THE BOOK WAS DRENCHED

Pages are missing

INTERNATIONAL ATOMIC WEIGHTS FOR 1943[1]

Element	Symbol	Atomic number	Atomic weight	Element	Symbol	Atomic number	Atomic weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	95.95
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.2
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	30.98
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Protactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92.91	Rubidium	Rb	37	85.48
Copper	Cu	29	63.57	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.2	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.06
Gadolinium	Gd	64	156.9	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32.06
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180.88
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Ho	67	164.94	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.39
Indium	In	49	114.76	Thorium	Th	90	232.12
Iodine	I	53	126.92	Thulium	Tm	69	169.4
Iridium	Ir	77	193.1	Tin	Sn	50	118.70
Iron	Fe	26	55.85	Titanium	Ti	22	47.90
Krypton	Kr	36	83.7	Tungsten	W	74	183.92
Lanthanum	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutecium	Lu	71	174.99	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.22

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[1] *J. Am. Chem. Soc.*, **65**, 1446 (1943).

INTERNATIONAL CHEMICAL SERIES

LOUIS P. HAMMETT, PH D, *Consulting Editor*

PHYSICAL CHEMISTRY
FOR COLLEGES

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PHYSICAL CHEMISTRY FOR COLLEGES

A Course of Instruction
Based upon the Fundamental Laws of Chemistry

by E. B. MILLARD
Professor of Physical Chemistry
Massachusetts Institute of Technology

Sixth Edition

McGRAW-HILL BOOK COMPANY, INC.
NEW YORK AND LONDON
1946

PHYSICAL CHEMISTRY FOR COLLEGES

PRINTED IN THE UNITED STATES OF AMERICA

THE MAPLE PRESS COMPANY, YORK, PA.

PREFACE TO THE SIXTH EDITION

The author has again attempted the difficult task of presenting physical chemistry to beginners with such simplicity that they can understand it after careful study, and yet with such precision that they will acquire a sound background with which to continue in the field beyond the introductory course.

Such an attempt requires compromises that may not be acceptable to all in any representative group of teachers, regardless of the level at which the text is written. Moderate changes toward or away from pedantic accuracy will shift the boundaries of the group that is pleased without greatly changing the number in the group. An arbitrary choice among the many important topics of physical chemistry as to which should be treated "thoroughly," which "briefly," and which omitted is a matter on which there will be differences of opinion, as is the amount of detail which constitutes thoroughness.

In this sixth edition the selection and order of topics are the same as in the preceding edition, the level of treatment is somewhat more precise, and there is a moderate redistribution of emphasis among the topics. The greater part of the text has been written anew, with the inclusion of new experimental material where it was available; the remainder of the text has been carefully studied and brought up to date to the extent that limitations of space and the author's ability permit. The first treatment of thermodynamics has been amplified and is now a separate chapter, and more emphasis is placed on thermodynamics in some of the other chapters as well. Opportunities for introducing additional thermodynamics at several points in the text will be evident to teachers who prefer to do so, but these opportunities are not thrust upon teachers who prefer to reserve most of the thermodynamics until the student has acquired some background in physical chemistry. In the last two chapters most of the important topics of the text are brought together through the use of free-energy calculations in order to provide a thorough review and summary with which to close the introduction to physical chemistry. Some of the problems in the fifth edition have been retained, some amplified, some omitted, and new problems have been added.

It is a pleasure to acknowledge the helpful suggestions received from teachers of the text, especially those from associates at the Massachusetts Institute of Technology.

E. B. MILLARD

CAMBRIDGE, MASS.,
May, 1946.

PREFACE TO THE FIRST EDITION

This book has been prepared to bring before college students certain of the more important aspects of physical chemistry, together with accurate modern data which illustrate the applicability of its laws to the phenomena observed in the laboratory. It has been assumed that the student is familiar with inorganic and analytical chemistry, that he has had an adequate course in college physics, and that the simple processes of calculus are familiar to him.

No attempt has been made to cover the whole of physical chemistry in a single volume; its most important topics have been treated at such length as the size of the volume allows, and numerous references to recent periodical literature are included for those who would pursue any given topic further.

The limitations of the orthodox laws of physical chemistry have been emphasized more than is commonly done in beginning courses of physical chemistry. To this end the illustrative data have been carefully chosen from modern experimental work, in order to minimize the "experimental errors" which are so often used to conceal real deviations of a law from the facts it is intended to express. A trusting belief in inadequate physical laws will only retard the scientific progress of a student, and weaken his faith in adequate laws; whereas a wholesome appreciation that physical chemistry is an unfinished and growing science may stimulate thoughtfulness and research. The proper time to encourage a research attitude is in the very beginning of a student's chemical career.

A qualitative treatment of the subject, so-called descriptive physical chemistry, may be obtained from the text alone; but careful consideration and study of the numerous tables of data will be required if anything approaching an appreciation of quantitative physical chemistry is desired. A quantitative point of view has been maintained as far as possible, even in the descriptive material.

Rather more tabulated data have been presented than might seem necessary in a beginning text. This is done to furnish the basis for numerous problems of a quantitative character. Many such problems should be solved in the course of a term, since they stimulate interest and increase the usefulness of the material taught in the class room. The problems at the end of each chapter will not be sufficient to test the ability of general classes; they are type problems in many instances, and should be supplemented by others designed by the teacher to suit the needs and ability of his particular class Problems should often be assigned for which data must be obtained directly from tables in the text. Much of the value of problem working is lost when a student knows he must use all of the data given him and no other; this too often results in suggesting the entire solution of the problem. Moreover, fresh problems must be given every year if fresh interest in physical chemistry is maintained, this can be done only when ample data are at hand Some of the more difficult problems at the end of a chapter should be worked by the instructor in class.

References to original sources are not intended primarily as citations of authority for statements made; they are first of all suggestions for further reading. With this in mind, most of the references are to periodicals in English, and to those which are available in small libraries The author has not hesitated to draw upon little known periodicals when the material to be obtained in them suited the needs of the text; he has not ignored foreign publications in the search for material; but for obvious reasons much of the best data is published in the widely circulated journals, and to these most of the reference work is confined.

The author is greatly indebted to Prof. James F. Norris and to Mr. Charles R. Park for reading the manuscript and making many helpful suggestions and criticisms based on their teaching experience. Their assistance has aided materially in detecting errors. He is also indebted to many other friends for kindly interest and encouragement during the preparation of the manuscript. It will be considered a favor if those who find errors of any kind in the text will communicate them to the author.

E. B. MILLARD.

CAMBRIDGE, MASS.,
March, 1921.

CONTENTS

PHYSICAL CHEMISTRY FOR COLLEGES

CHAPTER I

INTRODUCTION

DETERMINATION OF ATOMIC WEIGHTS

The title "physical chemistry" is almost universally accepted for the field of science that is concerned with the physical effects that attend or alter chemical changes Important aspects of physical chemistry are the influence of temperature, pressure, concentration, and relative proportions upon the rate and completeness of chemical reactions; the heat or work which they may produce; the structure of atoms or molecules as revealed by spectroscopy; the prediction from the properties of individual substances of the extent to which they will react if conditions are favorable; and, in general, the scope and limitations of the laws or theories that apply to chemical systems. Even this long list is not a complete description of the field; other topics of almost equal importance could well be added

As a preliminary to the study of mixtures or of reacting systems, it is convenient to know how the properties of single substances change with pressure or temperature, the conditions under which they are gaseous or liquid or crystalline, the conditions under which they exist at equilibrium in two or more states of aggregation, their heats of formation, and other properties.

Since it is obviously impossible to study experimentally every chemical system at every temperature, every pressure, and every concentration, one of the main functions of physical chemistry is the formulation of laws and theories that show the relation among the properties of chemical systems and the testing and revision of these theories and laws as experimental studies reveal minor or serious faults in them. The laws of thermodynamics, which are in no sense the "property" of chemists, have been most helpful in developing physical chemistry, but they could not have given this help to the extent that they have without accurate experimental data of the most varied kind. Notwithstanding the diligent work of thousands of chemists for many years, the supply of data is still inadequate; and notwithstanding the diligent work of many theorists for many years the theoretical foundation of physical chemistry is still inadequate. But research and study are continuing at an increasing rate, and while the prospect of complete theory or of complete experimental solution of the problems is remote, the progress already made is both impressive and useful.

Physical chemistry correlates mathematics, physics, and chemistry, using general methods of treating specific cases and thus providing a classification that puts less stress on memory. What is said of a selected system may be said of hundreds of particularized systems, almost without modification It is only for this purpose that "principles" are important and only in this sense that the principles or generalizations of chemistry have come to be called *physical chemistry* Thus physical chemistry is not a subdivision of chemistry like inorganic or organic chemistry, but a theoretical foundation for all of chemistry.

The following pages are intended to be a first survey of its vast field, with emphasis upon what has been accomplished and with some indication of what yet remains to be done Of necessity many topics have been treated briefly and others have been omitted entirely in order to keep the length of text within reasonable limits; but numerous references to the original sources are given in the footnotes, and suggestions for further reading are given at the ends of the chapters. Since the experimental facts are more important than theories, we shall speak of the deviations of theories or laws from the facts, rather than the deviations of the facts from the theory.

Laws of Nature (Results of Experience).—Some of the general laws of chemistry appear to be absolutely exact; they describe faithfully the results of most carefully conducted experiments, and the apparent deviations of these laws become less and less as the manipulative skill employed in testing them increases. Among these laws may be mentioned the law of the indestructibility of matter (conservation of matter), the law of definite proportions, Faraday's law of electrolysis, and the laws of thermodynamics. Other so-called "laws" fail to describe actual conditions, and the deviations are not due to experimental errors in the data. The deviations may be small under certain conditions and larger under other conditions. Such "laws" are useful approximations, which show the properties of substances in a qualitative way and which more or less accurately show their quantitative behavior. Thus, no simple law is known that shows exactly how the pressure of a quantity of gas changes as the volume or temperature changes. An approximation is known that shows these changes for most gases at moderate pressures within 1 or 2 per cent but is seriously in error at high pressures. Hence, it is as necessary to have a wholesome appreciation of the limited applicability of this "law" as it is to know the law itself.

As the various laws are stated, we shall state the experimental facts which confirm them or which show the extent of their errors and so endeavor to learn whether judgment is required in the use of a "law" or whether it is rigidly accurate under all circumstances. For this purpose a sense of proportion is essential. If a law appears to be exact in all but one case from a hundred thousand, as is true of the law of definite proportions, this "exception" may point to a new fact. In these circumstances one must examine the data more carefully or reconsider the fundamental assumptions or look for an unjustified interpretation. If the "exception" reveals a new fundamental fact, as is true here, much detailed study may be required before its full significance is appreciated. But while this study is in progress, it would be absurd to allow this "exception" to divert one's attention from the practically universal validity of this law. On the other hand, Avogadro's law and Boyle's law are "limiting laws," which become more nearly exact as the pressure of the gas is reduced but which are not strictly true at atmospheric pressure. They may be quite inaccurate at high pressures, and due account of the deviations must be taken in considering compressed gases. Some approximate laws describe the results of experiment quite accurately under certain conditions but deviate to a larger extent under other conditions. When this is so, the limiting conditions under which the law is accurate to within 1 or 2 per cent will be stated.

The statements put forward as laws of nature are sometimes the result of experience alone (empirical laws). There is always a possibility that some future experiment will demonstrate the untruth of what we have considered as a law, but the probability of this becomes less and less as the number of experiments increases. No change has ever been observed in the total mass of the substances involved in a chemical reaction; *i.e.*, no matter is destroyed in being changed into other forms.[1] As the methods of experiment have become more and more refined, and as the experimenters have become more skillful in their work, this law remains unshaken as a statement of universal experience, and it is now commonly accepted as an exact law of nature. Other simple laws, such as Boyle's law and Charles's law for gases, are also the result of experience; but as the experimental methods have become more refined, real deviations of these laws from the facts observed have been discovered. These experiments point to a failure of the supposed laws to explain completely the behavior of substances and are not to be traced to errors of experiment.

Proper reserve should always be exercised in drawing general conclusions from a set of experimental data. The phenomena of nature are often more complex than we think, and what appears to be a general law may be true only under restricted conditions. To state such a law without mentioning the qualifying circumstances under which it is applicable is to misrepresent the facts.

Theories are plausible beliefs advanced to explain observed facts. They serve to guide further experiments in a given field. Thus the theory that a gas consists of molecules, separated from one another by considerable distances and in rapid motion, offers a ready explanation of the compressibility of gases, of their diffusion, of their ability to mix with other gases in all proportions, and of practically all their properties. The evidence in favor of the theory is abundant and convincing; no facts are known that contradict it; and deductions based on this theory are in accord with the results of experiment. It is therefore universally accepted as a fact but is referred to as the kinetic *theory* of gases.

Many such theories are found in chemistry. They are

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[1] The exception to this statement that became so conspicuous in the summer of 1945 had been known for years. It was, and still is, so exceptional as to leave the conservation of matter one of the most valuable, if not the most valuable, guiding principle in chemistry.

accepted so long as they are in accord with the facts; they may be altered to fit new discoveries, but they should be discarded in favor of newer and more satisfactory ones when they seriously conflict with the results of experiments. Before proceeding to a study of new laws and theories, it will be advantageous to review some of those already studied in earlier courses in chemistry.

Indestructibility of Matter.—It is a familiar fact that matter may be changed into various forms by combination and rearrangement of the elements in various ways without any loss in the total mass of material The many operations of analytical chemistry depend on the validity of this fact; but since there is no reason why there *might* not be a change of mass during chemical change, it has been necessary to test this belief experimentally before accepting it. Perhaps the best known tests are Landolt's experiments[1] extending over a period of 20 years and devoted to a careful study of 15 different chemical reactions, which were examined with great skill and patience. The reacting substances were enclosed in the separate arms of sealed vessels, such as that of Fig. 1, to prevent the possibility of mechanical loss of material. The tubes were weighed on a very sensitive balance, a counterpoise of the same size and shape being used. Then, by tipping the vessel, the two solutions were brought in contact a little at a time. After the reaction had been completed, the vessel was weighed again. The weighings were made several times, and an average was taken. As a result of his work, Landolt concluded that, if there was a change in mass during chemical reaction, it was less than the error of weighing, which was 1 part in about 10,000,000.

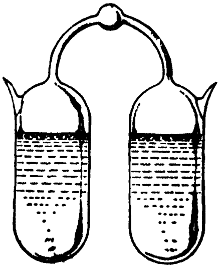

FIG. 1.

The later work of Manley[2] on the reduction of silver nitrate by ferrous sulfate was carried out with extreme care. His experiments showed that the change in weight attending chemical reaction was less than 1 part in 32,000,000, which is less than the probable error in weighing. In another series of experiments Manley showed that the reaction between barium chloride and

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[1] *Z. physik. Chem*, **12,** 1(1893); *Sitzber. preuss. Akad. Wiss.*, **1908,** 354.

[2] *Phil. Trans. Roy Soc. (London)*, (*A*) **212,** 227 (1913).

sodium sulfate was attended by a change in mass of less than 1 part in 100,000,000. In the light of these experiments there is no reasonable doubt that mass is conserved in chemical changes; we may, therefore, state that matter (anything which has mass) does not change in mass during chemical change.

One of the postulates of Einstein's theory of relativity states that matter is converted into energy under certain circumstances. The extraordinary velocities of some of the particles produced in nuclear reactions (which are briefly discussed in Chap. XVI) confirm experimentally the conversion of minute quantities of matter into energy. The astonishing amount of energy radiated by the sun is also claimed to be due to the conversion of matter into energy, with the loss of 3.6×10^{11} tons of mass per day required. Recently a few grams of matter were converted into an enormous amount of energy under circumstances that attracted world-wide attention and set off an equally large amount of speculation as to future developments; some of them are very attractive indeed. For the purposes of this text, we may well leave the future to the future and confine our attention to the chemical reactions with which we are likely to be concerned. In these reactions, mass is conserved within our limits of measuring it. The relation between the loss of mass and the energy produced is $\Delta E = \Delta mc^2$, where c is the velocity of light, 3×10^{10} cm per sec. Hence, if the total energy evolved by the combustion of 12 grams of carbon to carbon dioxide came from the destruction of matter the loss in mass would be about 10^{-8} gram, which is far beyond the precision of any weighing device yet discovered.

Elements and Compounds.—The number of kinds of matter is very great indeed, but attempts to resolve matter into its ultimate constituents by chemical means have brought to light about 92 substances that cannot be resolved, or at least that have not yet been resolved, into simpler substances. These substances are called *elements*. The number of experiments performed upon most of the known elements is so great as to make it improbable that they consist of two substances which may be separated later by some chemical process.

The separation of elements into isotopes, which are atoms of different mass and practically identical chemical properties, will be discussed briefly in Chap. XVI. We may mention here that deuterium, or hydrogen of atomic weight 2, has been separated in a practically pure state from natural hydrogen,[1] that neon (atomic weight 20.18) has been separated into portions of atomic weight 20 and 22, and that lithium (atomic weight 6.94) has been separated into portions of atomic weight 6.0 and 7.0; there are other instances of more or less complete separation of elements. The separation of chlorine (atomic weight 35.45) into portions of which one contained 99 per cent of the isotope of mass 37.0 has also been reported.[2] The isotopes of hydrogen are called protium and deuterium (symbol D). Deuterium oxide, or "heavy water," contains about 20 per cent of "heavy" hydrogen, as compared with 11 per cent hydrogen in ordinary water; it boils at 101.42°, freezes at 3.8°, has a density of about 1.1, and its surface tension, vapor pressure, latent heat, and other properties differ from those of ordinary water.

Lead of atomic weight ranging from about 206.0 to 208.0 has also been found in small quantities in some rare minerals, probably as the result of radioactive changes. These isotopes are the result of "natural" processes, in the sense that they have not been carried out in a laboratory for the purpose of making this separation, and they are accordingly naturally occurring exceptions to the constancy of atomic mass.

As may be seen from the periodic table in Chap. XIV, it is improbable that there are many undiscovered elements of atomic weight less than uranium, and there is yet no evidence of natural elements of higher atomic weights.[3] The discovery of "element 93" or "element 94" would cause no change in the periodic arrangement of the elements. It is customary to regard isotopes as different forms of the same element and to assign them all to a single place in the periodic table. But the discovery of another alkali element having an atomic weight between those of sodium and potassium, for instance, is most improbable, as is the discovery of any new element for which no place is available in the periodic table.

Law of Definite Proportions.—This law states that the quantity of an element which will combine with a given weight of another

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[1] Urey and Teal, *Rev. Modern Phys.*, **7**, 34–94 (1935).

[2] Hirschbold-Wittner, *Z. anorg. allgem. Chem.*, **242**, 222 (1939).

[3] "Synthetic" atoms of higher atomic weight have been prepared by methods that will be discussed in Chap. XVI.

element to form a pure chemical compound is a fixed quantity, regardless of the method of preparation of the compound. In other words, the percentage of each element in a pure compound is always the same, and the presence of an excess of one element does not result in the formation of a compound containing more of it. The atomic theory was suggested to Dalton by this law, and the theory furnishes a ready explanation of the law. Identical whole atoms of an element, by combining with identical whole atoms of another element, must yield molecules of a fixed composition.

Table 1 shows data[1] on the synthesis of silver bromide from carefully purified silver and bromine, together with the weight of bromine combined with each gram of silver. Elaborate precautions were taken to ensure the purity of the substances weighed and to avoid mechanical loss during the synthesis.[2]

The synthesis was conducted by supplying ammonium bromide to a weighed quantity of silver that had been converted into nitrate, until no more bromine would combine with the silver, after which the silver bromide was collected and weighed.

Other examples of the law of definite proportions are shown in Table 1. A quantity of iron was converted into ferric oxide and heated with an excess of oxygen until no more would combine with it.[3] The ferric oxide was weighed, then heated in a current of hydrogen until all the oxide had been completely reduced to iron, which was then weighed. The synthesis of tin tetrabromide is also shown in Table 1. It will be seen again that the composition of the product is constant, insofar as it is possible for the best quantitative chemistry to determine it [4]

Molecular Theory.—The theory that matter of all kinds consists of very small particles or molecules is now commonly

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[1] BAXTER, *J. Am. Chem. Soc*, **28,** 1322 (1906)

[2] Students will note that six significant figures are given in most of the weights in Table 1. This is justified in view of the elaborate precautions that atomic-weight work requires. All the reagents are purified with great care, and manipulative precautions are taken with which students of ordinary quantitative analysis are quite unfamiliar For an excellent description of such work, see Baxter, *Proc Am. Acad Arts Sci.*, **40,** 419 (1904), and **41,** 73 (1905), in connection with the atomic weight of iodine. Students who read these papers with care will find themselves well repaid.

[3] RICHARDS and BAXTER, *Proc. Am. Acad. Arts Sci.*, **35,** 253 (1900).

[4] BONGART and CLASSEN, *Ber.*, **21,** 2900 (1888).

TABLE 1.—DATA ILLUSTRATING DEFINITE PROPORTIONS

Weight of silver	Weight of silver bromide formed	Grams of bromine combined with each gram of silver
5 01725	8 73393	0 74078
5 96818	10 38932	0 74079
5 62992	9 80039	0 74077
8 13612	14 16334	0 74080
5 07238	8 82997	0 74079
4 80711	8 36827	0 74081
5 86115	10 20299	0 74078
6 38180	11 10930	0 74078
6 23696	10 85722	0 74079
9 18778	15 99392	0 74078
8 01261	13 94826	0 74079
8 59260	14 95797	0 74079
8 97307	15 62022	0 74079
		Average 0 74079

Weight of iron	Weight Fe_2O_3	Per cent Fe in Fe_2O_3
2 78115	3 97557	69 956
3 42558	4 89655	69 959
3 04990	4 35955	69 959
4 99533	7 14115	69 951
4 49130	6 42021	69 956

Weight of tin	Weight of $SnBr_4$ formed	Per cent tin in $SnBr_4$
2 8445	10 4914	27 113
4 5735	16 8620	27 123
4 5236	16 6752	27 119
3 0125	11 1086	27 116
2 8840	10 6356	27 113
3 0060	11 0871	27 123

accepted as a fact. This theory is in complete accord with all the known facts of chemistry; it explains in a simple way all our chemical reactions; and it forms the basis of modern chemical thinking. The molecules of which a substance consists cannot be divided into smaller particles without a complete change in the properties of the resulting particles. They are the limit of divisibility for a given kind of matter. When there are two or more kinds of molecules or molecular species present, the mass of matter is called a mixture The usual criterion of a mixture is that it may be prepared in varying proportions, while a pure substance always has the same composition.

If all the molecules of a pure substance are of the same species, every molecule must have the same composition as the whole mass of pure substance. Two matters at once claim interest: the relative weights of the molecules of different substances, and the way in which the molecules are formed from their constituent elements

The relative molecular weights cannot be determined from comparisons of single molecules on account of their small size, but equally satisfactory results may be obtained if we have a way of counting out the same number of molecules of each substance for comparison We consider next a procedure that accomplishes this purpose

Avogadro's Law.—A provisional statement of this important law, which will require some modification to put it into exact form, is that equal volumes of gases at the same temperature and pressure contain the same number of molecules. If this law is accepted, we may determine the relative weights of the molecules of two gases by comparing the weights of equal volumes at the same temperature and pressure. In order to put these comparisons on a numerical scale, the next step is obviously to select some substance as a reference standard, and chemists by common consent have adopted 32 as the "molecular weight" of oxygen.[1] Since they employ the gram as a unit of weight, 32 grams of oxygen is therefore accepted as a "gram-molecular weight," or a gram molecule. On account of the extensive use of this term, it has been abbreviated to "mole," which is written without a period. It is not an abbreviation of the word "molecule," but a separate new word meaning gram-molecular weight or formula weight. Molecular weights based on gas densities are usually free from any uncertainty as to the formula of the substance, but we shall call 18 grams of liquid water or 58.5

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[1] Strictly speaking, it is 16 00 as the *atomic* weight that was arbitrarily accepted as the standard. Since oxygen is diatomic, its molecular weight is 32.00.

grams of sodium chloride a mole without commitment as to whether a molecule of this composition actually exists or not.

A molecular weight of a gas is that weight of it which occupies the same volume as 32 grams of oxygen at the same temperature and pressure. If we define a molecular volume of gas as the volume occupied by 32 grams of oxygen, we may then define the molecular weight of any gas as that weight which fills a molecular volume. The facts (1) that most of the precise data on gas densities are reported at 0°C. and (2) that most texts on elementary chemistry give the molal volume for 0°C and 1 atm. pressure as 22.4 liters often leave students with the unfortunate misconception that Avogadro's law applies only to "standard conditions," even though the language in the texts correctly states that only the *same* temperature and pressure are required At 1 atm pressure a molecular volume of gas is 24.4 liters at 25°C., 30 6 liters at 100°C , and 22.4 liters at 0°C.; but a molecular volume is also 24 4 liters at 0°C. and 0.92 atm., or 30 6 liters at 0°C. and 0 73 atm., or 22 4 liters at 100°C. and 1.37 atm., for all these figures are the volumes of 32 grams of oxygen under the conditions stated A molecular weight of any gas is the weight required to fill any of these volumes at the corresponding temperature and pressure, and we may of course compute the weight of a molecular volume from the weight of any convenient volume.

Avogardro's law is an example of a "limiting law" which becomes more nearly exact as the pressure at which the gases are compared is reduced but which may be largely in error at high pressures or near the condensation point of a gas. For "permanent" gases at 1 atm. and ordinary temperatures the number of molecules per unit volume is the same within about 1 per cent. But the fractional expansion for a given pressure decrease at constant temperature is not quite the same for all gases, and therefore precise molecular weights may be determined through Avogadro's law only at low pressures. (The procedure for accomplishing this comparison will be given in detail presently.) We may now state Avogadro's law in a workable and exact form: Equal volumes of gases at the same temperature and the same *very low pressure* contain the same number of molecules. The necessity for this form of statement may be illustrated by the ratio of the density of N_2O to that of oxygen at 0°, which is 1.9782/1 4289 = 1.3844 for the gases at 1 atm. and 0.9855/0.7142 = 1.380 at ½ atm. The limit that this ratio of densities at equal pressures approaches as the pressure approaches zero is 1 3765. Hence, 32.000 × 1.3765 = 44.020 is the molecular weight of N_2O at such a low pressure that Avogadro's law is exact [1]

Atomic Weights.—An atomic weight of an element is the smallest weight of it found in a gram molecule of its compounds. Since a molecule must contain a whole number of atoms of each element, a gram-molecular weight must contain a whole number of atomic weights of each element. Thus, the accepted values of atomic weights represent the smallest quantity of each element found in a gram molecule of any compound so far; the possibility of discovering a compound with less of the element per molecular weight always exists, but the probability of this discovery becomes less as the number of compounds studied increases. There are many ways in which the value of an atomic weight may be checked, such as by its specific heat, its place in the periodic system, and its characteristic X-ray spectrum It is most improbable that any of the atomic weights now accepted will need to be divided by a whole number. The currently accepted atomic weights are given in Table 4 and repeated on the inside front cover for convenient reference.

The molecules of helium, argon, the other gases of the zero group in the periodic table, and most metals in the vapor state consist of a single atom, so that atomic weights are identical with molecular weights for these substances Oxygen, nitrogen, chlorine, and hydrogen, or, in general, any element whose condition in the vapor state is indicated by the symbol E_2, have atomic weights that are half the molecular weights.

Atomic weights, by which chemists always mean gram-atomic weights of course, are not proportional to weights of atoms unless all the individual atoms have the same mass. As will be explained in Chap XVI, there is no particle in chlorine that weighs 35 46/(6 03 × 10^{23}), even though 35 46 is the correct "atomic weight" of chlorine. The individual atoms have weights corresponding to 35 00 and 37.00 on the oxygen scale, but the mixture of these particles in the proportion of about 3:1 bears the name of the *element* chlorine. All the occurrences of chlorine in nature are of the same composition within 1 part in 10,000 or more, and the mixture behaves

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[1] The data are by Moles and Toral, through the report of the International Committee on Atomic Weights, *J. Am. Chem Soc.*, **60,** 739 (1938)

like a single substance in *every* chemical process. Samples of chlorine collected from widely separated sources, and from rocks that have probably never been in contact with the ocean, show no detectable variation in atomic weight from chlorides derived from the sea Samples of lead from minerals not associated with radioactive materials have been collected from sources all over the earth in a further test of the constancy of atomic weights. The atomic weight of lead from these materials was most carefully determined [BAXTER and GROVER, *J Am Chem Soc* , **37,** 1027 (1915)] and found to be 207 21 ± 0 01 (see Table 90) It will be shown later that common lead consists mainly of isotopes of mass 206 00, 207 00, and 208 00, but the figure 207 21 in Table 4 is still the proper atomic weight of lead The long series of radioactive changes, of which the decay of radium itself is the best known, results in an isotope of lead of atomic weight 206 0. Another series of such changes of which thorium is the parent element ends in an isotope of lead of atomic weight 208 0 Hence, in lead from radioactive materials the atomic weight values vary from nearly 208 0 to nearly 206 0, depending upon the source Some data bearing upon these "radiogenic" leads are given in Table 91

The atomic weights of elements that do not form gaseous compounds are determined from exact chemical analysis of their compounds, together with supplementary data that show the formula of the compound. For example, 63.57 grams of copper combine with 16 00 grams of oxygen to form cupric oxide, and 63.57 is the combining weight of copper. This is also shown to be the atomic weight of copper when it is established that these elements combine in the atomic ratio 1:1. It is found that 50 768 grams of iodine combine with 16.00 grams of oxygen to form a stable pure substance which is shown by supplementary data to be iodine pentoxide, I_2O_5, whence the atomic weight of iodine is 126.92. The analytical data alone show only that 50.768 grams is the weight of iodine combining with 16 00 grams of oxygen; they furnish no way of deciding what multiple or submultiple of this weight is the actual atomic weight.

Although the most direct method of determining precise atomic weights would be the analysis or synthesis of oxides, very few of the elementary oxides may be prepared in a sufficiently pure form for this purpose. Metallic halides are more readily purified, and ratios such as ECl:Ag may be used to determine atomic weights if the atomic weights of Cl and Ag are accepted. But these atomic weights involve those of other elements. The basic quantities are the atomic weights of 11 elements, which are related to one another through 71 ratios that have been most carefully determined. From these ratios, F. W. Clarke[1] derives 43 estimates of the atomic weight of silver, 32 for chlorine, 16 for bromine, 22 for nitrogen, etc , and finally determines the basic values of the 11 atomic weights, H, C, N, S, Cl, Br, I, Li, Na, K, and Ag.

In place of attempting to follow this rather involved calculation, we may illustrate the principle by some simpler calculations involving three of the fundamental ratios, as follows:

$$\begin{aligned} \mathrm{I:O} &= 50.768.16.000 \\ \mathrm{I_2O_5\ 2Ag} &= 100\ 64\ 623 \\ \mathrm{Ag\ Cl} &= 100.32\ 867 \end{aligned}$$

Accepting the formula of I_2O_5, the first ratio establishes

$$\mathrm{I} = 126.92$$

The second ratio then establishes Ag = 107.88; and the third ratio establishes Cl = 35.45. From the ratio Ag I = 100.117 6433, independently determined,[2] these atomic weights are confirmed; from the ratio AgCl.AgI = 100.163.8062, another confirmation is obtained.[3]

Once these atomic weights are established, the ratio ECl:Ag may be used on another substance, say KCl, for which the ratios are[4] Ag·KCl = 100.69.1085 and AgCl KCl = 100 52.016. The molecular weight of KCl that is here established may be checked from the ratio $KClO_3$:KCl = 100.60.836, which goes back to the fundamental standard of oxygen.

Some of the common procedures for determining atomic weights will now be described

Atomic-weight Methods. *a. From Gas Densities Alone*—When the number of atoms in a molecule of an elementary substance has been established, the atomic weight may be determined by dividing the molecular weight by the proper whole number. Similarly, the atomic weight of bromine may be determined by subtracting from the molecular weight of hydrogen bromide the atomic weight of hydrogen, since its molecule is

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[1] *Mem. Nat. Acad. Sci.*, **16** (3), part V, pp 1–418 (1922), this particular operation is given on p 116 of the memoir.

[2] BAXTER and LUNDSTEDT, *J. Am Chem. Soc.*, **62,** 1829 (1940).

[3] BAXTER and TITUS, *ibid*, **62,** 1826 (1940).

[4] BAXTER and HARRINGTON, *ibid.*, **62,** 1836 (1940).

known from combining volumes to contain one atom of each element. We have seen above that Avogadro's law is a useful approximation at atmospheric pressure and an exact law at very low pressures and hence that, in order to determine precise molecular weights, densities must be determined at low pressures. The pioneer work of Guye and his students has been supplemented by that of several other groups to such an extent that gas densities are among the most precise methods of determining molecular weights. It has been found that the ratio of density to pressure is a linear function of the pressure, and hence, by plotting d/p against p and extrapolating to zero pressure (or at least to very low pressures), one may determine the density of a gas under conditions such that it is substantially an ideal gas.

TABLE 2.—DENSITY OF CARBON DIOXIDE AT 0°

Pressure, atm	Density, grams per liter	**Ratio** d/p
1	1 976711	1 97676
⅔	1 314823	1 97226
½	0 985018	1 97010
⅓	0 655922	1 96788
¼	0 491678	1 96676
⅙	0 327606	1 96566
0		1 96346

As an example of the precision that may be attained we quote some data[1] for CO_2 at 0° in Table 2. When these ratios of d/p are plotted against the pressure, as is done in Fig. 2, they fall on a straight line that may be extended to zero pressure to determine the limiting density. This limiting density d/p is 1.96346; and when similar data for oxygen[2] are treated in the same way, the limiting ratio of d/p is found to be 1.42767. The ratio of these limiting densities is the ratio of their molecular weights according to Avogadro's law, which is exact at the limit; and

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[1] DIETRICHSON, MILLER, and WHITCHER, not yet published.

[2] BAXTER and STARKWEATHER, *Proc Nat Acad. Sci*, **14,** 50 (1928); see also **10,** 479 (1924); **11,** 231, 699 (1925), **15,** 441 (1929) for data on other gases. The data for oxygen at 0° are as follows:

Pressure, atm	1 000	¾	½	¼
Density, grams per liter	1 42896	1 07149	0 71415	0.35699

since the molecular weight of oxygen is 32.000 by definition, the molecular weight of CO_2 is 32.000(1.96346/1.42767), or 44.010, and C = 12.010.

This method is particularly suited to accurate atomic-weight determinations on the gases of the "zero" group in the periodic table, since these elements do not form compounds Thus for neon and argon the limiting ratios d/p at 0° are 0.90043 and 1.78204, respectively;[1] and the molecular weights are 20.183 for neon and 39.944 for argon Since the molecules are monatomic, these are also the atomic weights.

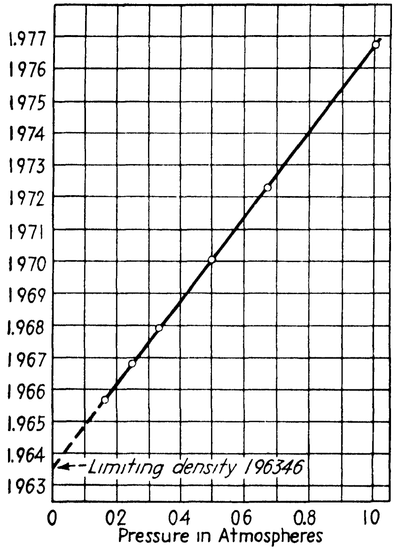

FIG. 2—Limiting density of CO_2 at 0°

b From Molecular Weights and Compositions by Weight — When large numbers of gaseous compounds of any element are examined, the smallest weight of an element found in a mole of any of its compounds is called the atomic weight of that element Since determinations of molecular weight are not usually performed with great accuracy, careful analytical data are used to supplement this work. An example will make the procedure clearer

In Table 3 are given some approximate data for gaseous nitrogen compounds, using only whole numbers. It is seen from this table that no nitrogen compound contains less than 14 grams of nitrogen per molecular weight; this is, then, the approximate atomic weight. But it is not an *exact* value, since it is derived from rough data Accurate values may be determined from gravimetric analysis of nitrous oxide, nitric oxide, or nitrosyl chloride; from the limiting densities of N_2O, NO, or NH_3; from the ratios $Ag:AgNO_3 = 100:157.48$, $NaCl:NaNO_3 = 100:145.418$, $N_2O_5:K_2O = 100:87.232$, all of which indicate N = 14.008. None of these gravimetric ratios would show whether N = 14 or

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[1] BAXTER and STARKWEATHER, *ibid.*, **14**, 50 (1928), **15**, 441 (1929).

N = 28, but the latter value is excluded by the densities of NO and NH_3, so that N = 14.008 is the proper atomic weight for nitrogen

TABLE 3.—NITROGEN CONTENT OF COMPOUNDS

Substance	Weight of a molal volume of gas	Per cent nitrogen in the compound	Weight of nitrogen in a mole of gas
Nitric oxide.............	30	47	14
Ammonia.	17	82	14
Nitrous oxide	44	64	28
Nitric acid	63	22	14
Nitrosyl chloride. . .	66	21	14
Hydrazine....	32	87	28

c From Analytical Data and Specific Heats.—The metals and some other elements do not form gaseous compounds at temperatures suited to accurate work, and determinations of their atomic weights rest on other considerations. But the weight of a metal that combines with 16 grams of oxygen is either an atomic weight, two atomic weights, half an atomic weight, or two-thirds or three-fourths or two-fifths of an atomic weight, depending on whether the formula of the oxide is EO, E_2O, EO_2, E_2O_3, E_3O_4, or E_2O_5. Analysis of the oxide will give, therefore, an exact value of the atomic weight or a simple fraction of it, and it requires only a rough determination in some other way to indicate which multiple of the weight combined with 16 grams of oxygen is the true atomic weight. The *law of Dulong and Petit* furnishes such a method of fixing the multiple for heavy elements. This law states that for metals and the heavy elements the atomic heat capacity at room temperature is about 6.2, that is, that the quantity of heat required to raise an atomic weight of an element through 1° is the same for all solid elements. From the data of Table 1 we see that iron oxide is 69.956 per cent iron; hence the weight of iron combined with 16 grams of oxygen is

$$x:16 = 69.956:(100.00 - 69.956)$$

or $x = 37.256$. This is either the atomic weight of iron or a simple fraction of it. The specific heat of iron is 0.115, and 6.2

divided by 0.115 is 54, which is approximately the true atomic weight. It will be seen that 37.256 is about two-thirds of 54, whence the true atomic weight is 1.5×37.256, or 55.88.

The atomic weight of bromine has been established by several methods at 79.92. From this we may compute the atomic weight of silver from the data of Table 1, since an atomic weight of silver combines with a whole number of atomic weights of bromine. Thus

$$\mathrm{Ag}:\mathrm{Br} = 1.000:0.74078 = x:79.92$$

whence $x = 107.88$. The specific heat of silver is 0.056, and 6.2 divided by 0.056 is 110. Thus the true atomic weight of silver is 107.88.

An example of a more complete set of experiments is the following one, which serves to determine the atomic weights of silver, chlorine, and lithium with reference to oxygen. By reducing lithium perchlorate to chloride it was found[1] that 100 grams of the former gave 39.845 grams of the latter. The formula of the perchlorate is $LiClO_4$, whence it follows that the molecular weight of lithium chloride is $x:(x + 4 \times 16.000) = 39.845:100.000$, or $x = 42.393$. The lithium chloride was then treated with silver nitrate solution made from a weighed quantity of silver, from which it was found that each gram of lithium chloride required 2.54460 grams of silver, giving the atomic weight of silver as 2.54460 times the molecular weight of lithium chloride, or 107.871. This will be seen to be in accord with its atomic weight calculated above from the synthesis of silver bromide. Then, by weighing the silver chloride formed, the ratio of silver to silver chloride was found to be 1:1.3287, from which the atomic weight of chlorine is given by $107.871:(107.871 + y) = 1.000:1.3287$, or $y = 35.454$. Returning now to the ratio of lithium chloride to perchlorate we see that the atomic weight of lithium may be calculated from the atomic weight of chlorine just found, since

$$LiClO_4:LiCl = (z + 35.454 + 4 \times 16.000):(z + 35.454) = 100.000:39.845$$

whence $z = 6.939$.

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[1] RICHARDS and WILLARD, *J. Am. Chem. Soc.*, **32**, 4 (1914).

d. From X-ray Spectra.—The frequency of the characteristic X radiation emitted by an element when it is bombarded with electrons serves to fix the position of the element in the periodic table and so to determine its atomic weight from the combining weight. We shall see in Chap. XIV that when the square root of this frequency is plotted against the atomic number, which is the order number of the elements in the table, a straight line results. This discovery of Moseley's places beyond doubt the positions of the elements in the table.

e. From the Mass Spectrograph.—Since a discussion of this procedure is given in Chap. XVI, it will be mentioned only briefly here. The method depends upon the fact that a charged particle is deflected, upon passing through an electric field, to an extent depending upon the ratio of charge to mass, in addition to other factors. By proper design of the apparatus, molecules or atoms of equal charge are caused to record their deflections upon a scale linear with respect to mass, from which precise determinations of atomic mass are derived. The atomic masses of hydrogen and iodine, as measured by this method, are 1.00813 and 126.933, respectively; the chemically determined atomic weights are 1.0081 and 126 92, respectively. This method measures the masses of the individual isotopes rather than those of the naturally occurring mixtures which chemists call the elements, but the comparison of the atomic weight of iodine from the two methods is justified by the fact that this element consists of a single species of atom A similar comparison for neon, whose atomic weight by the limiting density method is 20.183, shows from mass spectrographic data that this element consists of 90 per cent of atoms of mass 19 997, 9 73 per cent of mass 21.995, and 0.27 per cent of mass about 21 (the precise mass has not been determined). These isotopic masses are referred to that of the most abundant oxygen isotope as 16.000 and must be corrected to the chemical scale by allowance for the small amount of the heavier isotopes before being compared with the data based upon natural oxygen. The multiplying factor for this correction is 1.00027.

f. From Lattice Constants and Crystal Densities.—The recent precise determinations of lattice constants of crystals from X-ray diffraction give another method of determining relative atomic weights or molecular weights that is most promising, although it has not yet been applied to many substances. A single illustration must suffice here Both LiF and NaCl have the crystal structure shown in Fig 22, the edge of a cube containing 4LiF[1] is $a = 4.0181 \times 10^{-8}$ cm., and the edge of a cube containing 4NaCl is $a = 5.6301 \times 10^{-8}$ cm. The densities at 25° are 2 6390 for LiF and 2.1623 for NaCl, and so the ratio of the weight of 4LiF to 4NaCl is the ratio of a^3d for the two substances:

$$\frac{a_{\text{LiF}}{}^3 d_{\text{LiF}}}{a_{\text{NaCl}}{}^3 d_{\text{NaCl}}} = \frac{(4\ 0181 \times 10^{-8})^3 2.6390}{(5\ 6301 \times 10^{-8})^3 2.1623} = 0\ 44364$$

If the atomic weights of Li, Na, and Cl are accepted, F = 18 994, which is in close agreement with the accepted value, 19.00 in Table 4 In these determinations the *relative* lattice constants are readily determined to six significant figures and the densities to about the same precision. Since atomic weights and molecular weights are relative quantities, this method may develop into the most precise one for atomic weights.

Atomic-weight Table.—The table of international atomic weights published each year is based upon careful study of all available data by a Committee on Atomic Weights of the International Union of Chemistry.[2] The importance assigned to each determination in computing the weight for general use depends upon the number of individual experiments in a series and the probable accuracy of the work. The most recent atomic weights obtainable are given in Table 4 All the figures stated are significant. Thus 14.008 for nitrogen indicates that this atomic weight is accurate to a thousandth of a unit; 197.2 for gold indicates that the second decimal place is still uncertain

Units and Standards.—It will be convenient to define and record here the numerical values of some quantities for use throughout the book. We shall use the centimeter-gram-second (c.g.s.) system of units and the centigrade temperature scale in our calculations, following the usual custom of physicists and

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[1] JOHNSTON and HUTCHINSON, *Phys Rev*, **62,** 32 (1942) In the original paper the data are given to six figures

[2] Summaries of current work on which changes are based appear with the report each year. This is reported in *J Am Chem Soc.* and other periodicals. A summary of all of the atomic-weight work done prior to 1920 is given in *Mem. Nat Acad Sci*, **16** (3), part V, pp 1–418 (1922)

chemists The chief advantages of this c.g.s. system are that (1) each unit used is a decimal multiple of the smaller unit, (2) a unit volume of water has unit weight, and, especially, (3) the recorded data of physical chemistry are published in these units.

TABLE 4.—INTERNATIONAL ATOMIC WEIGHTS FOR 1943[1]

Element	Symbol	Atomic number	Atomic weight	Element	Symbol	Atomic number	Atomic weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	95.95
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.2
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	30.98
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Protactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92.91	Rubidium	Rb	37	85.48
Copper	Cu	29	63.57	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.2	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.06
Gadolinium	Gd	64	156.9	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32.06
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180.88
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Ho	67	164.94	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.39
Indium	In	49	114.76	Thorium	Th	90	232.12
Iodine	I	53	126.92	Thulium	Tm	69	169.4
Iridium	Ir	77	193.1	Tin	Sn	50	118.70
Iron	Fe	26	55.85	Titanium	Ti	22	47.90
Krypton	Kr	36	83.7	Tungsten	W	74	183.92
Lanthanum	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutecium	Lu	71	174.99	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.22

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[1] *J. Am. Chem Soc.*, **65**, 1946 (1943).

But daily use of the English units may make it easier to understand the first statement of a new law in familiar units and to obtain sooner a sense of proportion. Students of engineering may study applied mechanics in English units and physical chemistry in metric units at the same time, and considerable confusion of quantities is an inevitable result. When ratios or relative quantities are concerned, one set of units will do as well as another. The units and conversion factors stated below are for the convenience of students in working problems, and they are stated with sufficient precision for this purpose. It will be of little use to know that a cubic centimeter is 1 000027 ml. or that the density of water at 4°C. is not unity but 0 999973 in this connection.

Mass or **weight** usually will be expressed in *grams*, though milligrams ($\frac{1}{1000}$ gram) and kilograms, or *kilos* (1000 grams), are sometimes more convenient units

The acceleration of gravity is 980.66 cm. per sec.

Volume is to be stated in liters or milliliters. A milliliter of water at 4°C. has a mass of 1 gram.

Force is expressed in dynes, a *dyne* being the force that will impart to 1 gram mass a velocity of 1 cm per sec in a second.

Pressure is defined as the force acting on a unit area The absolute unit of pressure is 1 dyne per sq. cm ; a convenient multiple is the *bar*, which is 1,000,000 dynes per sq. cm.[1] In spite of the convenient size of this unit, which is closer to the average atmospheric pressure than the standard "atmosphere," the latter remains the common unit of pressure in scientific work. The main obstacle to its adoption is that the "steam point" is defined as the boiling point of water under a pressure of 1 atm. and established as 100° on the centigrade temperature scale. A standard *atmosphere* is a pressure that will support a column of mercury 76.00 cm. high at 0° when $g = 980.66$; it is 1.01325 bars. This multiplicity of pressure units is frequently a source of confusion, but custom has not sanctioned the elimination of any of them so far.

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[1] Occasionally the pressure of 1 dyne per sq. cm is called a bar, and the quantity defined as a bar above is called a *megabar*. The c.g.s. unit of pressure is also called a barye Since the quantities differ by 10^6, no confusion will arise. The definition which we have given is used in the "International Critical Tables" and by the U.S. Weather Bureau.

Work or Energy.—Small quantities of work or energy will be expressed in calories (abbreviated *cal.*), and large quantities in kilocalories (abbreviated *kcal.*). The quantities are, respectively, the amount of heat required to raise one gram of water one degree centigrade, and 1000 times this quantity. For our purposes it will not be necessary to consider whether the quantities are in "15° cal." or "mean calories," for the ratio of one to the other is 1.00017, and almost none of the experimental data we shall consider are precise enough to raise the question of which calorie has been used. Similarly, we shall use 4.18 joules as equivalent to 1 cal. without considering whether we mean 1 "absolute joule" or 1 "international joule," for the ratio of one to the other is 1.0004. The work done when a piston of 1 sq. cm. area moves 1 cm. against a pressure of 1 atm. is called "1 ml.-atm." and is the work done for each milliliter increase in volume during evaporation against the atmospheric pressure. One calorie is 41.3 ml.-atm., or 1 ml.-atm. is 0.0242 cal.,[1] or 1 liter-atm. is 24.2 cal.

Temperature will be given on the centigrade scale, which takes the ice point as 0° and the steam point as 100°; or on the Kelvin, or absolute centigrade, scale, which takes 273.16° as the ice point and 373.16° as the steam point. It will usually be sufficient to take 273° as the quantity to add to centigrade temperatures to convert them to absolute, or Kelvin, temperatures.

A mole, or formula weight, of substance will ordinarily be used to describe a quantity of reacting substance. For gases this is the quantity that fills the same volume as 32 grams of oxygen at the same temperature and pressure; for liquids or solids it will be the quantity corresponding to the usual chemical formula. We shall refer to 142 grams of Na_2SO_4 as a mole of sodium sulfate, whether or not a molecule of this composition actually exists; and we shall call 18 grams of water a mole in the liquid state

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[1] For those working in English units, the following conversion factors will be useful:

1 foot = 30.480 centimeters
1 pound = 453.59 grams
1 pound per square inch = 68,947 dynes per square centimeter
1 British thermal unit (60°F.) = 1054.6 joules
1 gallon = 3.785 liters
1 cubic foot = 28.317 liters
1 atmosphere pressure = 14.69 pounds per square inch
1 atmosphere pressure = 29.92 inches mercury
$T_R = t_F + 459.7$

whether liquid water consists of H_2O molecules or $(H_2O)_n$ molecules. The volume of 18 grams of water (or of 98 grams of sulfuric acid) will be called a molal volume, and the heat capacity of-18 grams of water will be called its molal heat capacity.

The ideal gas constant will be explained in the next chapter, but its numerical value is recorded here as

$$R = 8\,315 \text{ joules/mole-}^\circ\text{K}$$

or 0.08206 liter-atm./mole-°K., or 1.987 cal./mole-°K. In most of our calculations these figures may be used as 8.32, 0.082, and 1.99, respectively.

Concentration.—This word is used somewhat loosely in chemistry to designate several ways in which the composition of a solution is expressed; it may mean moles or equivalents of a solute in a unit weight or volume of solvent or of solution. For the purposes of this book two ways of expressing concentration will serve every ordinary need. We shall define the *molality* of a solute as the number of moles of solute per 1000 grams of solvent, and $0.1m$. will thus indicate 0.1 mole of solute in 1000 grams of solvent. Compositions so expressed do not vary with the temperature, and they are readily convertible into mole fractions, which will be defined later. Certain properties of solutions depend upon the quantity of solute per unit *volume of solution*, and the moles of solute per liter of solution will be called the volume concentration or simply the concentration of the solution. Since solutions expand slightly when heated, it is necessary in precise work to specify the temperature at which the concentration is given. An equivalent of solute per liter of solution will be called a normal solution, as in volumetric analysis. In dilute *aqueous* solutions the difference between molality and concentration is small, but it is not to be ignored in precise calculations; and for solvents other than water the difference is always important. For example, a solution of 0.1 mole of dissolved substance in 1000 grams of chloroform has a volume concentration of 0.15.

To illustrate these definitions, a solution containing 5 per cent sulfuric acid by weight has a density of 1.0300 at 25°; it contains 52.63 grams of H_2SO_4 per 1000 grams of water and is

$$\frac{52.63}{98} = 0.537m.$$

The volume of 1052.63 grams of this solution is 1.0219 liters, and its *concentration* is 0.537/1.0219 = 0.525 moles per liter of solution, or 1.050 equivalents per liter of solution. In the notation that we shall use, $m = 0.537$, $C = 0.525$, and $N = 1.050$.

Ionic Strength.—For certain purposes in connection with ionized solutes the composition is expressed as the ionic strength μ, which is half of the sum of each ion concentration multiplied by the square of the valence of the ion. Thus, 0.1*m*. $BaCl_2$ has an ionic strength $\mu = \frac{1}{2}(0.1 \times 2^2 + 0.2 \times 1^2) = 0.3$; in 0.12*m*. $CuSO_4$, $\mu = \frac{1}{2}(0.12 \times 2^2 + 0.12 \times 2^2) = 0.48$; in 0.3*m*. HCl, $\mu = \frac{1}{2}(0.3 \times 1^2 + 0.3 \times 1^2) = 0.3$.

Problems

Numerical data for some of the problems must be sought in the text. A table of logarithms will be found in the back cover of the book

1. (*a*) Calculate the molecular weight of KBr from the following series of weighings.

Wt $KBrO_3$	7 44818	10 69361	10 36524	9 78481
Wt KBr	5 30753	7 62021	7 38620	6 97233

(*b*) Calculate the atomic weight of silver from the following series:

Wt. KBr	6 93122	7 62092	7 38622	6 97265
Wt. Ag	6 28281	6 90813	6 69531	6 32040

(*c*) Calculate the atomic weights of K and Br from these data and the ratio in Table 1 [McAlpine and Bird, *J Am. Chem Soc*, **63,** 2960 (1941)]

2. The average of nine determinations of the ratio of carbon to oxygen is 0 375262 Calculate the atomic weight of carbon corresponding to this ratio, and compare it with the atomic weight from the limiting density on page 16 [Baxter and Hale, *J Am Chem Soc*, **58,** 510 (1936).]

3. The ratio $AsCl_3:3Ag$ is given as 0 56022 in *J. Am. Chem. Soc.*, **53,** 1629 (1931), and as 0 56012 in *ibid*, **55,** 1054 (1933); the ratio $AsCl_3:I_2$ is given as 0 714200 in *ibid*, **57,** 851 (1935) Should the atomic weight of arsenic be revised? (The atomic weights of silver and iodine have been unchanged for many years.)

4. Potassium chlorate contains 39 154 per cent of oxygen, and a gram of silver when converted into silver nitrate will react with 0.691085 gram of potassium chloride (*a*) Calculate the molecular weight of potassium chloride and the atomic weight of silver from these data. (*b*) Calculate the atomic weight of chlorine from that of silver just found and the ratio of silver to silver chloride given in the text. (*c*) Calculate the atomic weight of potassium from the composition of potassium chlorate and this atomic weight of chlorine.

5. Pure silicon tetrachloride was decomposed with sodium hydroxide solution, and the chloride was precipitated with silver nitrate made from weighed portions of silver. [*J. Am. Chem. Soc.*, **42,** 1194 (1920).]

Weight $SiCl_4$	Weight silver	Ratio $SiCl_4$:4 Ag
10.4353	26.4952	0.39386
5.9785	15.1830	0.39376
8.7905	22.3213	0.39381
6.8352	17.3562	0.39383

Calculate from each experiment the molecular weight of silicon tetrachloride, and calculate an average value of the atomic weight of silicon, using as the atomic weights of silver and chlorine 107.880 and 35.457. Calculate the percentage deviation of this value from that for silicon in Table 4.

6. The ratio of density in grams per liter to pressure in atmospheres at 0° for silicon tetrafluoride is

p	1.00	0.750	0.500
d/p	4.69049	4.67877	4.66705

(*a*) Determine the molecular weight of silicon tetrafluoride from these data and such others as are required in the calculation. (*b*) Calculate the atomic weight of silicon, taking the value for fluorine from Table 4. [MOLES and TORAL, *Z. anorg. allgem. Chem.*, **236,** 225 (1938).]

7. (*a*) The chloride of an element reacts with silver to form silver chloride, and in a certain experiment 3.418 grams of the chloride required 8.673 grams of silver. From this fact, what is the lower limit for its atomic weight if Ag = 107.88 and Cl = 35.457? (*b*) Given the further fact that at 1 atm. and 140°C this (gaseous) chloride has a density of about 5 grams per liter, what is the upper limit of its atomic weight? (*c*) What other facts would be required to determine its atomic weight with certainty?

8. The density-pressure ratio of phosphine gas at 0° is as follows:

Pressure, Atm.	*d/p*
1.0000	1.5307
0.7500	1.5272
0.5000	1.5238
0.2500	1.5205

Calculate the molecular weight of PH_3 and the atomic weight of phosphorous, taking the value of hydrogen from Table 4. [RITCHIE, *Proc. Roy. Soc.* (*London*), (*A*) **128,** 55 (1930).]

9. The average of 15 determinations of the ratio $POCl_3$:3Ag is given as 0.473833. Calculate the atomic weight of phosphorus from this ratio, and compare with that of Problem 8. [HONIGSCHMID and MENN, *Z. anorg. allgem. Chem.*, **235,** 129 (1937).]

10. Some of the gas-density data on nitrogen compounds are as follows:

Pressure, atm	Density at 0°				
	NH_3 (1)	NH_3 (2)	NH_3 (3)	N_2O (4)	N_2 (5)
1.000	0.77169	0.77143	0.77126	1.9804	1.25036
$\frac{2}{3}$	0.51182		0.51161	1.3164	0.83348
$\frac{1}{2}$	0.38293	0.38281	0.38282	0.9861	
$\frac{1}{3}$	0.25461		0.25458	0.6565	0.41667

On the basis of these data, should a change be made in the atomic weight of nitrogen, which for many years has been given in the international tables as 14.008? [The sources of data are (1) Moles and Batuecas, *Anales soc. españ. fis. quím.*, **28,** 871 (1930), (2) Moles and Sancho, *ibid.*, **32,** 931 (1934), (3) *J. Am. Chem. Soc.*, **55,** 1 (1933), (4) *J. chim. phys.*, **28,** 572 (1931), (5) Baxter and Starkweather, *Proc. Nat. Acad. Sci.*, **14,** 57 (1928).]

11. The ratio 2Ag : $ZnBr_2$ is 100 : 104.380, and $ZnBr_2$ contains 29.030 per cent zinc. (*a*) Calculate the molecular weight of zinc bromide, using 107.880 as the atomic weight of silver. (*b*) Calculate the atomic weights of zinc and bromine.

12. The specific heat of zinc is 0.092, and zinc oxide contains 80.311 per cent zinc. Calculate a new atomic weight of zinc, and compare with that from Problem 11.

13. The following data may be used to calculate values of the atomic weight of phosphorus: $3AgCl : PCl_3 = 100 : 31.951$, and $Ag_3PO_4 : 3AgCl = 100 : 102.704$. Calculate atomic weights of phosphorus corresponding to each of these data, and compare with the result from Problems 8 and 9.

14. (*a*) The chloride of a certain element *E* boils at 346°C under 1 atm pressure, and the density of the vapor is about 8.0 grams per liter under these conditions. What may be concluded as to the atomic weight of *E* and the formula of its chloride from these facts alone? (*b*) This chloride contains 53.60 per cent chlorine. With this additional fact what may be said of the atomic weight of *E* and the formula of the chloride? (*c*) The oxide of *E* contains 20.68 per cent oxygen. What additional information is furnished by this fact? (*d*) The specific heat of *E* is 0.033. What is the atomic weight of *E*? What are the formulas of its chloride and oxide?

15. (*a*) The chloride of an element requires 1.7853 grams of silver in solution to react with 1.0000 gram of it. What is the lower limit of the atomic weight of this element? (*b*) At 200°C and 1 atm the specific volume of this gaseous chloride is 200 ml. per gram. What is the upper limit for the atomic weight of the element? (*c*) The specific heat of the element is 0.09 cal. per gram. What is the atomic weight of the element? What is the formula of its chloride?

16. The density of chlorine (in grams per liter), the pressure (in atmospheres), and the ratio of pressure to density at 50° are as follows:

p	0.3134	0.6524	0.9893	1.605	2.0184
d	0.8410	1.756	2.673	4.361	5.509
d/p	2.683	2.692	2.702	2.717	2.789

Calculate a value for the atomic weight of chlorine from the limiting density at 50°, assuming limiting densities proportional to absolute temperatures for gases. [Ross and Maass, *Can. J. Research*, **18**, *B*, 55 (1940).]

CHAPTER II

ELEMENTARY THERMODYNAMICS

The purpose of this chapter is to outline very briefly the laws of thermodynamics and the fundamental concepts on which they are based, to derive a few thermodynamic equations that have been found useful in physical chemistry, and to stimulate those who are interested to read further.[1] As the name implies, thermodynamics relates to the flow of heat and the conversion of heat into work or, in general, the conversion of energy from one form to another form For our convenience we classify the forms of energy to be considered as heat and work, heat being that form of energy which flows under a temperature gradient, and work including the action of a force through a distance, expansion against an opposing pressure, production of electric currents, etc., in short, all forms of energy other than heat. For our further convenience we define heat as *positive* when it is *absorbed by* a system and work as *positive* when it is *done by* the system. We measure heat and work in the same units of calories or joules

By including a discussion of thermodynamics in a treatise on physical chemistry we do not imply that thermodynamics is an aspect of this field alone; for the laws apply in all fields, whether physics, engineering, or some other science; they are as general as the law of conservation of matter. But since the physical aspects of chemical changes are our chief concern, most of the applications of thermodynamics that we shall study will be illustrated by chemical reactions.

The laws of thermodynamics are powerful tools with which

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[1] See for example, STEINER, "Introduction to Chemical Thermodynamics," McGraw-Hill Book Company, Inc., New York, 1941; WEBER, "Thermodynamics for Chemical Engineers," John Wiley & Sons, Inc , New York, 1939; MACDOUGALL, "Thermodynamics and Chemistry," John Wiley & Sons, Inc., New York, 1939; LEWIS and RANDALL, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc , New York, 1923.

to show the relation of observed physical quantities to one another, but they do not of themselves specify the properties of material systems. In order to make them useful, we must supplement them with adequate experimental data or with suitable approximations when data are lacking.

Precise definitions of the terms used in thermodynamics must be given as a necessary preliminary to this outline; these definitions must be carefully read and the distinctions stated or implied in them must be carefully followed if the statements of thermodynamics are to have any clear meaning. In order to simplify these statements, certain quantities are designated by letters, as p for pressure, v for volume, T for absolute temperature, E for energy content The notation used in this outline is standard or as nearly standard as is possible,[1] and the definitions and conventions as to signs are likewise those in common use.

Definitions.—A *system* is defined as any combination of matter that we wish to study; a *closed system* is one that is not exchanging matter with any other system; an *isolated system* is one that exchanges neither matter nor energy with any other system. For convenience we usually give our attention to a single fixed quantity of matter which we designate as "the system" and call all other systems with which it may exchange energy "the surroundings"

The *state of a system* is fixed when we specify so many of its properties that all of them have definite values For example, if we specify the pressure, temperature, quantity, composition, and state of aggregation of a homogeneous (one phase) system, all its other properties, such as volume, density, and energy content, are also fixed; and the system is in a definite state Its state will also be fixed if we specify the volume in place of the pressure or the density in place of the quantity of matter But the properties most readily measured are those first listed, and they are the properties we shall ordinarily specify to fix the state of a system. If the system is of more than one phase (partly solid, partly liquid or vapor), one must specify the quantity and composition of each phase A change in one or more of the properties

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[1] The quantity which is called E in this text is sometimes designated by U, and the quantity **F** given later is designated by G in some books In Gibbs's notation, which is occasionally used, $E = \epsilon$, $H = \chi$, **F** $= \zeta$ and $A = \psi$.

of a system is a *change in state*, and of course all the properties of a system are not independently variable.

A *process* is not completely described by a change in state but is described by specifying the change in state and giving additional information as to the mechanism or how the pressure, temperature, or other property varied as the change proceeded. For illustration, a *change in state* is described by the following scheme:

$$\left.\begin{matrix}\text{10 grams air}\\ 20°,\ 5\text{ atm}\end{matrix}\right\} \rightarrow \left\{\begin{matrix}\text{10 grams air}\\ 20°,\ 1\text{ atm}\end{matrix}\right.$$

This is, moreover, an *isothermal* change in state, for the initial and final temperatures are the same But in order to describe the process we must also say whether the temperature remained constantly at 20° (which would make it an *isothermal process*) or whether the temperature varied as expansion took place and was afterward brought to 20° (which would not be an isothermal process). We must state whether the expansion was so conducted that the pressure overcome was always infinitesimally less than the pressure of the air (a *reversible process*) or whether the pressure overcome was less than the maximum (an *irreversible process*)

An *adiabatic process* is one in which no heat is exchanged between the system and the surroundings. The change in state described in the preceding paragraph could not take place adiabatically, since even during expansion into a vacuum (so that no work was done) there would be a slight change in temperature. This is not to say that air cannot expand adiabatically, but only that the initial and final temperatures will not be the same when it expands adiabatically.

Some further explanation of a *reversible process* in the thermodynamic sense will not be out of place. The isothermal operation of an electric cell against an opposing potential infinitesimally less than its own is a reversible process, or one in which the maximum amount of work is done. In general, a process is reversible when the pressure or temperature or other intensive property of the operating system differs infinitesimally from the pressure or temperature or other property of the system against which it operates. Thus an irreversible process is not one that may not be reversed—it is one that may not be reversed by infinitesimal changes in the variable properties of the system.

The transfer of heat from a body at T to a second body at $T - dT$ may be reversed by making the temperature of the second body $T + dT$, and such a process is called a reversible transfer of heat. Although, of course, no heat would pass between bodies at *exactly* the same temperature, it is customary to call the transfer reversible or isothermal when the temperature difference is infinitesimal.

A *cyclical process* is one in which the system returns to its initial state after completing a series of changes. Cycles, like other processes, may be conducted reversibly or irreversibly. In evaluating some quantities, such as heat absorbed or work done, it will be important to state whether the cycle was reversible or irreversible.

Temperature will usually be described on the absolute centigrade or Kelvin scale, on which the melting point of ice is 273.1°K. and the boiling point of water at 1 atm. is 373.1°K., and such temperatures will be denoted by T. Centigrade temperatures, based on 0° as the melting point of ice and 100° as the boiling point of water, will be denoted by t so that the boiling point of oxygen will be written $t = -183°\text{C.}$ or, more commonly, $T = 90°\text{K.}$ Thus the relation between the two temperatures is $t + 273.1 = T$. The means of determining this quantity 273.1° will be given in the next chapter.

Laws of Thermodynamics.—The "first law" of thermodynamics asserts the conservation of energy and denies the possibility of obtaining work without the expenditure of energy of some kind, the "second law" imposes some limitations on the conversion of heat into work, and the "third law" specifies the limit that one particular thermodynamic quantity approaches as the temperature approaches absolute zero. No "fourth law" has so far been suggested. We now consider the three laws in order.

The first law of thermodynamics is already familiar under the name "conservation of energy." It may be stated in a variety of ways. For example, the energy content of an isolated system is a constant, or energy is not created or destroyed in any process, or the energy content is a point function of the state of a system. If we denote by E the total energy in all forms associated with a system, any increase in the energy content of this system requires a corresponding decrease in the energy content of some other system. A fixed quantity of matter does not have a definite quantity of energy associated with it under every condition, of course, for its energy content varies with the state of the system.

A system *in a specified state* has a definite energy content; and when the system changes from state 1 to state 2, its energy content changes from E_1 to E_2 by exchange of energy with its surroundings. This may be written

$$\Delta E = E_2 - E_1 \tag{1}$$

Upon restoring the system to state 1 its energy content again becomes E_1 by another exchange of energy, which is quantitatively the reverse of the first one. In other words, the energy content of a system in a specified state is a property of the system. Hence, one form in which we may express the first law is that, in any *cycle* of changes whereby a system is restored to its initial state, the summation of the energy exchanges with the surroundings is zero. In mathematical language

$$\oint dE = 0 \tag{2}$$

and dE is an exact differential. We may also say that the energy content E is a point function of the state of a system, since ΔE depends only upon the change in state, not upon the path followed or the mechanism by which the change takes place. We have classified the several forms of energy as heat and work, and we have defined heat absorbed by the system as positive and work done by the system as positive. If we express heat and work in the same units,[1] the equations for the first law are

$$\oint dE = \oint (dq - dw) \tag{3}$$

$$dE = dq - dw \tag{4}$$

$$\Delta E = q - w \tag{5}$$

Although it is true that ΔE and hence $(q - w)$ depend upon the change in state taking place and not upon the manner in which this change is brought about, it is not true that q and w individually are independent of the manner in which the change is brought about. For example, a quantity of compressed air might expand and do useful work, or it might expand without the

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[1] The necessary conversion factors are given on p. 23.

performance of any work; but work would be required from an outside source to compress the air again, regardless of the manner of its expansion. Let the change in state be

$$\left.\begin{matrix}\text{10 grams air} \\ \text{5 atm., 20°}\end{matrix}\right\} \rightarrow \left\{\begin{matrix}\text{10 grams air} \\ \text{1 atm., 20°}\end{matrix}\right.$$

The first law states that $\Delta E = q - w$ regardless of the path; hence more heat would be absorbed by the air during the expansion in which work was produced than in the expansion in which no work was done. The first law does not state how much work such an expansion could do, nor does it give a numerical value to ΔE for this change in state; but it does state that the heat absorbed must be equal to ΔE for the process doing no work and to ΔE plus heat equivalent to whatever work is done in an expansion doing work. The system may remain at 20° during the expansion; or its temperature may change during the process; but if its final temperature is 20°, ΔE will have the same value for any path, while q and w are indefinite quantities until we specify exactly how the change occurs. It should be understood that while ΔE has a definite value for this change in state, we are unable to calculate its value from thermodynamics without the help of experimental data or suitable approximations, and we are unable to calculate q or w without information as to the exact mechanism of the expansion, whether it took place into a vacuum, reversibly against the maximum pressure that could be overcome, against the atmosphere, or in some other way, and whether the temperature remained constant throughout or varied during the expansion.

We shall see in the next chapter that for an *ideal gas*

$$\left(\frac{\partial E}{\partial v}\right)_T = 0$$

and since the deviation of air from the ideal gas law is slight in this pressure range, ΔE is *approximately* zero. From *experiments* on the expansion of air we find ΔE is slightly more than 2 cal. for this change in state. But q and w, while almost equal for the specified change in state, are not even roughly determined when ΔE is determined. If the vessel containing 10 grams of air at 20° and 5 atm. (about 1.65 liters) is connected to an evacuated vessel of such volume (about 6.6 liters) that the final pressure after isothermal expansion is 1 atm., $w = 0$ and $q = \Delta E = 2$ cal.; if the expansion takes place reversibly at constant temperature, $w = \int p\,dv = 325$ cal., and $q = 327$ cal.; if the expansion takes place isothermally against the atmospheric pressure, $w = p_e \Delta v = 162$ cal., and $q = 164$ cal.

Since the minimum amount of work that must be done upon the system to produce the change in state

$$\left.\begin{matrix}\text{10 grams air}\\ \text{1 atm., } 20^\circ\end{matrix}\right\} \rightarrow \left\{\begin{matrix}\text{10 grams air}\\ \text{5 atm., } 20^\circ\end{matrix}\right.$$

by an isothermal process is 325 cal. and the actual requirement exceeds this amount, the work done *by the system* for this change in state is $-(325 + x)$ cal., and we may set no value for x without exact knowledge of the process. For this change in state $\Delta E = -2$ cal., and therefore q will be equal to or greater than -327 cal. Thus, while E is a point function, a property of the system in a specified state, and dE is an exact differential, the quantities q and w depend upon the mechanism whereby the change takes place, and not alone upon the change in state.

We consider next another thermodynamic quantity called the enthalpy or heat content,[1] designated by H and defined by the equation

$$H = E + pv \tag{6}$$

Since E, p, and v are all properties of a specified system, H is also a property of a system, a quantity whose value is a point function of the state of the system. The change in enthalpy attending any change in the state of a system depends only upon the change

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[1] The word "enthalpy," rather than heat content, has long been used abroad for H, and its use in the United States is increasing. The term "heat content" has the unfortunate implication that a change in H requires the absorption of an equivalent amount of heat, and this is true only under certain conditions. For illustration, the isothermal expansion of a gas with the performance of work absorbs a quantity of heat nearly equivalent to the work done when the pressures involved are moderate, so that both q and w are much larger than ΔH. Some objection is raised against the word enthalpy because of its similarity in sound to entropy, which has an entirely different meaning. This is readily met by a little care in speaking. If enthalpy is accented on the second syllable (entropy being usually accented on the first syllable), no serious difficulty will arise. We shall use the terms enthalpy and heat content interchangeably in this book, but with enthalpy as the preferred word.

in state, not upon the path Such changes may be shown by the equation

$$\Delta H = \Delta E + \Delta(pv) \tag{7}$$

and for a cycle of changes $\oint dH = 0$, as was true of the energy content.

When a change in state takes place at constant pressure and without the performance of any work other than mechanical work, $w = p(v_2 - v_1)$, and $\Delta(pv) = p(v_2 - v_1)$, whence it will be seen that $\Delta H = q - w + \Delta(pv) = q$ for a *constant-pressure* change in state. Thus, in a constant-pressure reaction, for example, the heat absorbed by a chemical change is equal to ΔH. In succeeding chapters in this book, and especially in Chap. VIII, where the heat effects of chemical reactions are considered in detail, we shall use ΔH to describe the heat effects attending constant-pressure processes.

Heat Capacity.—The heat capacity of a system is the ratio of the heat absorbed to the rise in temperature attending the heat absorption, but two facts make it necessary to be more specific in the definition: (1) A given quantity of heat will not produce the same temperature rise in a system for all initial temperatures; in other words, the heat capacity is a function of the temperature. (2) For a given initial temperature the temperature rise produced by a definite quantity of heat depends upon the manner of heating, whether at constant pressure or constant volume. We define the heat capacity at constant volume as

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v \tag{8}$$

The heat capacity at constant pressure is defined by the equations

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \quad \text{or} \quad C_p = \left(\frac{\partial E}{\partial T}\right)_p + p\left(\frac{\partial v}{\partial T}\right)_p \tag{9}$$

of which the second follows from the first and the definition

$$H = E + pv$$

In the second definition $(\partial E/\partial T)_p$ is of course not C_v, which is $(\partial E/\partial T)_v$. In order to find its value we note that the energy content of a system of constant composition is a function of two independent variables, and we may take them as T and v,

$$E = f(T, v)$$

for which the total differential is

$$dE = \left(\frac{\partial E}{\partial T}\right)_v dT + \left(\frac{\partial E}{\partial v}\right)_T dv \tag{10}$$

and

$$\left(\frac{\partial E}{\partial T}\right)_p = \left(\frac{\partial E}{\partial T}\right)_v + \left(\frac{\partial E}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p$$

Upon substituting this relation in equation (9) defining C_p, we have

$$C_p = \left(\frac{\partial E}{\partial T}\right)_v + \left[p + \left(\frac{\partial E}{\partial v}\right)_T\right] \left(\frac{\partial v}{\partial T}\right)_p \tag{11}$$

Since the first term is equal to C_v, from equations (8) and (11) we find

$$C_p - C_v = \left[p + \left(\frac{\partial E}{\partial v}\right)_T\right] \left(\frac{\partial v}{\partial T}\right)_p \tag{12}$$

The second law of thermodynamics imposes certain limitations upon the flow of heat from one system to another and upon the conversion of heat into work. The limitations do not appear from the first law, which says nothing about any such restrictions so long as the quantities of energy as heat or work exchanged between systems are equivalent. As an illustration of such a restriction, if a given quantity of water at 25° be divided into two nearly equal parts, one part might be heated to 50° by cooling the other part to 0° (the slight inequality of the parts being required by the variation in heat capacity of water with temperature), and this process might occur spontaneously for anything the first law of thermodynamics has to say. A heat engine and generator immersed in a lake might deliver large amounts of electric energy at the expense of the heat energy of the water, and so long as the cooling of the lake gave a calorie to the heat engine for each 4.18 joules of electrical energy produced, the requirements of the first law would be met in the process. But these processes and numerous others are declared impossible by the second law and found to be impossible by experience.

In place of attempting to state the second law of thermodynamics in a form that will be applicable to all circumstances, we shall state several facts that together will constitute a sufficient formulation of it for the purposes of this text. (1) No work may be produced by a complete *cycle* operating in surroundings of constant temperature. (2) Heat will not flow spontaneously from an object of lower temperature to one of higher temperature. (3) When work is produced by a *cycle* operating between two absolute temperatures T_1 and T_2, the maximum amount of work to be derived from the cycle is

$$w_{\max} = q_1 \frac{T_1 - T_2}{T_1} \tag{13}$$

where q_1 is the heat absorbed at the higher temperature T_1. It will be observed that only a fraction of the heat absorbed at T_1 may be converted into work, and that the remainder is rejected at a lower temperature T_2 (4) No process is possible by which heat is changed into work without some other attending process. This attending process may be a change in the state of the system when the process is isothermal, which excludes the *cyclical* isothermal conversion of heat into work as was stated in (1) above. It may be the transfer of heat to a lower temperature, as in that fraction of the heat not converted into work in illustration (3).

Carnot's Cycle.—In order to derive the equation that limits the fraction of the heat convertible into work, let us assume that we have two very large heat reservoirs from which heat may be withdrawn or to which heat may be given. One of these reservoirs is maintained at the higher temperature t_1 and the other at the lower temperature t_2. We may assume also a working system called a "Carnot engine," *i.e.*, some system that can absorb heat and produce work or evolve heat when work is done upon it. In order to make the processes described seem real, we may suppose this engine to consist of a quantity of gas or other compressible fluid confined in a cylinder fitted with a frictionless piston, but we need make no assumptions as to the properties of the substance contained in the engine. In the "Carnot cycle," the engine passes through a series of reversible changes constituting a complete cycle, *i.e.*, such a series that at its completion the original state of the engine is restored in every particular.

During this cycle, a quantity of heat is absorbed from the reservoir at t_1, a portion of the heat is converted into work, and the remainder of the heat is rejected to the reservoir at t_2. Since in a cycle of changes $\oint dE = 0$ for the operating system by the first law of thermodynamics, the summation of the work done in all the steps of the cycle must be equal to the difference between the heat absorbed and the heat rejected. The steps in the cycle are as follows:

1. Let the working system be put into thermal contact with the heat reservoir at t_1 and withdraw a quantity of heat q_1 by a *reversible* isothermal expansion.

2. Let the system expand *reversibly* and adiabatically until its temperature falls to t_2.

3. Let the system be put into thermal contact with the heat reservoir at t_2 and give to the reservoir a quantity of heat $-q_2$, by a *reversible* isothermal compression. Note that, according to our standard convention, q is always the heat absorbed by the system, so that giving $-q_2$ cal. to the reservoir corresponds to $+q_2$ cal. *absorbed by the system at* t_2. It is inherent in the operation of a heat engine which produces work that some of the heat is rejected at the lower temperature, and q_2 is thus a negative quantity of *heat absorbed* by the system at the lower temperature.

4. Let the system be compressed *reversibly* and adiabatically until its temperature rises to t_1 and the system is restored to its initial state.

Since every stage of the cycle took place reversibly, the work obtained is the maximum obtainable by such a series of changes. The system has undergone a complete cycle, for which $\oint dE = 0$, and so by the first law,

$$w_{\max} = q_1 + q_2$$

Upon dividing both sides by q_1, we obtain as a measure of the fraction of the heat absorbed at t_1 that was converted into work

$$\frac{w_{\max}}{q_1} = \frac{q_1 + q_2}{q_1} \tag{14}$$

This measures the efficiency of the process, if we define efficiency as the fraction of the total heat convertible into work.

We now show that the efficiency of a *reversible engine* operating on a Carnot cycle depends only on t_1 and t_2. Let us suppose that, of two Carnot engines A and B operating *reversibly* between t_1 and t_2, the first, A, is more efficient. Let A perform a Carnot cycle and B a reversed Carnot cycle. We can adjust the engines so that the amount of heat $-q_2{}^A$ given to the heat reservoir at t_2 by the engine A equals numerically the heat $+q_2{}^B$ withdrawn from the reservoir at t_2 by the engine B, and, by so doing, we can restrict the heat effects to the reservoir at t_1. Since A is supposed to be more efficient, w_A will be greater than w_B, and hence by the first law $q_1{}^A$ is greater than $q_1{}^B$. If these engines are coupled together and considered as a single heat engine, the net result of one cycle will be the production of a quantity of work $w_A - w_B$ and the absorption of a quantity of heat $q_1{}^A - q_1{}^B$ from the heat reservoir at t_1. But this would constitute the conversion of heat into work by an isothermal cycle, which is declared impossible by the second law. Hence, A cannot be more efficient than B, and the efficiencies of all *reversible* engines operating between t_1 and t_2 are functions of t_1 and t_2 only. That is,

$$\frac{w_{\max}}{q_1} = \frac{q_1 + q_2}{q_1} = f(t_1, t_2) \qquad \text{or} \qquad \frac{q_1}{q_2} = f(t_1, t_2) \tag{15}$$

In this equation $q_1 + q_2$ is less than q_1, for we have already seen that q_2 is negative, since heat is always rejected at the lower temperature.

In order to make this relation quantitative, it is necessary to show what function of the temperature governs the fraction of heat converted into work and to select a scale on which to express the temperature. The simplest relation would be obtained from a temperature scale on which the fraction of the heat converted into work would also be the fractional decrease in temperature. Such a thermodynamic temperature scale would be defined by the equation

$$\frac{q_1 + q_2}{q_1} = \frac{T_1 - T_2}{T_1} \tag{16}$$

The temperature scale so defined is identical with the absolute temperature scale derived from the expansion of an ideal gas at constant pressure and already familiar from earlier work in chemistry.

The form in which this equation appears is not the usual one, but it is consistent with the conventions regarding q. The more common form designates q_1 as the heat *absorbed* at T_1 and q_2 as the heat *evolved* at T_2, so that the law then appears in one of the forms

$$\frac{q_1 - q_2}{q_1} = \frac{T_1 - T_2}{T_1} \qquad \text{or} \qquad \frac{q_1}{T_1} = \frac{q_2}{T_2}$$

It was in this form that Clausius stated it. This form emphasizes the fact that only a portion of the heat is converted into work; but its notation is inconsistent with respect to q, and it is not well adapted to a derivation of the entropy concept to which we shall come in a moment.

By combining equations (15) and (16) we obtain the desired statement of the law limiting the conversion of heat into work through a reversible cycle, namely,

$$w_{\max} = q_1 \frac{T_1 - T_2}{T_1} \tag{13}$$

This equation shows that the complete conversion of a quantity of heat into work by a cycle of changes is impossible, since this would require absolute zero for a rejection temperature. The lower temperature T_2 for the practical operation of a cyclical heat engine is the prevailing climatic temperature, which will ordinarily be between 275 and 300°K., and therefore the fraction of the heat that may be converted into work by a cycle of changes may be increased only by using higher initial temperatures. While there is almost no difficulty in obtaining temperatures much higher than the *effective* T_1 in the operation of a steam boiler (for example), there are practical difficulties in finding a suitable working material for use in the "engine" and suitable structural materials with which to build boilers and engines.

Entropy.—For the purpose of defining another useful thermodynamic function, we may put equation (16) into the form

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0 \tag{17}$$

which shows that the summation of q/T for the *reversible* cycle is zero, or, in mathematical language,

$$\oint \frac{dq_{\text{rev}}}{T} = 0 \tag{18}$$

This relation defines a function, a property of the system, which is called entropy and usually designated by S, such that

$$S = \int \frac{dq_{\text{rev}}}{T} + \text{const.} \qquad \text{or} \qquad dS = \frac{dq_{\text{rev}}}{T}$$

whence, for a change in state,

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{dq_{\text{rev}}}{T} \tag{19}$$

It should be noted that for irreversible processes $\int dq/T$ is not the entropy, or any definite quantity. This is not to say that ΔS for a system undergoing a change irreversibly is different from ΔS for the reversible process; for the value of S is a point function of the state of the system, and ΔS is independent of the path. But $\int dq/T$ is not a measure of the entropy change, and $\int dq_{\text{rev}}/T$ is a measure of the entropy change.

As an illustration, consider the change in state:

$$\left.\begin{matrix} I_2(s) \\ 386°\text{K., 1 atm.} \end{matrix}\right\} \rightarrow \left\{\begin{matrix} I_2(l) \\ 386°\text{K., 1 atm.} \end{matrix}\right.$$

for which ΔH is 3650 cal. Since the stated temperature is the melting point of iodine, the change in state takes place reversibly when iodine crystals are heated, and $\Delta S = 3650/386 = 9.54$ entropy units (usually written 9.54 e.u., meaning 9.54 cal. per mole per deg.), and for the reverse change $\Delta S = -9.54$ e.u. But if liquid iodine is undercooled to 376°K. and crystallization occurs at this temperature, the value of ΔS is not ΔH for the irreversible change divided by 376°. The difference between the entropies of liquid iodine and crystalline iodine at 376°K. may be obtained by (1) calculating ΔS for the reversible heating of crystalline iodine from 376 to 386°K. from equation (19), (2) reversible melting of the iodine at 386°K., for which ΔS has been calculated above, (3) calculating ΔS for the reversible cooling of liquid iodine from 386 to 376°K. from equation (19), and adding these three quantities. The calorimetric effect observed when undercooled iodine crystallizes, divided by 376, would not be equal to the ΔS calculated above; moreover, the temperature could not be maintained at 376°K. during the irreversible change.

The quantity S is a very important one in thermodynamics.

Although a clear concept of entropy is not to be obtained by a slight acquaintance with it, time is probably gained if cultivation of this acquaintance is begun early and continued throughout physical chemistry. Accordingly, we shall make occasional use of entropy in the calculations of this book, and the student will find many others in more advanced courses. But most beginners find it easier to understand derivations in which reversible expansion against a pressure, heat absorption, electric potential, and other familiar quantities are involved than derivations based upon the more elusive concept of entropy. Since this book is addressed to beginners in physical chemistry, it will be our usual custom to derive the equations without the use of entropy and to repeat the derivations of some of the equations using the entropy concept.

The Third Law of Thermodynamics.—A simple and almost accurate statement of this law is that the entropy of any pure crystal is zero at the absolute zero of temperature.[1] If this theorem is accepted, one may determine the entropy of a substance at any temperature by integrating equation (19) with absolute zero as the lower limit and taking S at 0°K. as zero. Through equations that will be developed in a later chapter, the entropies so obtained enable one to calculate chemical equilibrium from thermal data alone. In order to integrate equation (19) we may write it in the form

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p\,dT}{T}$$

for constant-pressure changes. If the lower limit it taken as $T_1 = 0°\text{K.}$, the heat capacity must be known as a function of the temperature to within a few degrees of absolute zero and up to the

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[1] An exact statement of the third law given by Eastman [*Chem. Rev.*, **18**, 272 (1936)] is: Any phase cooled to the neighborhood of the absolute zero, under conditions such that unconstrained thermodynamic equilibrium is attained at all stages of the process, approaches a state of zero entropy. He follows this statement with an admission that it is unnecessarily restrictive, since many constrained systems also approach zero entropy. The inaccuracy of the simple statement given above may be removed by a sufficiently stringent definition of the term "pure crystal." The definition excludes only a few substances in which we shall have no interest in this simple discussion. See Kelley, *Bulletin U S. Bur. Mines*, **434**, 3 (1941), for a discussion of these exclusions.

desired temperature. Graphical integration from a plot of C_p/T against T or of C_p against 2.3 log T over the temperature range of the data gives the entropy increase in this range. The small entropy increase in the range from 0°K to the lowest temperature at which C_p has been measured is calculated from an equation that need not concern us here,[1] since the quantity is usually not more than 0.1 e.u. C_p not only approaches zero at 0°K., but C_p/T also approaches zero at 0°K.; therefore, the molal entropies are all finite.

For a substance that has no phase transitions and does not melt below the temperature at which S is desired, the entropy is given by the equation

$$S_T = \int_0^T \frac{C_p\,dT}{T} \tag{20}$$

and for one that has no phase transitions other than fusion at T_f, the entropy of the liquid at T is

$$S_T = \int_0^{T_f} \frac{C_s\,dT}{T} + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T} \frac{C_l\,dT}{T} \tag{21}$$

in which C_s is the heat capacity of the solid and C_l the heat capacity of the liquid. For substances undergoing solid-solid transitions or that evaporate below the desired temperature, additional terms such as $\Delta H_{\text{trans}}/T_{\text{trans}}$ or $\Delta H_{\text{evap}}/T_{\text{evap}}$ must be included, and separate integrations of $(C_p/T)dT$ must be performed over the temperature ranges between transitions. It must be remembered that $S = \int dq_{\text{rev}}/T$, not $\int dq/T$, when the heating takes place irreversibly. This restriction makes it necessary to conduct the heating so slowly that no irreversible heat effects are included.

The necessary low-temperature heat capacities have now been measured for many substances, and standard entropies at 298°K. are available in sufficient quantity for calculations of numerous equilibriums through equations that will be given later.[2]

It may be profitable to repeat with emphasis a statement made at the beginning of this brief discussion: The laws of thermo-

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[1] See, for example, Steiner, *op. cit.*, Chap. XV.

[2] See, for example, Kelley, *U.S. Bur. Mines Bull*, **434** (1941), for the low-temperature heat capacities and 298° entropies of inorganic substances.

dynamics are among the most useful tools that the chemist has available. But one cannot build with tools alone, he requires materials as well, and for chemists the materials are the accumulated experimental data of physics and chemistry. For illustration, the change of entropy of a substance at constant pressure is related to the heat capacity of the substance by the equation $dS = C_p\, dT/T$, but if we have no data expressing C_p as a function of the temperature we may not integrate the equation.

Thermodynamic Properties.—The properties of a system that we have considered so far are the intensive properties, pressure p and temperature T, and the extensive properties, volume v, energy content E, enthalpy H, and entropy S. They are not, of course, the only properties of a system in a specified state, nor are they independently variable We have already had some equations that express relations among them, and presently we shall define two more quantities in terms of those listed above. In giving a definition, the usefulness of the property alone justified doing so; for example, a thermodynamic property might be defined as $X = E - pv$, in place of the enthalpy, which is defined as $E + pv$ But $E - pv$ is not a useful property for many calculations, and $E + pv = H$ is a property, independent of the path followed during a change in state, that measures the heat absorbed at constant pressure. Since most processes are conducted at substantially constant pressure, H is a useful property to define, and changes in H attending chemical reactions or other changes are useful quantities for tabulation. If the common procedure were to conduct changes at constant volume, there would be little use for the quantity H; and since there is no apparent use for a quantity defined by $E - pv$, there is no need to define it.

Two useful quantities will now be defined, the first by the equation[1]

$$A = E - TS \tag{22}$$

and a second property $\mathbf{F}$, which is related to A in the same way that H is related to E, by the equation

$$\mathbf{F} = H - TS \tag{23}$$

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[1] This A is the property that Helmholtz calls the free energy, but most American publications call the quantity $\mathbf{F}$, defined by equation (23), the free energy, following Lewis, in *J. Am Chem Soc.*, **35**, 1 (1913).

which is equivalent to $\mathbf{F} = A + pv$, since $H = E + pv$. This quantity **F** is the "Gibbs's free energy" and is written G in some books to emphasize this fact. We shall call it simply the "free energy," following Lewis and most American writers. These two definitions complete the list of thermodynamic properties that we shall have to use in this text, the full list being p, v, T, E, H, S, A, and **F**. Each of the two new definitions applies to a quantity that experience has shown to be useful. For reasons that will appear as we proceed, **F** is more convenient than A in most of the calculations of physical chemistry, and hence **F** is the quantity we shall use. If constant volume were a common procedure, A would be a more useful quantity than **F**. We turn now to some equations involving these quantities.

Some Thermodynamic Equations.—In specifying a few restrictions which we wish to impose upon the first law of thermodynamics in deriving equations applicable to reversible processes, we imply, not that there are any restrictions to the applicability of the first law itself, but only that we wish to impose some for our present convenience. We confine our attention to *reversible* changes in state taking place in closed systems in which gravitational effects are negligible, in which there are no distortional effects or electric fields large enough to be important, and in which the only form of work considered is reversible expansion at a single piston. Under these conditions $dq = dq_{\text{rev}} = T\,dS$ and $dw = p\,dv$, so that the equation for the first law becomes

$$dE = T\,dS - p\,dv \tag{24}$$

Another equation, subject to the same restrictions, is obtained by differentiating the enthalpy equation $H = E + pv$,

$$dH = dE + p\,dv + v\,dp$$

and substituting the value of dE from (24),

$$dH = T\,dS + v\,dp \tag{25}$$

In the previous section we defined the quantity A by the equation

$$A = E - TS \tag{22}$$

Differentiating,

$$dA = dE - T\,dS - S\,dT \tag{26}$$

and, by substituting the value of dE from (24),

$$dA = -S\,dT - p\,dv \tag{27}$$

For an isothermal process the first term on the right side of this equation is zero, and dA is seen to be the negative of the isothermal work,

$$dA = -dw_{\max} \qquad (t \text{ const.}) \qquad (28t)^1$$

The quantity A is sometimes called the isothermal work content, and an equation is written

$$\Delta A = A_2 - A_1 = -w_{\max} \qquad (29t)$$

which is a correct statement, subject to the condition that the process is isothermal. But it must be kept in mind that when the process is not isothermal the maximum work is not measured by ΔA, even though A is a property of a system and ΔA depends upon the change in state regardless of the path.

As has been said before, the equations involving the free energy **F** are more useful in physical chemistry than the equations involving A, or at least they are more commonly used. The definition of **F** has already been given, namely,

$$\mathbf{F} = H - TS \tag{23}$$

which gives upon differentiation

$$d\mathbf{F} = dH - T\,dS - S\,dT \tag{30}$$

Substituting the value of dH from equation (25) and canceling terms that are equal and of opposite sign,

$$d\mathbf{F} = -S\,dT + v\,dp \tag{31}$$

For isothermal expansion or compression in a system of constant composition, the first term on the right is zero, and the relation is

$$\Delta\mathbf{F} = \int v\,dp \qquad (t \text{ const.}) \qquad (32t)$$

Two other equations applicable to isothermal changes in state for which we shall have frequent use in later chapters follow from the equation defining **F**:

$$\Delta\mathbf{F} = \Delta H - T\,\Delta S \qquad (t \text{ const.}) \qquad (33t)$$

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[1] The letter t included with the number of an equation indicates the restriction of the equation to changes at constant temperature.

and

$$\Delta \mathbf{F} = \Delta A + \Delta(pv) \qquad (t \text{ const.}) \qquad (34t)$$

Most of the partial derivatives that can be formed from the thermodynamic quantities have no practical interest, but a few of them are very useful indeed. For example, the relations

$$\left(\frac{\partial E}{\partial S}\right)_v = T \quad \text{and} \quad \left(\frac{\partial E}{\partial v}\right)_S = -p$$

follow at once from equation (24) above. Relations involving four of the thermodynamic quantities may be derived almost without limit, but again very few of them are interesting. The following are some of Maxwell's relations, and they will frequently be useful:

$$-\left(\frac{\partial T}{\partial v}\right)_S = \left(\frac{\partial p}{\partial S}\right)_v$$

$$\left(\frac{\partial v}{\partial S}\right)_p = \left(\frac{\partial T}{\partial p}\right)_S$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial S}{\partial v}\right)_T$$

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial v}{\partial T}\right)_p$$

Most of the equations that have now been given will appear later as the need for them arises, and a few more will be derived in later chapters.

All the equations of thermodynamics are exact, but many of the useful ones are differential equations. Before integrating those containing more than two variables, it will be necessary to express all but two in terms of the selected two variables and to be sure that the quantities assumed constant remain constant. The necessary data for expressing the volume as a function of temperature and pressure (for example) are sometimes lacking, and an approximation must therefore be used. This is a perfectly legitimate procedure whenever one is willing to accept the errors inherent in the approximation, but the "equation" that results from combining an exact thermodynamic equation with an approximation is not strictly an equality at all. It may (and usually does) give a result that is all that is required. As an illustration, the volume of a gas at moderate pressure is very nearly $v = nRT/p$; and if one substitutes this relation into equation (32t) to calculate $\Delta\mathbf{F}$ for the expansion of a gas from p_1 to p_2 at T, the result is

$$\Delta\mathbf{F} = nRT \ln \frac{p_2}{p_1} \qquad (t \text{ const.}) \qquad (35t)$$

If both p_1 and p_2 are moderate or low pressures and if T is far from the condensation temperature, the use of this equation will give a definite value to $\Delta\mathbf{F}$ for the specified change in state, which is all that would ordinarily be required. But equation (35t) is not a "thermodynamic equation"; it is a satisfactory approximation based upon a thermodynamic equation and the *ideal* gas law.

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Problems

1. The entropy of oxygen gas at 298°K. and 1 atm. is 49.0 cal. per mole per deg. Calculate its entropy at 373°K. and 1 atm., taking

$$C_p = 6.5 + 0.001T \text{ cal. per mole per deg.}$$

for the heat capacity in this temperature range.

2. The standard entropy of $CO_2(g)$ at 298°K. and 1 atm. pressure is 51.08 and $C_p = 7.70 + 0.0053T - 0.83 \times 10^{-6}T^2$. Calculate the entropy of $CO_2(g)$ at 798°K. and 1 atm. pressure.

3. The volume of a mole of liquid water at 373°K. and 1 atm. pressure is 18.8 ml., that of a mole of water vapor under the same conditions is 30,200 ml., and the latent heat of evaporation at 373°K. is 9700 cal. per mole. Calculate ΔH and ΔE for the change in state

$$H_2O(l, 373°\text{K.}, 1 \text{ atm.}) = H_2O(g, 373°\text{K.}, 1 \text{ atm.})$$

4. Calculate $\Delta\mathbf{F}$, ΔA, and ΔS for the change in state described in Problem 3.

5. For the isothermal change in state

$$O_2(g, 298°\text{K.}, 1 \text{ atm.}) = O_2(g, 298°\text{K.}, 0.1 \text{ atm.})$$

ΔH and $\Delta(pv)$ are negligible, $pv = RT$ for the gas, and $R = 1.99$ cal./mole-°K. Calculate $\Delta \mathbf{F}$, ΔA, and ΔS for this change in state.

6. The heat capacity of solid bromine, in calories per mole per degree, changes with the Kelvin temperature as follows:

T	15	25	30	50	75	100	150	200	245	266
C_p	1.83	4 12	5 18	8 16	9 66	10 54	11 75	12 87	13.92	15 12

The molal latent heat of fusion of bromine is 2580 cal per mole at 266°K, and the heat capacity of liquid bromine is 17 cal per mole per deg. (*a*) Plot C_p/T against T for the solid, join the points with straight lines (as a sufficient approximation for illustrating the integration), and determine S_{266} for $\mathrm{Br}_2(s)$ (*b*) Determine S_{298} for $\mathrm{Br}_2(l)$ [Data from LATIMER and HOENSHEL, *J. Am. Chem Soc.*, **48,** 19 (1926)]

7. The atomic heat capacity of silver changes with the Kelvin temperature as follows:

T . . .	15	40	50	60	80	100	150	200	250	298
C_p	0 160	2 005	2.784	3 420	4 277	4 820	5 490	5 800	5 989	6.092

Plot C_p/T against T for each of these temperatures, join the points by straight lines (as a sufficient approximation to illustrate the method of integration), and determine the entropy of silver at 298°K. [Meads, Forsythe, and Giauque, *J Am Chem Soc*, **63,** 1902 (1941), find 10 21 from an exact treatment of this and other data]

8. Calculate the entropy of diamond at 298°K from the heat-capacity data in Table 23.

CHAPTER III

PROPERTIES OF SUBSTANCES IN THE GASEOUS STATE

This chapter will present first the simple equations that approximately describe the behavior of gases and gas mixtures at low or moderate pressures and then the more complex equations that apply at higher pressures. Through these laws we establish the temperature scale, determine molecular weights, estimate heat capacities, measure chemical equilibrium and the rates of reactions, and obtain other important information. The "ideal gas" will receive due attention, and we shall emphasize the important fact that "ideal" gas behavior is approached but not attained, as is true of almost any ideal; that the concept of an ideal gas is useful under certain conditions and a source of hazard if carried outside the bounds of its applicability. The ideal gas law usually does well enough when applied at pressures near or below atmospheric pressure, it *may* do well enough at higher pressures, but it may also be in error by 50 per cent or more at 50 atm. pressure.

A gas is a fluid that distributes itself uniformly throughout any space in which it is placed, regardless of the amount of gas or space so long as the space is large enough to prevent partial condensation to liquid. Thus a substance may or may not be a gas, according to the conditions of temperature and pressure; a more accurate expression would be "a substance in the gaseous state." It is this phrase that is to be understood when the word gas is used. All the substances that we ordinarily call gases have been liquefied and solidified by suitable reduction in the temperature. Many of the common liquids and solids may be changed to the gaseous state at high temperature and at low pressures. The common metals, most metallic halides, and many simple organic compounds are readily changed to gases by heating; but salts of oxygenated acids, complex organic compounds and metallo-organic compounds usually decompose before their vapor pressures reach 1 atm.

Mixtures of two or more kinds of molecules exhibit in the gaseous state most of the physical properties of a gas containing only one kind of molecules; they follow the laws that describe the behavior of single gases and may usually be treated as a single gas. For example, in its *physical* properties dry air at low pressures acts as if it were a single substance of molecular weight 29 at all temperatures above 100°K.

Structure of a Gas.—The fact that a small quantity of liquid yields a very much larger volume of vapor at the same temperature and pressure is evidence that the molecules in the vapor are separated from one another by distances that are large compared with the diameters of the molecules Eighteen grams of liquid water occupies 18 8 ml in the liquid state at 100° and 1 atm. pressure, but these same molecules occupy about 30,200 ml when changed to a gas at this temperature and pressure. Thus in the gaseous phase[1] the volume available for the use of each molecule is about 1600 times what it was in the liquid state. We do not believe that the volume of the molecules has changed to any great extent during evaporation, but only that the free space around them is larger. This will be taken up in more detail in connection with the kinetic theory of gases later in this chapter.

The molecules of a gas are not stationary but are moving about in space with very high velocities. They collide with each other frequently and strike the walls of the containing vessel, giving rise to the pressure exerted by the gas If the volume of a gas is increased, the number of molecular impacts on a given area is decreased, a smaller number of molecules strikes any area

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[1] The homogeneous parts of any system that are separated from one another by definite physical boundaries are often called its *phases* For example, ice, liquid water, and water vapor are the phases, or states of aggregation, common to water A solution is a single phase because there are no visible boundaries between solvent and dissolved substance. A mixture of several gases constitutes a single phase; for gases mix in all proportions, and there is no physical boundary between one gas and another A mixture of crystals forms as many phases as there are kinds of crystal present, since each is divided from the others by definite boundaries. When a single solid substance is capable of existing in two different crystalline modifications, each of these is considered a separate phase. Rhombic and monoclinic sulfur, red phosphorus and yellow phosphorus, gray tin and white tin are familiar examples of pure substances forming two definite solid phases, though many others also exhibit this property.

of the wall in a given time, and the pressure decreases. The pressure of a gas at constant volume increases as the temperature rises, which means that there are more collisions of the molecules with the walls in a unit of time and hence that the velocity of the molecules increases at higher temperatures. The pressure exerted by a gas does not decrease with time; therefore, the collisions between molecules are perfectly elastic, and no decrease in average velocity results from a collision. The "empty space" between molecules bears some resemblance to that between the spokes of a rapidly revolving wheel. The spokes do not fill all the space in which they revolve, but the whole of this space is effectively occupied, so that nothing else can be kept in it. In the same manner, other molecules cannot be inserted into the "empty" space between molecules without increasing the number of collisions and hence the pressure of the gas.

The treatment of gases at moderate pressures and at temperatures well removed from their condensation points is comparatively simple, for all of them have properties in common, which are expressed approximately by a few simple laws.

Boyle's law states that at any constant temperature the volume occupied by a quantity of gas is inversely proportional

TABLE 5.—PRESSURE-VOLUME RELATIONS OF HELIUM[1] AT 0°

Pressure, mm. of Hg	Volume, cc.	pv product	Per cent deviation from average (56,580)
837.63	67.547	56,579	−0.0018
794.81	71.191	56,583	+0.0056
761.56	74.293	56,579	−0.0018
732.17	77.278	56,581	+0.0018
613.09	92.279	56,575	−0.0087
561.40	100.777	56,576	−0.0071
520.37	108.720	56,575	−0.0087
462.54	122.320	56,576	−0.0071
310.31	182.341	56,582	+0.0036
237.84	237.895	56,581	+0.0018
169.48	333.881	56,586	+0.0105
147.16	384.539	56,589	+0.0159

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[1] BURT, *Trans. Faraday Soc.*, **6**, 19 (1910). Baxter and Starkweather confirm Boyle's law for helium at 0° from their densities, 0.17845 gram per liter at 1 atm., and 0.08923 at 0.50 atm. [*Proc. Nat. Acad. Sci.*, **12**, 20 (1926).]

to the pressure exerted upon it, provided that the composition of the gas does not change through dissociation or polymerization when the pressure changes. Very careful experiments have shown that the law is not exact but is a limiting law that describes the behavior of a gas more closely as the pressure decreases. At pressures near or below atmospheric, the deviations from Boyle's law are quite small for most gases, as may be seen from Table 5 and the limiting-density data in Chap. I. At 0°C. the *pv* product for CO_2 at ½ atm. is 1.0033 times that for 1 atm., and the *pv* product for oxygen at ½ atm. is 1.00047 times the value for 1 atm. The *pv* products for some other gases are shown in Fig. 3 and Table 6 in both of which *pv* is taken as unity at 0°C. and 1 atm. pressure.

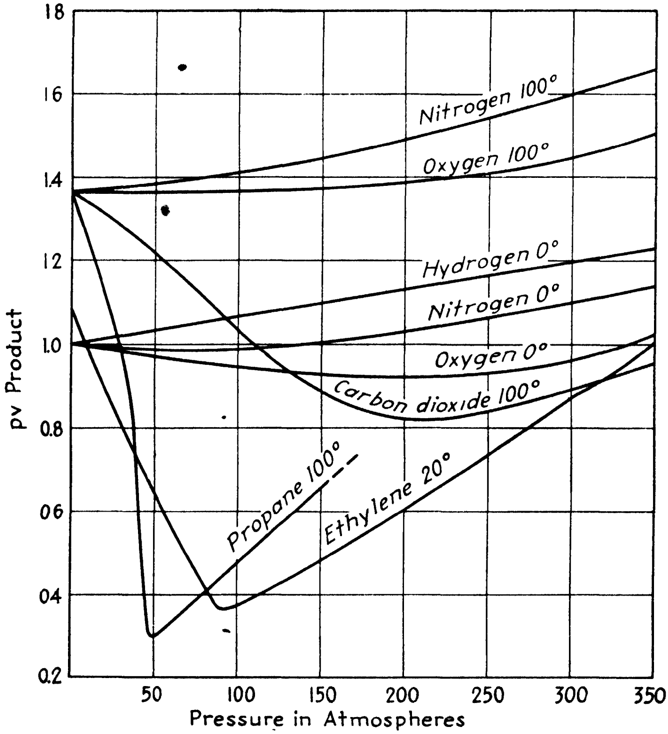

FIG. 3.—Deviations from Boyle's law at high pressures.

The *pv* product for most gases at constant temperature at first decreases with increasing pressure, then passes through a minimum, and finally increases with increasing pressure; but for hydrogen and helium the *pv* product increases with increasing pressure without passing through a minimum when the constant temperature is above room temperature. At low temperatures the *pv* products for these gases also pass through minima.

TABLE 6.—CHANGE OF *pv* PRODUCT WITH PRESSURE[1]
($pv = 1\ 000$ at 0° and 1 atm)

p, atm.	Oxygen		Carbon dioxide	Hydrogen		Ethylene		Nitrogen	
	0°	100°	100°	0°	100°	20°	100°	0°	100°
1	1 000	1 368	1 372	1 000	1 366	1 082		1 000	1 367
50	0 959		1 206	1 033	1 403	0 629	1 192	0 985	1 389
100	0 926	1 375	1 030	1 064	1 436	0 360	1 005	0 985	1 411
150			0 878			0 485	0 924		
200	0 914	1 400	0 815	1 134	1 511	0 610	0 946	1.036	1 496
300	0 963	1 453	0 890	1 205	1 584	0 852	1 133	1 136	1 597
400	1 051	1 532	1 039	1 276	1 656	1 084	1 356	1 256	1 711

There is for every gas a temperature, called the Boyle temperature, above which $[\partial(pv)/\partial p]_T$ is positive and below which it is negative, as the pressure approaches zero. Thus, at the Boyle temperature the plot of *pv* against *p* for constant temperature is horizontal at its lowest pressures, but this is not to say that it is horizontal at high pressures.

When gases with more complex molecules are studied, the deviations from Boyle's law become much larger. We quote the data for ethyl ether[2] at 300°C. as an illustration of this fact.

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[1] Quoted from "International Critical Tables," Vol III, pp. 9*ff*.

[2] BEATTIE, *J. Am. Chem Soc* , **49,** 1128 (1927) Data for other substances may be found in the "Landolt-Bornstein Tables"; in the *Communications of the Physical Laboratory of the University of Leiden* in Holland (available in English); in the tables published by the Smithsonian Institution; in Vol. III of the "International Critical Tables"; and in *Proc. Am. Acad. Arts Sci.*, **63,** 229–308 (1928). Bartlett [*J Am. Chem. Soc* , **52,** 1363 (1930)] carries experiments on N_2, H_2, and the mixture $N_2 + 3H_2$ to 1000 atm Data are sometimes presented in "Amagat units," in which the unit is the mass of 1 liter at 0° and 1 atm. pressure, or in "Berlin units," in which the unit volume is at 0° and a pressure of 1 meter of mercury.

(It should be noted that the *pv* product for a mole of ideal gas at 300°C. is 47.0, for comparison with the *pv* product in the last line of the table.)

Pressure, atm	16 732	19 276	22 708	27 601	35 194	48 430
Molal volume, liters	2 593	2 222	1 852	1 482	1 111	0 741
Product	44 38	42 83	42 05	40 89	39 10	35 87

At 300°C. and pressures of 1 atm or less, ether vapor conforms to Boyle's law within 1 per cent; at lower temperatures and these same high pressures, its deviations are greater than those shown above.

Law of Gay-Lussac (or Charles).—When a quantity of gas at an initial low pressure is heated at constant volume, the pressure is a linear function of the temperature. For example, if the pressure were 0.100 atm. at 0°, it would be 0.1366 atm. at 100° for a gas that was ideal and very nearly this pressure for all gases that are chemically stable. The increase of pressure per degree is 0.00366 of the pressure at 0°, for any low pressure; and since the reciprocal of this quantity is 273, the pressure at any temperature *t* is $(273 + t)/273$ times the pressure at 0°. This law, like Boyle's law, is a limiting law that becomes exact as the gas pressure becomes very small For "permanent" gases near atmospheric pressure, it is in error by less than 1 per cent, but it may be largely in error at high pressures. Some data are given in Table 6.

The important point to be noted is that this same coefficient applies to *all gases* that are chemically stable. Other materials such as solids also have nearly linear temperature coefficients of expansion, but they are different for different substances. But nitrogen, hydrogen, helium, ammonia, *every gas* increases its pressure at constant volume and a low pressure by 36.6 per cent of the pressure at 0° when heated to 100°. Since the pressure increase is due to an increased energy of a fixed number of molecules with increasing temperature, the convergence of all the energies toward zero at the same temperature (−273°C.) indicates that this is a temperature of "absolute" zero in the sense that no temperature can be lower. Since the temperature scale based on gas behavior, as defined in the next section, coincides with the "thermodynamic" temperature scale defined from Carnot's cycle on page 40, it is necessary to fix the position of the ice point on this scale with precision.

Determination of the "Ice Point" on the Absolute Scale.—The *ice point* is defined as the temperature at which ice and water saturated with air are in equilibrium at 1 atm. pressure, and the *steam point* is defined as the temperature at which liquid water and water vapor are in equilibrium at 1 atm. pressure. On the centigrade scale the interval between them is defined as 100°. In order to fix these points on an absolute scale through the properties of an ideal gas, we define α_v as $(p_{\text{steam}} - p_{\text{ice}})/p_{\text{ice}}$, which is the fractional increase of pressure at constant volume for the fundamental interval of 100°. Since this quantity varies with the pressure at 0° for an actual gas, the expansion coefficient is plotted against the pressure at the ice point and extrapolated to zero pressure. The following figures[1] are for nitrogen, with the pressure in meters of mercury:

p	0 99959	0 75117	0 60020	0 45032	0 33409	zero
α_v	0 3674118	0 3670689	0 3668750	0 3666780	0 3665327	(0 3660852)

The reciprocal of the extrapolated value of α_v is 2.7316; therefore, $100/\alpha_v$ is 273.16, which is the temperature of the ice point on the gas scale. It is the figure that is added to centigrade temperatures to convert them into absolute temperatures. Although this is sometimes called the value of absolute zero, there is no implication that such a temperature has been reached; and the experiments on which the value is based were performed at 0 and 100°C. The mean value of all experiments made since 1900 to determine the ice point is 273.16.

Since the fundamental interval between the ice point and the steam point is 180° on the Fahrenheit scale, absolute zero on this scale is $180/0.366085 = 491.69°$ below the ice point; and since the ice point is 32°, Fahrenheit temperatures are converted to absolute or "Rankine" temperatures by adding 459.69° to the Fahrenheit reading.

The absolute centigrade temperature scale, which is defined as proportional to the pv product of an ideal gas and which is very nearly proportional to the pv product for actual gases at low

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[1] Beattie, "Symposium on Temperature of the American Institute of Physics," p 74, 1940. Other less precise data for other gases support these figures at the limit; for example,

Pressure, atm	10	5	1	Limit
α_v for helium	0 3635	. . .	0.3658	0 3661
α_v for oxygen	0 3842	0 3752	0 3679	0 3660

pressures, is often called the Kelvin scale in honor of the celebrated physicist. Although Kelvin's originally defined scale was the thermodynamic scale, which is proportional to the fraction of heat convertible into work in a reversible cycle, these scales are identical. We shall use the terms 273.16° abs. and 273.16°K. interchangeably in the text to indicate the temperature at which ice and water saturated with air are in equilibrium at 1 atm. pressure. In this book the usual custom of denoting temperatures is followed, centigrade temperatures by t, and absolute temperatures by T. Thus $T = 273.16 + t$; and unless the highest precision is required, we shall be content to write $T = t + 273$ as an adequate figure.

Measurement of Temperature.—If a quantity of gas at constant volume has a pressure p_0 in melting ice, a pressure p_{100} when surrounded by water boiling at 1 atm., and a pressure p_t at some other temperature t, then this temperature may be determined from the equation

$$t = 100 \frac{p_t - p_0}{p_{100} - p_0} \qquad (v \text{ const }) \qquad (1a)$$

A corresponding set of measurements of the volume of a quantity of gas at constant pressure at the two standard temperature points and at temperature t leads to the expression

$$t = 100 \frac{v_t - v_0}{v_{100} - v_0} \qquad (p \text{ const.}) \qquad (1b)$$

If the actual gases were ideal gases, these scales would be identical and each would give exact temperatures. But pressure measurements on actual gases at constant volume do not yield exact absolute temperatures, nor do they give quite the same temperatures as the constant-pressure scale. Adequate, but rather complex, means are available for correcting these measurements so that their readings yield correct temperatures. On the absolute scale, these relations may be written

$$\frac{T}{T_0} = \frac{v}{v_0} \; (p \text{ const.}) \qquad \text{or} \qquad \frac{T}{T_0} = \frac{p}{p_0} \; (v \text{ const.}) \qquad (1c)$$

These scales are known, respectively, as the constant-pressure gas scale and the constant-volume gas scale. They both give true absolute temperatures to within small fractions of a degree. It should be noted that equation (1c) is true only if the expansion per degree is $1/273$ of the volume at zero. This is not true of equation (1*a*), in which it is necessary only that the temperature coefficient of pressure increase at constant volume is linear throughout the temperature range; *i.e.*, it is necessary only that $p = kt + a$; equation (1*c*) requires that a is $273k$.

If m is the measure of any property of a substance that changes linearly with temperature, its value is m_0 at the ice point, m_{100} at the steam point, and m_t at any temperature. Then the temperature is defined by an equation similar to (1*a*) above, namely,

$$t = 100\frac{m_t - m_0}{m_{100} - m_0} \tag{1d}$$

But since such a property is hard to find (actually none is known that is *exactly* linear), all thermometric scales require slight corrections when high precision is desired. The corrections are smaller for the gas scale over a wide range than for most other thermometric substances. For illustration, if nitrogen gas at 1000 mm. and 0°C. is used to measure temperatures through equation (1*a*), when the thermometer indicates 473.00° the Kelvin temperature is 472.975°; when the thermometer indicates 873 00° the Kelvin temperature is 872 75°. The correction at 473°K. for a platinum resistance thermometer would be about 4.3° and for a mercury thermometer something like 2°, depending upon the glass used in its construction.

We shall see in the next chapter that the vapor pressure of a pure liquid is a function of the temperature alone, and thus a vapor-pressure thermometer is another means of measuring temperatures. But since the vapor pressure is very far from a linear function of temperature, the scale will not be linear. For example, the vapor pressure of water changes more between 99 and 100° than it does between 0 and 25°; and so an equation of the form given in (1*d*) would be quite unsuitable. (The actual relation is nearly $\log p = A/T + \text{const.}$)

Certain other "fixed points" on the thermometric scale have been established by international agreement for the purpose of calibration, such as 90.19°K. for the boiling point of oxygen; 32.38°C., or 305.54°K., for the transition point of $Na_2SO_4.10H_2O$; 444.60°C., or 717.76°K., for the boiling point of sulfur.[1]

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[1] See Burgess, *J. Research Natl. Bur. Standards*, **1**, 635 (1928), for other fixed points and a discussion of the international thermometric scale.

Ideal Gas Law.—By combining the two laws just given we obtain the equation

$$\frac{pv}{T} = \text{const.}$$

in which the numerical value of the constant depends on the units chosen for expressing p and v and on the quantity of gas under consideration If we take a mole of gas as the standard quantity, then the numerical value of the constant in a given set of units is independent of the nature of the gas and is usually denoted by R. The equation then becomes, for one mole of ideal gas,

$$pv_m = RT \tag{2}$$

This equation is part of the definition of an ideal gas, and it is also an approximate relation for actual gases. Equation (2) alone is not a full definition of the ideal gas, and therefore we give here for the sake of completeness the remaining equations that complete the definition

$$\left(\frac{\partial E}{\partial v}\right)_T = 0 \qquad \text{or} \qquad \left(\frac{\partial H}{\partial p}\right)_T = 0 \tag{3}$$

Our discussion of this part of the definition will come later in this chapter after we have considered equation (2) further. A *mole* of gas is chosen as a unit in preference to a gram, since the molecular weight of any gas occupies the same volume as the molecular weight of any other gas. Engineers commonly use 1 lb. of gas as the unit quantity in their calculations and employ a different constant for each gas. This is less convenient than the use of molal quantities, which require the same constant for all gases.

Since the volume of n moles of gas is obviously n times the volume of one mole, the equation may be written to describe the behavior of any quantity of gas in terms of the one constant R.

$$pv = nRT \tag{4}$$

The numerical value of the ideal gas constant R depends only on the units chosen to express p and v. It should be noted that R has the dimensions of work, since the product pv is force per unit area × volume, or force × distance; and the quantities n

and T are numbers.[1] Suppose a cylinder of area a, is fitted with a tight piston. When this piston moves through a distance h against a pressure of p on each square centimeter of the piston, the force exerted is pa and it acts through the distance h; but since ah is the volume of the cylinder, pah is pv and this has the dimensions of work.

The *limiting* density (ratio of density to pressure at very low pressure) for oxygen was given as 1.42767 grams per liter at 0° on page 15, and from this value the molal volume of oxygen in the state of an ideal gas at 0° and 1 atm. is

$$32.000/1.42767 = 22.414 \text{ liters}$$

Hence, the pv product of an ideal gas is 22 414 liter-atm. per mole at 0°, and this is equal to RT, whence $R = 22.414/273.16$, or

$$R = 0.08206 \text{ liter-atm./mole-°K.}$$

The *actual* density of oxygen at 0° and 1 atm. corresponds to a molal volume of 22 394 liters, and upon dividing this pressure-volume product by 273.16 we obtain $R = 0.08198$ by applying the ideal gas law to a gas that deviates slightly from the ideal. For most calculations R may be rounded off to 0.082 liter-atm. per mole per deg. When pressure is expressed in dynes per square centimeter, the ideal constant is

$$R = 8.315 \times 10^7 \text{ ergs/mole-°K.}$$

When the pressure is in atmospheres and the volume is in milliliters per mole,[2]

$$R = 82.06 \text{ ml.-atm /mole-°K.}$$

We record for later use two other values,

$$R = 8.315 \text{ joules/mole-°K.}$$

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[1] The usefulness of equation (4) is not confined to the c g s. system of units. Pressure may be expressed in pounds per square foot and the quantity of gas in pound-moles As explained on p 57, $t_F + 460 = T_R$, where the subscript R indicates the Rankine, or Fahrenheit absolute, scale. Using this absolute scale, with pressure in pounds per square foot, volume in cubic feet, and quantity of gas in pound-moles, the value of the constant R in equation (4) is 1544 ft.-lb./lb.-mole-°R

[2] A milliliter-atmosphere is the work necessary to move a piston of 1 sq. cm. area through a distance of 1 cm. against a pressure of 1 atm. One small calorie is equivalent to 41.3 ml -atm.

and

$$R = 1.987 \text{ cal./mole-}^\circ\text{K.}$$

Equation (4) describes the behavior of most gases under moderate variations in pressure and temperature with an accuracy of about 1 or 2 per cent. An *ideal gas* is one the behavior of which would be exactly in accordance with this equation. No such substance is known, but all actual gases approach the condition of the ideal gas more closely as the pressure decreases and as the temperature increases. The "ideal gas" is thus the limiting condition for all gases, and equation (4) is called the ideal gas law or ideal gas equation. The term "perfect gas" is also commonly employed in this connection, but "ideal" serves to keep constantly before us the imaginary character of such a substance. In a later section we shall consider gases under conditions of high pressures and at temperatures near the condensation point, where the ideal gas law applies only roughly. But for calculations at temperatures well removed from condensation points and at moderate pressures (up to 5 atm , for example) the deviations of gases from the equation $pv = nRT$ are commonly less than 2 per cent, though they may be greater for some gases.

The fact that conformity to the ideal gas law improves with increasing temperature is well illustrated by the data for propane,[1] which are plotted in Fig. 4. Propane ($CH_3CH_2CH_3$) boils at about −42°C., so that all the curves are for temperatures above the boiling point but not above the condensation temperature for some of the pressures. For example, propane condenses to a liquid at 28 atm. and 80°C., and the sharp minimum in the curve for 100°C. is very close to the critical temperature and pressure above which no condensation is possible. At 60 atm. and 100°C. the value of pv/RT for a mole of propane is only 0.25; at 60 atm. and 325°C. it is about 0.92. Since thermal decomposition of propane is observed at about 350°, the experiments could not be carried to higher temperatures.

Large deviations from the ideal gas law at low pressures usually indicate a change in the number of moles present. Of course, equation (4) cannot be expected to describe the changes of p or v with T if the number of moles present is also changing.

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[1] DESCHNER and BROWN, *Ind. Eng. Chem.*, **32**, 836 (1940).

For example, phosphorus pentachloride vapor partially decomposes according to the equation $PCl_5 = PCl_3 + Cl_2$, and the extent of the dissociation depends upon the temperature and pressure. On the other hand, simultaneous measurements of p, v, and T for a weighed quantity of such a material afford a means of determining the number of moles present for these conditions. A numerical example is given in a later paragraph. Such apparent "deviations" are only examples of the misapplication of a law to conditions for which it was not derived and to which there is no reason to expect it to apply.

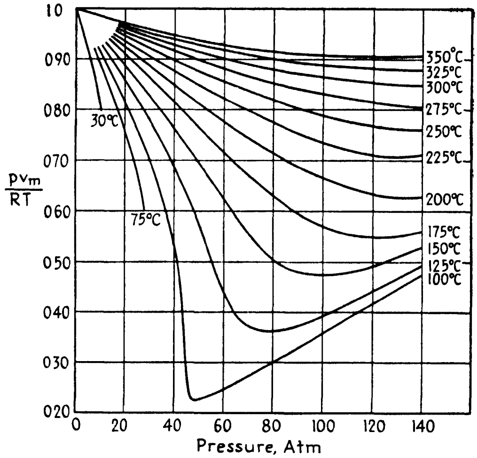

FIG 4 —p-v-T relations of propane.

Mole Fraction.—A common method of expressing the composition of a mixture is in terms of the number of moles of each substance present, divided by the total number of moles of all substances present. As an example, the composition of the earth's atmosphere may be computed in terms of the mole fractions of the constituents. Analysis shows that 100 grams of dry air contains 23.25 grams of oxygen, 75.5 grams of nitrogen, and 1.24 grams of argon. On dividing each of these weights by the molecular weight of the substance we find 0.727 mole of oxygen, 2.70 moles of nitrogen, and 0.032 mole of argon, a total of 3.459 moles in 100 grams of air. The mole fraction of oxygen is $0.727/3.459 = 0.210$, that of nitrogen is $2.70/3.459 = 0.781$, and that of argon is $0.032/3.459 = 0.009$.

At 20°C. and 1 atm. pressure the volume of 32 grams of oxygen is 24 liters. By mixing 6.76 grams of oxygen, 21.88 grams of nitrogen, and 0.36 gram of argon a total volume of 24 liters at 20° and 1 atm. is obtained, and the mixture has properties identical with air. The mixture contains 0.210 mole of oxygen, 0.781 mole of nitrogen, and 0.009 mole of argon, a total, therefore, of 1 mole. We may thus properly speak of this 24 liters of air as a mole of air, though it contains less than a mole of any one substance. By multiplying the number of moles of each substance in a mole of air by its molecular weight and adding, we find that a mole of air weighs 29.0 grams. This "molecular weight of air" is useful in applying the ideal gas law to air and in calculating molecular weights of gases from the densities expressed as multiples of the density of air under the same conditions. For most approximate calculations it is sufficient to assign air the composition 0.21 mole of oxygen and 0.79 mole of nitrogen, since both nitrogen and argon are chemically inert.

As one more illustration, we shall consider a mixture of 0.18 mole of hydrogen, 0.31 mole of iodine vapor, and 1.76 mole of hydrogen iodine, a total of 2 25 moles of gas. In this mixture the mole fraction of hydrogen is $0.18/2.25 = 0.080$, that of hydrogen iodide is $1.76/2.25 = 0.782$, and that of iodine vapor is $0.31/2.25 = 0.138$.

Gas Dissociation.—The extent of dissociation (or of polymerization, or of reaction in general) in a gas mixture at moderate or low pressure may often be determined from the pressure, volume, and temperature of a known quantity of mixture of known initial composition. For example, the density of phosgene and its dissociation products at 823°K. and 1 atm. total pressure is 0.820 gram per liter, and the calculated density of undissociated phosgene is 1.475 grams per liter under these conditions. This actual density is sometimes called an "abnormal" density or a "deviation" from the ideal gas law. It is neither an abnormality nor a deviation, but the density of a mixture formed through the incomplete chemical reaction

$$COCl_2(g) = CO(g) + Cl_2(g)$$

which increases the number of moles for a given weight and so leads to an increase in volume and a decrease in density for a given pressure and temperature. The measured density affords a means of determining the extent of the dissociation. Consider one mole of undissociated $COCl_2$, which is 99 grams, as a working basis, and let x be the moles of CO formed. From the chemical equation we see that x is also the moles of Cl_2 formed and the number of moles of $COCl_2$ decomposed, and so the composition of the mixture is

$$\begin{array}{rl} x = & \text{moles CO} \\ x = & \text{moles Cl}_2 \\ 1 - x = & \text{moles COCl}_2 \\ \hline 1 + x = & \text{total moles from 99 grams} \end{array}$$

The volume of 99 grams of mixture of density 0.82 gram per liter is $99/0.082 = 120.7$ liters, and upon substituting into $pv = nRT$ we have

$$1 \times 120.7 = (1 + x)0.082 \times 823$$

whence $x = 0.80$, and this is the fraction of phosgene dissociated at this temperature and pressure.

Any material basis for the calculation will serve as well as any other, and we might have used 0.82 gram or $0\ 82/99 = 0.0083$ mole of $COCl_2$ in 1 liter for the calculation. The composition of the mixture is

$$\begin{array}{rl} y = & \text{moles CO} \\ y = & \text{moles Cl}_2 \\ 0.0083 - y = & \text{moles COCl}_2 \\ \hline 0.0083 + y = & \text{total moles per liter} \end{array}$$

From the ideal gas law we find 0.0149 mole per liter at 823°K. and 1 atm., whence $y = 0.0066$ and the fraction dissociated is $0.0066/0.0083 = 0.80$ as before.

One more illustration will serve to show that the choice of a material basis for calculation is merely one of convenience. At 823°K. and 1 atm. a molal volume of gas is 67.4 liters, and $67.4 \times 0.82 = 55.2$ grams per molal volume. In this volume we have

$$\begin{array}{rl} z = & \text{moles CO} \\ z = & \text{moles Cl}_2 \\ 1 - 2z = & \text{moles COCl}_2 \end{array}$$

Upon multiplying each of these quantities by the appropriate molecular weight, we obtain as the weight of a mole of mixture $28z + 71z + 99(1 - 2z) = 55.2$ from which we find $z = 0.445$ mole CO and Cl_2 and $1 - 2z = 0.11$ mole $COCl_2$; and the fraction dissociated is $0.455/(0.455 + 0.11) = 0.80$ at 823°K. and 1 atm. total pressure. At some other temperature and pressure the method would be the same, though the fraction dissociated would not be 0.80, but another value.

Since this method in any of its forms depends upon measuring the total moles of gas in a mixture through the ideal gas law, it is obviously not applicable to reactions in which there is no change in the number of moles. Dissociations such as $2HI = H_2 + I_2$ and $2NO = N_2 + O_2$ must be measured in some other way.

Partial Pressures.—The partial pressure of a gas in a mixture is defined as the product of its mole fraction and the total pressure of the mixture. If p is the total pressure on a mixture of several components, a, b, c, . . . , whose mole fractions are x_a, x_b, x_c, . . .

$$p_a = px_a \qquad p_b = px_b \qquad p_c = px_c \tag{5}$$

In the dissociation problem treated at the top of page 65, the partial pressure of phosgene was $p(1 - x)/(1 + x)$, for example. In any mixture of gases the ratio of the partial pressures is thus the ratio of the number of moles of each in the mixture, or

$$\frac{p_1}{p_2} = \frac{n_1}{n_2}$$

Dalton's law states that the total pressure of a mixture of gases is equal to the sum of the pressures of the separate component gases when each is at the temperature and each occupies the total volume of the mixture. The pressures of the separate pure gases are called the Dalton pressures.

Suppose the three bulbs A, B, and C of Fig. 5 to be of equal volume v and filled with n_O moles of oxygen, n_N moles of nitrogen, and n_H moles of hydrogen, respectively, at the temperature T. Now let the stopcocks a and b be opened and the whole mixture be forced into the bulb A. The pressures p_O, p_N, p_H of the unmixed gases can be computed by the ideal gas law to be

$$p_O = \frac{n_O RT}{v} \qquad p_N = \frac{n_N RT}{v} \qquad \text{and} \qquad p_H = \frac{n_H RT}{v}$$

By Dalton's law, the pressure p of the mixture in the bulb A is the sum of the pressures of the unmixed gases.

$$p = p_O + p_N + p_H = (n_O + n_N + n_H)\frac{RT}{v}$$

Thus the equation for a mixture of ideal gases has exactly the same form as that for a pure gas. From the relations given, we see that each partial pressure is the product of mole raction and total pressure,

$$p_O = px_O \qquad p_N = px_N \qquad p_H = px_H$$

For ideal gases the Dalton pressure of a gas in a mixture is equal to its partial pressure; for mixtures of real gases at low pressure they are approximately equal.[1]

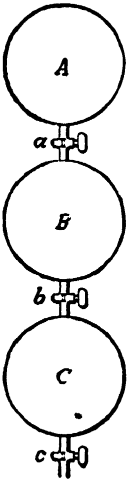

FIG. 5.

It has been possible to find a few materials that allow the free passage of the molecules of one gas but not of other gases and so to measure partial pressures directly. Thus Ramsay[2] found that when a palladium bulb filled with nitrogen at 280° was surrounded by a stream of hydrogen the pressure within the bulb increased almost as much as the total pressure of hydrogen outside of the bulb. His experiments were not continued until equiibrium was attained, and the partial pressure of hydrogen within the palladium bulb never reached the total hydrogen pressure outside. In a series of rather hasty experiments, he found that the partial pressure of hydrogen inside the bulb varied from 87 to 98 per cent of the pressure outside and that the actual figure depended somewhat upon the condition of the palladium.

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[1] For a thermodynamic treatment of gas mixtures we are interested in the equilibrium pressure of a gas in a mixture [Gillespie, *J. Am. Chem. Soc.*, **47**, 305 (1925)]. The equilibrium pressure of a gas is the pressure that it would exert through a membrane permeable to it alone. For mixtures of deal gases the equilibrium pressure is equal to the partial pressure; for mixtures of real gases at low pressure they are approximately equal.

[2] *Phil. Mag.*, **38**, 206 (1894).

Lowenstein[1] made use of the permeability of platinum to hydrogen at higher temperatures in studying the extent of dissociation of water vapor. A platinum tube connected to an oil manometer was surrounded by water vapor contained in an electrically heated furnace. As platinum allows the free passage of hydrogen molecules through it, but not of oxygen or water vapor, the manometer should show the partial pressure of hydrogen. By means of this method it was found that, at 1500°, water vapor is about 0.1 per cent dissociated into hydrogen and oxygen, which agrees with other methods of measuring the dissociation

With the exception of these experiments at high temperatures upon mixtures containing hydrogen, there are no direct measurements of partial pressures, because of the lack of suitable semipermeable membranes. The chief support for the belief that correct equilibrium pressures or partial pressures are calculated from the product of total pressure and mole fraction comes from the study of chemical equilibrium itself. This topic will be discussed fully in later chapters; here we need say only that equilibrium compositions calculated from Dalton's law in gas mixtures at moderate pressures are in agreement with measured equilibrium compositions based upon analytical chemistry or other means.

It is not to be expected that Dalton pressures will be additive at high pressures, for the individual gases are not ideal at high pressures; and such data as we have confirm this idea. For example, in mixtures of argon and ethylene at 30 atm. total pressure the actual pressures are less than the sum of the Dalton pressures by 0.75, 0.85, and 0.45 per cent, respectively, when the mole fractions of ethylene in the mixture are 0.25, 0.50, and 0.90.

Mixtures of nitrogen and ammonia at total pressures of 10 to 60 atm. also show that Dalton's law is inaccurate at high pressures. In a steel bomb the pressure of NH_3 developed by the dissociation of solid $BaCl_2.8NH_3$ is 7.123 atm. at 45°, and this ammonia pressure remains almost constant when nitrogen is added to the bomb.[2]

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[1] *Z. physik. Chem.*, **54**, 715 (1906).

[2] Data from Lurie and Gillespie, *J. Am. Chem. Soc.*, **49**, 1146 (1927), **53**, 2978 (1931); the increase of dissociation pressure with total pressure is calculated by a method similar to that on p. 109 for the vapor pressure of water.

In the following table the first line gives observed total pressure of $N_2 + NH_3$ in atmospheres, the second line gives the pressure of NH_3 in equilibrium with $BaCl_2\,8NH_3$ and $BaCl_2$ at 45°, and the third is the product of total pressure and mole fraction of NH_3. Ammonia itself deviates from the behavior of an

Total pressure	10 13	13 27	23 70	32 82	60 86
$p(NH_3)$	7 14	7 16	7 22	7 27	7 44
$px(NH_3)$	7 28	7 51	7 85	8 13	9 03
Per cent difference	1 9	4 8	8 7	11 8	21 4

ideal gas by about 7 per cent at 45° and 7 atm., and larger deviations are shown in the presence of nitrogen, which increases the total pressure.

These data are quoted to show that while the ideal gas law is a useful and convenient simplification at low pressures, it is not to be used outside of certain limits without appreciable error. It does not apply *exactly* to any gaseous system, but it ordinarily yields calculations within 1 per cent of the truth with gases or gas mixtures at pressures not much above 1 atm.

Change of Barometric Pressure with Altitude.—The decrease of pressure in any fluid of density ρ with increase in height above a chosen reference point is shown by the equation

$$-d\rho = \rho g\, dh$$

in which $\rho\, dh$ is the mass of a layer of unit cross section and thickness dh and g is the acceleration of gravity. For an ideal gas $\rho = m/v = Mp/RT$, whence, for changing barometric pressure with altitude h, we have

$$-\frac{dp}{p} = \frac{Mg}{RT}\,dh \tag{6}$$

If a uniform temperature is assumed for the air column, we may integrate the equation between the limits p_0 at h_0 and p at an altitude h, as follows:

$$2.3 \log \frac{p_0}{p} = \frac{Mg}{RT}(h - h_0)$$

Substituting $R = 8.32 \times 10^7$, $T = 293$ for an assumed temperature of 20°C., $h = 160{,}900$ cm. for 1 mile, $M = 29$ for air, and $g = 980$ cm. per sec.^{2}, we find the pressure to be 0.83 atm. 1 mile above sea level. Similarly, the pressure is found to be 1.019 atm. at the bottom of a 500-ft. shaft by taking $h = -15{,}000$ cm.

Avogadro's Law.—We have already seen in the previous chapter that equal volumes of gases at atmospheric pressure and at the same temperature contain almost the same number of molecules. At very low pressures equal volumes at the same temperature contain exactly the same number of molecules, as shown by the agreement of atomic weights derived from gas densities with those based on other methods. The fact that the volumes of gases entering into chemical reactions are equal or simple whole multiples of one another and of the volume of the gaseous products is also evidence of the correctness of the law. These volume ratios alone led Avogadro to propose the law in the first place. But convincing confirmation of the law came from determinations of the actual number of molecules in a gram molecule. We turn now to some of the methods by which this was accomplished.

Avogadro's Number.—The early experiments upon the behavior of colloidal particles, which showed that if they approximated molecules in their properties the number of molecules in a gram molecule was 6×10^{23} or 7×10^{23}, are now of historical interest only. But the scattering of solar radiation in the upper atmosphere, the energy of the products of radioactive decomposition, the radiation laws, and other data also pointed to these figures, 6×10^{23} being nearer the probable number than 7×10^{23}. We may review briefly three methods of obtaining this number,[1] of which the first is so convincingly direct as to leave no room for doubt of its validity and the second and third yield the most precise values available.

The radioactive decay of radium expels charged helium atoms (alpha particles) of such high velocity that the impact of a single atom upon a screen of zinc sulfide produces a flash of light that is visible in a microscope. There are other ways in which the effect may be observed. By adjusting the quantity of radium and the distance to the counting mechanism so that an actual count could be made, it was found that the enormous number

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[1] A review of the early experiments which led to estimates of Avogadro's number is given by Dushman in *Gen. Elec. Rev.*, **18**, 1159 (1915); the more precise modern values are reviewed by Birge in *Phys. Rev. Suppl.*, **1**, 61 (1929); and by Virgo in *Science Progress*, **27**, 634 (1933).

1.36×10^{11} alpha particles were emitted each second from a gram of radium.[1] In other experiments it was found that 0.156 ml. of helium (0° and 1 atm.) was produced per gram of radium per year. Upon multiplying 1.36×10^{11} by the number of seconds in a year, one obtains the number of atoms of helium in 0.156 ml. and, by proportion, the number in 22.4 liters, which is 6.16×10^{23} atoms per molal volume of this monatomic gas.

A second method involves Faraday's law of electrolysis, the important aspect of which for this purpose is the deposition of silver from silver nitrate by electrolysis. This reaction is

$$Ag^+ + e^- = Ag$$

and careful experiments have shown that 96,489 coulombs of electricity deposit one atomic weight of silver. The charge of an electron is 1.598×10^{-19} coulomb.[2] The number of electron charges in a faraday of electricity is the number of atoms of silver in an atomic weight, or Avogadro's number, which is thus $96{,}489/1.598 \times 10^{-19} = 6.03 \times 10^{23}$.

The third method involves determining (1) the wave length of X rays from a ruled grating, (2) the spacing of atomic planes in a crystal by using these planes as a diffraction grating for the X rays, (3) the density of the crystal, from which, together with the atomic weights of the elements, one determines (4) the gram-molecular volume. For sodium chloride, the edge of a cube containing 4 atoms of sodium and 4 atoms of chlorine is 5.638×10^{-8} cm., the density is 2.163, the molecular weight is 58.454, and $4 \times 58.454/2.163 = 108.10$ cm.^{3} is the volume of 4 molecular weights of sodium chloride. Avogadro's number is then found by dividing 108.10 by the cube of 5.638×10^{-8}, which gives 6.032×10^{23}. A more recent determination based on the spacing of calcite[3] gives 6.0245×10^{23}.

Viewed in the light of this number the attainment of a "vacuum" seems quite hopeless; for the lowest pressures ever measured, after the most efficient removal of gas from a container,

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[1] The figures are quoted from Sir Ernest Rutherford's lecture printed in the annual report of the *Smithsonian Institution*, **1915**, p. 167.

[2] Millikan, *Ann. Physik*, **32**, 34, 520 (1938), gives the electronic charge as 4.796×10^{-10} e.s.u., which is 1.598×10^{-20} abs. coulomb or 1.598×10^{-19} int. coulomb, since the absolute ampere is 10 int. amp.

[3] BEARDEN, *J. Applied Phys.*, **12**, 395 (1941).

are about 10^{-6} dyne per sq. cm. (this is approximately 1/1,000,000,000,000 atm.), and in this "vacuum" the number of molecules per milliliter is greater than the population of the earth. As a further illustration of the astonishingly large number of molecules in a weighable quantity of matter, it may be observed that, if 1 gram of water were spread uniformly over the surface of the entire earth, there would be 3500 molecules per sq cm.

Molecular-weight Determinations—Direct Method.—When the ideal gas equation is written $pv = (m/M)RT$, it will be seen that the molecular weight M of a gas may be determined from the weight m of a known volume at some definite temperature and pressure. A glass bulb of 300 to 500 ml. capacity is evacuated and carefully weighed, then filled at a fixed temperature and pressure with the gas under consideration, and weighed again The precise data on pages 15 and 27 illustrate an extension of this method, which has been useful for many other gases. But it should not be concluded that its application to all substances is free from complications. We record here for illustration the observed temperature and pressure (in millimeters of mercury) for 0.2429 gram of formic acid vapor in a bulb of 5218 ml capacity and the "molecular weight" obtained from the data for each temperature.

t°C...	10	20	30	40	50	60	70
p, mm.	10 1	11 02	12 13	13 42	14 90	16 50	18 10
M..	81 4	77 3	72 4	67 6	62 9	58 5	54 9

The vapor of formic acid is a mixture of HCOOH and $(HCOOH)_2$ molecules in proportions varying with the temperature, and each of the figures in the third line above gives the weight of a molal volume of the mixture under the stated temperature and pressure. The data do not illustrate a failure of the ideal gas law; they provide a means of determining the composition of the vapor. If all the molecules were HCOOH, the pressure would be 17.9 mm. at 10° and 21.7 mm. at 70°.

Dumas's Method.—If the substance whose vapor density is desired is a liquid at room temperature, about 10 ml. of it may be placed in a weighed bulb with a long capillary stem. All the bulb except its tip is then immersed in a constant-temperature bath (usually boiling water), and the air and excess liquid are expelled from the bulb. When all the liquid has been vaporized, the bulb is sealed and the barometer is read. At the moment of sealing, the bulb is filled with vapor at the barometric pressure and at the temperature of the bath. Thus T and p are known, and m is determined by weighing the sealed bulb again and v by filling the bulb with water and weighing again. As the bulb when first weighed is filled with air that is expelled by the boiling liquid, it is necessary to compute the weight of air expelled and subtract it from the first weighing in order to obtain the weight of the *empty* bulb.

Actual data on carbon tetrachloride may be used to illustrate the method of calculation

Bulb (filled with air)	51.43 grams
Bulb with CCl_4 vapor	52.86 grams
Bulb filled with water	411 grams

The difference between the weight of the bulb when filled with water and the weight filled with air is 360 grams, and this is substantially the volume of the bulb in milliliters. The weight of air contained in the bulb at its first weighing was not present at the second weighing. Its weight may be obtained by substituting in the equation $pv = nRT$, from which it will follow that 0.015 mole of air, or 0.43 gram, was present. The empty bulb, therefore, weighed 51.00, and hence 1.86 grams of carbon tetrachloride vapor filled the volume of 360 ml. and exerted a pressure of 1 atm. at 100°C when the bulb was sealed. Upon substituting these values in $pv = (m/M)RT$, M is found to be 160, which should be compared with 154, the formula weight. The difference is mostly due to the fact that the vapor of CCl_4 is not ideal under the experimental conditions, and closer agreement is not to be obtained by more careful experimentation. The method of limiting densities would give 154 if correctly applied to CCl_4 at 100°C.

Victor Meyer's Method.—This procedure is adapted to substances that vaporize at somewhat higher temperatures than those suited to Dumas's method; indeed, it can be applied at temperatures up to the softening point of porcelain or quartz. In principle, the method consists in vaporizing a weighed quantity of the liquid or solid substance in a vessel filled with hot air or nitrogen at such a temperature that the substance vaporizes readily. The hot bulb is made much larger than the volume that the substance will occupy as a vapor, and when vaporization takes place a mole of air is expelled for each mole of vapor formed. For convenient measurement, the expelled air is collected in a burette over water. From the barometric pressure,[1] volume, and temperature of the air in the burette the number of moles of air expelled is calculated from $pv = nRT$, and since this is also the number of moles formed by a known weight of substance vaporized in the hot tube, $M = m/n$. The method may not be applied to dissociating substances; for the vapor mixes with the hot nitrogen in the tube, and the extent of dissociation is altered by dilution at constant temperature. Dumas's method and the direct method are free from this restriction.

KINETIC THEORY OF GASES

The purpose of the paragraphs that follow is to consider the properties of the molecules in a gas and to develop equations in terms of the mass and velocity of the molecules that apply to the behavior of gases and that can be tested by experiment. Since the number of molecules in any quantity of gas upon which experiments can be performed is exceedingly large, we are to be concerned with average velocities or average kinetic energies rather than with those of individual molecules.

Fundamental Equation.—The molecules of a gas are not at rest but move about through the confining space with great rapidity,[2] colliding frequently with each other and with the walls of the vessel surrounding them. This statement is supported by the fact that when two gases are brought in contact and the mixture is allowed to stand it finally becomes homogeneous throughout. If a quantity of chlorine be placed in the bottom of a vessel by displacing part of the air in it, a distinctly greenish layer will be seen. When this is allowed to stand for some time, the green layer diffuses upward throughout the whole

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[1] The partial pressure of the air is of course the barometric pressure less the vapor pressure of water, which is given in Table 14.

[2] The average velocity of molecules in air is about ⅓ mile per sec., but the average straight-line distance traveled between collisions is only about 0.0001 mm., the number of hits per second for each molecule being thus about 5,000,000,000. Actual velocities of molecules were determined by Stern [Z. *Physik*, **2**, 49 (1920)] and found to agree with those expected from the kinetic theory.

vessel and there is no longer any visible boundary between the two gases. This mixing is not dependent on stirring but will take place if the vessel is kept absolutely quiet and at a constant temperature, in spite of the different densities of the gases.

The pressure exerted on the walls of a container by a gas is entirely due to collisions that take place between the moving molecules and the walls. It is known that the pressure does not decrease if a gas is allowed to stand indefinitely in a closed space at constant temperature and that a gas does not continuously absorb heat from the surroundings to supply the energy of motion of its molecules. This can be true only if the molecules are perfectly elastic as regards their collisions with one another; for otherwise the collisions would absorb energy, and the intensity of motion would gradually decrease and cause the pressure to fall off. The pressure is perfectly constant on all the walls at all times, and therefore the bombardment of the walls must be uniformly distributed.

Within a gas the molecules move about in the utmost chaos, with no regularity whatever, and at widely different velocities. A molecule that has a high velocity at one instant may suffer a collision that changes its direction and velocity at any moment. Indeed, the path of each molecule is absolutely haphazard, and the state of a gas must be thought of as absolute confusion. But it is convenient in visualizing the behavior of molecules, as regards pressure exerted on the surrounding walls, to consider their motions along three axes perpendicular to the faces of a confining cube and to consider the mean[1] velocity of all the

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[1] By applying the laws of probability Maxwell has shown that the distribution of velocities among a large number of molecules which have a given mean velocity is shown by the equation

$$y = \frac{4}{\sqrt{\pi}} x^2 e^{-x^2}$$

where y denotes the probability of a velocity whose magnitude is x, the most probable velocity being taken as unity. Figure 6 shows this curve graphically. The arithmetic average velocity is 1.13 times the most probable velocity; and the "mean" velocity is 1.22 times the most probable one. By "mean" is

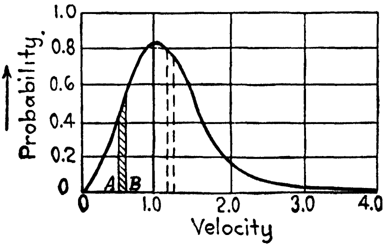

FIG. 6.

molecules, in place of the rapidly changing velocity of a single molecule.

For convenience in deriving the desired equation, we may assume a cubical container of edge l, of which one corner is the "origin," and resolve the motions of the molecules along the rectangular x, y, and z axes meeting at this corner. The root-mean-square velocity $\sqrt{\Sigma u^2/n}$, which we shall call the mean velocity u, or the velocity from which to compute the average kinetic energy of a molecule, is evidently related to the velocities resolved along these axes by the equation

$$u^2 = u_x^2 + u_y^2 + u_z^2$$

Let n be the number of molecules in the container, and let m be the mass of one molecule Consider one face of the cube, perpendicular to the x axis, which a molecule approaches with a velocity whose x-component is u_x and from which it recedes with a velocity whose x-component is $-u_x$ after colliding with the wall. The change in momentum caused by this impact is $2mu_x$, and this momentum will be imparted to the wall by every molecule striking it. Before the molecule can strike this wall again, it must travel the distance $2l$ to the opposite face and back, which will require $2l/u_x$ sec. In other words, the number of impacts on this wall by one molecule will be $u_x/2l$ per second or $nu_x/2l$ impacts per second for all the n molecules.

The total momentum imparted to the wall per second will be the product of the change in momentum per hit and the number of hits per second, which is $2mu_x(nu_x/2l)$. Since the force f exerted on the wall is the rate at which momentum is imparted to it,[1] we have as a measure of this force

$$f = \frac{2mu_x \times nu_x}{2l} = \frac{mnu_x^2}{l}$$

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meant that velocity which would give the average probable kinetic energy. This is the square root of the average of the squares, or root-mean-square (r.m.s) velocity, and is denoted by u in the above text.

Since the area under the curve in Fig 6 is unity, the fraction of all of the molecules which have velocities between $0A$ and $0B$ is denoted by the shaded area. For a further discussion of these matters see Dushman, *Gen. Elec. Rev.*, **18,** 952 (1915).

[1] Force has the dimensions ml/t^2, and momentum is ml/t; hence $ml/t \times 1/t$ is the rate of imparting momentum to a surface.

Since experiment shows that the force acting upon the walls of the container is the same for all walls, it follows that the velocities resolved along the three axes must be equal, so that $u_x^2 + u_y^2 + u_z^2 = u^2 = 3u_x^2$ Upon making this substitution. and dividing both sides of the equation by l^2, we have

$$\frac{f}{l^2} = \frac{mnu^2}{3l^3}$$

Note now that the left side of the equation, f/l^2, is the pressure and that l^3 is the volume v of the container, so that the equation becomes

$$p = \frac{\frac{1}{3} mnu^2}{v}$$

Since for a mole of gas pv is equal to RT [equation (4)], we may write

$$pv_m = \tfrac{1}{3}mnu^2 = RT \qquad (7)$$

which is the fundamental equation of the simple kinetic theory. If p is in dynes per square centimeter, v is in milliliters, m in grams, u in centimeters per second, n is Avogadro's number (6.03×10^{23}), and R has the value $8\,315 \times 10^7$ ergs/mole-°K. Since mn equals M, the molecular weight, this equation may also be written

$$pv_m = \tfrac{1}{3}Mu^2 = RT \qquad (7a)$$

If we write equation (7) in the form

$$\tfrac{2}{3}n \times \tfrac{1}{2}mu^2 = RT$$

it will be seen that $\frac{2}{3}n$ is constant for a molal volume (Avogadro's law); and hence $\frac{1}{2}mu^2$ must be the same for all gases when T is constant, since nothing has been assumed as to the kind of gas molecules. Thus $\frac{1}{2}mu^2 = f(T)$.

When two different gases at the same temperature are mixed there is almost no change in temperature; consequently, the average kinetic energy of the molecules ($\frac{1}{2}mu^2$) must be practically the same for all gases at the same temperature and must increase at the same rate for all gases. If the kinetic energy of a gas molecule depends only on its temperature and is independent of the nature of the gas,

$$pv = \tfrac{2}{3} \times \tfrac{1}{2}m_1u_1^2n_1 = \tfrac{2}{3} \times \tfrac{1}{2}m_2u_2^2n_2$$

If $p_1v_1 = p_2v_2$ at a given temperature, the same volume of the two gases must contain the same number of molecules, that is, $n_1 = n_2$, since $\frac{1}{2}m_1u_1^2 = \frac{1}{2}m_2u_2^2$, and this is the law of Avogadro.

Thus we see that our fundamental equation (7) is in substantial agreement with the known facts concerning gaseous substances at moderate pressures.

Rate of Effusion of Gases.—At any given temperature the kinetic energies of two kinds of molecules should be the same according to our equation; *i.e*.,

$$\frac{1}{2}m_1u_1^2 = \frac{1}{2}m_2u_2^2$$

or

$$\frac{u_1}{u_2} = \sqrt{\frac{m_2}{m_1}} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{d_2}{d_1}} \tag{8}$$

since the masses of the molecules are proportional to the molecular weights M_1 and M_2 and to the densities d_1 and d_2. This equation states that the velocity of the molecules should be inversely proportional to the square root of the density of the gas. Since effusion through a small hole is a manifestation of molecular motion, the correctness of this equation may be tested by comparing the rates of effusion of gases through a given opening. The statement in equation (8) is Graham's law of effusion of gases. Some of his data are quoted in Table 7 to show that this consequence of equation (7) is proved by experiment.

TABLE 7.—RATE OF EFFUSION OF GASES[1]

Gas	Density relative to air	Time of effusion relative to air	Square root of density	Velocity of effusion relative to air	Velocity calculated from square root of density
Air.....	1.0000	1.000	1.0000	1.000	1.000
Oxygen	1.1056	1.053	1.0515	0.950	0.951
N_2......	0.9714	0.984	0.9856	1.016	1.015
CO.....	0.9678	0.987	0.9838	1.012	1.016
CH_4....	0.5549	0.765	0.7449	1.322	1.342
CO_2....	1.5290	1.218	1.2350	0.821	0.809
N_2O....	1.5290	1.199	1.2350	0.834	0.809

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[1] GRAHAM, *Phil. Trans. Roy. Soc. (London)*, **136**, 573 (1846). See Edwards, *Natl. Bur. Standards Tech. Paper*, **94** (1917), for a description of an improved experimental method; also Kemp, Collins, and Kuhn, *Ind. Eng. Chem.*, Anal. Ed., **7**, 338 (1935).

The following calculations will illustrate the method of applying equation (8) under a small (constant) driving pressure. Suppose that 100 ml. of air will effuse through a pinhole in a thin plate in 75 sec. and that under the same conditions 100 ml. of another gas escape in 92 sec. Since the faster moving molecules will escape at a higher rate, the velocities are inversely proportional to the relative times of escape and equation (8) becomes

$$\frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$$

Upon substituting 75 sec. for t_1, 92 sec. for t_2, and 29 for M_1 it is found that M_2 is 44.

Heat Capacity of Monatomic Gases at Constant Volume.—Since a quantity of gas is usually described by the number of moles in the calculations of physical chemistry, we shall be concerned with the molal heat capacity, which is the ratio of the heat absorbed by a mole of gas to the rise in temperature produced, $C = dq/dT$. But since q depends upon the manner of heating, some further specification is required to make the heat capacities definite. The only processes that concern us are heating at constant volume and heating at constant pressure, for which the definitions are

$$C_v = \left(\frac{dq}{dT}\right)_v = \left(\frac{\partial E}{\partial T}\right)_v$$

and

$$C_p = \left(\frac{dq}{dT}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p$$

For gases at moderate pressures the equations

$$\left(\frac{\partial E}{\partial v}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial H}{\partial p}\right)_T = 0$$

are substantially true; therefore, C_p is the same for any constant pressure, and C_v is the same for any constant volume.

An increase of temperature increases the *kinetic* energy of translation of the molecules by an amount that may be calculated from equation (7). This will not be equal to the increase in the energy content E unless the other forms of energy do not change. The total energy content of a gas includes kinetic, rotational, vibrational, electronic, and all other forms; and since $C_v = dE/dT$, this will not be equal to dE_{kin}/dT unless the energy absorbed in other forms is zero. Thus dE_{kin}/dT is the minimum value that C_v may have. For monatomic gases this is the actual value of C_v, but for all other gases the rotational energy is important even at room temperatures. For all gases the other forms become important at high temperatures. Similarly,

$$C_p = \frac{d(E + pv)}{dT}$$

by definition, and thus the heat capacities of all gases at constant pressure will be greater than those for constant volume. The calculation for a monatomic gas will now be given.

Let u_1 be the mean velocity of the molecules at the absolute temperature T_1 and u_2 the mean velocity at the higher temperature T_2 after the quantity of energy ΔE has been absorbed by a mole of the gas. The increase in kinetic energy of all the molecules is

$$\Delta E = \tfrac{1}{2}nmu_2^2 - \tfrac{1}{2}nmu_1^2$$

where n is Avogadro's number of molecules in a mole of gas; and this increase in kinetic energy is equal to the heat added Since we are concerned with a molecular weight of gas, the product nm is equal to the molecular weight of the gas M. From equation (7a) we obtain

$$p_1v_m = \tfrac{1}{3}Mu_1^2 = RT_1$$

and

$$p_2v_m = \tfrac{1}{3}Mu_2^2 = RT_2$$

By multiplying each of these equations by $\tfrac{3}{2}$ and subtracting the first from the second, we obtain

$$\tfrac{1}{2}Mu_2^2 - \tfrac{1}{2}Mu_1^2 = \tfrac{3}{2}R(T_2 - T_1) \tag{9}$$

as the difference between the kinetic energies of the molecules at the temperatures T_2 and T_1. This is equal to the heat absorbed, which is equal to the molal heat capacity of the gas multiplied by the increase in temperature; that is,

$$\Delta E = C_v(T_2 - T_1).$$

On substituting these quantities in equation (9), we have

$$\Delta E = C_v(T_2 - T_1) = \tfrac{1}{2}M(u_2^2 - u_1^2) = \tfrac{3}{2}R(T_2 - T_1) \qquad (10)$$

whence the molal heat capacity at constant volume is

$$C_v = \tfrac{3}{2}R = 2.98 \text{ cal. per deg.} \qquad (11)$$

By multiplying both sides of equation (7*a*) by $\tfrac{3}{2}$, we obtain an expression for the kinetic energy of the molecules,

$$\tfrac{1}{2}Mu^2 = \tfrac{3}{2}RT = E_{\text{kin}}$$

and if increase in kinetic energy is the only effect of energy absorption upon heating at constant volume, the value of C_v is obtained by differentiating this equation,

$$\frac{dE_{\text{kin}}}{dT} = \tfrac{3}{2}R = C_v$$

Since the relation $(\partial E/\partial v)_T = 0$ is part of the definition of an ideal gas, it will be seen that $(\partial E/\partial T)_v = C_v$ is also independent of the volume. This relation is also nearly true for actual gases at pressures of a few atmospheres; we may therefore write that $\partial C_v/\partial v = 0$.

Heat Capacity of Monatomic Gases at Constant Pressure.—If the gas is heated from T_1 to T_2 at constant pressure, expansion attends the heating and work is done against the external pressure. Since the increase of kinetic energy is the same whether heating occurs at constant volume or constant pressure, the latter process requires the absorption of additional heat equivalent to the work done. This work is $p(v_2 - v_1)$, which for a mole of gas is $R(T_2 - T_1)$, whence

$$C_p(T_2 - T_1) = \tfrac{3}{2}R(T_2 - T_1) + R(T_2 - T_1)$$

or

$$C_p = \tfrac{5}{2}R = 4.97 \text{ cal. per deg.} \qquad (12)$$

This equation, like equation (11), is applicable only to gases in which none of the energy absorbed in heating is used to increase the rotational or vibrational energy of the molecules or to overcome attractive forces between molecules; and only monatomic gases meet these requirements. The experimental data of Table 8 will be seen to agree with the heat capacities calculated in equations (11) and (12).

TABLE 8.—MOLAL HEAT CAPACITIES OF MONATOMIC GASES

Substance	C_p	$C_p - R = C_v$	Experiments by
Mercury vapor	4.97	2.98	Kundt and Warburg
Helium	5.10	3.11	Behn and Geiger
Argon	4.99	3.00	Niemeyer
Argon	4.97	2.98	Pier
Argon	5.07	3.07	Heuse[1]

Ratio of C_p to C_v for Monatomic Gases.—In addition to evidence from experiments on the temperature change during expansion into a vacuum (to be discussed presently), there is another way in which the correctness of equations (11) and (12) may be tested. It will be remembered that these equations were derived on the assumption that all the energy added to the gas increased the kinetic energy of the molecules or performed work in overcoming the pressure of the atmosphere during expansion. Let us assume for the moment that there is some unknown absorption of energy in addition to those stated. The equation $C_p - C_v = R$ has been established by experiment; and the quantity of energy $\frac{3}{2}R$ must be absorbed to increase the kinetic energy of the molecules and account for the experimentally proved increase in pressure with the temperature. Let x denote the energy required for other purposes. Then the ratio of specific heats at constant pressure and at constant volume is

$$\frac{C_p}{C_v} = \frac{\frac{5}{2}R + x}{\frac{3}{2}R + x} = \frac{5R + 2x}{3R + 2x} = \gamma$$

It is possible to determine the ratio of these two specific heats from the velocity of sound in a gas,[2] and the ratio for monatomic

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[1] *Ann. Physik*, **59**, 86 (1919).

[2] Laplace has shown that the hydrodynamic equation for the velocity of sound in a medium of density ρ is

$$(\text{vel})^2 = +\left(\frac{\partial p}{\partial \rho}\right)_q = -\left(\frac{v_s^2 \partial p}{\partial v}\right)_q \qquad (1)$$

where v_s is the specific volume of the medium. For an adiabatic expansion, such as attends the passage of sound through a gas, pv_s^γ = const., or $\ln p + \gamma \ln v_s = \ln$ const., where γ is the ratio C_p/C_v for the gas in which sound travels. Upon differentiating, gases is 1.667. Now this is $\frac{5}{3}$, and hence x in the above equation must be zero. Thus the heat-capacity equations are supported by the results of experiment.

Heat Capacity of Diatomic Gases.—The definitions of heat capacity that have already been used for monatomic gases apply to all gases, namely,

$$C_v = \frac{dE}{dT} \quad \text{and} \quad C_p = \frac{dH}{dT}$$

and of course the relation $pv_m = RT$ applies to them. By combining this equation with the definition $H = E + pv$, we find $H = E + RT$ for a mole of gas; and, upon differentiating with respect to T, we have

$$\frac{dH}{dT} = \frac{dE}{dT} + R$$

which gives the difference between C_p and C_v for any gas as

$$C_p - C_v = R$$

whether the gas is monatomic or polyatomic, so long as it conforms to the relation $pv = nRT$. This same relation follows from equation (12) on page 37, which was

$$C_p - C_v = \left[p + \left(\frac{\partial E}{\partial v}\right)_T\right]\left(\frac{\partial v}{\partial T}\right)_p$$

since $(\partial E/\partial v)_T = 0$ for gases and $p(\partial v/\partial T)_p = R$ from the gas law.

$$\frac{dp}{p} + \gamma\frac{dv}{v_s} = 0$$

$$\frac{\partial p}{\partial v} = -\gamma\frac{p}{v_s} = -\gamma\frac{pv_s}{v_s^2} \qquad (2)$$

In an ideal gas the specific volume is RT/pM, and the product of pressure and specific volume is RT/M, whence (2) becomes

$$\frac{\partial p}{\partial v} = -\gamma\frac{RT}{Mv_s^2}$$

and (1) becomes

$$(\text{vel})^2 = \frac{RT}{M}\gamma$$

If the molecules of a gas contain more than one atom, considerable quantities of energy may be absorbed in increasing rotation of the molecules or in increasing internal vibrations, *i.e.*, displacement of one of the atoms relative to another. Experiment shows that the pressure of the diatomic and triatomic gases increases with the absolute temperature in the same way as that of the monatomic gases, which could be true only if the kinetic energy of the molecules increases with increasing temperature in the same way. The heat absorbed and converted into rotation or vibration of the molecules is in addition to that required to increase the kinetic energy or to do work of expansion; therefore, the heat capacities are higher for diatomic gases. If we call the extra energy absorption during heating the "internal heat capacity," C_{int}, the equations that apply are

TABLE 9.—MOLAL HEAT CAPACITY RATIO FOR GASES

Substance	t	p, atm	C_p	$\gamma = C_p/C_v$
Air	18	1	6 95	1 40
Air	18	100		1 58
Air	− 79	100		2 20
N_2	18	1	6 94	1 40
N_2	18	100		1 56
O_2	18	1	6 97	1 40
O_2	−180	1		1 45
Cl_2	18	1	8 15	1 36
HCl	18	1	7 07	1 41
SO_2	18	1	9 71	1 29
CO_2	18	1	8 75	1 30
CO_2	18	60		3 52
CO_2	− 75	1	8 08	1 37
C_2H_6	18	1	11 6	1 28
Ether	35	1	27 7	1 08

$$C_v = \tfrac{3}{2}R + C_{\text{int}}$$

and

$$C_p = \tfrac{3}{2}R + R + C_{\text{int}}$$

These equations show that C_p/C_v will be less than $\tfrac{5}{3}$ if C_{int} is appreciable. Since $C_p/C_v = 1.4$ for diatomic gases, we estimate $C_{\text{int}} = R$ for them as a first approximation. A clue, though not a complete explanation, is furnished by the law of equipartition of energy, which says that C_v is $\frac{1}{2}R$ for each "degree of freedom" of the molecule. Monatomic gases have three degrees of translational freedom; and since $C_v = \frac{3}{2}R$ for them, they have no appreciable rotational energy; diatomic gases have three degrees of translational freedom and two of rotational freedom, which should give $C_v = \frac{5}{2}R$, $C_p = \frac{7}{2}R$, and $C_p/C_v = 1.4$ if no energy is absorbed in other ways. These figures are close to the experimentally determined heat capacities of H_2, N_2, O_2, CO, NO, and HCl at ordinary temperatures, which is an indication that there is no appreciable internal heat capacity other than rotation at ordinary temperatures. The molal heat capacities of $Br_2(g)$ and $I_2(g)$ at constant pressure are 9.0 at ordinary temperatures which shows that these gases have "internal heat capacity" other than rotation; the usual interpretation is vibration of the atoms in the molecule. For the other diatomic gases C_p increases at higher temperatures, which is an indication that vibrational effects become more important as the temperature rises. The increase for chlorine is conspicuous, C_p changing from 8.1 at 300°K. to 8.6 at 500°K. and to 8.9 at 2000°K., probably because the vibrational heat capacity changes rapidly with rising temperature. Equations for the change of heat capacity with temperature are given in Table 56 and some data for C_p/C_v are given in Table 9.

Mass of Gas Striking a Unit of Surface.—As shown on page 76, pressure is the momentum imparted to a unit area in unit time. If w is the mass of gas striking a unit of surface in unit time and u_x is the velocity resolved on the x axis perpendicular to this surface, the pressure is $p = 2wu_x$. In a gas the velocities resolved upon the three axes are equal, for the pressure is the same on all walls of the vessel; therefore,

$$u^2 = u_x^2 + u_y^2 + u_z^2 = 3u_x^2$$

From equation (7*a*),

$$RT = \frac{1}{3}Mu^2 = Mu_x^2$$

and by combining these relations, the mass of gas striking unit surface each second is given by the equation

$$p = 2w\sqrt{\frac{RT}{M}} \qquad \text{or} \qquad w = \frac{p}{2}\sqrt{\frac{M}{RT}} \tag{13}$$

where w is the mass of gas in grams per second per unit surface,

p is the pressure of the gas in dynes per square centimeter, M is the molecular weight of the gas, T is the absolute temperature, and R has the value 8.315×10^7 ergs/mole-°K. Langmuir[1] has derived a more exact expression for the mass of gas striking a unit area during each second, by taking into account the distribution of velocities around the most probable one. His equation differs from the one above only by a numerical constant. The more exact equation is

$$w = p\sqrt{\frac{M}{2\pi RT}} \tag{14}$$

We may illustrate the application of this equation by calculating the mass of oxygen striking each square centimeter of a surface exposed to air under ordinary conditions. The partial pressure of oxygen is 0.21 atm., or 21.2×10^4 dynes per sq. cm., T is 293, and the other quantities have been given above. By substituting these quantities into equation (14), we find w is 3.1 grams per sec.

Energy Absorbed in Expansion, Joule Effect.—The fact that the pressure-volume product of gases at constant temperature is nearly constant for moderate pressure changes indicates that the attraction between molecules is relatively small under these conditions. But if during an expansion the molecules exert considerable attractive (or repulsive) forces on one another, these forces will resist (or assist) the expansion. In the expansion of a compressed gas taking place in an isolated system and arranged so that no work is done (a "Joule expansion"), the attractive forces of the molecules for one another must be overcome at the expense of the kinetic energy of the molecules and the temperature will not remain constant if these forces are appreciable. Consider a vessel of 6 liters capacity containing a mole of gas at 20°C. and connected by a tube, containing a closed stopcock, to an evacuated vessel of 18 liters capacity, and assume the whole system isolated so that no heat can enter or leave it. When the stopcock is opened, gas passes into the empty vessel until the pressure is the same (about 1 atm.) in both. No heat is absorbed, and no work is done by the system, so that ΔE is zero; and if no "internal" work is done against the attractive forces, the temperature will still be 20°. These facts may be

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[1] *Phys. Rev.*, **2**, 329 (1914).

expressed by the equation $(dE/dv)_T = 0$, which is part of the definition of an ideal gas.

Experiments on the Joule expansion of actual gases show that the temperature changes during the expansion. For these expansions ΔE is zero, but the temperature is not constant; therefore, ΔE for the *isothermal* expansion is ΔE for heating the gas to the original temperature at constant volume, or $\int C_v\, dT$. Attempts to measure the temperature changes during Joule expansions have been unsuccessful because of heat transfer from the container to the expanded gas, heats of adsorption and desorption, and other difficulties. One may calculate what the temperature change would be if these effects were absent from other experiments on actual gases, but the observed temperature changes differ from the calculated ones. Even so, the experiments show that for isothermal expansion of a real gas $(dE/dv)_T$ is not zero, and they indicate that molecular attraction is one of the main causes. The calculated temperature change for carbon dioxide expanding as indicated above is about 1°.

Joule-Thomson Effect.—One of the best means of showing the change of internal energy of a gas upon expansion consists in passing it through a tube thermally insulated from its surroundings and obstructed by a porous plug, as shown in Fig. 7. There will thus be a pressure difference on the two sides of the plug; and if the expansion is attended by an energy change, the temperature on the two sides of the plug will not be the same. The change in temperature, called the "Joule-Thomson effect" after its discoverers,[1] depends upon the initial temperature and for a given temperature varies with the initial pressure.

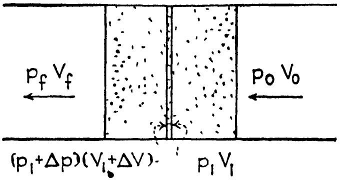

FIG. 7.

The gas in its passage through the plug will come to a steady condition, provided that the pressure and temperature before the plug remain constant and the pressure on the far side is constant. To secure the steady state the tube and its plug must be nonconductive for heat, or corrections will be required to allow for flow of heat along the tube or plug. Assuming the ideal conditions, an examination can be made of the physical change

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[1] *Phil. Trans.*. **149**, 321 (1854).

of state in the gas as it passes at a slow constant rate through the uniformly porous plug. Referring to Fig. 7, consider sections through the plug, and fix attention on one where the pressure on the right side is p_1 and the volume v_1. As the gas flows, the pressure changes to $p_1 + \Delta p$ and the volume to $v_1 + \Delta v$. The gas in each thin section does work on the section ahead, and we have the following difference for the work done upon the gas:

$$p_1v_1 - (p_1 + \Delta p)(v_1 + \Delta v)$$

or, since we consider work done *by the system* as positive,

$$w = p\,\Delta v + v\,\Delta p + \Delta p \cdot \Delta v$$

In the limit of infinitely thin sections, there is obtained for the element of work, products of small quantities being dropped, the expression

$$dw = d(pv)$$

This equation applies to a process where heat has no access to the system, and hence $-dw$ must equal the energy change in the gas, dE. We obtain therefore the special thermodynamic equation for the Joule-Thomson effect,

$$dE = -d(pv)$$

This equation may be integrated, and the following relation is obtained for the conditions before and after the plug, as represented in Fig. 7:

$$E_0 + (pv)_0 = E_f + (pv)_f$$

The quantity that it is desired to obtain from the Joule-Thomson experiment is the change of temperature in relation to the corresponding change in pressure, that is, dT/dp under the condition that H or $(E + pv)$ is constant. The following exact equation[1] is valid:

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{T(\partial v/\partial T)_p - v}{C_p}$$

We see that a qualitative statement about the effect may be made at once, since the heat capacity at constant pressure, C_p, is always positive and $(\partial v/\partial T)_p$ is positive. The sign of $(\partial T/\partial p)_H$ will

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[1] For its derivation, see Glasstone, "Physical Chemistry," p. 279.

therefore be positive or negative according as $T(\partial v/\partial T)_p$ is greater than v or less than v, and $(\partial T/\partial p)_H$ will be zero when $T(\partial v/\partial T)_p = v$. The temperature at which these quantities are equal is the inversion temperature; and unless a compressed gas is cooled below this temperature, its expansion through a porous plug will not produce further cooling.

The Joule-Thomson *coefficient* for various gases is commonly recorded[1] in degrees centigrade per atmosphere of pressure change, dT/dp, and is positive when cooling takes place, since the pressure always decreases in these experiments. The coefficient depends upon the initial pressure and the initial temperature of the expanding gas, as shown by the data for carbon dioxide in Table 10.

TABLE 10.—JOULE-THOMSON COEFFICIENTS, $(dT/dp)_H$, FOR CARBON DIOXIDE[2]

p, atm t, °C.	1	20	60	100	140
300	0 2650	0 2425	0 2080	0 1872	0 1700
200	0 3770	0 3575	0 3400	0 3150	0 2890
100	0 6490	0 6375	0 6080	0 5405	0 4320
80	0 7350	0 7240	0 6955	0 5973	0 4050
60	0 8375	0 8325	0 8060	0 6250	0 2625
40	0 9575	0 9655	0 9705	0 2620	0 1075
20	1 1050	1 1355	0 1435	0.0700	0 0420
0	1 2900	1 4020	0.0370	0.0215	0 0115

Liquefaction of Gases.—At high pressures, and especially at low temperatures, the cooling effect available from a Joule-Thomson expansion may be quite large. By employing an insulated expansion apparatus in which efficient heat interchange takes place between the outgoing expanded gas and the entering high-pressure gas, sufficient cooling may occur to cause liquefaction. Since the gases are warmed by compression, it is advantageous to cool the compressed gas by passing it through refrigerated tubes before the cooling effect of expansion takes place. There

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[1] See "International Critical Tables," Vol. V, p. 144, for data.

[2] ROEBUCK, MURRELL, and MILLER, *J. Am. Chem. Soc.*, **64**, **400** (1942).

is a "critical temperature" for each gas, above which no liquid forms under any pressure, and for ordinary gases this is far below room temperature. For example, the critical temperature of oxygen is −118°C., and even at this low temperature the pressure required for condensation is about 50 atm. In the manufacture of liquid air, if the compressed air enters the expansion chamber at about 200 atm. and 0°, during its expansion to atmospheric pressure the temperature falls to −182° and about 11 per cent of the air liquefies. By cooling the compressed air to −50° before expansion takes place, the yield of liquid is approximately doubled.

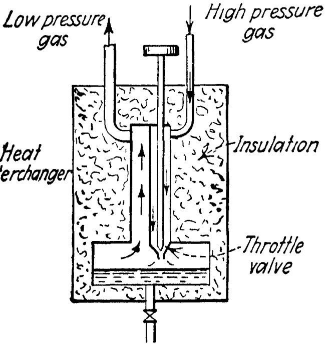

FIG. 8.

The liquefying apparatus is in principle a special porous-plug apparatus (see Fig. 8) in which heat interchange is brought about between the expanded gas and the incoming high-pressure gas. It will be assumed that the apparatus is so insulated as to prevent heat flow and that the low-pressure outgoing gas is brought to exactly the same temperature as the incoming high-pressure gas by the heat interchanger. Under these conditions we are dealing with a constant-enthalpy process, but we must consider the fluid in the three states, high-pressure gas at p_{start} and T_{start}, liquid at p_{liq} and T_{liq}, and exit gas at p_{exit}, $T_{\text{exit}} = T_{\text{start}}$. Let x represent the fraction of the incoming gas that becomes liquefied. We may then write the enthalpy-balance equation as follows:

$$H_{\text{start}} = H_{\text{liq}}x + H_{\text{exit}}(1 - x)$$

Solving for x, the simple equation is obtained,

$$x = \frac{H_{\text{exit}} - H_{\text{start}}}{H_{\text{exit}} - H_{\text{liq}}}$$

A larger cooling effect may be obtained in the production of liquid air by expanding the cold compressed air in an engine, and so decreasing the energy content of the gas through the performance of work. The Claude method employs this procedure, which has some theoretical advantages over the method based on overcoming molecular attraction alone, such as operation at a lower pressure and greater efficiency in operation. There are practical difficulties in its operation, of which the design and proper lubrication of an engine running at a low temperature may be mentioned. In actual practice there is not much difference between the efficiencies of the two methods.

Mixtures of gases that have been liquefied may be separated by fractional distillation in the same way as other liquids are fractionated. The operation requires careful control of temperatures, but it is in common use for the preparation of industrial oxygen, nitrogen, argon, and neon. One other striking example of its application is in the separation of helium from natural gas, most of which contains not more than 1 per cent of helium.

Deviations from the Ideal Gas Law.—The simple equation for ideal gases, $pv = nRT$, is not valid at high pressures, and many expedients have been suggested for taking the variations into account. One common procedure is to add terms in increasing powers of the pressure and determine empirically the numerical values of the coefficients from the measured pressure of the gas. Such equations contain parameters that are coefficients of the pressure terms valid for a given temperature but are different at different temperatures. The equations for oxygen will be a sufficient illustration. Upon taking $pv = 1.000$ at 0° and 1 atm., the pv product at 0° for any other pressure (in atmospheres) is

$$pv_{273} = 1.0010 - 0.000994p + 0.00000219p^2$$

and at 20°C. the pv product for any pressure, again upon taking $pv = 1.000$ at 0° and 1 atm., is

$$pv_{293} = 1.07425 - 0.000753p + 0.00000150p^2$$

Another common procedure is to include terms that allow for molecular attraction and "incompressible" volume, or that part of the volume which is not reduced by increased pressure. Of the many such equations proposed (probably more than a hundred), we consider a few that are typical of them all.

van der Waals' Equation.—Since liquids, in which the molecules are much closer together than in gases, are very slightly compressible, it seems reasonable that compression of a gas changes only the volume of free space between the molecules. At high pressures this "volume of the molecules," or "incompressible volume," becomes a considerable portion of the total volume; therefore, a better representation of the observed compressibility of a gas is obtained by writing

$$p(v_m - b) = RT$$

in which b is understood to be a volume correction, not the volume that the molecules would have in the liquid state

The Joule-Thomson coefficients indicate a "cohesive pressure" that is overcome during expansion at the expense of energy, and thus a correction for attractive forces is evidently required. It would have the same effect qualitatively as an increase in pressure, which may be indicated by writing an equation of the form

$$(p + A)(v_m - b) = RT$$

The Joule-Thomson coefficients in Table 10 show that the cohesive pressure decreases with rising temperature for a given pressure, which indicates that the cohesive pressure is a function of the volume. This is supported by the known fact that the deviations of actual gases from the ideal law become smaller as the pressure becomes smaller, whereas, if A is a constant, its importance would become greater relative to p at lower pressures. If we consider the layer of molecules about to strike a given wall at any instant of time, we see that the attraction holding them back will be proportional to the number of molecules attracting them. Since the number about to strike at any instant is also proportional to the number present, it follows that this attractive force is proportional to the square of the density of the gas or inversely proportional to the square of the volume occupied by a mole of gas. Our equation may then be written with a/v_2 in place of A, when we have[1]

$$\left(p + \frac{a}{v_m^2}\right)(v_m - b) = RT \tag{15}$$

This is van der Waals' equation for the behavior of a mole of gas, though the argument on which it is based is not the same as that used in its original derivation.

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[1] The equation will usually be required in this form. When any quantity other than a mole is involved, the equation for n moles of gas is

$$\left[p + a\left(\frac{n}{v}\right)^2\right](v - nb) = nRT$$

In order to show the meaning of the equation more clearly, it is sometimes written in the form

$$p = \frac{RT}{v_m - b} - \frac{a}{v_m^2}$$

in which the first term is the "thermal" pressure and the second is the "cohesive" pressure. An increase in b relative to v_m at a given temperature would obviously increase the thermal pressure above RT/v_m, and a decrease in v_m would increase the value of a/v_m^2.

The equation of van der Waals is more difficult to handle than is the ideal gas law; it is a cubic in v, and it contains characteristics of the particular substance. The best means of determining the numerical values of a and b is through two measurements of pressure and volume for a substance at a known temperature.

TABLE 11.—VAN DER WAALS' CONSTANTS a AND b
(For pressures in atmospheres and molal volumes in milliliters)[1]

Substance	a	b Ml per mole	a/v_m^2, atm., when v_m is	
			500 ml.	5000 ml
H_2	0.19×10^6	23.0	0.76	0.008
O_2	1.36×10^6	31.6	5.44	0.054
N_2	1.31×10^6	37.3	5.24	0.052
CO_2	3.61×10^6	42.8	14.4	0.14
CO	1.43×10^6	38.6	5.72	0.057
SO_2	6.69×10^6	56.5	26.8	0.27
C_2H_6	6.0×10^6	69.9	24.0	0.24
H_2O	5.87×10^6	33.2	23.5	0.23
NH_3	4.05×10^6	36.4	16.2	0.16

For example, when the molal volume of CO_2 is 1320 ml., the pressure is 15.07 atm. at 273°K. and 18.40 atm. at 321°K. Upon substituting these measured quantities into van der Waals' equation and solving for values of a and b that satisfy these condi-

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[1] For other data see *Z. physik. Chem*., **69**, 52 (1910), and "Landolt-Börnstein's Tables," pp. 253–263, 1923. Since the unit of volume used in these tables is a molal volume at 0° and 1 atm., the values of a given there should be multiplied by $(22{,}400)^2$ and those for b by 22,400, if they are to correspond to the units used in this table.

tions, we find $a = 4.6 \times 10^6$ and $b = 47$ ml. per mole. But if this process is repeated with other data for CO_2, somewhat different values of a and b are obtained, which shows that van der Waals' equation is not a complete representation of the properties of gases. It will readily be seen that the values of a and b that apply to CO_2 do not apply to some other gas, such as NH_3 or SO_2, since the volume and attractive force depend upon the substance. Data for various gases will be found in Table 11

Many of the recorded data for a and b are derived from the critical constants through a "reduced" equation of state that will be given in the next chapter. The quantities so derived are less suitable for pressure calculations at temperatures and pressures far removed from critical conditions than are a and b based on actual gas densities, since van der Waals' equation is not valid in the critical region.

The experimental facts (1) that a is not zero or negative for hydrogen and (2) that the Joule-Thomson expansion of hydrogen is attended by a rise in temperature show that b is not alone a volume correction but that repulsive forces of some kind are involved.[1]

For a constant molal volume the cohesive pressure a/v_m^2 in van der Waals' equation has the same value for a given gas at all temperatures, and for all temperatures and pressures the "incompressible volume" correction has the same value for a given substance. It seems more probable that these corrections are temperature functions, rather than constants, and the deviations of calculated pressures from observed pressures also show that some further corrections are required. The equation is a second approximation that indicates the type of correction needed but furnishes inadequate correction. If the same a and b are used over wide ranges of temperature and pressure, van der Waals pressures are sometimes in error more than ideal gas pressures; but in general a pressure calculated from van der

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[1] For a change of pressure from p_1 atm. to p_2 atm., the temperature change in a Joule-Thomson expansion is, nearly, $\Delta T = \left(\frac{2a}{RT} - b\right)\left(\frac{p_1 - p_2}{C_p}\right)$ if the van der Waals equation is accepted. It will be seen that ΔT is zero only when $2a/RT = b$. The "inversion" temperature for hydrogen is about −80°C., while that for most other gases is above room temperature. Thus, at temperatures below −80°C. hydrogen is cooled by expansion as is true of other gases.

Waals' equation will be more nearly correct than a pressure calculated from the ideal gas law.

As an illustration, we calculate the pressure for ethyl ether at 303°C. when the volume is 2120 ml. per mole and for which the measured pressure is 20.4 atm. Using the values of a and b in Table 11, we calculate from van der Waals' equation that the pressure is 20.3 atm., and from $p = RT/v_m$ we calculate the pressure to be 22.3 atm. Thus the ideal gas law pressure is 9 per cent above the actual pressure, and the van der Waals pressure is 0.5 per cent less than the actual pressure. Some other calculations involving these equations are shown in Table 13.

When the pressure becomes small and the volume of a mole of gas correspondingly large, the term a/v_m^2 becomes so small in comparison with p that it may be neglected; also, the volume b is negligible in comparison with the molal volume v_m, and it may be neglected. The equation of van der Waals thus reduces to the simple gas law at large molal volumes

Keyes's Equation.[1]—This equation, which agrees quite well with observed experimental data, may be written

$$\left(p + \frac{a}{(v_m - l)^2}\right)(v_m - \delta) = RT \qquad (16)$$

where a and l are constants characteristic of each substance and the logarithm of δ is a function of the volume, $\delta = \beta e^{-\alpha/v}$. Calculations based on this equation are rather difficult to carry out, but the agreement between observed and calculated pressures is excellent.

The Beattie-Bridgeman Equation of State.—When it is necessary to calculate pressures to within a few tenths of 1 per cent, the Beattie-Bridgeman equation[2] is recommended. It is

$$p = \frac{RT}{v_m} + \frac{\beta}{v_m^2} + \frac{\gamma}{v_m^3} + \frac{\delta}{v_m^4} \qquad (17)$$

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[1] KEYES, F. G., *Proc. Nat. Acad Sci* , **3,** 323 (1917)

[2] *J. Am. Chem. Soc* , **49,** 1665 (1927); **50,** 3133 (1928); *Proc. Am. Acad. Arts Sci.*, **63,** 229 (1928). A close approximation when volumes are to be calculated is

$$v_m = \frac{RT}{p} + \frac{\beta}{RT} + \frac{\gamma}{R^2T^2}p + \frac{\delta}{R^3T^3}p^2 \qquad (18)$$

in which the Greek letters have the same significance as in the other form of the equation in which the Greek letters represent constants and temperature functions as follows:

$$\beta = RTB_0 - A_0 - \frac{Rc}{T^2}$$

$$\gamma = -RTB_0b + A_0a - \frac{RB_0c}{T^2}$$

$$\delta = \frac{RB_0bc}{T^2}$$

In this equation R is 0.08206 liter-atm./mole-°K., v_m is the molal volume in liters, and the quantities A_0, a, B_0, b, and c are constants for a given gas but different for each gas. The values of these constants are given in Table 12.

Calculations made to check the validity of this equation show that it agrees with measured pressures up to 100 atm., and at temperatures of -150°C. or above, to within 0.3 per cent or less except near the condensation pressures for the temperatures used. Some of the calculated pressures for carbon dioxide are given in Table 13.

TABLE 12.—CONSTANTS OF THE BEATTIE-BRIDGEMAN EQUATION

Gas	A_0	a	B_0	b	$10^{-4}c$
He	0.0216	0.059 84	0.014 00	0.0	0.0040
Ne	0.2125	0.021 96	0.020 60	0.0	0.101
A	1.2907	0.023 28	0.039 31	0.0	5.99
H_2	0.1975	−0.005 06	0.020 96	−0.043 59	0.0504
N_2	1.3445	0.026 17	0.050 46	−0.006 91	4.20
O_2	1.4911	0.025 62	0.046 24	0.004 208	4.80
Air	1.3012	0.019 31	0.046 11	−0.011 01	4.34
CO_2	5.0065	0.071 32	0.104 76	0.072 35	66.00
CH_4	2.2769	0.018 55	0.055 87	−0.015 87	12.83
$(C_2H_5)_2O$	31.278	0.124 26	0.454 46	0.119 54	33.33
C_2H_4	6.1520	0.049 64	0.121 56	0.035 97	22.68
NH_3	2.3930	0.170 31	0.034 15	0.191 12	476.87
CO	1.3445	0.026 17	0.050 46	−0.006 91	4.20
N_2O	5.0065	0.071 32	0.104 76	0.072 35	66.00

Other Equations for Gases.—The equations that have been given above are not the only ones that have been proposed to represent the changes of pressure and temperature of a gas with volume; many others have been suggested, and new ones are being proposed from time to time.[1] A compressed gas is a complex system in which attractive and repulsive forces operate between the molecules and in which the "volume of the molecules" is a function of temperature and total volume. In a dilute gas these effects are not as important as they are in the compressed gas, of course, but they are not negligible if high precision is desired.

TABLE 13.—OBSERVED AND CALCULATED PRESSURES FOR CARBON DIOXIDE[2]
(Density in moles per liter, pressure in atmospheres)

t, °C.	Density	½	1	2	3	4
100°	Actual p	14.75	28.47	53.30	75.06	94.45
	$p = RT/v$	15.3	30.6	61.2	91.8	122.4
	Eq. (15)	14.74	28.3	52.5	72.8	89.5
	Eq. (17)	14.77	28.42	53.21	74.68	93.62
70°	Actual p	13.45	25.69	47.01	64.77	79.50
	$p = RT/v$	14.45	28.9	57.8	86.7	115.6
	Eq. (15)	13.85	26.6	48.8	66.9	81.8
	Eq. (17)	13.46	25.74	47.07	64.68	79.37
40°	Actual p	12.15	22.94	40.86	54.58	64.79
	$p = RT/v$	12.8	25.6	51.3	76.9	102.6
	Eq. (15)	12.2	23.2	41.7	55.9	66.1
	Eq. (17)	12.14	22.94	40.83	54.44	64.67
20°	Actual p	11.26	21.03	36.56	47.49	54.57
	$p = RT/v$	12.0	24.0	36.0	48.0	60.0
	Eq. (15)	11.35	21.5	38.0	50.5	58.0
	Eq. (17)	11.26	21.05	36.59	47.43	54.53

For engineering purposes, one may use an empirical treatment of the data by defining a quantity

$$\mu = \frac{pv_m}{RT} \tag{19}$$

which may be plotted against the pressure or some function of the pressure, as was done in Fig. 4 for propane. Another common device is to plot μ against the "reduced pressure," which is the ratio of the actual pressure to the critical pressure (the vapor

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[1] A review of some of these equations, with historical notes, is given in *J. Chem. Education*, **16**, 60 (1939).

[2] BEATTIE and BRIDGEMAN, *Proc. Am. Acad. Arts Sci.*, **63**, 229 (1928).

pressure for the highest temperature at which condensation is possible), for such a plot is linear for many gases. Whichever device is used, a separate line is drawn for each temperature or for temperatures at convenient intervals for interpolation.

References

Current research on gases frequently appears in the *Philosophical Magazine*, *Proceedings of the Royal Society of London*, *Communications of the Physical Laboratory of the University of Leiden*, *Wissenschaftliche Abhandlungen der Physikalischen-Technischen Reichsanstalt*, *Journal of the American Chemical Society*, *Zeitschrift fur Physik*, and *Physical Review*

Further treatment of the topics in this chapter may be found in books by Glasstone, "Text Book of Physical Chemistry," New York, 1940, and Kennard, "Kinetic Theory of Gases," McGraw-Hill Book Company, Inc , 1938.

Problems

Numerical data for solving some of the problems must be sought in tables in the text.

1. (*a*) Calculate the volume of a balloon with a lifting power of 400 kg at 20° and 1 atm , if the balloon is filled with hydrogen (*b*) Repeat the calculation for helium as the gas filling the balloon (*c*) Calculate the volume of the helium balloon in the stratosphere at −60°C and 0 1 atm.

2. When air is passed through a bed of fuel, part of the oxygen reacts to form CO and the remainder to form CO_2, and a molal volume of the emerging gas weighs 29 grams. Assume air to contain 21 mole per cent oxygen and 79 mole per cent nitrogen, and calculate the composition of the emerging gas.

3. When 0 00413 mole of bromine is introduced into a flask of 1050 ml. volume at 300°K. containing NO at an initial pressure of 0 229 atm., a chemical reaction as shown by the equation $2NO + Br_2 = 2NOBr$ takes place incompletely, and the final pressure becomes 0 254 atm (*a*) What fraction of the NO originally present has formed NOBr? (*b*) What is the partial pressure of the residual bromine vapor? (*c*) When this same mixture is heated to 500°K. in the same flask, the total pressure becomes 0 529 atm. Under these conditions what fraction of the original NO is combined with bromine?

4. (*a*) Calculate the weight of air in a 200-ml. incandescent light bulb if the pressure at 20°C. is 1 dyne per sq cm. (*b*) Calculate the number of molecules in the bulb.

5. (*a*) Calculate the velocity of oxygen molecules in air at 25°C. (*b*) Calculate the velocity of nitrogen molecules in air at 25°C. (*c*) At what temperature would the velocity of oxygen molecules be 1 mile per sec. (1610 meters per sec.)? (*d*) At what temperature would the velocity of hydrogen molecules be 1 mile per sec ?

6. From the data on page 72 calculate what fraction of the formic acid vapor has reacted according to the equation $2HCOOH = (HCOOH)_2$ at each of the temperatures.

7. (*a*) If 100 ml. of nitrogen under a constant pressure will flow through a given orifice in 155 sec., what is the molecular weight of a gas of which 100 ml. under the same pressure will flow through the same orifice in 175 sec.? (*b*) Assuming the gas to be a mixture of nitrogen and argon, calculate the mole fraction of argon in it.

8. Calculate the mass of CO_2 striking each square centimeter of a leaf in air containing CO_2 at a partial pressure of 0 0010 atm at 25°C.

9. (*a*) Calculate the value of the gas constant R from the limiting density data for CO_2 on page 15 (*b*) Calculate another value of R from the density of helium given in the footnote on page 53.

10. The ratio C_p/C_v for CO_2 at 293°K is 1 30 for 1 atm. pressure. Calculate the "internal heat capacity," the energy absorbed on heating and not used for increasing the translational kinetic energy of the molecules or for doing work

11. In the manufacture of SO_3 by the contact process 8 0 moles of air (assumed 21 mole per cent oxygen and 79 mole per cent nitrogen) enter a sulfur burner for each atomic weight of sulfur burned, and the density of the emerging mixture of SO_2, SO_3, O_2, and N_2 is 0 605 gram per liter at 700°K and 1 atm total pressure. Calculate the partial pressures of SO_3, SO_2, and O_2 in the mixture

12. A capsule containing 0 356 gram of a solid was dropped into a Victor Meyer bulb at 400°C , expelling 33 2 ml of air, measured over water at 20° and 1 atm total pressure Calculate the molecular weight of the substance at 400°

13. When 6 40 grams of SO_2 and 4 26 grams of chlorine are introduced into a 3-liter flask, partial union as shown by the equation $SO_2 + Cl_2 = SO_2Cl_2$ takes place, and the total pressure at 463°K becomes 1.69 atm Calculate the partial pressure of each gas in the mixture.

14. The vapor of acetic acid contains single and double molecules in equilibrium as shown by the reaction $(CH_3COOH)_2 \rightleftarrows 2CH_3COOH$. At 25° and 0 020 atm pressure the pv product for 60 grams of acetic acid vapor is 0 $541RT$, and at 40° and 0 020 atm. it is $0.593RT$. Calculate the fraction of the vapor forming single molecules at each temperature. (*Ans.:* 0.186 at 40°) [MacDougall, *J Am Chem. Soc.*, **58**, 2585 (1936).]

15. A glass bulb of 373 ml. volume, with a long capillary stem, weighs 29 450 grams when open to the air at 20° and 1 atm. In a molecular-weight determination by Dumas's method an excess of a volatile liquid is placed in the bulb, which is then heated in boiling water until the air and the excess of substance are expelled. The bulb is sealed and after cooling is found to weight 30 953 grams. Calculate the molecular weight of the substance.

16. One mole of ethane (C_2H_6) is exploded with 15 moles of air, and the products are cooled to 320°K. and 1 atm. total pressure. Assume that air is 21 mole per cent oxygen and 79 mole per cent nitrogen, that the only substances present are $CO(g)$, $CO_2(g)$, $N_2(g)$, $H_2O(g)$, and $H_2O(l)$, that all the gases are ideal, that the *volume* of condensed water is negligible, and that the vapor pressure of water at 320°K. is 0 10 atm. Calculate the volume of the mixture, the weight of condensed water, and the partial pressure of each of the gases.

17. When 0.296 mole of iodine is added to a space of 34.6 liters at 422°K. containing 0.413 mole of NOCl, partial reaction as shown by the equation

$$2NOCl(g) + I_2(g) = 2NO(g) + 2ICl(g)$$

takes place and the final pressure becomes 0.866 atm. Calculate the partial pressure of NO in the final mixture.

18. Lead nitrate decomposes on heating according to the chemical equation $Pb(NO_3)_2(s) = PbO(s) + N_2O_4(g) + \frac{1}{2}O_2(g)$. When the gaseous products are brought to 323°K., 45 per cent of the N_2O_4 is decomposed into NO_2 and the partial pressure of oxygen in the mixture is 0.184 atm. (*a*) Calculate the partial pressures of NO_2 and N_2O_4. (*b*) Calculate the weight of a liter of the gaseous mixture at 323°K.

19. When 3 atomic weights of phosphorus and 7 moles of chlorine are brought together at 523°K. the phosphorus is completely converted to a mixture of PCl_3 and PCl_5. At a final total pressure of 5 atm. 55 per cent of the phosphorus is in the form of PCl_3. (*a*) Calculate the density of the mixture in grams per liter at 523°K. and 5 atm. pressure. (*b*) Calculate the partial pressure of chlorine in the mixture.

20. When 1 mole of N_2 and 1 mole of H_2 react to equilibrium at 623°K., the chemical reaction $N_2 + 3H_2 = 2NH_3$ takes place incompletely and the density of the mixture is 3.10 grams per liter at a final total pressure of 10 atm. (*a*) What is the partial pressure of ammonia? (*b*) What fraction of the hydrogen reacted?

21. (*a*) Calculate the molecular volume of carbon dioxide at 70°C. and 23.56 atm and from this the specific volume in milliliters per gram, assuming it to be an ideal gas. (*b*) Calculate the molecular volume under these conditions by means of van der Waals' equation, solving the cubic by trial and using the measured specific volume, 25 ml. per gram, as a first estimate

22. The pressure in a liter flask containing 0.500 gram of NO_2 changes with the temperature as follows:

T, °K	521	615	658	714	795	820
p, atm.	0.488	0.628	0.705	0.810	0.965	1.000

The deviation of this pressure from that to be expected of NO_2 as an ideal gas is due to the incomplete chemical reaction $2NO_2 = 2NO + O_2$. (*a*) Plot the observed pressure against the absolute temperature, and show the pressure to be expected of undissociated NO_2 by a dotted line on the same diagram. (*b*) Derive a relation between the pressure to be expected of the undissociated gas, the increase over this pressure, and the fractional dissociation; and apply this relation to the diagram to determine the fraction dissociated at each temperature. (*c*) Calculate the partial pressure of each substance in the mixture at 820°K.

23. When a mixture of $2CS_2$ and $5Cl_2$ is heated, 90 per cent of the chlorine reacts as shown by the equation $CS_2(g) + 3Cl_2(g) = CCl_4(g) + S_2Cl_2(g)$. Calculate the volume of the resulting mixture at 373°K. and 1 atm. total pressure, and the partial pressure of each gas in the mixture.

24. When a mixture of $2CH_4$ and $1H_2S$ is heated, the reaction

$$CH_4(g) + 2H_2S(g) = CS_2(g) + 4H_2(g)$$

takes place incompletely, and the final volume is 259 liters at 973°K. and 1 atm. Calculate the partial pressure of each gas in the mixture.

25. (*a*) Calculate the pressure in atmospheres at which ammonia has a specific volume of 50 0 ml per gram at 200°C., assuming it an ideal gas. (*b*) Recalculate the pressure from van der Waals' equation. The measured pressure under these conditions is 41 9 atm.

26. The total pressure in a liter flask containing 1.159 grams of N_2O_4 is 0 394 atm at 25°, 0 439 atm at 35°, and 0 489 atm at 45°. Practically all the deviation from the ideal gas law is due to the incomplete dissociation of N_2O_4 into NO_2 Calculate the extent of this dissociation at 25° and at 45°. [VERHOEK and DANIELS, *J. Am. Chem. Soc.*, **53**, 1250 (1931).]

CHAPTER IV

PROPERTIES OF SUBSTANCES IN THE LIQUID STATE

The purpose of this chapter is to consider the vapor pressures, surface tensions, latent heats, viscosities, critical constants, and other properties of liquids. Since all gases may be changed to liquids by suitable changes in temperature and pressure and many liquids may be changed to gases or solids, it is evident that a liquid is only a substance in the liquid state under certain conditions. Under other conditions it may be a solid or a gas, and under suitable conditions a liquid may exist in equilibrium with both solid and vapor of the same composition or with either phase in the absence of the other. There is for every vapor a certain "critical temperature" above which it may not be condensed to liquid under any pressure. This critical temperature is 374.2°C. for water vapor, 31.1°C. for carbon dioxide, −118.7°C. for oxygen, and some characteristic temperature for every vapor. Below this critical temperature and above the "triple point" at which solid, liquid, and vapor are in equilibrium, there is for each temperature a single pressure at which liquid and vapor may be in equilibrium. This "vapor pressure" is also different for each substance at a given temperature; it is 57.0 atm. for carbon dioxide at 20° and 0.0231 atm. for water at 20°; and since 20° is above the critical temperature of oxygen, no pressure, however great, will cause oxygen to liquefy at 20°C.

Substances in the liquid state have greater densities, greater internal friction, larger cohesive pressures, and much smaller compressibilities than they have in the gaseous state. Many of the changed properties are due to greater attractive forces acting between the molecules. The molecules probably have the same kinetic energies as those characteristic of the gaseous state at the same temperature; but they have much shorter paths between collisions, much less freedom of motion, and much greater damping effects upon their motion. In contrast to the crystalline state that most liquids assume at still lower temperatures, liquids have no shape, no form elasticity but only internal friction. They usually have larger compressibilities, larger temperature coefficients of expansion, higher specific heats, and smaller densities than the substances in the crystalline form.

Our knowledge of the liquid state is much less complete than that of the gaseous state or the crystalline state, in spite of diligent study by competent physicists and chemists for many years. No experimental measurements yet enable us to calculate directly the attractive forces that cause condensation of a vapor to liquid or the cohesive forces between molecules in a liquid, but experiments on the angle and intensity of scattering at a given angle for molecular or atomic beams appear to be promising. It is estimated that the attractive force between molecules varies inversely as the seventh power of the distance between nonpolar molecules, but at close approach there are also repulsive forces acting between them. Such "calculated" attractions as we have rest upon assumptions of uncertain validity. From a review of numerous papers attempting to correlate the properties of liquids or to calculate some of their properties, Herzfeld[1] finds that calculations often disagree with measured properties by 50 per cent to fourfold. Evidently new experimental methods are urgently needed. We turn to a brief consideration of some of the experimental facts and such interpretations as are available

Liquid Solubilities.—Although gases mix with one another in all proportions without seriously influencing the properties of each gas (such as partial pressure), this is not true of all liquids. Some pairs of liquids, such as alcohol and water, chloroform and carbon tetrachloride, benzene and xylene, do mix in all proportions; other pairs, such as aniline and water or ether and water, mix only to a limited degree; still others, such as benzene and water or alcohol and mercury, do not dissolve in each other to an appreciable extent In the gaseous state all these substances mix in all proportions, but this is doubtless because of the greater separation of the molecules and the consequent lack of strong forces acting between them. In the liquid state, where molecules are very close to each other, specific attractive forces act between them, and these forces seem to govern the extent to which one liquid will dissolve in another. No general rules for solubility of liquids are free from exceptions, but it is usually true that

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[1] *J. Applied Phys* , **8**, 319 (1937); 43 references to recent work.

liquids of the same chemical type (two hydrocarbons, two liquid metals, or water and alcohols) are soluble in each other, while liquids of quite different natures exhibit slight attractions for each other. Thus when benzene (C_6H_6) dissolves in toluene (C_7H_8), the attractive forces between molecules are probably changed but little, because of the chemical similarity of the substances.

"Slightly soluble" liquids usually increase in solubility as the temperature rises; they often become completely soluble in one another at a sufficiently high temperature, but this temperature may be above the boiling point of the mixture for 1 atm. pressure. At 20°C. a saturated solution of phenol in water contains about 8 per cent phenol; when a larger percentage is present, a second liquid layer containing 72 per cent phenol and 28 per cent water is in equilibrium with the solution containing 8 per cent phenol and 92 per cent water. With rising temperature the compositions of the two layers approach one another, and above 66.8°C. the liquids mix in all proportions to form a single solution. Water and aniline also form two layers, which at 100°C. contain, respectively, 7.2 and 90 per cent aniline by weight. Complete solubility of each in the other is reached at 167°C. with the application of sufficient pressure to prevent evaporation.

Liquid solubilities also change slightly with pressure at constant temperature, but climatic variations in atmospheric pressure produce only negligible changes. Application of 100 atm. pressure raises the critical solution pressure of phenol in water by about 4.6°, and the effect of pressure upon other systems is likewise small.

Vapor Pressure.—The vapor pressure of a pure liquid is that pressure at which the liquid and vapor are in equilibrium. This equilibrium pressure, or saturation pressure, is a function of the temperature alone and is independent of the relative quantities of liquid and vapor present. Different liquids have different vapor pressures at a given temperature, and the vapor pressures change with temperature at different rates; but for a given pure substance at a given temperature there is only one pressure at which liquid and vapor are in equilibrium. If the volume of a vapor is gradually decreased at a constant temperature that is below the critical temperature, the pressure increases until the vapor pressure for that temperature is reached; after this further decrease in volume at constant temperature causes more condensation to liquid, and no increase in pressure is observed until condensation is complete.

Mixtures of liquids, and solutions in general, also have vapor pressures; but they depend upon the nature and relative proportions of the substances in the solution at a given temperature. We shall consider these vapor pressures in a later chapter, but we are now considering only the vapor pressures of pure liquids—one-component systems in which liquid and vapor have the same composition and exist together at a single pressure for a fixed temperature.

Vapor pressures of readily purified substances may be used to calibrate pressure gauges. For illustration, the equilibrium pressure between liquid CO_2 and its vapor at 0°C. is 34.041 atm.; and since 0°C. is the most readily reproduced standard temperature, a pressure gauge that does not read 34.041 atm. for the vapor pressure of CO_2 packed in a mixture of ice and water is in error by the amount its reading deviates from this pressure.

In the absence of liquid, the pressure of a vapor may be anything less than the vapor pressure for the prevailing temperature and retain this value indefinitely. Thus the difference between a vapor pressure and the pressure of a vapor is neither a pedantic distinction nor a play upon words; it is an important difference that must be clearly understood. An illustration or two may be helpful. Consider a flask of 12.045 liters at 50°C. containing a gram of water, which exerts a pressure of 0.1217 atm. Since this pressure is the vapor pressure of water at 50° and this volume is the specific volume of saturated water vapor at 50°, we have a pressure of water vapor equal to the vapor pressure. If we double the volume occupied by a gram of water vapor, the pressure of water vapor will become 0.0607 atm.; we no longer have saturated vapor, but the vapor pressure of water at 50° is still 0.1217 atm. If we increase the temperature to 70° and keep the volume 12.045 liters, the pressure will become 0.129 atm. but this pressure is not the vapor pressure of water at 70°C. or a quantity from which it may be calculated. The vapor pressure of water at 70°C. is 0.3075 atm., a pressure found by experiment upon water in equilibrium with its vapor at 70°C. If we cool the flask to 20°C., part of the water vapor will condense and the pressure of water vapor at equilibrium is 0.02307 atm., which is also the vapor pressure of water for this temperature. Doubling the volume at 20° would not evaporate all the gram of water, and therefore the pressure of water vapor and the vapor pressure would still be the same. But if the volume were increased beyond 57.87 liters (the specific volume of saturated vapor at 20°C.), the pressure of water vapor would decrease as indicated by the gas laws and would no longer be equal to the vapor pressure.

In the presence of air or of any inert slightly soluble gas at low pressure, the equilibrium pressure or saturation pressure of a liquid is substantially the same as its vapor pressure in the absence of the gas. Thus, in a mixture of 0.023 mole of water vapor and 0.977 mole of air at 20° and 1 atm total pressure, the partial pressure of water vapor is the same as its vapor pressure. If this mixture is heated to 30° at 1 atm., the partial pressures are unchanged; but since the vapor pressure of water at 30° is 0.0419 atm., the air at this temperature is 55 per cent saturated. Two other common expressions for the moisture content of the mixture at 30° are that the relative humidity is 55 per cent and that the dew point is 20°C.

Equilibrium between a liquid and its vapor, like any other condition of equilibrium, is not a stationary state but a condition of reactions at equal rates in opposite directions. Thus at 20° the pressure exerted by a gram of water in a volume of 1 liter, or 10 liters, or 50 liters is 0.02307 atm., but at each volume we must suppose that water is evaporating and water vapor is condensing at the same rate to keep this pressure constant. If the volume is quickly decreased, there is a temporary increase in pressure, which increases the rate of condensation while the rate of evaporation remains constant; and with the passage of time the pressure returns to 0.02307 atm. after the removal of enough heat to restore the temperature to 20°.

Measurement of Vapor Pressures.—In theory the measurement of a vapor pressure over a range of temperatures is a very simple operation; namely, one measures on a gauge the pressure under which liquid and vapor exist at equilibrium for each temperature. But there are many experimental difficulties in carrying out this simple operation in such a way as to yield precise data. Removal of the last traces of dissolved air from a liquid (which requires prolonged shaking with periodical pumping out of air, followed by repeated distillation under very low pressure) is necessary if the gauge is to show the pressure of vapor alone and not the pressure of vapor plus air. Containers and precise gauges that will withstand high pressures, be inert to the liquid, and possess the requisite mechanical, thermal, and elastic properties are difficult to design and construct. All these problems have been solved, and reliable vapor-pressure data are available for water and most of the fluids used in refrigeration. Vapor pressures of most of the common liquids at temperatures below their boiling points have also been measured, but one must exercise some judgment in selecting data, for some of the pressures were measured before the experimental difficulties involved were fully appreciated.

Vapor pressures for several substances are given in Table 14.

Air-bubbling Method.—Vapor pressures of liquids at temperatures well below their boiling points may be measured with fair precision by saturating a known quantity of air or nitrogen with the liquid, passing the mixture of air and vapor through an absorbing agent, and weighing the absorbed vapor. For example, if 10 liters of air at 20°C. and 1 atm. are bubbled through several tubes of water at 20°C and the water in the saturated air is absorbed in sulfuric acid and weighed, it will be found that 0.178 gram of water saturated the air. Reducing these figures to moles, 0.416 mole of air and 0.00984 mole of water vapor emerged from the saturating vessel at 20°C. and 1 atm. The partial pressure of water vapor in the mixture, on the basis of Dalton's law of partial pressures, is $0.00984/0.4258 = 0.023$ atm., which is also the vapor pressure of water at 20°. If the experiment is repeated at 25°, 0.0132 mole of water vapor will saturate 0.416 mole of air and the vapor pressure will be found to be 0.031 atm. But one may not find by this method that the vapor pressure of water is 0.02307 atm. at 20° and 0.031254 atm. at 25°, no matter how carefully the experiments are performed, for the ideal gas law does not apply to this mixture of gases with the requisite precision.

Change of Vapor Pressure with Total Pressure.—In the air-saturation method of measuring vapor pressure, the total pressure acting on the liquid phase is 1 atm., while at equilibrium in an evacuated space the pressure on the liquid is only 0.023 atm. at 20°. There is a very slight increase of vapor pressure caused

TABLE 14—VAPOR PRESSURES OF LIQUIDS
(In millimeters)[1]

t, °C.	H_2O	CCl_4	C_2H_5OH	Ethyl ether	C_6H_6	n-C_8H_{18}	SO_2
10	9 21	..	23 6	291 7	.	5 62	2 256*a*
15	12 79	.	32 2	360 7	..		.
20	17 53	91	43 9	442 2	.	10 45	3 288*a*
25	23 75	113 8	59 0	537 0	.		.
30	31 82	141.5	78 8	647 3	119 6	18 40	4 498*a*
35	42 17	174 4	103 7	775 5	148 2		..
40	55 31	213.3	135 3	1.212*a*	182 7	30 85	6 125*a*
45	71.86	258 9	174 0	......	223 2	. .	. ..
50	92.50	312 0	222 2	1.680*a*	271 3	49 35	8.176*a*
55	118 04	373 6	280.6	..	340 7	.	. ..
60	149.38	444 3	352.7	2 275*a*	391 66	77 55	10 73*a*
70	233.69	617 43	542 5	3.021*a*	551 0	117 9	13 87*a*
80	355.18	1.10*a*	812.6	3.939*a*	757 6	174 8	17 68*a*
90	525 82	1 46*a*	1.562*a*	5 054*a*	1 42*a*	253 4	22 27*a*
100	1.000*a*	1.92*a*	2.228*a*	6 394*a*	1 76*a*	353 6	27 71*a*
110	1 414*a*	2 47*a*	3 107*a*	7 987*a*	2 29*a*	... .	34 09*a*
120	1 959*a*	3 20*a*	4 243*a*	9 861*a*	2 93*a*	.	41 43*a*
130	2.666*a*	3 95*a*	5.685*a*	12.05*a*	3.71*a*	... .	49 70*a*

TABLE 15.—VAPOR PRESSURE, VOLUME, AND ΔH FOR WATER

Vapor pressure, atm.	T, abs.	Specific volume of		dp/dT, atm. per degree	ΔH, cal. per gram
		liquid	vapor		
0 1217	323	1 0121	12045.0	0 006039	568.9
1.0000	373	1 0434	1673 2	0 0357	539.0
4.6977	423	1.0906	392 46	0 1260	504 9
15 352	473	1.1565	127.18	0 3211	463.3
39 256	523	1 2512	50 06	0 6629	409.6
84 776	573	1 4036	21.62	1.1942	334.9
163.164	623	1.7468	8.802	2.0031	213.2
218 5	647.3	3 15	3.15	....	0

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[1] Pressures marked *a* are in atmospheres. The data for water are from Smith, Keyes, and Gerry, *Proc. Am. Acad. Arts Sci.*, **69,** 137 (1934); for CCl_4 and C_6H_6 below 1 atm. from Scatchard, Wood, and Mochel, *J. Am. Chem. Soc*, **61,** 3206 (1939); for other substances from "International Critical Tables." Some additional data for water are

t, °C.......	16	17	18	19	21	22	23	24
p, mm... .	13.63	14.53	15 48	16.48	18 65	19 83	21 07	22 38

by this increase of pressure on the liquid. The equation for this increase is[1]

$$\left(\frac{\partial p}{\partial P}\right)_T = \frac{v_l}{v_g} \tag{1}$$

where p is the vapor pressure, P the total pressure, v_l the molal volume of the liquid, and v_g the molal volume of saturated vapor at T. The equation may be integrated between limits, after separating the variables, by neglecting the slight compressibility of the liquid and assuming $v_g = RT/p$ for the vapor. Then the equations are

$$d \ln p = \frac{v_l}{RT}\, dP$$

and

$$2.3 \log \frac{p_2}{p_1} = \frac{v_l}{RT}\,(P_2 - P_1) \tag{2}$$

If air at 100 atm. presses upon liquid water at 25°, the partial pressure of water vapor in the air at equilibrium will be about 1.07 times the vapor pressure when no air is present, as will be found when the appropriate quantities are substituted in this equation. For air at 1 atm. in contact with water, the increase in vapor pressure with the total pressure (about 0.07 per cent) is commonly neglected.

Change of Vapor Pressure with Temperature.—The vapor pressures of liquids increase with increasing temperature, and the increase per degree also increases as the temperature rises. Data showing the vapor pressures of some common liquids are given in Table 14.[2] The rate at which the vapor pressure changes with the absolute temperature is given by the following exact equation, called the Clapeyron equation:

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[1] The equation follows from equation (32) on p. 47 in view of the fact that ΔF is zero for any phase change taking place isothermally at equilibrium, since $d\mathbf{F}_l$ then equals $d\mathbf{F}_g$ when the pressure changes and

$$v_g\, dp = v_l\, dP \qquad (t \text{ const.})$$

which rearranges to give (1) above.

[2] For the vapor pressures of most substances that have been studied, see "International Critical Tables," Vol III, pp. 201–249; a review of the data on vapor pressures of inorganic substances is given by Kelley in *U.S. Bur. Mines Bull.*, **383** (1935).

$$\frac{dp}{dT} = \frac{\Delta H}{(v_g - v_l)T} = \frac{\Delta H}{T\,\Delta v} \tag{3}$$

In this equation ΔH is the quantity of heat absorbed in vaporizing v_l ml. of liquid to form v_g ml. of saturated vapor, dp/dT is the rate at which the vapor pressure increases with the temperature, and Δv is the increase in volume attending evaporation.

The Clapeyron equation follows from equation (31) on page 47, which was

$$d\mathbf{F} = -S\,dT + v\,dp$$

We note that for the isothermal evaporation of a liquid under its vapor pressure $\Delta\mathbf{F} = \Delta H - T\,\Delta S = 0$ from equation (33*t*) on page 47; therefore, the free energies of liquid and vapor change with temperature by the same amount. The equations for each phase are

$$d\mathbf{F}_g = -S_g\,dT + v_g\,dp$$
$$d\mathbf{F}_l = -S_l\,dT + v_l\,dp$$

and upon equating them and rearranging, we have

$$\frac{dp}{dT} = \frac{S_g - S_l}{v_g - v_l}$$

But $S_g - S_l = \Delta S$, which is $\Delta H/T$ when evaporation takes place isothermally and reversibly; and, upon making this substitution above, we obtain

$$\frac{dp}{dT} = \frac{\Delta H}{T\,\Delta v} \tag{3}$$

Clapeyron's equation follows from the third "Maxwell relation" given on page 48; but since the system is monovariant when a liquid and its vapor are at equilibrium, there is only one independent variable and the equation becomes

$$\frac{dp}{dT} = \frac{dS}{dv} = \frac{\Delta S}{\Delta v}$$

Upon multiplying numerator and denominator of the right side by T and noting that $T\,\Delta S = \Delta H$, the equation is then

$$\frac{dp}{dT} = \frac{\Delta H}{T\,\Delta v} \tag{3}$$

The Clapeyron equation may also be derived from a cycle of changes whereby heat is transferred from one temperature to another by a reversible cycle involving the phase change and for which the maximum work is given by equation (13) on page 38,

$$dw = q\frac{dT}{T}$$

where q is the heat absorbed at the higher temperature. Let the cycle consist of the following steps: (1) Evaporate a quantity of liquid reversibly under its vapor pressure p at T, for which the work done is $w_1 = p(v_g - v_l)$ and the heat absorbed is ΔH. (2) Cool the vapor to $T - dT$; by this means the pressure becomes $p - dp$ and the volume of saturated vapor becomes $v_g - dv_g$, for which $w_2 = -(p - dp)dv_g$ or $-p\,dv_g$ if the second-order quantity is neglected. (3) Condense the vapor to liquid reversibly under its vapor pressure $p - dp$ at $T - dT$, for which

$$\begin{aligned} w_3 &= (p - dp)[(v_l - dv_l) - (v_g - dv_g)] \\ &= pv_l - p\,dv_l - pv_g + p\,dv_g - v_l\,dp + v_g\,dp \end{aligned}$$

if the second-order quantities are neglected. (4) Heat the liquid to T, for which $w_4 = p\,dv_l$. The summation of these work quantities is $(v_g - v_l)dp$; and, upon substituting this quantity for dw and ΔH for q in the equation above, we have

$$\frac{dp}{dT} = \frac{\Delta H}{(v_g - v_l)} = \frac{\Delta H}{T\,\Delta v}$$

which is again equation (3).

This equation, while derived for the change of vapor pressure of a liquid with changing temperature, came from fundamental equations of the second law of thermodynamics applying to any equilibrium phase change in a system of constant composition. We shall also use it later for the change of melting point of a solid with pressure, for the vapor pressures of solids, and for any change for which the pressure is a function of temperature alone.

The Clapeyron equation does not apply when the pressure is a function of some quantity other than temperature. For example, the pressure at which $Na_2CO_3(s)$, $NaHCO_3(s)$, $H_2O(g)$, and $CO_2(g)$ are at equilibrium depends upon the composition of the gas phase as well as upon the temperature, and thus the Clapeyron equation does not apply to this system at every composition.

For calculations involving equilibrium between a liquid and its vapor at pressures near or below 1 atm. and over small ranges of temperature, the Clapeyron equation may be put into a more convenient form by the use of some approximations. The derived equation is, of course, valid only to the extent that the approximations are valid. If we assume that v_l is negligible in comparison with v_g, that $v_g = RT/p$, and that ΔH is a constant, the equation becomes

$$\frac{dp}{dT} = \frac{p\,\Delta H_m}{RT^2} \qquad \text{or} \qquad d \ln p = -\frac{\Delta H_m}{R}\, d\left(\frac{1}{T}\right) \tag{4}$$

in which ΔH_m is now the *molal* latent heat, since Δv is taken as RT/p and not nRT/p.

A plot of ln p against $1/T$ for the vapor pressure of water between 323 and 373°K. is substantially linear, and equation (4) shows that its slope should be $-\Delta H_m/R$, from which we find $\Delta H_m = 10{,}100$ cal. The true value of ΔH_m is 10,250 cal. at 323°K. and 9700 cal. at 373°K. At higher pressures the curvature of the plot becomes apparent, and larger deviations are found. Between 473 and 573°K. saturated water vapor deviates widely from ideal gas behavior, and ΔH_m changes 25 per cent. In this range a plot of ln p against $1/T$ shows some curvature, and the slope at 523°K. gives $\Delta H_m = 9100$ cal., while the correct ΔH_m at this temperature is 7370 cal. Thus the fact that the curvature is small is not proof of the validity of the simplifying assumptions. At these high pressures the decrease in ΔH_m is somewhat compensated by the fact that Δv is less than RT/p, so that a plot of ln p against $1/T$ is nearly straight but of the wrong slope. We must understand that these deviations are due to the assumptions made in obtaining equation (4) from (3), and not to any defect in equation (3), which is exact. If measured volumes of liquid and vapor and the correct slope of the vapor-pressure-temperature curve at 523°K. are substituted into equation (3), the correct ΔH_m will be found, namely, 7370 cal.

Over moderate ranges of temperature in which the vapor pressure is near or below 1 atm. the vapor pressure may be expressed as a function of the temperature with reasonable approximation by the integral of equation (4),

$$\log p = -\frac{\Delta H}{2.3RT} + \text{const.} \tag{5}$$

The change of ΔH with temperature is usually expressed by an equation in ascending powers of T; therefore, for higher precision, vapor pressures are expressed by equations of the form

$$\log p = \frac{A}{T} + BT + CT^2 + D + \cdots \tag{6}$$

and the coefficients A, B, C, D are adjusted to fit the data for the chosen units of pressure. As an illustration, the vapor pressure of SO_2 below 273°K., in centimeters of mercury, is given by the equation[1]

$$\log p = -\frac{1867.52}{T} - 0.015865T + 0.000015574T^2 + 12.0754$$

For another substance the equation would have a different set of numerical quantities but would be of the same form.

For some purposes the integral between limits of the approximate equation (4) is convenient. If ΔH is sufficiently constant over the interval involved,[2] the integral is

$$2.3 \log \frac{p_2}{p_1} = \frac{\Delta H_m}{R}\left(\frac{T_2 - T_1}{T_2 T_1}\right) \tag{7}$$

As the pressures appear in a ratio, p_2/p_1, they may be expressed in any units, but $R = 1.99$ cal. when ΔH_m is in calories per mole. By substituting $p = 0.0946$ atm. for 45°C. and $p = 0.1553$ for 55° in this equation, ΔH_m for water at 50° is calculated as 10,300 cal., which is satisfactory. As another example, the vapor pressure of benzene is 700 mm. at 77.43° and 777.2 mm. at 80.82°, whence $\Delta H_m = 7600$ cal., which should be compared with 7600 by direct experiment at 80.1°.

Boiling Point.—The boiling point of a liquid is defined as the temperature at which its vapor pressure is 1 atm. The temperature at which a liquid is observed to boil in the laboratory is a

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[1] GIAUQUE and STEPHENSON, *J. Am. Chem. Soc*, **60,** 1389 (1938).

[2] The change of ΔH_m (in calories) with the temperature for water is as follows:

t	0°	50°	95°	100°	105°	200°	300°
ΔH_m	10,760	10,250	9760	9700	9640	8360	6030

variable quantity depending upon the existing barometric pressure, and it is often necessary to apply a correction to such observed boiling temperatures in order to change them to standard boiling points. This correction is usually small, but in places of high altitude it may be several degrees; failure to make such corrections in reporting boiling points has led to small errors in recorded data. It is partly for this reason that the melting point of an organic substance (which is not appreciably affected by moderate changes of pressure) is a better guide to its purity than the boiling point.

The rise in boiling point of a pure liquid per millimeter increase in external pressure is nearly the same fractional amount of the absolute boiling point for all substances, about 0.00010. In using this approximate rule to compute a boiling point at 1 atm. from that observed at some other pressure, one should subtract $0.00010T\ (p - 760)$ from the observed temperature. For illustrations, water[1] boils at 100.73° under a pressure of 780 mm., and $20 \times 373 \times 0.00010$ is 0.75°; benzene[2] boils at 79.80° under a pressure of 753.1 mm., and $6.9 \times 354 \times 0.00010$ is 0.25°, whence the calculated boiling point at 760 mm. is 80.05° and the observed one is 80.09°.

For pressures far removed from atmospheric, this simple rule will not give the proper correction. Thus at 525 mm. pressure the boiling point of water calculated according to this rule is 91.2°; the experimental boiling point under this pressure is 90.0°. When it is desired to calculate boiling points at pressures considerably removed from 1 atm., the approximate form of the Clapeyron equation (7) will give results of reasonable accuracy; thus in the example just considered, by substituting 9700 cal. for ΔH_m, 1.99 cal. for R, 373 and 760 for T_2 and p_2, 525 for p_1, and solving for T_1, we find $T_1 = 362.8$, whence t is

---

[1] The change in boiling temperature of water with changing barometric pressure is as follows:

p, mm	700	720	740	780	800
t, °C	97.712	98.492	99.255	100.729	101.443

[2] **Smith** and **Matheson**, *J. Research Natl. Bur. Standards*, **20**, 641 (1938), give the boiling temperature of benzene at various pressures as follows:

p, mm	674.4	699.6	712.6	739.4	753.1	764.8	777.2
t, °C	76.26	77.43	78.02	79.20	79.80	80.29	80.82

calculated to be 89.7°, compared with 90° by experiment. These calculations will illustrate the errors to be expected from the use of these two approximate rules.

An equation giving the boiling point of water to within about 0.001° in the pressure range 700 to 830 mm. is[1]

$$t = 100 + 0.03697(p - 760) - 1.959 \times 10^{-5}(p - 760)^2$$

Latent Heat of Evaporation.—Recorded latent heats are usually for evaporation at 1 atm. pressure and are written ΔH, so that enthalpy increase for evaporation would be a more precise term. For evaporation into an evacuated space $q_v = \Delta E = \Delta H - \Delta(pv)$, and at moderate pressures Δv is nearly the volume of vapor formed, which is nRT/p. We shall confine our discussion to evaporation at constant pressure, for which the latent heat is ΔH.

The experimental determination of latent heats is very simple in theory and very difficult in practice. One need only measure the quantity of heat added to a liquid at its boiling point and the quantity of vapor formed. But, in order to be sure that all the added heat is used in evaporation, one must prevent heat flow through apparatus in which temperature gradients exist or apply corrections for them, prevent reflux of condensed vapor to the evaporator, prevent entrainment of spray in the escaping vapor, and prevent superheating of the vapor. If the calorimeter is run as a condenser, one must eliminate spray without superheating the vapor, avoid incomplete condensation, prevent or correct for heat flow along the condenser coil, and meet other difficulties. All these problems have been solved[2] and accurate latent heats of evaporation for water have been measured over a wide temperature range, but a glance at the reference quoted will show that much skill and patience were required.

Exact latent heats may also be obtained from the Clapeyron equation through the use of measured volumes of liquid and saturated vapor and from dp/dT obtained by differentiating the vapor-pressure equation with respect to temperature. The many experimental difficulties were troublesome in this method

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[1] Michels, Blaisse, Seldham, and Wouters, *Physica*, **10**, 613 (1943).

[2] See for example, Osborne, Stimson, and Flock, *J. Research Natl Bur. Standards*, **5**, 411 (1930); Osborne, Stimson, and Giddings, *ibid.*, **18**, 389 (1937); **23**, 197 (1939).

as well, but they have been solved;[1] and the method has been used to determine latent heats for water that agree with those based on direct calorimetry to within 1 part in 3000. Data of nearly as good quality are available for a few other substances used in refrigeration over suitable temperature ranges, but most of the recorded latent heats are for 1 atm. pressure and the normal boiling point.[2] Those based on vapor pressures or from direct calorimetry are usually reliable to 2 or 3 per cent, but many of the latent heats of evaporation in tables have been derived from boiling-point changes for solutions through equations that will be derived in Chap. VI. Some of these are also reliable to 2 or 3 per cent, but many of them are in error by something like 10 per cent, and tables do not usually indicate sources of data or probable errors. For example, the latent heat of evaporation for a mole of bromine at 59°C. is given in the common reference books as 7280, 7410, 7000, 7200, and 7520 cal., with no means of deciding which value is best.

Latent heats of evaporation decrease with rising temperature and become zero at the critical temperature. The rate at which the latent heat decreases also becomes greater at higher temperature, as may be seen from the data for water in Table 15 and for alcohol on page 140.

Molal latent heats are roughly the same for liquids of the same boiling point and are higher for liquids of higher boiling point. This fact is expressed in the so-called "Trouton's rule," which states that the molal latent heat in calories is 22 times the absolute boiling point of the liquid. This approximation may be written

$$\frac{\Delta H_m}{T} = 22 \qquad \text{or} \qquad \Delta S_{\text{evap}} = 22 \tag{8}$$

It is at best only a rough estimate, as shown by the fact that in a tabulation for 153 liquids the average Trouton "constant" was 22.1 and 40 of the liquids deviated from this average by more than 10 per cent. From this rule the estimated ΔH_m for water is 8200 cal., compared with 9700 by experiment; the esti-

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[1] See, for example, SMITH, KEYES, and GERRY, *Proc. Am. Acad Arts Sci.*, **69**, 137, 285, (1934), **70**, 319 (1936).

[2] The best compilation of latent heats is by Kelley, *U.S. Bur. Mines Bull.*, **383** (1935).

mated ΔH_m for benzene is 7800, compared with 7600 by experiment. Large deviations are usually found for liquids in which the dipole moments are capable of associating the hydrogen bonds.[1]

Critical Conditions.—There is a *critical temperature* for each substance above which it cannot be condensed to a liquid phase at any pressure. At any temperature below the critical temperature a vapor condenses when the applied pressure reaches the vapor pressure for that temperature. Since the vapor pressures of most substances at the critical temperature are less than 100 atm. and much higher pressures are readily reached, it seems suprising that higher pressures cannot cause condensation above a sharply defined temperature that is usually about 1.5 times the boiling point on the absolute scale for 1 atm. pressure. Yet there is ample experimental evidence that no condensation to liquid occurs above the critical temperature, even at extreme pressures. There are additional facts showing that there is a temperature above which liquid does not exist, such as that (1) the densities of liquid and saturated vapor become identical at the critical temperature, (2) the surface tension approaches zero at this temperature, (3) the latent heat of evaporation becomes zero at this temperature, and (4) the isotherms near the critical volume have different characteristics above and below this temperature (see Figs. 10 and 11).

The *critical pressure* is the last point on the vapor-pressure curve, the *critical density* is the density of both liquid and saturated vapor at the critical temperature, and the *critical volume* is the volume of a gram of liquid (or vapor) at the critical temperature and pressure.

The so-called "law of Guldberg-Guye" states that the critical temperature is 1.5 times the boiling point, both temperatures being on the absolute scale; that is, $T_c/T_b = 1.5$. The ratio is between 1.45 and 1.55 for many liquids, but wider deviations are not uncommon; for example, the ratios are 1.72 for water, 1.88 for oxygen, and 1.69 for ammonia, so that the "law" is only a rough approximation. Some data for liquids are given in Table 16.

Law of Average Densities.—As the temperature rises, the density of saturated vapor increases rapidly, owing to the increase

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[1] HILDEBRAND, *Proc. Phys. Soc.* (*London*), **56**, 221 (1944).

TABLE 16.—DATA FOR LIQUIDS

Substance	Absolute boiling point	Absolute critical temperature	ΔH_m, cal per mole at 1 atm.	Critical pressure, atm	Critical density, g per ml
Acetic acid	391.4	594.8	5800	57.2	0.351
Acetylene	189.5	309		62	0.231
Ammonia	239.7	405.6	5560	111.5	0.235
Argon	87.4	151	1500	48	0.531
Benzene	353.3	561.7	7600	47.7	0.304
Butane (*n*)	273.7	425.2	5320	37.5	0.225
Carbon dioxide	[1]	304.3	[1]	73.0	0.460
Carbon monoxide	81.1	133.0	1480	34.5	0.301
CCl_4	349.8	556.3	7290	45.0	0.558
Chlorine	240	417.2	4410	76.1	0.573
Ethane	184.8	305.4	7800	48.2	0.203
Ethanol	351.4	516.2	9400	63.1	0.275
Ethyl chloride	285.3	460.4	5960	52	0.33
Ethyl ether	307.7	466.0	6220	35.5	0.263
Ethylene	169.3	282.8		50.9	0.22
Helium	4.2	5.2	24	2.3	0.069
Heptane (*n*)	371.5	540.2	7650	27.0	0.243
Hexane (*n*)	342.1	507.9	6830	29.6	0.234
Hydrogen	20.5	33.3	215	12.8	0.031
Methane	111.7	190.7	2040	45.8	0.162
Methanol	337.8	513.2	8420	98.7	0.272
Methyl chloride	249.3	416.3	5170	65.8	0.37
Neon	27.2	44.5	415	25.9	0.484
Nitrogen	77.3	126.1	1330	33.5	0.311
Octane (*n*)	397.7	569.4	8100	24.7	0.233
Oxygen	90.1	154.4	1595	49.7	0.430
Pentane (*n*)	309.3	470.3		33.0	0.232
Propane	228.6	377.4		42.0	0.226
Sulfur dioxide	263.0	430.4	6070	77.7	0.52
Sulfur trioxide	317.7	491.5	9500	83.6	0.630
Toluene	383.6	593.8	7980	41.6	0.292
Water	373.1	647.3	9700	218.5	0.318

of vapor pressure of the liquid. The density of the liquid phase decreases as the temperature rises, at first slowly, then more rapidly as the critical temperature is approached. At the critical temperature the density of liquid becomes the same as that of the saturated vapor. In this region there is considerable diffi-

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[1] Vapor and liquid not in equilibrium at 1 atm pressure.

culty in distinguishing the separate phases, and an exact determination of the critical density is difficult. It has been found that, as the critical temperature is approached, the average of the density of the liquid and its saturated vapor is a linear function of the temperature. This statement will be clearer from Fig. 9, which shows the density of liquid argon and its coexisting saturated vapor. By plotting this average density against the temperature and drawing a straight line through the points it is easy to determine the point at which this line intersects the curve showing the density of each phase and thus to read the critical density. This statement is known as the law of Cailletet and Mathias, after its discoverers, or as the law of rectilinear diameters, since the diameter of the density curve is a straight line.

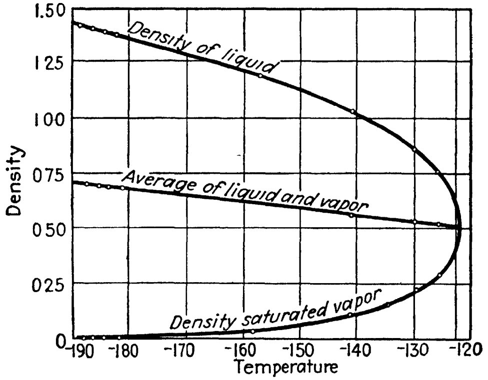

FIG. 9.—Densities of liquid argon and its saturated vapor.

Isotherms in the Region of Condensation.—When pressure is plotted against molal volume at a series of constant temperatures, a diagram such as Fig. 10 results. For a temperature T_1, which is below the critical temperature, the pressure increases with decreasing volume along CD until the vapor pressure for T_1 is reached at the point C. Under this constant pressure the volume decreases from C to B while condensation takes place. In the region between C and B the "molal volume" is governed by the fraction condensed and is thus not a function of p and T alone. At a higher temperature such as T_2, condensation occurs at a higher pressure, the molal volumes of saturated liquid and saturated vapor are more nearly equal, and ΔH_m is smaller.

These changes all continue until the critical temperature T_3 is reached, and at this point $v_{\text{liq}} = v_{\text{vapor}}$ and $\Delta H_m = 0$. The behavior of a fluid in this region is shown by measurements on ethane,[1] which are plotted to scale in Fig. 11 for temperatures very close to the critical temperature. It will be noted that the critical isotherm at 32.27°C., which is tangent to the two-phase area, is horizontal at the critical temperature. At this point

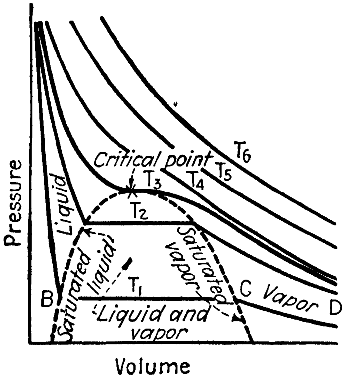

FIG. 10.—Isotherms on a pressure-volume plane

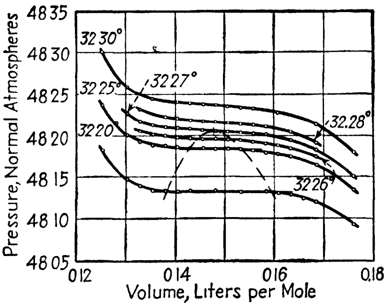

FIG. 11.—Isotherms of ethane in the critical region.

$$\left(\frac{\partial p}{\partial v}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0$$

Reduced Equation of van der Waals.—Since at the critical temperature $(v - v_c) = 0$, one may expand the equation $(v - v_c)^3 = 0$, which gives

$$v^3 - 3v_cv^2 + 3v_c^2v - v_c^3 = 0$$

write van der Waals' equation in the expanded form

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

and, by equating the coefficients of the various powers of v, derive the relations

$$a = 3v_c^2p_c \quad \text{and} \quad b = \frac{v_c}{3}$$

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[1] BEATTIE, SU, and SIMARD, *J. Am. Chem. Soc.*, **16**, 924 (1939).

Such a procedure is often used to obtain numerical values of these "constants" a and b; but since van der Waals' equation near the critical region is not reliable, the values of a and b so derived will not be suitable for calculations involving this equation at temperatures and pressures far removed from the critical region.

The critical data for carbon dioxide in Table 16 lead to the values $a = 8.4 \times 10^6$ and $b = 32$ ml. per mole; and if the constants so derived are used to calculate the pressure at which carbon dioxide has a molal volume of 880 ml. at 323°K., the calculated pressure is 21.5 atm. compared with the observed pressure of 26 4 atm. The values of a and b in Table 11 lead to a calculated pressure of 26.9 atm. for these conditions.

If the "reduced" temperature is defined as $T/T_c = \theta$, the "reduced" volume as $v/v_c = \varphi$, and the "reduced" pressure as $p/p_c = \pi$, so that the quantities are expressed as fractions of the critical quantities for each substance in place of being in the same units for all substances, one obtains van der Waals' *reduced equation of state*,

$$\left(\pi + \frac{3}{\varphi^2}\right)(3\varphi - 1) = 8\theta \tag{9}$$

It will be observed that there are no quantities appearing directly in the equation which are properties of any particular substance; but, of course, the reduced quantities themselves have the characteristic constants p_c, v_c, and T_c in them. Thus a reduced pressure of unity is 73 atm. for carbon dioxide, 52 atm. for ethyl chloride, 218 atm. for water, etc. These reduced quantities lead to certain simple relations more suited for plotting than the actual data; for example, reduced isometrics (plots of π against θ for constant φ) fall on the same straight line for all the hydrocarbons, CH_4, C_2H_6, C_2H_4, C_3H_8, C_5H_{12}, and C_7H_{16}.

Plots of $\mu = pv_m/RT$ against the *reduced* pressure for a range of *reduced* temperatures for all saturated hydrocarbons above methane are identical for each reduced temperature. This fact indicates that reduced temperatures, pressures, and volumes are "corresponding states" and thus indicates that there is some fundamental "law of corresponding states." But since the reduced equation of van der Waals does not yield exact pressures or volumes, it will be clear that some further modification or some other equation of state is required to show fully what this law is.

Surface Tension.[1]—The familiar fact that drops of liquid are nearly spherical indicates some kind of tension within the surface that acts to reduce the surface area to the smallest value consistent with existing conditions. This force is due to molecular attraction. A molecule in the bulk of a liquid is attracted equally in all directions by surrounding molecules in a region of equal density, but a molecule in the surface is attracted toward the liquid phase more than toward the vapor phase of smaller density, and there is a resultant force acting upon it in the interface. Surface tension is measured in dynes per centimeter of film edge, and the surface free energy is the work required to increase the surface area 1 sq. cm.; *i.e.*, we measure surface *tension* in dynes per centimeter and surface *free energy* in dynes per square centimeter.

For any pure liquid the surface tension has a fixed value at a fixed temperature. It may be measured by the height to which a liquid rises in a capillary tube of known radius, by the maximum weight of a drop that will hang from a circular tip, by the pressure required to form bubbles at the end of a submerged tube, by the force required to pull a submerged ring out of a surface, and by other methods. Surface tensions of solutions may also be measured by these methods, but they depend upon the nature and concentration of dissolved substance as well as upon the temperature. We shall see later that the composition of a surface layer may be quite different from that of the bulk of the solution; therefore, when the surface is extended, sufficient time must be allowed for the new surface to come to equilibrium with the underlying liquid before the surface tension is measured. Serious errors in some of the recorded data are due to failure to allow sufficient time, which may be hours rather than minutes for some solutions.

The rise of a liquid in a capillary tube that is wet by the liquid may be used to measure its surface tension. If γ is the surface tension in dynes per centimeter and h is the height to which a

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[1] For a detailed treatment of this subject see Rideal, "An Introduction to Surface Chemistry," Cambridge University Press, London, 1926; for a general survey of experimental methods, see Dorsey, *Natl. Bur. Standards Sci. Paper*, **21**, 563 (1936).

liquid of density d rises above the horizontal surface in a tube of radius r, the equation connecting these quantities is

$$\gamma = \tfrac{1}{2}rhdg \qquad (10)$$

This equation results from equating the surface tension to the weight of liquid supported by it when equilibrium of forces is reached. The length of film edge is the circumference of the tube, $2\pi r$; hence the upward force is $2\pi r\gamma$, and this is balanced by a volume of liquid $\pi r^2 h$ of density d acted upon by the force of gravity g. It follows from this that $2\pi r\gamma = \pi r^2 hdg$; and, upon solving for γ, equation (10) results. It has been assumed in this derivation that the angle of contact between the liquid and the surface it wets is zero, or otherwise the upward force would be $2\pi r\gamma$ times the cosine of this contact angle. The fact that the surface tensions of water and most liquids as determined by the capillary-rise method without correction for an appreciable angle of contact are in agreement with those from other methods indicates that the angle is zero for these liquids.[1] But, for liquids that do not wet the material of the capillary tube, equation (10) without correction for the contact angle will give incorrect results.

The chief error in capillary-rise measurements comes from uncertainty of the radius r, owing to irregular diameters of the capillary tubes. In the method as modified by Jones and Ray[2] and shown diagrammatically in Fig. 12, the meniscus is brought to the same part of the capillary tube for each measurement by adjusting the level of liquid in the large tube. Thus a capillary rise h_0 for a liquid of known surface tension (such as water) with the meniscus in the capillary at the index point serves to determine the radius *at this point*, whereas the length of a weighed mercury thread in the capillary would yield only the *average* radius of that part of the tube which it occupies.

When a liquid of smaller surface tension than water is put in the apparatus in such quantity that the meniscus in the capillary rests at the index point, a larger quantity of liquid is required to bring the level in the large tube to the position shown by the

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[1] For methods of measuring the contact angle, see Ferguson, "Fifth Report on Colloid Chemistry," *Brit. Assoc. Advancement Sci. Rep.*, **1923**, 1–13.

[2] JONES and RAY, *J. Am. Chem. Soc.*, **59**, 187 (1937).

dotted line in Fig. 12. In precise work the density d in equation (10) should be written $(d - \beta)$, where β is the density of the vapor. Then, indicating the quantities for water with subscripts w and omitting subscripts from the corresponding quantities for the unknown liquid, we have from equation (10)

$$\frac{\gamma}{\gamma_w} = \frac{rg(d - \beta)h}{rg(d_w - \beta_w)h_w} \tag{11}$$

When capillary rise is determined for a liquid-liquid interface between two insoluble liquids, the term $(d - \beta)$ becomes $(d_1 - d_2)$, the difference in density of the two liquids. Such interfacial tensions are important factors in determining the stability of emulsions. The surface tensions of some common liquids are given in Table 17.

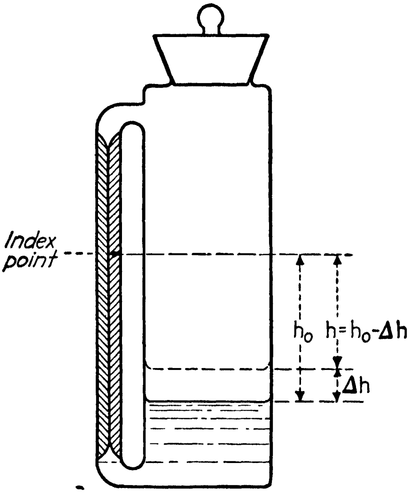

FIG. 12.—Apparatus for measuring capillary rise. (*Jones and Ray.*)

TABLE 17.—SURFACE TENSION OF SOME PURE LIQUIDS
(Measured in dynes per centimeter at 20° by the capillary-rise method)

Water.	72.62	Toluene	28.58
Benzene . . .	28.88	Isobutyl alcohol	22.85
Methyl alcohol	22.61	Ethyl butyrate	24.54
Ethyl alcohol	22.27		

Surface Tension and Drop Weight.[1]—The maximum weight of drop that will *hang* from the end of a rod or other tip is determined by the surface tension of the liquid. But the simple theory that equates the product of the tip circumference and surface tension to mg, the product of the mass of the drop that *falls* and gravity, is incorrect; for a considerable portion of the hanging drop adheres to the tip when the remainder falls. The mass of the *ideal drop*, m_i, which gives the correct surface tension through the relation

$$2\pi r\gamma = m_i g \qquad (12)$$

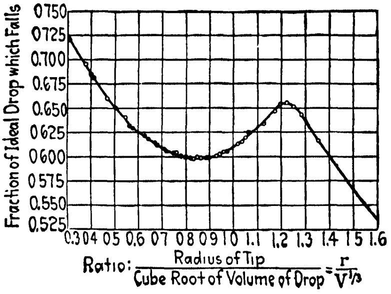

FIG 13.

is a function of the mass of the actual falling drop, the diameter of the tip, and the cube root of the volume of the drop;[2] that is, m_i (ideal) $= m/f(r/V^{1/3})$. In Fig. 13 the fraction of the ideal drop that falls is plotted against $(r/V^{1/3})$. Once the volume of the actual falling drop has been determined by experiment, the ratio of the tip radius to the cube root of its volume is calculated; and then the fraction by which the volume of the actual drop must be divided to give the volume of the ideal drop is read from the curve. Its mass when substituted in the equation

$$\gamma = \frac{m_i g}{2\pi r}$$

gives the correct surface tension. In order to emphasize more fully the imaginary character of the ideal drop whose mass is m_i, it is better to write this surface tension equation in the form

$$mg = 2\pi r\gamma f\left(\frac{r}{V^{1/3}}\right) \qquad (13)$$

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[1] For a discussion of the method and a survey of the literature upon it, see Harkins and Brown, *ibid*, **41**, 499 (1919)

[2] HARKINS, *ibid.*, **38**, 228–253, **39**, 354–364, 541–596 (1917), **41**, 499 (1919). *Cf.* Lohnstein, *Z. physik. Chem.*, **84**, 410 (1913), for a criticism of the method. Tabulated values of a function F, such that $\gamma = (mg/r)F$, are given for various values of V/r^3 in "International Critical Tables," Vol. IV, p. 435. For recent studies see Hauser, *J. Phys. Chem.*, **40**, 973 (1936), **41**, 1017 (1937).

where m is the mass of the *actual falling* drop determined by experiment.

The drop-weight method has the advantage of employing a much larger liquid surface than the capillary method When suitable precautions are taken in the experiments and when the drop volumes or drop weights are properly used in the calculations, the method gives surface tensions that are comparable in precision with those derived from capillary rise. The details of manipulation allow of less latitude than has commonly been supposed;[1] for example, a tip diameter should be chosen such that $(r/V^{1/3})$ is between 0.7 and 1.0; and adequate time must be allowed for orientation of the molecules at the interface and adjustment of the molecular forces before the drop falls. This time is seldom less than 5 min. per drop, and for soap solutions falling into oil it may exceed 20 min. per drop, as shown by variation in the drop size with time when drops are allowed to form too fast.

Other experimental methods include measuring the force required to draw a straight wire or a wire ring vertically out of a horizontal surface (du Nuoy method)[2] and the pressure required to initiate bubble formation on a submerged tip. Both these methods, like the drop-weight method, require the formation of new interfacial surface so slowly that orientation reaches equilibrium.

Surface tensions of mixtures of liquids are not linear functions of the concentration at constant temperature. In mixtures of benzene and cyclohexane, for example, the plot of surface tension against concentration passes through a minimum; other mixtures do not show such minima but are not linear.

Surface Tension and Temperature.—The empirical equation of Ramsay and Shields shows the change of molecular surface energy with temperature, where the molecular surface energy is proportional to the product of surface tension and the molecular volume to the two-thirds power. The equation is

$$\gamma(Mv)^{2/3} = k(t_c - t - d)$$

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[1] Harkins and Brown, *J. Am. Chem. Soc.*, **41**, 499 (1919); Hauser, Edgerton, Holt, and Cox, *J. Phys. Chem.*, **40**, 973 (1936); Aubry, *Compt. rend.*, **208**, 2062 (1939)

[2] See Dale and Swartout, *J. Am. Chem. Soc.*, **62**, 3039 (1940), for a "twin-ring" modification of this method into a means of precise measurement.

where t_c is the critical temperature, t is the temperature at which γ is measured, d is a "correction factor" of 6° (required for unexplained reasons), k is a constant, and $(Mv)^{2/3}$ is proportional to the surface of a mole of liquid. Some results of applying the equation are shown in Table 18.

TABLE 18.—CRITICAL TEMPERATURES CALCULATED FROM DROP WEIGHTS AT DIFFERENT TEMPERATURES[1]

Substance	Milligrams Weight per drop at		$m_t(Mv)^{2/3}$ at		k	t_c Calculated	t_c Experiment
	18°	60°	18°	60°			
Benzene.......	30.96	25.10	614.99	516.44	2.326	288	288
Quinoline......	48 10	43.09	1,156.42	1,057.23	2.329	520	
CCl_4.........	28.85	23.55	607.14	512.89	2.332	285	283
C_6H_5Cl. ...	35.87	30.48	780.31	682.00	2.328	360	359
Pyridine . .	40 37	34.14	751.71	654.35	2.330	347	

From the equation it is seen that the surface tension γ decreases as the critical temperature is approached and that it becomes zero when $(t_c - t)$ is equal to d. The quantity d is a correction factor of 6°, introduced into the equation to show that γ becomes zero at 6° below the critical temperature, instead of at the critical temperature as might be expected. The value of k in the equation is obtained from measurements of γ at different temperatures for one substance; it has the same value for all "normal" substances.[2]

Molecular Attraction.—In the simple gas law, it was assumed that there were no attractive forces acting between the molecules; and it was found that at high pressures this assumption was not correct. To allow for it, a term (a/v_m^2) was introduced into van der Waals' equation. Without the attractive forces that cause the vapor to condense (*i.e.*, an ideal gas being assumed), the pressure necessary to bring a mole of water vapor into a space of 18 ml. at 20°C. is given by $p \times 18 = 82 \times 293$, whence the pressure is 1340 atm., but the pressure exerted by water at 20°

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[1] MORGAN and THOMSSEN, *ibid*, **33**, 657 (1911).

[2] Research upon surface tension near the critical temperature involves difficulties that have not been fully realized by all who have experimented in this region. For a consideration of these matters, see Winkler and Maass, *Can. J. Research*, **9**, 65 (1933).

(its vapor pressure) is only about 0.02 atm. It appears that the attractive pressure, or *cohesive pressure,* must, therefore, be very large. The cause of molecular attraction is not at all understood but is believed to be due to stray electric fields caused by the electrons within the atoms.

TABLE 19.—INTERNAL PRESSURE (IN ATMOSPHERES) OF VARIOUS LIQUIDS

	Winther[1]	Traube[2]	Walden[2]	Lewis[3]	Mathews[4]
Ether.	1220	990	1360	1930	1970
Ethyl acetate.	1490	1140	1730	2640	2460
CCl_4	1820	1305	1680	2520	2660
Benzene	1790	1380	1920	2640	2940
Chloroform.	1680	1410	1950	2780	2910
CS_2	2200	1980	2400	2920	3950
Ethyl alcohol.	2030	2160	4000	. . . .	3600

Many equations have been put forward by various investigators for calculating the internal pressure of a liquid from a/v_m^2, from the latent heat of evaporation, and from other data. But the internal pressures so calculated are not in good agreement with one another. Table 19 shows the internal pressure[5] in atmospheres according to the calculations of various workers. It should be borne in mind that all these calculations are based on certain assumptions and that the actual internal pressure has not been measured directly. The deviations among the values for any one liquid will indicate the uncertainty of the assumptions made as to the way in which the attractive forces act; but all the calculations agree in showing that there is an internal pressure and that it is very great.

When van der Waals' equation of state is written in the form $p = [RT/(v_m - b)] - (a/v_m^2)$ it will be seen that the measured pressure p is the difference between two terms, of which the first may be called the thermal pressure and the second the cohesive pressure. For small molecular volumes both these terms are large compared with the difference between them, and under

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[1] From optical properties.

[2] From surface tension and van der Waals' a and b.

[3] From thermal data.

[4] From latent heats and surface tension.

[5] HILDEBRAND, *J. Am. Chem. Soc.*, **38**, 1459 (1916).

themselves so that the change of properties attending passage from one phase to the other will be as gradual as possible. For example, the hydrocarbon part of a molecule in an oil-water interface is probably directed toward the oil layer. Of course, there is no evidence that this arrangement persists for more than one molecular length. The "water-soluble" portion or active group ($—COOH$, $—OH$, $=CO$, $—CN$, $—CONH_2$, or inorganic radical) will be directed toward the water layer. This tendency may result in a preferential solubility of a dissolved substance *in the interface*. For example, the surface tension at a benzene-water interface is greatly decreased by very small amounts of soap, of which the composition may be represented roughly by the sodium salt of palmitic acid ($C_{15}H_{31}COONa$). The interfacial tension decreases from that of benzene-water (35 dynes) almost in proportion to the concentration of soap, falling to about 2 dynes for 0 01 *N* soap solution, after which further additions of soap cause only a slight decrease (to 1.8 dynes for 0.1 *N* soap, for example). A probable explanation is that the interface becomes nearly saturated with soap molecules oriented in such a way as to give the minimum surface tension through preferential solution in the interface long before the water layer as a whole is saturated. When this surface saturation is attained, the addition of more soap to the water layer causes only a little increase in the soap concentration in the interfacial layer and hence only a slight change in the surface tension. The behavior of soap solutions is complicated by other factors such as the alkalinity of the aqueous layer and the nature of the nonaqueous layer, which are best omitted from a preliminary discussion, but the most important properties of soaps are those which result from the formation of surface layers much richer in soap than the body of the solution.

Dr. Katherine Blodgett[1] has modified the monolayer technique so that parallel layers of barium stearate and other insoluble substances may be deposited one upon another to a total thickness of some 300 molecules.

Monolayers such as these are probably the most important single factor in determining the structure and properties of the water shells around the particles in hydrophyllic colloids, as we shall see in a later chapter. Similar layers are probably

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[1] See *Science*, **87**, 493 (1938), for references to papers upon this topic.

present upon most solid surfaces in contact with liquids or solutions. While there are many complications, such as changes produced by pressure or minute amounts of solutes, the fact that oriented monolayers form is the prime fact to be kept in mind.

X-ray Diffraction in Liquids.—In the next chapter a method for determining the distance between atomic centers in a crystal is described. We may anticipate this treatment here by a brief statement of the results of its application to liquids. The "pattern" shown by X-ray diffraction of liquids consists of one or more broad diffuse rings, differing markedly from the sharp rings so typical of a crystalline material. By making a Fourier analysis of the X-ray pattern of a liquid, a radial distribution curve is obtained that gives the distribution of atoms with respect to any average atom in the liquid. In such a distribution curve for liquid sodium, the first peak occurs at about 4×10^{-8} cm., and this distance corresponds approximately to the diameter of the sodium atom.[1] Measuring from the center of any sodium atom we should not expect to find the center of any other atom at a distance less than the "diameter" of the atom. At this distance we should expect to find several atoms, since any atom in a liquid will always be in approximate contact with several neighboring atoms.

A similar study of water shows an average distance 2.9 to 3.0×10^{-8} cm. between oxygens (the X-ray diffraction of hydrogen atoms is too feeble to indicate their positions), which is greater than the O-O distance in ice (2.76×10^{-8} cm.) in spite of the smaller density of ice. The interpretation is that in liquids a molecule has no permanent neighbors, but at any instant a few molecules are in approximate contact and others at greater distances are either approaching or receding.

The patterns obtained in a vitreous "liquid" such as a simple glass are also diffuse rings. In fused quartz or vitreous silica, which is an example of a simple glass, the X-ray results show that each silicon atom is tetrahedrally surrounded by four oxygens at a distance of 1.62×10^{-8} cm. Each oxygen is bonded to two silicons, the two bonds being roughly diametrically opposite. As far as nearest neighbors are concerned, the structure in the glassy form of silica is exactly the same as the crystalline

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[1] WARREN, *J. Applied Phys.*, **8**, 645 (1937).

forms. The glass differs from the crystal only in the fact that no definite scheme of structure repeats itself identically at regular intervals.

Application of X-ray diffraction to alcohols shows that the C-C distance[1] is 1.54×10^{-8} cm., which agrees with the length of hydrocarbon chain per atom of carbon determined in the oil-film experiments described in the previous section.

Problems

Numerical data for some of the problems must be sought in tables in the text

1. (*a*) Calculate the latent heat of evaporation per mole of water at 80° from the vapor pressures in Table 14, using the approximate Clapeyron equation. (*b*) Calculate this quantity from the slope of the vapor-pressure curve, 0.01893 atm. per deg. at 80°, and the specific volumes of liquid and saturated vapor, 1.029 and 3409.2 ml. per gram, respectively.

2. A cylinder fitted with a movable piston contains 5.4 grams of a saturated vapor, which occupies 1 liter at 350°K. (=77°C.) and 1 atm. pressure. (*a*) When the temperature is reduced to 323°K. and the volume remains 1 liter, part of the vapor condenses to liquid and the pressure becomes 0.41 atm. Calculate the weight of condensed liquid, assuming the vapor an ideal gas and neglecting the volume of the condensed liquid. (*b*) The latent heat of evaporation of the liquid is substantially constant in this temperature range. Calculate the quantity of heat that must be added to the vessel at 323°K. to evaporate the condensed liquid if the pressure is kept at 0.41 atm. through the motion of the piston.

3. Calculate the area covered by a monolayer of stearic acid spread upon water for each milligram of acid, whose formula is $C_{17}H_{35}COOH$.

4. The slope of the vapor-pressure curve of liquid nitrogen tetroxide at 294°K. (the boiling point) is 0.0467 atm. per deg. (*a*) Calculate the latent heat of evaporation per mole of vapor formed at the boiling point. (*b*) The vapor consists of N_2O_4 and NO_2 molecules, and the measured latent heat of evaporation of 92 grams of liquid is 9110 cal. at the boiling point. Calculate the degree of dissociation of N_2O_4 into NO_2 at 294°K. [GIAUQUE and KEMP, *J. Chem. Phys.*, **6**, 40 (1938).]

5. In the experiment described in Problem 15 (page 99) assume that the sealing was imperfectly performed, so that, when the bulb is cooled to 20° for weighing, some air enters the bulb, part of the substance condenses to a liquid, but none is lost. Under these conditions the bulb weighs 31.300 grams. Assume the vapor pressure of the substance to be 0.227 atm., and calculate the molecular weight of the vapor.

6. One mole of CH_4 is exploded with 9 moles of air (assumed 21 mole per cent oxygen and 79 mole per cent nitrogen), and the resulting mixture is assumed to contain only H_2O, CO, CO_2, and N_2. (*a*) Find the temperature at which this mixture is just saturated with water vapor (see Table 14).

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[1] HARVEY, *J. Chem. Phys.*, **7**, 878 (1939).

(*b*) The mixture is cooled to 25°C and 1 atm. total pressure. Calculate the weight of condensed water and the partial pressures of CO, CO_2, and N_2.

7. The volume of a quantity of air saturated with water vapor at 50° is 2.50 liters when the total pressure is 5.0 atm. (*a*) Calculate the final total pressure if this air is expanded over water at 50° until the total volume becomes 46 liters. (*b*) How many moles of water evaporate to establish equilibrium?

8. Benzene has a surface tension of 28.88 dynes at 20°, and its density is 0.879. What is the radius of a capillary tube in which benzene rises 1 cm.? How high would water rise in the same tube?

9. (*a*) Calculate the total pressure in a 10-liter flask containing 0.1 mole of CCl_4 and 0.3 mole of air when the temperature is 50, 40, 30, and 20°. (*b*) Determine from a suitable plot the temperature at which the mixture is just saturated with CCl_4.

10. The critical temperature of ethanol (C_2H_5OH) is 243°C., the critical pressure is 63.11 atm., and the following data apply at lower temperatures.

t, °C.	Vapor pressure, atm	Surface tension, dynes per cm	Liquid density, grams per ml	Saturated vapor density, grams per ml.	ΔH evaporation, cal. per mole
20	0.0577	22.75	0.7895		10,000
25	0.0776	22.32	0.7852		
50	0.2925	20.14			9,800
78.3	1.000		0.7365	0.00165	9,400
100	2.228	15.47	0.7157	0.00351	8,900
150	9.70	10.16	0.6489	0.0192	7,490
200	29.20	4.26	0.5568	0.0508	5,280
220	42.38		0.4958	0.0854	3,950
240	59.92		0.3825	0.1715	1,760

(*a*) Estimate the critical density from a suitable plot of the above data. (*b*) Calculate ΔH_m at 220° from the vapor-pressure data. (*c*) Calculate ΔH_m at 220° from the slope of the vapor-pressure curve, which is 0.750 atm. per deg. at 220°.

11. (*a*) Calculate the weight of ethanol evaporated when 100 liters of air at 50° and 1 atm. are bubbled through ethanol at 50° so slowly that equilibrium is reached and the mixture of air and ethanol emerges at 50° and 1 atm. total pressure. (*b*) Calculate the weight of ethanol condensed when this mixture is cooled to 25° and 1 atm. total pressure.

12. The vapor pressure of phenylhydrazine in atmospheres is given by the equation $\log p = 5.0238 - 2810/T$ in the range 365 to 415°K. Calculate ΔH_m, assuming the vapor an ideal gas. [WILLIAMS and GILBERT, *J. Am. Chem. Soc.*, **64**, 2776 (1942).]

13. Drop-weight experiments were made at 20° for water and for benzene with the following results:

Tip radius, centimeters	Drop weight for	
	Water, grams	Benzene, grams
0.1477	0.0469	0.0175
0.2680	0.0775	0.0297
0.3419	0.0964	0.0383

Calculate from these drop weights the surface tension of benzene and of water at 20°, and compare them with the measured results given in Table 17. [Harkins and Brown, *J. Am. Chem. Soc.*, **41,** 449 (1919).]

14. The slope of the vapor-pressure curve for formic acid is 6.3 mm. per deg. at 50°C. and 25 mm. per deg. at 100°C.; the vapor pressure is 130 mm. at 50°C. and 748 mm. at 100°C. (*a*) Calculate ΔH_m at each temperature, assuming the vapor to be an ideal gas. (*b*) The recorded latent heat of evaporation of formic acid at 100° and 1 atm. pressure is 120 cal. per gram. See page 72 for other data on formic acid, and suggest an explanation of the values obtained in (*a*).

15. (*a*) Calculate the molal latent heat of evaporation for water at 120° from the data in Table 14, assuming the vapor to be an ideal gas. (*b*) The slope of the vapor-pressure curve at 120° is 0.0621 atm. per deg., the specific volume of the vapor is 891.8 ml. per gram, that of the liquid is 1.06 ml. per gram. Calculate a more accurate value of ΔH for the evaporation of a mole of water at 120°.

16. The following data refer to ammonia:

T	Vapor pressure, atm.	Specific volume, ml.		ΔH, cal. per g.	dp/dT, atm. per deg.
		Liquid	Vapor		
233.1	0.708	1.45	1551	331.7	0.0378
238.1	0.920	1.46	1215		
293.1	8.459	1.64	149.5	283.8	0.270
298.1	9.986	1.66	128.4		
313.1	15.34	1.73	83.3	263.1	0.426
318.1	17.58	1.75	72.6		

(*a*) Calculate ΔH over the three 5° temperature intervals from the approximate Clapeyron equation. (*b*) Calculate ΔH at 233.1, 293.1, and 313.1°K. from the exact equation, and compare with the experimental values.

17. The slope of the vapor-pressure curve for acetic acid is 0.0187 atm. per deg. at 100°C., and the vapor pressure at this temperature is 0.548 atm. (*a*) Calculate the heat absorbed per molal volume of vapor formed at 100°C (*b*) The vapor consists of $(CH_3COOH)_2$ and CH_3COOH molecules, and the heat absorbed by the evaporation of 120 grams of acetic acid at 100°C. is 11,800 cal. Calculate the degree of dissociation of the dimer into the monomer at 100°C. and 0.548 atm., assuming this to be the only cause of the deviation.

18. (*a*) Air at 17° and 1 atm. pressure, 70 per cent saturated with water vapor, is pumped into a 1000-liter tank until the pressure becomes 6 0 atm. and the temperature rises to 27° The vapor pressure of water is 14 5 mm at 17° and 26.7 mm. at 27°. Assume the ideal gas law to apply, neglect the volume of condensed water in comparison with the volume of the tank, and calculate the weight of liquid water in the tank at 27° (*b*) Determine from a suitable plot the lowest temperature at which all the water in the tank would be in the form of vapor.

19. (*a*) Calculate the values of RT/v_m, and of $[RT/(v_m - b)] - (a/v_m^2)$ for water at 100° and a molal volume of 18 8 ml. (*b*) Calculate the pressure at which water vapor would have a molal volume of 30.16 liters at 100° from the ideal gas law and from van der Waals' equation. (The measured molal volume of water vapor at 100° and 1 atm. is 30 16 liters)

20. (*a*) One step in the manufacture of nitrocellulose cakes involves the removal of ethanol (C_2H_5OH) from the cakes by evaporation in a current of dry air If the air-ethanol mixture emerges from the drier at 35° and 1 atm. total pressure, 73 per cent saturated with ethanol, what weight of ethanol is evaporated for each 90 moles of air entering? (*b*) This mixture is passed over brine pipes at $-15°$ to recover the ethanol, and air emerges from the cooler at $-15°$ and 1 atm. 100 per cent saturated with ethanol What weight of ethanol is condensed from each 90 moles of air? (The latent heat of evaporation of ethanol is 10,000 cal per mole in this temperature range)

21. What volume of dry air at 20° and 1 atm. must be bubbled through *n*-octane at 50° in order to evaporate 10 grams of it, assuming the mixture of air and *n*-octane to emerge from the evaporator at 50° saturated with *n*-octane?

22. Hot air is passed over a product to remove CCl_4 from it, and the air emerges from the drier at 45°, 59 per cent saturated with CCl_4, and at 1 atm total pressure. (*a*) How many moles of air enter the drier for each mole of CCl_4 evaporated? (*b*) This mixture of air and CCl_4 is passed over refrigerated coils, which cool it to 0° to recover the CCl_4. Calculate the vapor pressure of CCl_4 at 0° and the fraction of CCl_4 recovered, assuming the total pressure to remain at 1 atm.

23. A refrigerator derives its cooling effect from the reaction

$$NH_3(l) = NH_3(g)$$

which takes place at -10°C. (263°K.). Assuming NH_3 to be an ideal gas and that ΔH is independent of temperature, calculate the heat absorbed in the refrigerator for each 100 liters of saturated vapor formed at -10°C.

24. The following data apply to equilibrium between liquid and vapor of carbon dioxide:

T, °K.	dp/dT, atm /deg	Molal volume, ml	
		Liquid	Vapor
223	0.273	38	2520
293	1.35	57	234

(*a*) Calculate ΔH_m at each temperature. (*b*) The vapor pressure of CO_2 at 293°K is 57 atm. Calculate the per cent error in taking $\Delta v = RT/p$ at 293°K.

25. Air 50 per cent saturated with ethanol at 20°C and 1 atm total pressure is pumped into a 100-liter tank until the total pressure becomes 10.0 atm. and the temperature rises to 30°. (*a*) Calculate the moles of liquid C_2H_5OH in the tank. (*b*) Find the lowest temperature at which the ethanol in the tank will be completely evaporated. (*c*) Find the total pressure in the tank at this temperature.

26. The vapor pressure of sulfur dioxide (in millimeters of mercury) changes with the absolute temperature as follows:

T	197.6	205.1	214.1	228.3	238.3	249.6	256.4	263.5
p	12.56	23.58	46.77	121.57	217.62	402.27	558.97	773.82

(*a*) Plot log p against $1/T$ over the entire temperature range, draw a smooth curve through the points, and state whether ΔH is a constant over the range. (*b*) Calculate ΔH from the vapor pressures at the two highest temperatures, assuming the vapor an ideal gas, and compare with the measured ΔH, which is 5960 cal per mole at 263.08°K., the boiling point. [GIAUQUE and STEPHENSON, *J. Am. Chem. Soc.*, **60,** 1389 (1938).]

CHAPTER V

CRYSTALLINE SOLIDS

The purpose of this chapter is to present very briefly such experimental facts on the properties of crystalline solids as we shall need in later chapters—their vapor pressures, thermal properties, and the arrangement of atoms in their crystals. Crystalline solids result when pure liquids are cooled to temperatures characteristic of the substances, when solutions of these substances are cooled or evaporated, or when vapors condense under such conditions that the liquid does not form. Iodine crystals, for example, may be formed in any of these ways: by cooling liquid iodine to 114.15°, by evaporating a solution of iodine in CCl_4, or by cooling iodine vapor that has a partial pressure of less than 94 mm., which is to specify that the temperature is below 114.15° when condensation begins. It is not definitely known that there are any noncrystalline solids that are stable over long intervals of time. But whether these exist or not, there are some substances that are evidently solid and not demonstrably crystalline. Since we are to consider the equilibrium properties of solids and since the noncrystalline solids are probably not in equilibrium states, we shall not consider them.

The change from liquid to solid at the melting point is attended by a moderate change in volume, by a decrease in energy content, and by the assumption of rigidity. Although the shape of the mass of crystals obtained from complete solidification of a liquid is usually that of the container in which it occurred, if partial solidification occurs, the crystals formed will have characteristic geometric forms. Under either circumstance the internal arrangement of atoms or molecules in the crystal conforms to a definite pattern. In crystals the molecules or atoms are held in fixed positions; and though they probably vibrate about these positions, they have no net motion in one direction, no mobility at ordinary temperatures. There is, however, abundant evidence of intercrystalline diffusion at higher temperatures, which are still far below those at which liquid forms. The viscosity of a crystal is substantially infinite; it may be crushed or sheared, but by the application of a reasonable force it may not be changed into another shape that it will retain when the force is removed.

If a crystal of a pure substance is heated at atmospheric pressure, it changes to a liquid sharply at its melting point and when cooled it assumes again its characteristic external shape and internal symmetry as it crystallizes at the melting point.

Since all pure liquids become crystalline when sufficiently cooled and most crystals become liquid when sufficiently heated (except those which decompose before reaching the melting point), we must understand that by a crystal we usually mean a state of aggregation rather than a chemical substance capable of existence only in solid form. The changes in volume and in energy content that attend the formation of solids from liquids are much smaller than those attending the condensation of vapors to liquids. These phase changes for pure substances occur at constant temperatures for any specified pressure, and the effect of pressure upon the temperature of the phase change from liquid to solid is much smaller than that for vapor to liquid. The density of a crystalline phase is commonly within 10 per cent of that of the liquid from which it forms, while the density of a liquid may be a thousand times that of the vapor from which it condenses at atmospheric pressure. Solids have characteristic vapor pressures that change with the temperature, as was true of liquids; and, of course, the vapor pressure of the solid is equal to that of the liquid at the triple point where all three phases, solid, liquid, and vapor, are in equilibrium.

Vapor Pressures of Crystalline Substances.—A solid phase in equilibrium with its saturated vapor is a monovariant system, one in which the equilibrium pressure is a function of the temperature alone, and hence the change of vapor pressure or "sublimation" pressure with changing temperature is shown by the Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta H_s}{T\,\Delta v} \tag{1}$$

in which ΔH_s is the heat absorbed by the phase change from solid to vapor and Δv is the increase in the volume of the vapor over that of the solid. By making the same assumptions as were used for the liquid-vapor change in the previous chapter, we may derive an approximate form of this equation suitable for low pressures. These assumptions are that the volume of solid is negligible compared with that of the vapor, that the volume of the vapor is RT/p, and that ΔH_s is constant over the range in which the equation is used. Since RT/p is the volume of 1 mole of vapor, ΔH_s must now be the heat absorbed in the formation of 1 mole of vapor. The equation and its integral between limits then become

$$d \ln p = \frac{\Delta H_s}{R} \frac{dT}{T^2} \qquad \text{and} \qquad 2.3 \log \frac{p_2}{p_1} = \frac{\Delta H_s}{R} \left(\frac{T_2 - T_1}{T_2 T_1} \right) \tag{2}$$

As an illustration of the change of vapor pressure of a solid with changing temperature we quote the data for iodine.[1]

t. . .	20°	25°	30°	40°	60°	80°	100°	114 15°(m. pt)
p, mm	0 201	0 309	0 467	1 027	4 276	15 04	45 97	94 18

By using the vapor pressures for 20 and 30° one may calculate ΔH_s per mole of iodine vapor formed at 25° from the approximate equation to be 14,960 cal. From more precise treatment of the data, the authors calculate ΔH_s = 14,880 cal. per mole of vapor formed.

Carbon dioxide is one of the few substances of which the solid phases have vapor pressures greater than 1 atm., as the following data show:[2]

T, °K	174 7	182 3	192 66	194 6	195 83	203	213	216
p, atm .	0 160	0 339	0 845	1 000	1 100	2 02	4 18	5 13

Since 216°K. is the triple-point temperature, 5.13 atm. is the last point on the vapor-pressure curve for the solid and the first point on the vapor-pressure curve for the liquid. Liquid carbon dioxide has no boiling point, since its liquid and vapor phases are not in equilibrium at 1 atm. pressure for any temperature. These vapor pressures afford a means of calculating the heat of sublimation from the exact Clapeyron equation (1), but they do not give a correct heat of sublimation when substituted into equation (2), since carbon dioxide deviates from ideal gas behavior

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[1] GILLESPIE and FRASER, *J. Am. Chem. Soc.*, **58,** 2260 (1936).

[2] GIAUQUE and EGAN, *J. Chem. Phys.*, **5,** 45 (1937).

at these temperatures and pressures. Thus, substitution of the pressures 1.10 atm. and 0.845 atm., with the appropriate temperatures, into equation (2) gives $\Delta H_s = 6400$ cal. per mole, while equation (1) gives $\Delta H_s = 6030$ cal. per mole at 194.6°K. As has been said before, an approximate equation is useful only to the extent that the assumptions inherent in it are valid. In this instance the assumption of ideal gas behavior is not valid, but in the illustration at the end of the preceding paragraph the same equation gave ΔH_s for iodine vapor within 0.5 per cent because at the higher temperatures and lower pressures involved the assumptions were closer to the truth.

Melting Point.—The temperature at which the liquid and solid phases of a pure substance are in equilibrium under a pressure of 1 atm. is defined as the melting point. Since the presence of a foreign substance in a liquid lowers the temperature at which equilibrium with the solid phase is reached, melting points are a useful indication of the purity of a preparation. Under the procedure usually followed the liquid is saturated with air, which is an "impurity" affecting the melting point slightly; but unless the very highest precision is required, the change produced by air may be neglected. For example, centigrade zero is defined as the temperature at which ice and water *saturated with air* are in equilibrium under 1 atm. pressure. Removal of the air would raise the equilibrium temperature to +0.0023°, which is thus the true melting point of ice. The effect of dissolved air on other substances is also of this order of magnitude.

Changes in barometric pressure produce only negligible changes in the melting point, but high pressures cause changes in melting points that may be large; for example, under 2000 atm. pressure ice and liquid water are in equilibrium at −22°.

A solid phase in equilibrium with its liquid is also a monovariant system to which the Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta H}{T\,\Delta v}$$

may be applied. If the pressure effect is desired in atmospheres per degree, Δv should be expressed in milliliters and ΔH in milliliter atmospheres (calories × 41.3). For example, when a gram of ice melts at 0° and 1 atm., there is a volume decrease of 0.09 ml. and a heat absorption of 79 cal., or 3260 ml.-atm.; upon substituting these quantities in the Clapeyron equation, dp/dT is found to be -132 atm. per deg., which is a change of the melting point of $-0.0075°$ per atm. This is not to say that some very high pressure would produce a change proportional to this figure. For example, the application of 2000 atm. would not change the melting point to $2000/(-132)$, or $-15°$, but to $-22°$ as was stated above. Such a calculation leaves out of account the important facts (1) that ice and water have different compressibilities so that Δv is not -0.09 ml. over the range of 2000 atm. and (2) that ΔH is not 79 cal. per gram over a 22° range. When Δv and ΔH are suitably expressed as functions of pressure and temperature, the Clapeyron equation leads to the correct temperature, as it always does when properly used.

Heats of Fusion.—The heat absorbed by the melting of a solid to a liquid at the melting point is called the heat of fusion or the "latent heat" of fusion. It is best determined by direct calorimetry but may be derived from the freezing-point depressions of solutions through some of the equations to be given in Chap. VI. Some of the recorded data based on the latter method are unreliable because of incorrect use of the data or the use of unreliable data, but such figures are often recorded in the same tables with directly measured heats of fusion and properly calculated ones. Since no reliable rules are known for estimating latent heats of fusion, one must select the sources of data with care or be prepared for discrepancies. The ratio $\Delta H_f/T$ of the

TABLE 21 —LATENT HEATS OF FUSION
(In calories per mole at the melting point)

Substance	T	ΔH_f	Substance	T	ΔH_f
Al	932	2550	Acetic acid	289.7	2690
Cl_2	238	1615	Ethylene dibromide	282.7	2570
H_2	14	28	Ethyl alcohol	158.7	1145
Pb	600	1224	Carbon tetrachloride	249.1	644
Mg	923	2160	*p*-Dichlorbenzene	325.8	4360
Hg	234	557	Nitrobenzene	278.8	2770
Sn	505	1720	Benzene	278.5	2365
H_2O	273	1436	Phenol	298.5	2720
LiCl	887	3200	Naphthalene	353.0	4550
NaCl	1073	7220	Diphenyl	382.3	4020
KCl	1043	6410	Benzophenone	321.6	4290
NH_3	196	1426	Anthracene	489.7	7800

molal latent heat of fusion to the absolute temperature varies widely for different substances, from 1.6 for cesium to 18.2 for $AlCl_3$, for example. Thus the ratio is not even a rough approximation, and it would be useless for checking the reliability of recorded data. A few measured heats of fusion are given in Table 21[1]

Heat Capacities of Crystalline Solids.—We shall consider only heat capacities at constant pressure, since virtually all the data are taken at constant pressure; and, in conformity to the common custom, we shall discuss the *atomic* heat capacity of elements and the *molal* heat capacity of compounds. Thus $C_p = dH/dT = 5.82$ for aluminum at 298°K. is the ratio of the heat absorbed (in calories) by an atomic weight of aluminum to the rise in temperature produced at or near 298°K, and $C_p = 4.80 + 0.0032T$ is an expression for the heat capacity of an atomic weight of aluminum, valid to 2 per cent, in the temperature range 273 to 932°K. Since $\Delta H = \int C_p\,dT$ between the appropriate temperature limits, the heat required to raise the temperature of an atomic weight of aluminum from 273 to 673°K. is the integral of the heat-capacity equation between these temperature limits, or 2560 cal. Use of the "room-temperature" heat capacity *over this range* of temperature would give $400 \times 5.82 = 2320$ cal, which is obviously not correct; but between 288 and 298°K. the equation gives 57.2 cal., and the single heat capacity gives 58.2 cal., either of which would be close enough in most calculations.

The restrictions as to temperature range and validity of a heat-capacity equation are important. Thus substituting $T = 298$ in the equation $C_p = 4.80 + 0.0032T$ gives 5.76, which is within 1 per cent of 5.82; but by substituting $T = 50$ in this equation one obtains $C_p = 4.96$, while the correct atomic heat capacity of aluminum at 50°K. is 0.92. The upper limit is set by the melting of aluminum at 932°K.; the lower limit is a conventional one arising from the custom of discussing "low-temperature" heat capacities and "high-temperature" heat capacities from different

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[1] The best critical summary of heats of fusion of inorganic substances is by K. K. Kelley in *U.S. Bur Mines Bull*, **393** (1936), from which the data in Table 21 were taken. Data for organic substances will be found in "International Critical Tables," Vol. V, pp. 132*ff*, in which the data are in joules per gram or kilojoules per formula weight. One kilojoule is 238.9 cal.

points of view. There is no implication that heat capacities change abruptly at the melting point of ice. One more illustration will serve to emphasize the necessity of heeding the restrictions stated with such equations For iron the equation $C_p = 4.13 + 0.00638T$ is valid to 3 per cent in the range 273 to 1041°K. The melting point of iron is 1803°K ; but the equation given is not to be used through the upper limit stated because of a phase transition to another form of iron, which takes place at 1041°K. with the absorption of "heat of transition," and the formation of a phase with a different heat capacity. Many other substances undergo phase transitions, some at low temperatures, some at high temperatures; some (including iron) undergo more than one solid-solid transition; and for all of them there is a constant-temperature absorption of heat at the transition temperature for which no allowance can be included in a heat-capacity equation.

TABLE 22—HEAT CAPACITIES OF SOME SOLID ELEMENTS
(In calories per atomic weight at 298°K and constant pressure)

Element	C_p	Element	C_p
Aluminum	5.82	Lead	6.39
Antimony	6.03	Lithium	5.65
Beryllium	4.26	Magnesium	5.71
Bismuth	6.10	Nickel	6.16
Cadmium	6.19	Potassium	6.97
Calcium	6.28	Silicon	4.73
Carbon (graphite)	2.06	Silver	6.10
Carbon (diamond)	1.45	Sodium	6.79
Copper	5.86	Sulfur (*r*)	5.41
Gold	6.03	Tin (white)	6.30
Iodine	6.57	Tungsten	5.97
Iron	6.03	Zinc	6.07

The atomic heat capacity of most of the solid *elements* at ordinary temperatures is about 6.2, a fact that has long been known as the "law of Dulong and Petit." As may be seen in Table 22, carbon, beryllium, and silicon are conspicuous exceptions, and most of the elements of atomic weight below 39 deviate by more than 10 per cent from this average figure. This "law" is thus only a rough approximation. Another rough approximation, known as "Kopp's law," states that the heat capacity of a solid compound is equal to the sum of the heat capacities of the elements of which it is composed. The sum of the atomic heat capacities of Cu and S is 11.17; the molal heat capacity of CuS is 11.43; for FeS the corresponding figures are 11.44 and 13.06, which shows that considerable error may be involved in accepting this "law." Fortunately, there is now little need for either of these "laws," since abundant modern heat-capacity data are available,[1] especially at low temperatures, because of the importance of standard entropies computed from them. It will be recalled from Chap. II that the entropy of a substance at (say) 298°K. is obtained by integrating $C_p\,dT/T$ from 0 to 298°K and that the heat capacity must be known as a function of temperature for this integration.

The heat capacities of all crystalline substances become zero at 0°K., but the rates at which they decrease at temperatures below 298°K. are quite different for different substances. For example, Sb, Au, and Fe all have atomic heat capacities of 6.03 at 298°K , but at 50°K they are, respectively, 3.0, 3.5, and 0.71 Their standard entropies at 298°K., which are obtained by integrating $C_p\,dT/T$ from 0 to 298°K., also illustrate this difference; they are 10.5 for Sb, 11.4 for Au, and 6.47 for Fe. Some low-temperature heat capacities are given in Table 23, and many others will be found in the reference quoted with the table.

So-called "high-temperature" heat capacities are commonly represented by equations such as $C_p = a + bT$ or $C_p = a + bT + cT^2$. Plots of heat capacity against temperature often have marked curvature at ordinary temperatures and become nearly linear (though not horizontal) at higher temperatures. Such variation is better shown by an equation of the form suggested by Maier and Kelley,[2] $C_p = a + bT - c/T^2$. Thus for zinc oxide the molal heat capacity is given by the equations

$$C_p = 6.63 + 11.26 \times 10^{-3}T - 4.72 \times 10^{-6}T^2$$

(2 per cent, 273 to 1600°K.)

$$C_p = 11.40 + 1.45 \times 10^{-3}T - 1.824 + 10^5/T^2$$

(1 per cent, 273 to 1573°K.)

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[1] For "low-temperature" heat capacities (0 to 298°K.) see the excellent compilation of Kelley in *U.S. Bur. Mines Bull*, **434** (1941); for "high-temperature" heat capacities (273°K. to the highest temperatures for which data are available) see Kelley, *ibid.*, **371** (1934).

[2] *J. Am. Chem. Soc.*, **54,** 3243 (1932).

TABLE 23—LOW-TEMPERATURE HEAT CAPACITIES[1]

Substance	10°K	25°K	50°K	100°K	150°K	200°K	298°K
Pb	0 66	3 36	5 11	5 83	6 06	6 20	6 39
C (diamond)	0 00	0 00	0 00	0 06	0 25	0 58	1 45
C (graphite)	0 00	0 04	0 11	0 40	0 77	1 20	2 06
I_2	0 93	5 12	8 79	10 96	11 86	12 42	13 14
Na	0 14	1 44	3 82	5 40	5 93	6 25	6 79
NaCl	0 04	0 58	3 82	8 44	10 15	11 09	12 14
KCl	0 10	1 30	5 04	9 38	10 89	11 58	12 31
AgCl	0 40	2 95	6 59	10 00	11 22	11 88	12 14
HgO (red)	0 19	1 94	4 31	6 89	8 39	9 46	10 93

In spite of the widely different coefficients, these equations are both valid for the heat capacity within the limits stated.

A glance at Fig. 15 will show that for elementary solids the change of heat capacity with temperature is not a simple matter governed by a universal rule. Yet qualitatively all these curves are at first convex toward the temperature axis, with the heat capacities at the lowest temperatures proportional to T^3; all have nearly straight portions followed by portions with concavity toward the temperature axis as the temperature increases; and at higher temperatures the curves become more nearly horizontal. Hence, one might expect to derive an equation of the same algebraic form, with one or two characteristic constants for each substance, showing this change. Upon the assumption that the atoms of an elementary crystal vibrate about their mean positions with a characteristic frequency, independent of T, and an intensity varying with T, Einstein derived an equation for

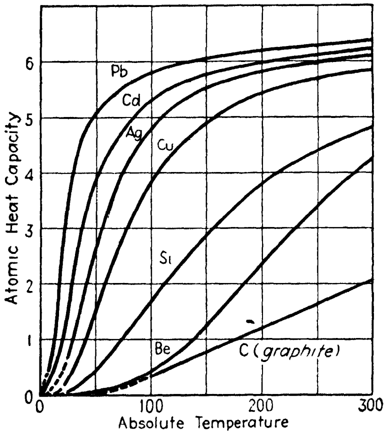

FIG 15.—Change of atomic heat capacity with absolute temperature

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[1] From Kelley, *U.S. Bur. Mines Bull.*, **434** (1941), in which the heat capacities of hundreds of substances are given. This bulletin is the best compilation of such data.

a curve of the right form. Nernst and Lindemann assumed two characteristic frequencies; Debye assumed a range of frequencies from zero to a certain maximum; others took into account the energy absorption of the electrons, changing "degrees of freedom" in vibration and other factors. All the equations were quite complex, and we shall give only the Debye equation[1] applicable at very low temperatures,

$$C_v = 77.94 \times 3R\left(\frac{T}{\theta}\right)^3 \tag{3}$$

where θ is proportional to the *maximum* vibration frequency of the atoms. At high temperatures the equation approaches $C_v = 3R$, which is in fair agreement with the horizontal portions of the curves in Fig. 15.

Much remains to be done upon the problem of heat capacity. Thus the atomic heats of sodium, potassium, and magnesium tend toward higher values than the $3R$ predicted by Debye's equation;[2] and the elements iron, nickel, cobalt, bismuth, tin, and chromium do not approach $3R$ as an upper limit of their atomic heat capacities;[3] but aluminum, copper, silver, zinc, and cadmium do approach such a limit. The excess heat capacity above $3R$ is not due to the partial heat capacity of the electrons[4] in the atoms, though no explanation is known for the excess above $3R$. By taking into account the decreasing "degrees of freedom" at low temperatures and the corresponding loss in thermal agitation of the atoms, A. H. Compton[5] derived a relation that is in good agreement with measured heat capacities over a wide range of temperature. Other suggestions, which need not concern us here, have appeared more recently.

Forces Acting between Atoms or Molecules.—While it must be said that our knowledge of these forces is inadequate, the available theory in its incomplete form allows the calculation or close approximation of the forces in some simple crystals. The

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[1] *Ann. Physik,* **39,** 789 (1913). For an excellent treatment of Debye's theory of specific heats, see Slater, "Introduction to Chemical Physics," McGraw-Hill Book Company, Inc , New York, 1939.

[2] LEWIS, *Proc. Nat Acad. Sci.,* **4,** 25 (1918).

[3] SCHUBEL, *Z. anorg. Chem.,* **87,** 89 (1914).

[4] EASTMAN, *J. Am. Chem. Soc.,* **48,** 552 (1926).

[5] *Phys. Rev.,* **6,** 377 (1915).

slight compressibilities of solids indicate that the molecules or atoms are already under very high compressive forces, so that the application of more pressure does not largely increase the total. The tensile strength of solids, particularly of the metals, is an indication of large forces holding the material together, but the true cohesive strength of a metal is not measured by the breaking tension of a standard test bar. The fact that crystals have constant axial ratios and interfacial angles shows the precise nature of the forces but does not enable us to calculate the forces. The application of X rays to crystal analysis has greatly increased our knowledge of crystalline solids, particularly of the regular arrangement of atoms, ions, or molecules into space-lattices, but these data have not yet led to calculations of the forces or indeed to a clear understanding of their nature. The work is still being pressed actively, both by experiment and by the application of all known theoretical means, and the results achieved so far are most promising even in their incomplete form.

Arrangement of Atoms in Crystals.—Before discussing the modern work on this subject, it will be instructive to consider briefly what knowledge preceded this work and to speculate upon the various possible arrangements that agree with this knowledge. It is a familiar fact that the crystals of different substances have different external forms. The crystallographer measures the angles between the faces of a crystal, and he refers the planes forming these faces to imaginary axes placed within the crystal. He finds that the intercepts of these planes, when the axes have been properly chosen, occur at distances from the origin which are to one another as simple whole numbers. The classification of crystals is more simple when their symmetry is considered with reference to the proper axes than when the faces are considered. For many crystals the axes are not at 90 deg. to one another, and often the axes are of unequal lengths.[1]

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[1] All crystals may be classified according to the following systems: (1) *cubic*, with the three crystallographic axes of reference of equal length and at right angles to one another; (2) *tetragonal*, with only two axes equal, but all at right angles; (3) *rhombic*, with three unequal axes at right angles; (4) *monoclinic*, with two axes at right angles and all of unequal length; (5) *triclinic*, with three oblique unequal axes; (6) *hexagonal*, with three axes in a plane intersecting at angles of 60 deg. and a fourth axis through the intersection and perpendicular to the plane; (7) *trigonal*, with three axes of equal length, at equal angles other than 90 deg. For a dis-

Some of the crystal faces may be parallel to one or two of the axes and so have no intercept at all upon them.

The constancy of crystal form in a given substance, regardless of the size of the crystals, suggests that a unit of packing is repeated over and over throughout the crystal, corresponding to some systematic arrangement of points or volume elements in space In elementary substances the unit might contain only a single atom, and single atoms or ions (rather than molecules) of compounds sometimes make up the "points" that form the basis of the "space-lattice," as it is called The repetition of this unit of packing in space constitutes the structure of the crystal.

It is interesting to speculate upon what arrangement the atoms may take. We have no information as to the shape of an atom or molecule,[1] but in the absence of information it will be instructive to assume that the atoms or other structural units that make up the crystal are incompressible spheres. We shall see later that certain metallic elements have the internal arrangement which spheres assume under pressure and shaking; but the internal arrangement of other elementary substances is not that taken by spheres. In binary compounds we must imagine spheres of different sizes for the two elements, and we may abandon the sphere concept entirely in connection with other compounds. Thus this useful concept, like any mechanical analogy, must not be pressed too far just because it is useful in a few simple instances.

The fact that a substance crystallizes in a cubic system does not mean that its atoms are arranged at the corners of imaginary cubes; but since all crystals may be described with reference to axes which are straight lines and since the natural faces of crystals

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cussion of the development of crystal faces referred to axes in the various systems, reference should be made to texts on crystallography or to any standard encyclopedia.

[1] Measured dielectric constants of liquids may be used to calculate dipole moments, which in turn yield some information as to the shape of the molecules of liquids. Such experiments have shown, for example, that H_2O and H_2S are triangular, by which we mean that the atomic centers are arranged at the corners of a triangle and not that the exterior of the molecule is a triangle with no third dimension. The atoms in CO_2 are arranged linearly, NH_3 is pyramidal, and chain hydrocarbons are linear, as has been found from the spreading experiments.

are planes, it seems proper to assume that the arrangement is one in which the constituent units lie in planes. It seems reasonable to suppose, also, that some of these planes, perhaps the most important, are parallel to the developed faces of the crystal. For example, in the piles of spheres shown at the bottom of Fig 16, the external form of the "crystal" is not that of a cube. The arrangement of the spheres may be shown to possess cubic symmetry in both of these arrangements, however, by removing some of the spheres and noticing the "unit cube" of black balls, which is the same in both arrangements. While the external form of the two piles of spheres is different, the internal arrangement is that of a face-centered cube for both pyramids. The different external shapes result from developing different planes. We shall return to a consideration of the problem in three dimensions after a brief examination of a simpler one in two dimensions

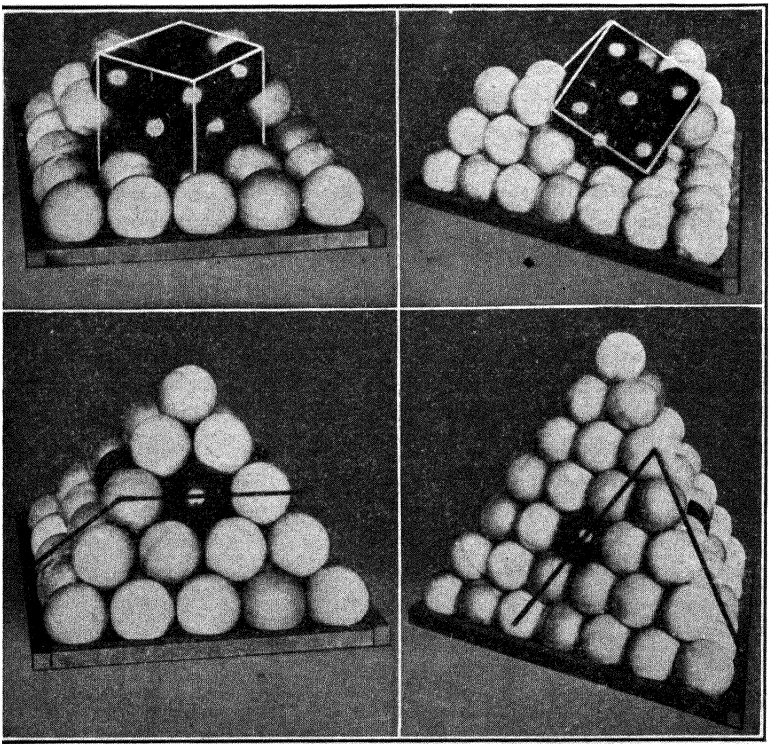

FIG 16 — Illustrating cubic close packing to illustrate the method of attack, but it may be suggested here that a determination of the relative spacings of these planes would give some information regarding the method of packing the atoms in a crystal.

It is a familiar fact that as one rides by an orchard[1] planted in some systematic way the confusion of tree trunks is resolved into straight rows of trees when the orchard is viewed from certain angles. As one rides on, confusion appears to replace regularity until presently at some other angle straight rows are seen again. It is probably a less familiar fact that the distance between the straight rows would be different in viewing the orchard at different angles, but a glance at Fig. 17 will show that this must be so. Now suppose that one is given the distance between these straight rows of trees as viewed from several *distant* points and that it is required to draw a plan of the orchard from these spacings. A set of such spacings is given in the first column of Table 24, with the largest distance given first and the others in order of decreasing distance; in the second column the ratio of each of these spacings to the largest one has been obtained by dividing each distance by 17.7 ft.

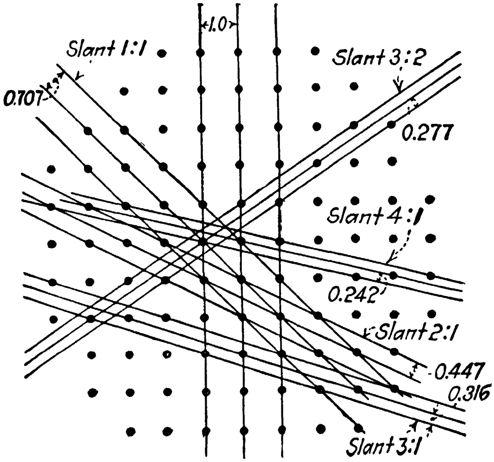

FIG 17.

The next step is to assume some simple plan and see whether the relative distances between straight rows are in agreement

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[1] The author is indebted to Dr. W. P. Davey for the illustration of the orchard [see *Gen. Elec. Rev.*, **28,** 586 (1925)].

with it. Let us assume as a beginning that the orchard is planted with trees at the corners of squares 17.7 ft. on a side and that the angles of view are illustrated in Fig. 17. The third column of Table 24 shows the ratios calculated for this simple square arrangement for the various angles, and it is obvious at once that some of the ratios correspond to such a plan and others do not. This is, therefore, not the correct plan, for a correct one must correspond to *all* the ratios observed; but it is probable that a square enters into the plan, since the first four ratios agree with the experimental ones. Incidentally, the table illustrates the need of sufficient data before reaching a definite conclusion, for had only the first four ratios been studied it would appear that the correct plan corresponded to a simple square. Let us next assume that the plan of the orchard consists of a tree at each corner of an imaginary square and an additional tree in the center of each square (a centered square such as the "five" face on dice). The spacing of the straight rows of trees as viewed from some of the points of observation would be changed, but it would be unchanged when viewed from some other points, such as the 1:1 ratio. Furthermore, the largest distance between rows would be less than the side of the assumed square, for a view directly at the side of the square would show a row corresponding to the trees in the centers of the squares. That this set of measurements corresponds to a "face-centered square" of 25 ft. is shown by the figures in the last column of Table 24. Once a method applicable to the spacing of planes of atoms in crystals has been developed, the problem in three dimensions may be

TABLE 24.—DISTANCE BETWEEN ROWS OF A SIMPLE SQUARE AND A CENTERED SQUARE

Distance between rows (feet)	Ratio from experiment (17.7 = 1)	Ratio calculated for simple square	Ratio calculated for face-centered square
17.7	1.00	1.00	1.00
12.5	0.71	0.707	0.707
7.9	0.45	0.447	0.447
5.6	0.32	0.316	0.316
3.4	0.19	0.277	0.195
3.0	0.17	0.242	0.171

attacked in the same way, by choosing some simple arrangement as a working basis and discarding it in favor of another as soon as it is found to be incorrect.[1]

To return now to the piles of spheres shown in Fig. 16, it will be seen from the black spheres that the arrangement is a face-centered cube, *i e.*, that each sphere in the face of the "unit" formed by black spheres is equidistant from four others in the same plane with it. The "crystal," therefore, has the same atomic plan as the orchard, if the proper planes are considered.

Application of X Rays to Crystal Structure.—This topic, like so many others that we consider briefly, is one about which a book should be read as an introduction to the fundamental theory and an outline of some of the simpler results.[2] Since only a few pages are available for the topic, it is necessary to omit entirely the historical development,[3] the means of measuring the wave lengths,[4] and the procedures by which the X-ray diffraction of single crystals or of crystalline powders has revealed the arrangement of atoms or ions or molecules in crystals.

The fascinating chain of scientific events that has so enriched our knowledge of crystals started in 1912 from the application of three fundamental facts to this problem: (1) X rays were shown to possess properties similar to light, of a wave length about 10^{-8} cm , and capable of penetrating matter that was opaque to visible light. (2) Avogadro's number (6×10^{23}) showed that atomic spacing in a crystal was of the order 10^{-8} cm. (3) The plane faces of crystals made it probable that there were planes of atoms or molecules regularly spaced throughout the crystal.

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[1] More general analytical methods have been developed which are applicable to the problem in three-dimensional space. See R. W. G. WYCKOFF, "The Structure of Crystals," 2d ed , Chemical Catalog Company, Inc., New York, 1931

[2] There are several excellent books available, of which Bragg, "The Crystalline State," and Wyckoff, *op cit* , are worthy of special mention.

[3] See Richtmyer, "Introduction to Modern Physics," 1934, Chap. XIII, for a brief but most excellent historical outline

[4] The wave length was at first derived from the relative spacings of planes parallel to the cube face, face diagonal, and cube diagonal [BRAGG, *J. Chem Soc.* (*London*), **109,** 252 (1916)] and later by diffraction from a ruled grating [COMPTON and DOAN, *Proc Nat. Acad. Sci.*, **11,** 598 (1925)]; see also RUARK, *Phys. Rev.*, **45,** 827 (1934); GOTTLING and BEARDEN, *Phys. Rev.*, **46,** 435 (1934).

These facts led von Laue to suggest to Friedrich and Knipping[1] that a crystal with its three-dimensional symmetry should be able to serve as a diffraction grating for X rays in the same way that a ruled grating may be used to diffract visible light. By passing a pencil of general X radiation for some hours through a crystal mounted in front of a photographic plate, they obtained on the plate a symmetrical pattern of spots about the image of the transmitted beam, from which they confirmed the wave-like properties of X rays, demonstrated the three-dimensional space-lattice of the crystal, and showed that the wave lengths in the beam were about 10^{-8} cm.

Following this discovery, means were developed for providing nearly "monochromatic" X rays, for precise measurement of the wave lengths, and for precise determination of atomic plane spacing in crystals. We may assume that the internal structure of crystals in three dimensions was then inferred in a way similar to that used in the "orchard" example, though, of course, other procedures have also been used. The fundamental equation relating the distance d between atomic planes, the wave length λ of the X rays, and the angle θ at which the "reflected" X-ray beam has its maximum intensity is

$$\lambda = 2d \sin \theta \tag{4}$$

which is known as Bragg's law.[2]

In order to derive the equation let the parallel dash lines of Fig. 18 represent the advancing wave front of a beam of X rays of a single wave length λ and the horizontal lines correspond to the planes of atoms in a crystal separated by the distance d If the beam is striking at such an angle θ that the "reflected" beam along the line hcg is not in phase, destructive interference results and the intensity of the reflected beam is very low Only when the angle θ is such that the difference in the paths ecg, mhg, akg, etc , is a *whole number* of wave lengths will the reflections from different planes

---

[1] See *Sitzber. kgl. bayer. Akad. Wiss* (1912); *Jahrb. Radioakt Elektronik*, **11**, 308 (1914), for the first papers on the topic. An excellent account of the later developments, experimental technique, and interpretation of the photographs is given in Wyckoff *op. cit.*, and especially in Bragg, *op cit.* For briefer accounts see Ruark and Urey, "Atoms, Molecules, and Quanta," pp. 209–236 (1930), or Richtmyer, *op cit.* Chap. XIII.

[2] *Proc. Cambridge Phil Soc.*, **17**, 43 (1912). The usual form of the law is $n\lambda = 2d \sin \theta$, where n is a whole number called the "order" and signifying the number of wave lengths by which the paths of the X-ray beam differ when there is constructive interference.

reinforce one another and give rise to an intense reflected beam, for the apparent reflection of X rays differs from ordinary reflection of light in that the beam penetrates *into* the crystal and gives rise to reflection from many planes. It will be seen also that, unless the planes of atoms are ***accurately*** spaced at the distance d, destructive interference would take place for all incident angles of the beam and there would not be any reflected beam of marked intensity. Suppose θ is so chosen that the reflected beam has maximum intensity, the difference in the paths ecg and bhg is a whole number of wave lengths $n\lambda$. As ec is equal to bj and hf is equal to hc, the difference in path $bhg - ecg = hc - hj$ and this is equal to $hf - hj$, or jf Now jf divided by cf is the sine of the angle θ, and cf is twice the interplanar distance, then it follows that

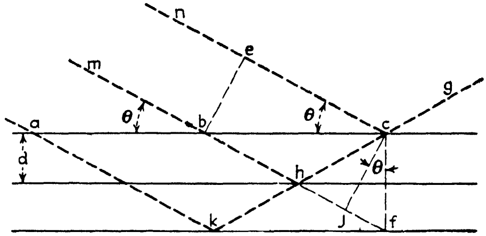

FIG 18

$$n\lambda = 2d \sin \theta$$

The Unit Cell.—In considering the internal structure of crystals it is convenient to imagine that the space is divided into *identical* unit cells of suitable dimensions such that each cell contains a unit of the pattern. The points at which atoms occur in this cell form the space-lattice which shows how the "design" is repeated. The cell is made as small as it may be and still be identical with every other cell. In the cubic system to which we shall confine most of our attention in this brief treatment, the unit cell is a cube; but in other types of crystals the planes bounding the cells may meet at angles other than 90 deg., and the lengths of the edges of the cells may not be equal. If one corner of a cell is taken as the origin, the edges of the cell along the x, y, and z axes are a, b, and c. In place of giving the actual lengths of these edges, it is usually sufficient to express them in terms of b as unity, but in the cubic system $a = b = c = 1$.

Types of Unit Cells.—The sketches[1] in Fig. 19 show the types of cell in the cubic system and the hexagonal close-packed cell.

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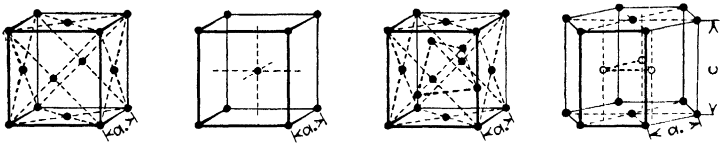
[1] From the Department of Metallurgy at Massachusetts Institute of Technology. The dimensions of the cells are in angstrom units, of which 1Å = 10^{-8} cm.

These cells have been drawn in the conventional manner, but it should be understood that in all of them the "corner" atoms are also the "corner" atoms of other cubes formed by extending the plane faces beyond the distances shown and that those in the faces of the cubes lie in the faces of the adjoining cubes. An element of space such as that shown for the face-centered cube contains one-eighth of each of the atoms shown at the eight corners and one-half of each of the atoms shown in the cube faces, or a total of 4 whole atoms. Similarly, the body-centered cube contains one-eighth of each of the eight corner atoms and all of the center atom, or a total of 2 atoms; the hexagonal cell contains 3 atoms entire, one-half of each of 2, and one-sixth of each of 12, or 6 altogether.



Face-Centered Cubic

N	ELEMENT	a.
13	Al	4 04
20	Ca	5 56
26	Fe (γ)	3 61
27	Co	3 55
28	Ni	3 54
29	Cu	3 60
45	Rh	3 82
46	Pd	3 95
47	Ag	4 06
58	Ce	5 12
77	Ir	3 80
78	Pt	3 93
79	Au	4 08
82	Pb	4 91
92	Th	5 04

Body-Centered Cubic

N	ELEMENT	a.
3	Li	3 50
11	Na	4 30
24	Cr	2 89
26	Fe (α)	2 86
42	Mo	3 14
73	Ta	3 27
74	W	3 15
19	K	5 20
23	V	3 04

Diamond Cubic

N	ELEMENT	a.
6	C	3 55
14	Si	5 42
32	Ge	5 63
50	Sn (gray)	6 46

Hexagonal Close Packed

N	ELEMENT	a	c/a
4	Be	2 29	1 58
12	Mg	3 22	1 62
30	Zn	2 67	1 86
48	Cd	2 96	1 89
22	Ti	2 97	1 59
40	Zr	3 23	1 59
58	Ce	3 65	1 63
27	Co	2 51	1 63
44	Ru	2 69	1 59
76	Os	2 71	1 59

FIG. 19.—Crystal structures of elements

The face-centered cubic arrangement is obtained by dividing the space in a crystal into closely packed cubes and placing an atom at each cube corner and at the center of each cube face. This arrangement is also called cubic close packing and is one of the two alternative arrangements that hard spheres of equal size assume when closely packed by pressure and shaking. The body-centered cubic arrangement has an atom at each cube corner and at the center of each elementary cube. Spheres so arranged are not so closely packed as in the face-centered cubic arrangement, and this arrangement is not stable for spheres. Hexagon close packing is obtained by dividing the space into equal, closely packed, right-triangular prisms, the bases of which are equilateral triangles and the altitudes 1.63 times the side of the triangles. An atom is located at each prism corner and at half of the prism centers. This is the second alternative arrangement assumed by equal spheres under pressure and shaking. As has been said before, the concept of a spherical unit is not necessarily the correct one, but the arrangements that have been described are those actually assumed by the atoms in a considerable number of crystals of elements and compounds.

The simplest arrangement of all would appear to be that obtained by dividing the space into equal elementary cubes with the center of a sphere at each cube corner. Such an arrangement is not stable for equal spheres that are pressed and shaken, and no *elementary* substance has this arrangement, though some compounds have structures of this kind, involving spheres of two different sizes, as we shall see later.

The Coordination Number.—In any symmetrical arrangement of spheres or points repeated in space of three dimensions, each sphere or point would have a certain number of "nearest neighbors," and this number is defined as the coordination number. For example, if a rectangular box of which the dimensions are whole multiples of 1 in. is filled with uniform spheres 1 in. in diameter in such a way that all the edge members of each layer touch the sides of the box, the arrangement has simple cubic symmetry, for each sphere is in contact with six others, its nearest neighbors.

In the body-centered cubic arrangement shown in Fig. 19, which could be produced in the box of spheres by shifting every other layer half the radius in two directions and decreasing the vertical spacing of the layers, the coordination number is 8. Each sphere in the second layer, for example, is in contact with four in the first layer and four in the third layer, these eight forming the "unit cube." Of course, the spheres in the second and fourth layers form "unit cubes" in which the spheres in the third layer are the center spheres, so that, except for the outside spheres touching the box, each one has eight nearest neighbors.

In the face-centered cube (Fig. 20) the coordination number is 12. Consider for a moment the spot in the front face of the cube from which the 4 spots F, G, B, and E are separated by half the diagonal of the cube face. Four others in the plane $a/2$ behind this front face are also half the diagonal of a cube face from it; and if we imagine another plane $a/2$ in front of the plane containing F, G, B, and E, it will also contain 4 spots at this distance from the one in the center of the face $FGBE$, making a total of 12 at the distance $a/\sqrt{2}$, or $0.707a$, from center to center.

In hexagonal close packing the coordination number is also 12, as may be seen from Fig. 19. The spot in the upper face, for example, has six spots in the plane of this face, three in the plane $c/2$ below it, and, of course, another three in the plane $c/2$ above this plane. Since hexagonal close packing has the same coordination number as that of the face-centered cube and both arrangements are stable for spheres, it might seem at first thought that the arrangements were identical and made to appear different by an artificial choice of volume element; but this is not true. Hexagonal close packing could be changed to face-centered cubic packing by moving the three "inside" spots of the hexagonal unit cells packed above and below the ones shown in Fig. 19 around the vertical axis 60 deg., but keeping them in the same horizontal plane. This may readily be seen by packing at least four layers of spheres in a glass box or frame; but it is somewhat difficult to imagine from the single cells sketched, and plane drawings of several cells are too confusing to be useful. The two arrangements give slightly different densities, which are nevertheless real, again confirming the fact that the arrangements are not quite the same.

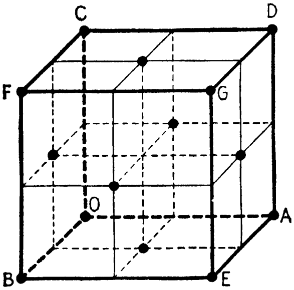


FIG 20.—Face-centered cubic unit

Other coordination numbers are also found in crystals. The lowest possible coordination number would, of course, be 1, corresponding to two spheres in contact, with these pairs arranged in a symmetrical lattice spaced at a distance greater than a sphere diameter. Another possible arrangement would be in linear chains, in which 2 would be the coordination number. In the diamond cubic arrangement sketched in Fig. 19, each sphere has four nearest neighbors arranged with the centers forming a tetrahedron around it. This will be clearer from Fig. 21, in which spheres are arranged in this same way.

From the distance between atomic centers in an elementary crystal and the coordination number, we may calculate the radii of equal spheres which will just be in contact when packed in this way. This calculated quantity is commonly called the atomic radius or distance of closest approach, though, of course, we have no knowledge that the atoms are actually spheres or actually of any recognizable "shape"

In the discussion of chemical compounds later in the chapter, especially of compounds in which the lattice unit is an ion, we shall consider ionic radii as well, and these will not in general be equal for the two ions in a crystal. The point which should be made here is that the atomic radius of sodium in sodium metal, for example, will not be the same as the radius of sodium ion in a sodium chloride crystal for several reasons, of which some will be given later.

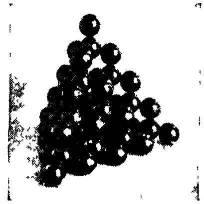


FIG 21 —Arrangement of spheres in tetrahedral symmetry (diamond-type lattice).

Arrangement of Atoms in Elementary Crystals.—Crystalline structures of the true metals are characterized by their extreme simplicity and by the closeness of packing. The common arrangements are face-centered cubic and hexagonal close packed, in each of which the coordination number is 12, representing the closest packing of spheres; and body-centered cubic with a coordination number of 8 and in which the packing is not quite as close as in the first two types. Some correlation of arrangement with physical properties has been observed; for example, the metals that are ductile and good conductors of heat and electricity (Cu, Ag, Au, Al) are face-centered cubic. But it is not safe to generalize that all face-centered cubic metals will have these properties to an exceptional degree compared with those of some other symmetry.

There is a tendency for members of the same group in the periodic table to show the same symmetry (for example, Li, Na, K; Cr, Mo, W; Cu, Ag, Au), but exceptions are found. It should be noted that the tetrahedral arrangement shown by C, Si, Ge, and gray Sn, all in the fourth column of the periodic table, is not shown by Pb, which is also in the triad with Ge and

Sn. The high melting point of carbon is less marked in the succeeding elements (Si melts at 1420°, Ge at 958°), though the hardness persists in Si to some extent and is especially conspicuous in SiC, which is of the same structure.

The nonmetallic elements N_2, O_2, Br_2, and I_2 have these diatomic molecules as the unit in the crystal, rather than atoms, which is to be expected from the stability of the molecules in the vapor. Chlorine has a different arrangement of molecules from bromine and iodine, which shows again that not all elements in one column of the periodic table have the same structure. The structure of crystalline fluorine has not yet been determined.

Only the simpler structures for elements are discussed here, but it will be understood that not all elements crystallize in the cubic system, and hence the structures of some of them are more complicated than one would infer from the examples given. The atoms in most of the elementary structures outside of the cubic system are arranged symmetrically with coordination numbers of 2, 4, 8, 12, etc., as is true of cubic crystals, but of course the axes are unequal or inclined at angles other than 90 deg., so that the "unit cell" is not a cube, but another geometric unit.

As has already been suggested, attempts to explain hardness, melting point, thermal or electrical conductivity, color, ductility, or other physical properties of crystalline elementary solids in terms of the arrangement of atoms in crystals have been only partly successful. Some of these properties depend upon the nature of the bonds between atoms and the part taken by the electrons in these bonds—doubtless upon other factors as well. Much experimental work is still being done, and many of the facts already known await satisfactory interpretation. The bare outline of some of the work given here will suffice to show its general nature; full accounts are available to those who wish to study further.[1]

Arrangement of Atoms in Binary Compounds.—When the elements forming a binary compound come from widely separated columns of the periodic table, the chemical bond is usually due to a complete (or nearly complete) transfer of an electron

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[1] STILLWELL, "Crystal Chemistry," McGraw-Hill Book Company, Inc., New York, 1938, and EVANS, "Introduction to Crystal Chemistry," Cambridge University Press, London, 1939, are suitable texts in which to read further on the correlation of properties to internal arrangement.

from one atom to another.[1] An alkali metal readily loses its one valence electron to chlorine or other halogen, which has seven valence electrons, so that the outer shell of eight is completed in the halogen. The crystals of such substances are presumably formed of ions and are termed ionic crystals. X-ray diffraction shows the positions of the atomic centers; but since the ions do not have equal "atomic radii," the conventional representation of the structure is by spheres of unequal size representing the two elements. It does not follow that the radius of sodium ion in sodium chloride is the same as that in sodium bromide, for the different atomic volume and the larger number of electrons in bromine alter the volume available to the sodium. It should not be assumed that NaCl and CsCl have the same internal arrangement (for they do not), nor does it follow that another compound of the type XY will have the arrangement of either NaCl or CsCl We consider briefly some simple examples.

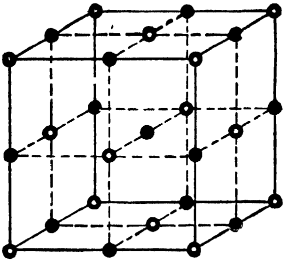

FIG. 22.—Sodium chloride structure

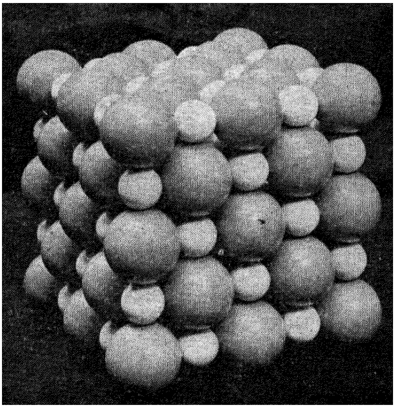

FIG 23 —Arrangement of atoms of sodium (small spheres) and chlorine in sodium chloride

In sodium chloride the ion centers of sodium and chloride ions alternate at the corners of equal cubes, as sketched in Fig.

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[1] The two types of bond which we need to consider are the so-called "polar bond," which results from a complete transfer of an electron from one atom or group to another, and the covalent or homopolar bond, which results from the sharing of a pair of electrons by two atoms, as in the compound Cl_2. In general, an atom of the nth group may share no more than $(8 - n)$ electrons. Thus in O_2 the atoms share two pairs of electrons, corresponding to a chemical valence of 2

22, which shows the conventional unit cube. A photograph of an arrangement of large dark spheres, representing chloride ions, and smaller white ones representing sodium ions is shown in Fig. 23, which is eight "unit cubes." It should be understood that the corner ions in Fig. 22 differ in no way from those in the face centers, for this pattern is repeated over and over again in space. One-eighth of each corner ion, one-half of each face-centered ion, one-fourth of each ion in the cube edge lies within the cube shown. The coordination number is 6, each ion of sodium having six neighboring chloride ions and each ion of chloride six neighboring sodium ions. Although the structure is apparently a simple cubic one, it is not commonly so called; for a cube having half the edge of that sketched in Fig 22 would not show the correct structure by repetition in space This is the structure of most alkali halides (though not of all of them) and of many oxides and sulfides. It is commonly called the "sodium chloride structure."

The radius assigned to sodium ion in sodium chloride is 0.96Å, and that assigned to chloride ion is 1 83Å It may be noted for comparison that the atomic radius of sodium atoms in sodium metal is 1.86Å.

Cesium chloride is a body-centered cubic structure in which half the atoms are different from the other half. It is also an ionic crystal, and one in which the assigned ionic radii are not equal. For each ion in this structure the coordination number is 8. The halides of cesium, thallium, and ammonium are other examples of ionic crystals of this type, but nonionic crystals of compounds are known that are of this type also. In the ammonium halides we have an example of an ionic group (NH_4^+) forming the unit of structure, and this is true of the structure of other compounds such as nitrates and carbonates.

As another illustration of a binary compound having an arrangement similar to that of an elementary substance, ZnS has the diamond structure with half the atoms unlike the other half. This structure is shown by many less polar binary solids. Presumably, but not certainly, the units in this structure are atoms rather than ions. As has been said before, one must not assume that chemically analogous compounds have the same structure; for example, ZnO does not have the same structure as ZnS, but SiC has the same structure as ZnS.

These examples will show the general nature of the arrangement in simple crystals, though not all binary compounds crystallize in the cubic system, of course, and not all the types have been listed. Further complications arise in more complex crystals, as would be expected, but the structures of many hundreds of crystalline solids have been worked out[1] by the application of X-ray diffraction.

Though correlation of crystal structure with physical properties is not a simple matter, since several different factors are involved, it is generally true that increasing distance between atomic centers in *ionic* crystals is attended by decreased hardness and lower melting point. In crystals of substances joined by homopolar bonds (shared electrons), these forces hold together the two atoms in the molecule, and the crystal structure derives its strength from other less intense forces that are described by the vague term "residual." Such crystals will usually be of much less strength and of lower melting point, though the correlation of properties to structure is more difficult for these substances.

Many inorganic crystals are probably not of the ionic type but consist of atoms. This is particularly true of crystals of intermetallic compounds, most of which have bonds similar to those in crystals of a single metal. Crystals of organic compounds usually consist of molecules arranged in space-lattices. The chemical bond is probably "covalent" in these substances, which is to say that two elements share one or more electron pairs, rather than transferring electrons more or less completely from one atom to another as in "polar" compounds such as sodium chloride. Since hydrogen atoms diffract X rays to a comparatively slight extent, the crystal study by this method usually locates the other atoms in an organic compound and leaves the position of hydrogen to be inferred.

Determination of Avogadro's Number.—Since wave lengths of X rays may be determined from ruled gratings, their diffraction by crystals furnishes a means of calculating Avogadro's number from the size of the "unit cell" in a crystal of known structure. For example, the "unit cube" shown in Fig. 22 contains 4 atoms of sodium and 4 atoms of chlorine. The edge

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[1] Most of them are described in Wyckoff, *op. cit.*, and in the 1935 supplement; nearly all of them are given in the six volumes of "Strukturbericht."

of this cube is 5.638×10^{-8} cm., or its volume is $(5.638 \times 10^{-8})^3$ cm³. The density of NaCl is 2.163, whence the volume occupied by 4 gram atoms of each element in the compound is

$$\frac{4(23\ 0 + 35.45)}{2.163}$$

or 108.1 cm³. The ratio of the volume of 4 "gram molecules" of NaCl to the volume of 4 "molecules" of NaCl is

$$\frac{108\ 1}{(5\ 638 \times 10^{-8})^3} = 6.03 \times 10^{23}$$

which is the number of molecules per mole.

Structure of Surfaces.—We have seen that in crystals the atoms or other structural units are held together in symmetrical patterns by something which may be called "bonds" These atomic or molecular forces, or "bonds," are exerted in all directions within the body of the crystal, no doubt chiefly upon the immediate neighbors, but possibly upon a second or third "layer" as well. Molecules or atoms in the surface of a crystal may be presumed to have these forces unsatisfied outside the crystal. If the crystal is in contact with its vapor at a sufficient pressure or with a solution of the substance at a sufficient concentration, it will add on other layers and grow in size. This growth of crystals, which may be readily observed in the laboratory, is evidence of the existence of the residual forces.

Lacking an opportunity to attach molecules of its own kind, the crystal may attach molecules of some other substance. The "bond" holding such molecules is possibly of a different character and less intense than a "bond" to a molecule that may fit into the crystal lattice, though we have no means of showing how the molecule may be held. Experimental evidence is available for the formation of attached layers of nitrogen upon mica,[1] of water vapor and other gases upon glass or silica, of many gases upon charcoal,[2] and of many solutes upon charcoal or other solids.

An initial monolayer might be held by the residual forces at the face of the crystal. The formation of a second layer could result only if the crystal forces reached out into space more than

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[1] Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).

[2] For example, see Coolidge and Fornwalt, *ibid*, **56**, 561 (1934).

molecular distances (which is considered improbable) or by the forces acting between the molecules of the attached substance. The latter effect would resemble condensation to a liquid phase, and adsorbed layers form upon surfaces when the pressure of the gas supplying the attached layers is a very small fraction of that necessary for true condensation.

Adsorption.—This term is commonly used to signify an attached layer upon a solid or liquid surface such as is discussed in the previous section. The mechanism of adsorption is described by Langmuir[1] as follows:

> . . . when gas molecules impinge against any solid or liquid surface they do not in general rebound elastically, but condense on the surface, being held by the field of force of the surface atoms. These molecules may subsequently evaporate from the surface. The length of time that elapses between the condensation of a molecule and its subsequent evaporation depends on the intensity of the surface forces. Adsorption is a direct result of this time lag. If the surface forces are relatively intense, evaporation will take place at only a negligible rate, so that the surface of the solid becomes completely covered with a layer of molecules. In cases of true adsorption this layer will usually be not more than one molecule deep, for as soon as the surface becomes covered by a single layer the surface forces are chemically saturated. When, on the other hand, the surface forces are weak the evaporation may occur so soon after condensation that only a small fraction of the surface becomes covered with a single layer of adsorbed molecules.
>
> In agreement with the chemical nature of the surface forces, the range of these forces has been found to be extremely small, of the order of 10^{-8} cm. That is, the effective range of the forces is usually much less than the diameter of the molecules. The molecules thus orient themselves in definite ways in the surface layer since they are held to the surface by forces acting between the surface and particular atoms or groups of atoms in the adsorbed molecule.

The atoms in the space-lattice may be thought of as resembling a "checkerboard" on which adsorbed molecules take up definite positions. Since not all the atoms in the crystal face are alike, not all the spaces will necessarily hold an adsorbed atom or molecule. Large molecules might occupy several spaces or at least prevent the occupation of adjoining spaces by other molecules. If nearly all the gas molecules striking a solid surface condense and if a molecule of gas striking another molecule of

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[1] *Ibid.*, **40**, 1361 (1918).

gas already adsorbed evaporates immediately (or rebounds elastically), the rate of condensation will be proportional to the pressure of the gas and to the fraction of the surface that is bare. The rate of evaporation will be the product of the rate for a saturated surface and the fraction of the surface covered; and at equilibrium the two rates will, of course, be equal.

At low gas pressures the amount of adsorbed gas usually decreases rapidly as the temperature is raised, since this greatly increases the rate of evaporation At high pressures the surface may be nearly covered with a monolayer, so that the adsorption varies only slightly with increasing temperatures.

Much of the experimental work tending to show that adsorbed layers are or are not monomolecular is difficult to interpret, owing to the uncertainty as to the actual area of adsorbing surface available. For the area of a square centimeter of "rough" surface has no meaning, and when molecular dimensions are considered smoothness may be an ideal beyond attainment.

Langmuir has derived an expression for the fraction of a solid surface covered by an adsorbed layer of molecules of gas at equilibrium, in terms of n_s, the number of molecules striking a square centimeter of surface each second [which may be computed from equation (14), page 86], the fraction x of these molecules that condenses upon the surface (usually near unity), and n_e, the number evaporating each second from a square centimeter of completely covered surface This relation is

$$\text{Fraction covered} = \frac{n_s x}{n_e + n_s x}$$

Experiments show that this relation is valid insofar as one is able to determine the quantities appearing in it. The chief difficulty lies in determining the actual area of the solid surface.

A more common but less accurate relation, the Freundlich equation, gives the quantity of adsorbed substance as

$$q = ap^{1/n} \tag{5}$$

where q is the quantity of adsorbed substance per unit area of surface, p is the pressure, and a and n are constants. Over narrow ranges of pressure the equation fits experimental data fairly well, though the term n is not a constant but a function of the pressure. This may be seen in Fig. 24, which is a plot of the data in Table 25. At low pressures the adsorption might well be expected to be proportional to the pressure (*i.e.*, to the number of molecules striking the surface), while as the pressure is increased the surface layer approaches saturation and there is no further increase of adsorption because there is no more uncovered surface at which the residual attraction of the surface atoms can act

TABLE 25.—ADSORPTION OF NITROGEN ON MICA AT 90° ABSOLUTE

Pressure (dynes per square centimeter)	Moles adsorbed × 10^6	Calculated from Freundlich equation	Per cent deviation of Freundlich equation
34.0	1.37	1.54	+11
23.8	1.28	1.31	+ 3
17.3	1.17	1.14	− 3
13.0	1.06	1.01	− 5
9.5	0.995	0.883	−12
7.4	0.90	0.795	−11
6.1	0.79	0.726	− 7
5.0	0.707	0.68	− 4
4.0	0.628	0.62	− 1
3.4	0.556	0.58	+ 4
2.8	0.500	0.536	+ 7

The calculated values were obtained from the equation $q_F = 8.4p^{0.417}$ At the lowest pressure the slope of the plot (log p against log q) corresponded to $1/n = 0.68$; at higher pressures it decreases to $1/n = 0.20$.

Langmuir's adsorption data for nitrogen are given in Table 25 as typical of modern work.[1] These results were obtained by a simple and ingenious method. A quantity of mica whose area was 5750 sq. cm. was placed in one of two connecting bulbs of nearly equal volume, and both bulbs were very carefully and completely exhausted. A small quantity of nitrogen was admitted to the empty bulb, and its pressure was determined. Then connection was established between this bulb and the one containing mica, and the pressure was measured again. The difference between the pressure to be expected from the relative volumes of the two bulbs and the pressure actually

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[1] A summary of the numerous papers of Langmuir and his associates during the last 20 years is given in *Science*, **87**, 493 (1938).

measured gave the quantity of nitrogen that had been adsorbed. Next, the tube connecting the two bulbs was closed, and the one containing no mica was carefully pumped out again. When the connecting tube was opened a second time, the difference between the expected and observed pressures was a measure of the amount of nitrogen adsorbed on the mica at the lower pressure.

In order to evaluate the constants of the Freundlich equation, log q was plotted against log p (solid line), and n was so chosen as to give a "straight line" through these points. As will be seen from Fig. 24, the Freundlich equation (represented by a dotted line) is not a very satisfactory one for expressing adsorption as a function of the pressure.

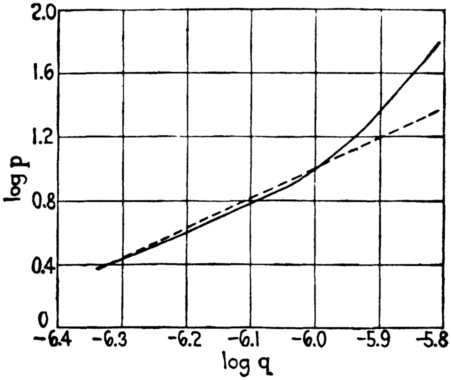

FIG. 24 —Adsorption as a function of pressure.

Adsorption decreases as the temperature is raised. Therefore, when it is desired to remove an adsorbed film of gas from a solid surface, this is usually done by pumping out at a high temperature. Thus the evacuation of double-walled flasks for the storage of liquid air is usually carried out at a temperature just below the softening point of the glass. Since adsorption increases at lower temperatures, the evacuation of a flask may be made fairly complete by attaching it to a bulb filled with charcoal and immersing the charcoal bulb in liquid air while gently warming the flask to be evacuated.

Experiments on adsorption of gases at high pressures and with materials of large surface for a given weight are more difficult to interpret, and the quantity of gas adsorbed by a unit weight of adsorbent is not a simple function of the pressure, as may be seen from the data expressed in Fig. 25 for nitrous oxide adsorbed on charcoal.[1]

While the formation of monolayers on solids is greatly influenced by the surface lattice of the solid, such layers forming on liquids are probably not dependent upon the structure of the underlying liquid. Oriented monolayers of solutes also form at liquid-liquid interfaces and at liquid-solid interfaces. These layers are of the greatest importance in determining the stability of emulsions and suspensions, in the concentration of minerals by froth flotation, and other processes. Some of these matters will be considered in a later chapter.

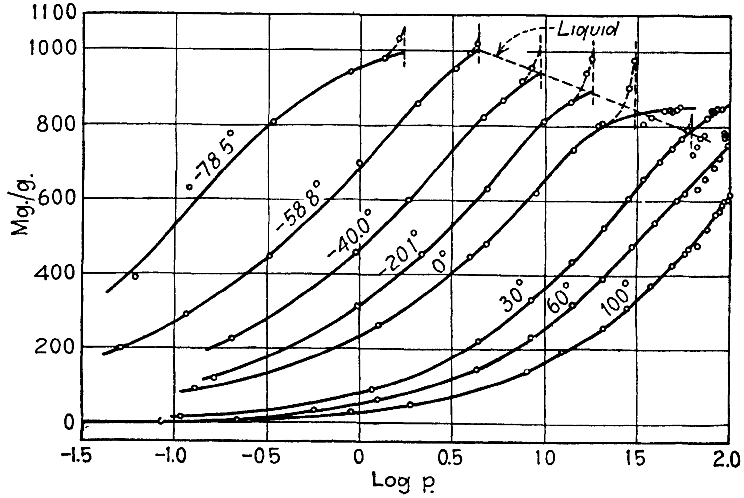

FIG. 25—Adsorption isotherms for nitrous oxide on charcoal.

Liquid Crystals.—Certain substances of complex organic nature melt to turbid liquids having quite different properties from those of ordinary liquids. As the temperature is further raised, a point is reached at which each liquid changes sharply to a clear liquid of ordinary properties. The substance thus shows, in addition to its usual melting point, another transition temperature at which it assumes the properties of liquids. While in this intermediate state, the liquid exhibits double refraction, a property characteristic of crystalline substances. When a

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[1] COOLIDGE and FORNWALT, *J. Am. Chem. Soc.*, **56**, 561 (1934).

beam of light passes through a doubly refracting substance, there are two emerging beams, only one of which follows the ordinary laws of refraction, and the rays are polarized. This occurrence is characteristic of substances which are not isotropic, *i.e.*, whose properties are not the same when measured in different directions. It follows that the intermediate "liquid" state is one in which the properties of the liquid are not the same in all directions. Lehmann[1] calls this intermediate condition the "liquid-crystalline" state; perhaps a better name would be doubly refracting liquids. Apparently weak forces such as those acting in crystals are at work arranging the molecules in a kind of space-lattice similar to that of crystals, but less definite in character. The sharp disappearance of this double refraction at a definite temperature bears a resemblance to the melting point of crystals, except that in this case the substance is already fluid.

An early explanation of liquid crystals (Nernst, Bose) was that there were "molecular swarms," but this idea has been found inadequate to explain the observations. Born[2] and Voigt[3] both consider that in liquid crystals there is an arrangement of the *molecules* in some particular way, perhaps parallel to one another with respect to some one axis, and that this is responsible for the behavior of liquids in this peculiar state. If there is a space-lattice, it differs sharply from the one found in solids. At the second transition point, or clearing point, this molecular lattice is lost, and with it the double refraction characteristic of anisotropic substances.

Over 170 substances showing two transition points[4] have been prepared. A study of them has shown no space-lattice detectable by the usual X-ray methods applicable to solid substances. These liquid crystals have optical rotatory powers as high as 4000 deg. for a film 1 mm. thick; a quartz plate of this thickness has a rotation of only about 25 deg. There is apparently no relation between the constitution of the compounds and their capacity for producing liquid crystals.[5] It may be that all

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[1] A review of his very numerous papers on this subject is given in *Physik. Z.*, **19,** 73 (1918).

[2] *Sitzber. kgl. preuss. Akad. Wiss.*, **1916,** 614.

[3] *Physik. Z.*, **17,** 76, 152 (1917).

[4] *Engineering,* **106,** 349 (1918); a review of the subject.

[5] CHAUDHARI, *Chem. News*, **117,** 269 (1918).

organic substances are capable of forming liquid crystals, but the temperature ranges of their existence are so small that they have escaped detection. This is rendered unlikely by the fact that some of the substances exhibit their peculiar properties through a range of 35°. A few examples are mentioned in Table 26.

TABLE 26.—SUBSTANCES FORMING LIQUID CRYSTALS[1]

Substance	Transition temperatures, degrees		Range of existence of liquid crystals, degrees
Cholesterin benzoate	145	179	34
p-Azoxyanisole	118	136	18
p-Azoxyphenetole	134	169	35
Pyridine nitrate	88	105	17
Quinoline nitrate	102	119	17
p-Methylaminobenzaldehyde phenyl hydrazone	170	190	20
p-Ethylaminobenzaldehyde phenyl hydrazone	160	181	21

Problems

1. The heat of fusion of monoclinic sulfur is 13 cal per gram, the melting point is 119°, the density of the solid is 1.960, and that of the liquid is 1.80. Calculate the melting point at 50 atm pressure.

2. The vapor pressure of ice is 4.58 mm. at 0° and 3.28 mm. at −4°. Calculate the heat of sublimation of ice.

3. Calculate the heat of sublimation of iodine at 110° from the vapor pressures on page 146.

4. The unit cell of chromium is a cube of edge 2.89Å, its density is 7.0. Calculate this density upon the assumptions of (*a*) face-centered and (*b*) body-centered structure.

5. (*a*) Calculate the weight of nitrogen gas necessary to cover the surface of a cube of 1-liter capacity with a layer one molecule deep, making a reasonable assumption as to the diameter of an atom, and assuming both atoms of the molecule in contact with the adsorbing surface. (*b*) How large an error would the loss of these molecules produce in the calculated pressure at 20° and 1 atm.?

6. MgO has been shown to have the sodium chloride arrangement, and the edge of a cube containing 4MgO is 4.20Å. Calculate its density.

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[1] ROTARSKI, *Ber.*, **41,** 1994 (1908).

7. Given the density of KI as 3.11, calculate the edge of a cube containing 4KI, assuming the sodium chloride arrangement. The measured edge is 7.1Å.

8. Copper crystallizes in the face-centered cubic arrangement, and the edge of the unit cube is 3 6Å. Show that the density calculated upon the assumption of this arrangement is in agreement with the measured density, which is 8.93.

9. Cesium chloride forms a body-centered cube arrangement, and the cube containing 1CsCl has an edge of 4 12Å Show that this arrangement is in conformity with its measured density and not in conformity with the arrangement in which most of the alkali halides crystallize The density of CsCl is 3 97.

10. The edge of the unit cell of lead is 4 92Å, and the structure is face-centered. Calculate the sine of the smallest angle at which constructive interference of X rays of wave length 0 708Å would occur for planes of atoms parallel to the cube face and to the face diagonal

CHAPTER VI

SOLUTIONS

The solutions that are to be studied in this chapter are liquid phases in which a gas, liquid, or solid solute is *molecularly* dispersed. Solutions in which the solute is ionized are considered in the next chapter; "solid solutions" are discussed briefly in Chap. XI; colloidal "solutions," in Chap. XVII. Such a subdivision of the general topic of solutions brings us to the simpler systems first. The experimental quantities used in studying solutions are solubility, partial pressure of solvent vapor above the solution, partial pressure of solute vapor, boiling point, freezing point, and osmotic pressure and the changes in these properties with changing temperature or pressure or composition. We shall develop equations relating some of these properties to others that are exact for very dilute solutions and useful approximations for stronger solutions; and it will be necessary to exercise some judgment in applying them to solutions that are not dilute, as it was necessary to use the ideal gas law with discretion at high pressures or low temperatures.

Solubility.—There are no fixed rules by which to predict whether a substance will dissolve in a given liquid or not or to what extent. The probability that a solution can be formed increases with the resemblance of the solvent to the dissolved substance; hence most closely related liquids mix with one another in all proportions. Chemically unlike substances, such as water and silver nitrate or water and sodium chloride, also form solutions over a wide range of compositions; yet silver chloride dissolves in water scarcely at all. Carbon bisulfide is soluble in all proportions in alcohol, but very slightly soluble in water, though water and alcohol are soluble in one another in all proportions. Hence direct experiment is the only method of determining solubility. The solubility of a substance in a given liquid is a function of the temperature and the pressure, though variations in atmospheric pressure produce only negligible changes in the solubilities of liquids and solids. Large variations in pressure may cause large changes in solubility even in these "condensed" systems, and the solubilities of gases change in direct proportion to the partial pressure at low pressures Most solubilities at constant pressure increase with increasing temperature, some decrease with increasing temperature, and a few do first one and then the other. Plots of solubility against temperature for a single crystalline form of solute are smooth curves. Sudden breaks in a solubility-temperature curve indicate a change in crystalline form or crystalline composition; for example, $Na_2SO_4.10H_2O$ changes to rhombic Na_2SO_4 without water of crystallization at 32.38°, and at this temperature there is an abrupt change in the curve showing the solubility of "sodium sulfate" as a function of temperature.

Concentration in Solutions.—The composition of a solution may be expressed in a great many ways, such as the number of moles or equivalents of dissolved substance (called the *solute*) per liter or per 1000 grams of dissolving liquid (called the *solvent*) or per liter or 1000 grams of solution. Unfortunately for clearness, each of these quantities is sometimes called a concentration; and since each such "concentration" is a convenient quantity in some kinds of work, no one of them has a greater claim to the term than any other. For our purposes two of these "concentrations" will fill almost every need. The *molality* of a solution is defined as the moles of solute per 1000 grams of solvent, and it will be better to form the habit of calling it the molality rather than the molal concentration. The *volume concentration* is defined as the moles of solute per liter of solution. Of course, the equivalent concentration is defined as the number of equivalents per liter of solution, as is customary in analytical chemistry and as will be requisite in considering some of the electrical properties of solutions. The molality of a solution has the advantage that it does not change with the temperature, whereas volume concentrations change with temperature owing to thermal expansion.

For many purposes the *mole fraction* of solvent or solute in a solution is a convenient method of expressing composition. This quantity is defined for any component as was the mole fraction in a gaseous mixture, namely, as the number of moles of it in a mixture, divided by the sum of the moles of all substances present.

An example will make these definitions clearer. A solution containing 10 per cent by weight of ethanol ($C_2H_5OH = 46.0$) has a density of 0.9839 grams per milliliter at 15.5°. A liter of this solution contains 98.39 grams, or $98.39/46.0 = 2.14$ moles of ethanol; and it contains 885.5 grams, or 49.4 moles of water. In this solution the *volume concentration* of ethanol is 2.14; its *molality* is $2.14/0.8855 = 2.42$; its *mole fraction* is $2.14/(2.14 + 49.4) = 0.0416$. Our standard notation for these quantities is $C = 2.14$, $m = 2.42$, and $x = 0.0416$.

Ideal Solutions.—The ideal solution, like the ideal gas, is a convenient fiction that is closely approached by some actual solutions at moderate or high concentrations and by most solutions at low concentrations of solute. There is no solution that conforms strictly to the laws of ideal solutions, just as there is no gas that conforms strictly to the equation $pv = nRT$. Yet each serves the same useful purpose; namely, it provides an ideal that is approached by actual system at low concentrations and a means of obtaining approximations when data are lacking. There are many solutions of which the actual properties are within 1 or 2 per cent of those calculated for an ideal solution and many circumstances in which a knowledge of the properties of the solution within this accuracy is desirable. There are also many solutions for which this is not true, and of which the properties must be determined by experiment. We shall consider both types in this chapter.

In an ideal solution of two liquids, the components dissolve in one another in all proportions, without the evolution or absorption of heat, to form a mixture the volume of which is the sum of the volumes of the components. In ideal solutions there is no distinction necessary between solvent and solute, but in actual solution it will be necessary to distinguish carefully between the "solvent," which is the component present in excess, and the "solute," which is the component present in small quantity. In mixtures such that "excess" and "small quantity" do not apply, it is usually necessary to determine the properties experimentally. The properties of ideal solutions may be calculated from those of the components through simple laws called the laws of ideal solutions. But the properties of many solutions of gaseous or solid solutes in liquid solvents at moderate concentrations may also be calculated from these simple laws, within the limitations of a few per cent. At low concentrations, or in "dilute" solutions, the agreement between calculation and experiment is even better. These laws are thus "limiting" laws from which we may calculate the properties of very dilute solutions but from which the deviations are important in some concentrated solutions and small in other concentrated solutions. The experimental data in the sections that follow will be chosen so as to represent both classes of solutions. As the laws are stated, their limitations will also be stated. Failure to appreciate the fact that many solutions do not conform to these ideal laws may lead to serious errors. Thus, the measured vapor pressures of solutions of CCl_4 in $SiCl_4$ agree with the calculated pressures within less than 5 per cent; but the measured vapor pressure of a solution of a mole of alcohol in a mole of water at 80° is 30 per cent greater than the one calculated for an ideal solution.

Vapor Pressure of the Solvent from Solutions. Raoult's Law. The partial pressure of *solvent vapor* at equilibrium with a solution at a fixed temperature is proportional to the mole fraction of the solvent in the solution. Stated in other words, the partial pressure of the solvent vapor decreases as the mole fraction of the solute increases, and the *fractional decrease* in solvent vapor pressure at a fixed temperature is equal to the *solute* mole fraction. If p_0 denotes the vapor pressure of the pure solvent and p the equilibrium pressure of solvent vapor above the solution, these statements of Raoult's law may be written as equations

$$p = p_0 x_{\text{solvent}} \qquad (t \text{ const.}) \qquad (1)$$

and

$$\frac{p_0 - p}{p_0} = x_{\text{solute}} \qquad (t \text{ const.}) \qquad (2)$$

These equations are only different algebraic forms of the same law, as may be seen by substituting $(1 - x_{\text{solvent}})$ for x_{solute} in (2) and solving for p, whereupon equation (1) will result.

It should be clearly understood that, in these equations for Raoult's law, p is the partial pressure of *solvent vapor*, and this will not be the total pressure of vapor in equilibrium with the solution if the dissolved substance is volatile. The partial pressure of solute vapor as described by Henry's law is given in the next section, and the total vapor pressure of a solution is the sum of the partial pressures of solvent plus solute. But the solvent vapor pressure at a fixed temperature is decreased by the addition of a solute whether or not the solute has an appreciable pressure.

It may be seen from Table 27 that Raoult's law gives correctly the lowering of vapor pressure of the solvent for *solvent* mole fractions from 1.00 to 0.983, which is to say for *solute* mole fractions from zero to 0.0176 or solute molalities up to unity. Some other aqueous solutions of nonionized solutes in water over this range show similar conformity within the experimental error. The largest deviation shown in Table 27 is 0.002 mm., which probably exceeds the experimental error of these measurements; but vapor pressures are difficult to determine experimentally and are only rarely accurate to this extent.

Table 27.—Aqueous Solutions of Mannitol at 20°[1]

Molality	Vapor-pressure lowering, mm.		Per cent deviation
	$p_0 - p$ observed	Calculated from $p_0m/(m + 55.54)$	
0.0984	0.0307	0.0310	+1.0
0.1977	0.0614	0.0622	+1.3
0.2962	0.0922	0.0930	+0.9
0.3945	0.1227	0.1236	+0.7
0.4938	0.1536	0.1545	+0.6
0.5944	0.1860	0.1857	−0.2
0.6934	0.2162	0.2162	0.0
0.7927	0.2478	0.2467	−0.4
0.8922	0.2792	0.2772	−0.7
0.9908	0.3096	0.3073	−0.7

The vapor pressures of aqueous solutions of sucrose calculated from Raoult's law are not in close agreement with experiment, as may be seen in Table 28. These experiments are probably as reliable as those quoted in Table 27, so that the differences are real deviations of Raoult's law. But Table 27 is more nearly typical of dilute aqueous solutions in general, and such vapor pressures as have been determined at molalities below unity usually agree with Raoult's law within the experimental error.

In nonaqueous solutions of nonvolatile solutes, Raoult's law

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[1] Frazer, Lovelace, and Rogers, *J. Am. Chem. Soc.*, **42**, 1793 (1920).

is usually reliable for solute mole fractions below 0.05, and occasionally over wider ranges. The following vapor pressures for benzene solutions of biphenyl ($C_{12}H_{10}$) at 70° are probably accurate to 1 per cent and so the data show conformity to Raoult's law within this range[1]

Mole fraction C_6H_6	1.000	0.930	0.890	0.848	0.786	0.699
$p(C_6H_6)$, mm	550	511	492	472	435	386
p_0x_{solvent}		511	490	466	432	385
Per cent deviation	.	.0	−0.2	−1.3	−0.7	−0.3

TABLE 28.—VAPOR PRESSURES OF AQUEOUS SOLUTIONS OF SUCROSE AT 30°[2]

Molality	Vapor pressure, mm	Mole fraction of solute	$\frac{p_0 - p}{p_0}$	Per cent deviation
0.993	31.22	0.0175	0.0194	10
1.65	30.76	0.0288	0.0338	13
2.38	30.21	0.0410	0.0520	21
3.27	29.43	0.0555	0.0746	25
4.12	28.72	0.0690	0.0980	29
5.35	27.55	0.0877	0.1326	33
6.36	26.70	0.1025	0.1612	37

Raoult's law may be written in terms of the weights of solvent and solute in a solution,

$$\frac{p_0 - p}{p_0} = x = \frac{m/M}{m/M + m_0/M_0} \qquad (t \text{ const.}) \qquad (3)$$

in which m_0 denotes the grams of solvent, M_0 its molecular weight, m the grams of solute, and M its molecular weight in the solution. This relation allows one to calculate molecular weights from vapor-pressure data; but since vapor pressures are more difficult to measure experimentally than are other properties related to them (boiling points and freezing points), vapor pressures are not ordinarily available for such calculations. The vapor pressure of benzene is 639.8 mm. at 75°, and the equilibrium pressure above a solution of 8.84 grams of naphthalene ($C_{10}H_8 = 128$) in 100 grams of benzene ($C_6H_6 = 78$) at 75° is 607.4 mm., whence $M = 129$ from equation (3). This calculation indicates that solutions of naphthalene in benzene

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[1] GILMAN and GROSS, *ibid.*, **60,** 1525 (1938).

[2] BERKLEY and HARTLEY, *Trans. Roy. Soc.* (*London*), (*A*) **218,** 295 (1919)

are nearly ideal, and other data[1] upon this system support this conclusion.

It should not be assumed that all solutions of nonvolatile organic solutes in benzene at low molalities will be ideal, for this is not true. The tendency of hydroxylated compounds to form double molecules (dimers) or higher complexes (polymers) in benzene has long been known, and is a reasonable explanation of vapor pressures higher than would be calculated from Raoult's law. If the molalities of phenol (C_6H_5OH) solutions in benzene are computed upon the assumption that the molecular weight of the solute is 94 and the molalities of solutions of naphthalene ($C_{10}H_8$) in benzene are computed upon the assumption that the molecular weight of the solute is 128, the molalities for solutions of equal vapor pressure will not be equal. Some of these "molalities" for equal vapor pressures at 25° are[2]

m (phenol)	0.2221	0.4014	0.6634	0.7369	1.036	1.368
m (naphthalene)	0.1989	0.3344	0.5070	0.5608	0.7314	0.9061
Ratio	1.117	1.199	1.307	1.313	1.416	1.509

Since these ratios are not whole numbers and since they increase with increasing molality, a reasonable interpretation is partial association of phenol into dimers to an extent that increases with the molality.

Vapor Pressure of the Solute. Henry's Law.—This law states that the solubility of a gas at a given temperature is proportional to the equilibrium pressure of the gas above the solution Expressed as a vapor-pressure law, it states that the partial pressure of a volatile solute in equilibrium with a dilute solution is proportional to its mole fraction in the solution. In the form of an equation Henry's law is

$$p_{\text{solute}} = kx_{\text{solute}} \qquad (t \text{ const.}) \qquad (4)$$

where p is the partial pressure of the solute vapor in equilibrium with a solution in which x is the mole fraction. It will be seen that this law resembles Raoult's law for the vapor pressure of solvent from a solution, the important difference being that the proportionality constant k is not the vapor pressure of the pure

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[1] WASHBURN, *Proc. Nat. Acad. Sci.*, **1,** 191 (1915); ROSANOFF and DUNPHY, *J. Am. Chem Soc*, **36,** 1416 (1914).

[2] LASSETTRE and DICKINSON, *ibid.*, **61,** 54 (1939).

solute. The value of k is a joint property of the solvent and solute; it must be determined by experiment for each solute in a chosen solvent at each temperature. Henry's law affords only a means of calculating a solubility at some new pressure or a solute pressure at a new mole fraction, when k is known for the system involved at the required temperature. The total vapor pressure above a solution will be the sum of the partial pressures of solvent vapor and solute vapor, and Henry's law applies only to the solute, as Raoult's law applies only to the solvent.

In dilute solutions the mole fraction of solute will be nearly proportional to its molality or its concentration, since $n_1/(n_1 + n_2)$ is nearly equal to n_1/n_2 when n_1 is small. For dilute solutions the pressure of solute will be proportional to the molality or the concentration if the solute conforms to Henry's law; this may be stated in equations such as

$$m = k''p \qquad \text{or} \qquad p = k'm \qquad \text{or} \qquad p = k'''C \quad (t \text{ const.}) \qquad (5)$$

but of course none of these constants will be equal to k in equation (4) above. The point is that in a dilute solution the equilibrium pressure of solute (in any units) is proportional to the quantity of solute in the solution (in any units).

This law applies to the distribution of a *single molecular species* between the vapor phase and the solution at moderate pressures and concentrations. It is not valid at high pressures, or for solutions in which the solute forms a compound with the solvent or is polymerized or ionized, without allowance for these effects. Solutions of SO_2 in $GHCl_3$, HCl in C_6H_6, H_2S in water, and CO_2 in water, for example, conform to Henry's law at moderate pressures; but aqueous solutions of HCl and SO_2 do not conform. Any convenient units may be employed to express the solubilities and pressures; but since there is no standard way of reporting such data, it will be necessary in consulting the literature to give careful attention to the units employed. The "Bunsen coefficient" α is the milliliters of gas, reduced to 0° and 1 atm., that dissolve in 1 ml. of solvent when the partial pressure of the solute is 1 atm.; hence, $\alpha p/22.4$ gives *concentrations* of solute in moles per liter of solvent, which will be substantially moles per liter of solution, and *molalities* of solute are given by $\alpha p/22.4d$ if d is the density of the solvent. In some tables of data the *total* *pressure* of solvent plus solute is given, and from these tables concentrations are calculated after subtracting the vapor pressure of the solvent from the total pressure. Such coefficients in terms of total pressure are frequently designated β. Equilibrium pressures may be in atmospheres, millimeters of mercury, or other units; liquid-phase compositions may be given in any one of a dozen ways. Some illustrative data will now be given.

The solubility of CO_2 in water[1] at 50° and at 100° is given in milliliters of gas (reduced to 0° and 1 atm.) per gram of water under the following total pressures:

Total pressure, atm	25	50	75	100
β = solubility at 50°	9.71	17.25	22.53	25.63
β = solubility at 100°	5.37	10.18	14.29	17.67

Upon dividing these solubilities by 22.4, they become molalities, and p_{CO_2} is obtained by subtracting 0.13 atm. from the total pressure at 50° and 1.05 atm.[2] at 100°. Since CO_2 is not an ideal gas at such pressures, it is not to be expected that Henry's law will apply exactly. The ratio of pressure to molality is

p_{CO_2}	25	50	75	100
$k' = p/m$, 50°	57	65	75	87
$k' = p/m$, 100°	104	110	117	127

Aqueous solutions of H_2S in water conform to Henry's law, as shown by the data[3] for 25°:

p, atm	1.00	2.00	3.00
molality	0.102	0.204	0.305
$m/p = k''$	0.102	0.102	0.102

This ratio m/p, which is constant for a given temperature according to Henry's law, changes with changing temperature, as is true of almost every equilibrium ratio. In this system the ratio m/p changes with the temperature as follows:

t	10°	20°	30°	40°	50°
$k'' = m/p$	0.153	0.116	0.092	0.075	0.064

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[1] WEIBE and GADDY, *ibid.*, **61**, 315 (1939).

[2] The vapor pressure increases with the applied total pressure and becomes 1.08 atm. at 100° for a total pressure of 100 atm. We subtract 1.05 as a sufficient correction at all pressures in this table.

[3] WRIGHT and MAASS, *Can. J. Research*, **6**, 94 (1932).

The molality of HCl is proportional to the pressure of HCl above the solution when the solvent is nitrobenzene, $CHCl_3$, CCl_4, chlorobenzene, benzene, or toluene. We quote the data for HCl in toluene[1] at 25°:

p, atm	0 282	0 250	0 158	0 0960	0 0338	
m	0 137	0 119	0 0762	0 0468	0 0167	
$p/m = k'$	2 05	2 11	2 07	2 06	2 16	av 2 09

It should be understood that this ratio is for a given solute and a given solvent, a joint property of both, for a single temperature. For example, the ratio p/m in the same units at the same temperature is 6.4 for HCl in carbon tetrachloride[2] and 1.02 for HBr in toluene.

Hydrogen chloride is largely ionized in aqueous solution, and there is no reason to expect proportionality between the partial pressure of HCl molecules and a molality of ions in a solution. Since there is no reliable way of measuring what fraction of the total dissolved hydrogen chloride is in the form of un-ionized molecules, it is impossible to say whether Henry's law applies to the HCl molecules or not. The data for 25° are as follows:[3]

Molality HCl	4	5	6	7	8	10
$10^4 p$, atm.	0 24	0 70	1 84	4 58	11 1	55 2
Ratio	16 7	7 1	3 3	1 5	0 72	0 18

When sulfur dioxide dissolves in water, both ionization and hydration occur, so that one would not expect the ratio m/p to be constant. If a fixed fraction of nonionized solute is hydrated, which is a reasonable expectation from the laws of chemical equilibrium, the ratio of $p(SO_2)$ to the molality of $(H_2SO_3 + SO_2)$ should be constant. The following table[4] gives for 25° total SO_2 in all forms as the molality, p the pressure of SO_2 in atmospheres above the solution, α the fraction of the solute which is ionized, so that $m(1 - \alpha)$ is the molality of un-ionized solute, and $K = m(1 - \alpha)/p$. It will be seen that this ratio is substantially constant, but that m/p is not constant.

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[1] O'Brien and Bobalek, *J. Am. Chem. Soc.*, **62**, 3227 (1940).

[2] Howland, Miller, and Willard, *ibid.*, **63**, 2807 (1941).

[3] Bates and Kirschman, *ibid.*, **41**, 1991 (1919).

[4] Johnstone and Leppla, *ibid.*, **56**, 2233 (1934).

Molality	0.0271	0.0854	0.166	0.287	0.501	0.764	1.027
$p(SO_2)$	0.0104	0.0450	0.097	0.179	0.333	0.526	0.723
α	0.524	0.363	0.285	0.230	0.184	0.153	0.134
$m(1 - \alpha)$	0.0129	0.0544	0.119	0.221	0.409	0.647	0.890
m/p	2.61	1.90	1.71	1.61	1.50	1.45	1.42
$K = m(1 - \alpha)/p$	1.24	1.21	1.22	1.23	1.23	1.23	1.23

It should be understood that this constant K is for a single temperature; the ratio of $m(1 - \alpha)$ to p changes with changing temperature as follows:

t	0°	10°	18°	25°	35°	50°
$K = m(1 - \alpha)/p$	3.28	2.20	1.55	1.23	0.89	0.56

The pressure of chlorine above an aqueous solution would be proportional to the molality of dissolved chlorine as such, but not proportional to the total chlorine that dissolves, since a considerable proportion of it reacts with water to form hypochlorous acid and hydrochloric acid. No corrections were required on page 187 for the *very small* fraction of carbonic acid or of H_2S ionized, and therefore Henry's law applies directly to these solubilities.

Distribution of a Solute between Liquid Phases.—Consider two mutually insoluble liquids in each of which a third substance is soluble, the molecular condition of the solute being the same in both solvents. The distribution law states that at equilibrium the ratio C_1/C_2 of the concentrations in the two solvents is a constant for a given temperature, whatever (small) quantity of solute is used. Like Raoult's law and Henry's law, the distribution law applies only to a single molecular species. The ratio C_1/C_2 will not be constant when the solute is ionized or polymerized or solvated in one solvent and not in the other, without allowance for these effects. Even when these effects are not known to be responsible, variations in the ratio C_1/C_2 are often found at high concentrations, so that the law is strictly applicable only in dilute solutions. When the distribution ratio varies with the concentration, a plot of C_1/C_2 against C_1 is a useful device for determining C_2.

In dilute solutions the distribution ratio at constant temperature may be expressed in several ways, such as molalities, mole fractions, or volume concentrations:

$$\frac{x_1}{x_2} = \text{const.} \qquad \frac{C_1}{C_2} = \text{const.} \qquad \text{or} \qquad \frac{m_1}{m_2} = \text{const.} \tag{6}$$

The numerical values of m_1/m_2 and C_1/C_2 will not be the same, of course, and it is important to know in what units a distribution ratio has been stated when it is used in calculations. There is no standard form for recording these ratios.[1]

Some illustrations are quoted in Tables 29 and 30, from which it will be seen that the ratios are substantially constant at low concentrations. Table 29 shows that the equilibrium ratio is a function of the temperature, as is true of all equilibrium ratios that are constant for constant temperatures.

If a gaseous solute at some fixed pressure is in equilibrium with two mutually insoluble solvents, the concentrations in each will be determined by the constant of Henry's law for each solvent. The distribution ratio is then the ratio of these constants, for the two liquid phases are in equilibrium with the same gas phase and so must be in equilibrium with each other. When two phases are in equilibrium with one another as regards some particular component and one of these is in equilibrium with a third phase, the other is also in equilibrium with this third phase. If the third phase is the solid solute itself, then when one liquid is saturated with the solid and in equilibrium with another liquid this second liquid must also be a saturated solution of the solute. Thus the distribution constant for a given substance between two solvents is the ratio of the solubilities of that sub-

TABLE 29.—DISTRIBUTION OF SUCCINIC ACID BETWEEN WATER AND ETHER[2]
(Concentrations are in moles of acid per 100 moles of solution)

15°			20°			25°		
Water layer	Ether layer	k	Water layer	Ether layer	k	Water layer	Ether layer	k
0.372	0.305	1.223	0.2025	0.1535	1.322	0.364	0.248	1.471
0.440	0.358	1.229	0.431	0.319	1.351	0.720	0.485	1.485
0.575	0.468	1.228	0.495	0.366	1.353	1.088	0.727	1.493
0.880	0.714	1.233	0.629	0.465	1.355	1.513	1.014	1.489
0.963	0.778	1.237	0.936	0.686	1.364			
.....	.....	.....	1.211	0.889	1.363			

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[1] Distribution ratios of many systems for volume concentrations are given in "International Critical Tables," Vol. IV, pp. 418*ff*.

[2] FORBES and COOLIDGE, *J. Am. Chem. Soc.*, **41**, 140 (1919).

TABLE 30.—DISTRIBUTION OF AMMONIA BETWEEN WATER AND CHLOROFORM[1]

At low concentration			At high concentration		
Concentration in water	Concentration in chloroform	C_w/C_c	Concentration in water	Concentration in chloroform	C_w/C_c
0.0443	0.00165	26.2	1.02	0.045	22.7
0 0220	0 00091	24.1	3.13	0.146	21.4
0 0110	0 00044	24.7	5.24	0.283	18.5
0.00572	0.00021	25.7	7.29	0.457	15.9
0.00275	0.00011	24.6	9.35	0.710	13.2
			12.25	1.227	10.0

stance in the two phases, provided that the distribution law holds for such concentrated solutions.

In order to emphasize the fact that distribution ratios are not constant when the solute is in a different molecular condition in the two solvents, we quote the data for acetic acid distributed between water and benzene at 25°. The acid is largely in the form $(CH_3COOH)_2$ in benzene and largely in the form CH_3COOH in water, and thus the distribution ratio in terms of total concentrations is not constant.

C_B	0.0159	0 0554	0 2250	0 9053
C_W	0 579	1 382	3 299	6 997
C_B/C_W	0 0274	0.0401	0 0776	0.1290

As has been said before, the distribution law applies strictly in dilute solutions only. The addition of large quantities of the distributed substance usually increases the mutual solubilities of the "insoluble" solvents and may so increase them as to form a single three-component liquid. For example, the distribution ratio of acetone between chloroform and water, which are substantially insoluble in one another, is 2.25 at 0°C., but the addition of 62 grams of acetone to 18 grams of chloroform and 20 grams of water forms a single liquid. Similar behavior is observed in the addition of pyridine to water and benzene and in the addition of alcohols to water and ethers.

Summary of Three Distribution Laws.—Raoult's law, Henry's law, and the "distribution law" are all distribution laws, each for a single species of molecule between two phases at the same

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[1] *Z. physik. Chem.*, **30**, 258 (1899). *J. Am. Chem. Soc.*, **33**, 940 (1911).

temperature. In a vapor the concentration in moles per liter is $C = n/v = p/RT$; and, by combining RT with the constant, Raoult's law becomes

$$\frac{C \text{ (solvent in vapor)}}{C \text{ (solvent in solution)}} = \text{const.}$$

Henry's law as stated in equation (5) may be put into the same form by the same device, namely,

$$\frac{C \text{ (solute in vapor)}}{C \text{ (solute in solution)}} = \text{const.}$$

and equation (6) is already in the form

$$\frac{C \text{ (solute in } L_1)}{C \text{ (solute in } L_2)} = \text{const.}$$

Vapor Pressures of Binary Liquid Mixtures at Constant Temperature.—When two liquids A and B form an ideal solution, the partial pressure of each component in the vapor in equilibrium with the solution at constant temperature is proportional to its mole fraction in the solution,

$$p_A = p_{0_A}x_A \qquad \text{and} \qquad p_B = p_{0_B}x_B \qquad (t \text{ const.})$$

where p_{0_A} and p_{0_B} are the vapor pressures of the pure components and x_A and x_B are their mole fractions in the solution. These partial pressures and the total vapor pressure, which is their sum, are shown in Fig. 26 for an ideal system.

When the components are present in the liquid phase mole for mole, the partial pressures in the equilibrium vapor will be $\frac{1}{2}p_{0_A}$ and $\frac{1}{2}p_{0_B}$, or cd and ce in Fig. 26. The total pressure is the sum of these partial pressures, or cf, and the equilibrium mole fractions in the vapor (which are denoted by y) are $y_A = cd/cf$ and $y_B = ce/cf$. As cd and ce are not equal, it will be evident that the vapor in equilibrium with an ideal solution at a given temperature does not have the same composition as the liquid. In general, the greater the difference between the vapor pressures of the two components, the greater the difference in composition between a liquid and a vapor in equilibrium with it.

Ideal solutions of this kind are formed only when the two components are chemically similar. For most pairs of liquids that mix in all proportions the deviations from ideal solutions are considerable when both constituents are present in large proportion, for example, when the mole fractions are between 0.1 and 0.9 for both. This may be due to the formation of complexes between solvent and dissolved substances, or to the dissociation of double molecules of solvent, either of which would render the mole fractions calculated from the composition by weight in error, or to other factors.

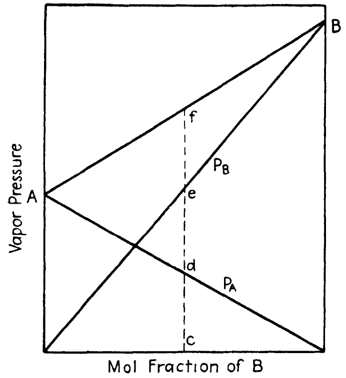

Fig. 26.—Vapor pressures in an ideal solution.

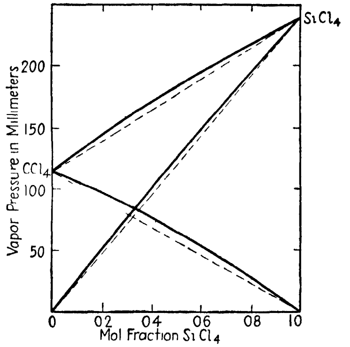

Fig. 27.—Vapor pressures of CCl_4 and $SiCl_4$ solutions at 25°.

The experimental procedure by which solutions and their vapors are studied consists in establishing equilibrium between the liquid and vapor phases at a fixed temperature, measuring the total vapor pressure, and analyzing the vapor. Although we cannot measure directly a partial pressure, the product of total pressure and mole fraction in the vapor is usually a sufficient measure of the partial pressure. We designate the mole fraction of a component in a liquid by x and the mole fraction of it in the

Table 31.—Vapor Pressures of Mixtures of $SiCl_4$ and CCl_4 at 25°

Total vapor pressure, mm	Mole fraction $SiCl_4$ in		$p_0x(SiCl_4)$	$py(SiCl_4)$	Per cent deviation
	Liquid	Vapor			
114.9	0	0			
153.0	0.266	0.436	63.4	66.7	5.0
179.1	0.472	0.648	112.4	116.1	3.3
198.5	0.632	0.773	150.5	153.4	1.9
238.3	1.00	1.00			

vapor by y. If the solution is ideal, the partial pressure of the A component is p_0x_A, and this is equal to py_A when the total vapor pressure is p and the mole fraction of A in the vapor is y_A. When the solution deviates from ideal behavior, we shall take $p_A = py_A$ as a measure of the partial pressure of A and call the difference between this quantity and p_0x_A the deviation of p_A from that for an ideal solution.

Mixtures of CCl_4 and $SiCl_4$ conform to the simple laws of ideal solutions quite closely, as may be seen from the data[1] in Table 31. These data are plotted in Fig 27, in which the solid lines show measured total pressures, and the products of these pressures and the mole fractions of $SiCl_4$ in the equilibrium vapors. The dotted lines show calculated total pressures and calculated partial pressures from Raoult's law for an ideal solution.

Mixtures of benzene and toluene[2] have vapor pressures from which the calculated ones deviate 6 per cent or less. Mixtures of benzene and cyclohexane[3] show closer conformity to the ideal laws. In all these systems the deviations are real ones, far outside of the experimental error; in all these mixtures the components are chemically similar, which is the favorable condition for ideal conformity.

We turn now to some systems which are more typical of solutions in general and in which large deviations are found at high mole fractions. Even in these systems we shall frequently find close conformity to Raoult's law when the mole fractions of solute are below 0.05, considering first one component and then the other as solvent according as it is present in a large mole fraction.

Mixtures of chloroform ($CHCl_3$) and ethanol (C_2H_2OH) are more nearly typical of solutions in general. Raoult's law yields nearly correct vapor pressures of ethanol when its mole fraction is between 0.8 and 1.0, but the pressures of chloroform from these mixtures deviate largely from the ideal. In such mixtures the chloroform pressures are nearly *proportional* to the mole fractions of chloroform, so that Henry's law applies, but the proportionality constant is not the vapor pressure of pure chloroform. Let

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[1] Wood, *ibid.*, **59**, 1510 (1937).

[2] Schulze, *Ann. Physik*, **59**, 82 (1919).

[3] Scatchard, Wood, and Mochel, *J. Phys. Chem.*, **43**, 119 (1939).

x_e denote the mole fraction of ethanol in the liquid phase, y_e the mole fraction in the equilibrium vapor, and p the measured total pressure. Then $p_{0e}x_e$ should be equal to py_e if Raoult's law applies and if the vapor is an ideal gas. The data[1] for that part of the system rich in ethanol are as follows for 45°, with pressures in millimeters:

x_e	1 000	0 9900	0 9800	0 9500	0.9000	0 8000
y_e	1 000	0 9610	0.9242	0 8202	0 6688	0 4640
p.	172 76	177 95	183 38	200 81	232 58	298 18
p_0x_e		171 03	169 30	164 12	155 48	138 20
py_e		171 01	169 57	164 70	155.54	137.90

Considering only this part of the data, one might conclude that since Raoult's law applies over a wide range the solution was ideal. But the partial pressure of chloroform in equilibrium with the solution in which x_e is 0.8 is $298.18 - py_e$, or 160.3 mm., and $p_{0c}x_c$ is 86.7 mm.

Turning now to mixtures rich in chloroform, we find that in the corresponding range of composition $p_{0c}x_c$ deviates somewhat more from py_c, as these figures for 45° show:

x_c.	1 000	0 990	0 980	0.950	0.900	0.800
y_c	1 000	0 9793	0.9626	0.9254	0 8868	0.8448
p, mm	433 54	438 59	442 16	449 38	455 06	454.53
p_0x_c		429 18	424 87	411 86	390 19	346.83
py_c		429.52	425 63	415 87	394.46	383.98

The difference between $p_{0c}x_c$ and py_c exceeds 1 per cent when x_c is 0.95; the corresponding difference between $p_{0e}x_e$ and py_e is below 0.4 per cent when x_e is 0.95. In the solution in which x_c is 0.8, $p_{0c}x_c$ deviates from py_c by about 10 per cent, but $p_{0e}x_e$ and py_e still agree within 0.4 per cent when x_e is 0.8.

Similar behavior is shown by many mixtures, with smaller[2] or even larger[3] deviations from the ideal. Without experimenting upon the mixture there is no way to decide whether or not a given mixture will form an ideal solution over a wide range of composition. There are only the general rules (1) that chemically similar components usually yield solutions that are approxi-

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[1] Scatchard and Raymond, *J. Am. Chem. Soc.*, **60,** 1278 (1938).

[2] Benzene and acetic acid, Hovorka and Driesbach, *ibid.*, **56,** 1664 (1934); benzene and CS_2, Sameshima, *ibid.*, **40,** 1503 (1918); CCl_4 and C_6H_6, Scatchard, Wood, and Mochel, *ibid.*, **62,** 712 (1940).

[3] Acetone and CS_2, Zawidski, *Z. physik. Chem.*, **35,** 172 (1900).

mately ideal and (2) that "dilute" solutions have vapor pressures which conform to Raoult's law and Henry's law.

Constant-temperature Distillation.—We have already quoted the equilibrium mole fractions of liquid and vapor for mixtures of ethanol and chloroform at 45° for "dilute" solutions. For the purposes of this section we quote the remaining data applying at 45° for mole fractions of ethanol between 0.2 and 0.8:

x_e	0.300	0.400	0.500	0.600	0.700
y_e	0.1850	0.2126	0.2440	0.2862	0.3530
p, mm	446.74	435.19	417.71	391.04	353.18

These data, together with the other equilibrium mole fractions already quoted, are plotted in Fig. 28 in which the total vapor pressure is plotted against the mole fraction of ethanol in the liquid phase as a solid line and the dotted line shows the equilibrium mole fraction of ethanol in the vapor for each total pressure at 45° on the same composition scale. For example, at 45° and 380 mm. total pressure, liquid of composition x_1 is in equilibrium with vapor of composition y_1; liquid of composition x_2 is in equilibrium with vapor of composition y_2 at 325 mm. and 45°. Such lines as x_1y_1 and x_2y_2 are called "equilibrium tie lines" or, more briefly, "tie lines," since they tie together the compositions of two phases at equilibrium. These lines apply to constant-temperature diagrams, each for a given pressure; but in a later section we shall also use tie lines on constant-pressure diagrams, each applying to a single temperature.

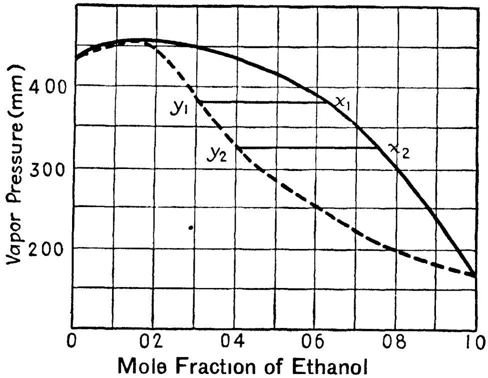

FIG. 28.—Constant-temperature distillation of mixtures of chloroform and ethanol at 45°

Diagrams such as Fig. 28 may be used to show approximately the composition of each phase when a moderate fraction of the total liquid is distilled at constant temperature. Starting with a liquid of composition x_1, which would yield a *first* vapor of composition y_1, suppose the distillation is continued at constant temperature and decreasing pressure until the liquid composition becomes x_2. The *last* portion of vapor leaving the liquid would have the composition y_2, and when the distillation range is not too great, $\frac{1}{2}(y_1 + y_2)$ will nearly represent the composition of the whole distillate It should be noted that the composition of the liquid residue is x_2 and not $\frac{1}{2}(x_1 + x_2)$ and that a line joining the compositions x_2 and $\frac{1}{2}(y_1 + y_2)$ is not an equilibrium tie line Fractional distillation for the purpose of separating a mixture into portions of different composition is more commonly carried out at atmospheric pressure and changing temperature, rather than at constant temperature, as we have done here, since the former procedure is more convenient and the latter is experimentally difficult. We shall consider this process in a later section, after discussing boiling solutions in which only the solvent is volatile from the solution.

Boiling Points of Solutions of Nonvolatile Solutes.—The boiling point of a solution is the temperature at which its total vapor pressure is 1 atm. Solutions from which both solute and solvent are volatile are discussed in the next section; and solutions from which only the solvent has an appreciable vapor pressure are discussed in this section. At any given temperature, such as the boiling point of the pure solvent, the vapor pressure of solvent from a solution will be less than p_0 for this temperature. It is thus necessary to heat a solution containing a nonvolatile solute to a temperature above the boiling point of the pure solvent before the solution will boil.

We have seen in previous sections that the vapor pressure is not a linear function of the temperature and that for ideal solutions the fractional decrease in solvent vapor pressure produced by a fixed mole fraction of solute is the same at all temperatures. Hence, plots of vapor pressures against a considerable range of temperature for a pure solvent and for a solution of a nonvolatile solute will yield lines that are neither straight nor parallel. Yet when such a plot is made over a range of 2° or so near the boiling point for the pure solvent and a solution in which the mole fraction of solute is 0.02, the lines are so nearly straight and parallel that a diagram similar to Fig. 29 results.

We shall use this diagram to determine the relation between $T - T_0$, the boiling-point elevation caused by the addition of a nonvolatile solute to a solvent of which the boiling point is T_0, and x, the mole fraction of solute. At T_0 the vapor pressure of the solution is less than 1 atm. by the distance *ab*. In order to bring the solution to its boiling point, it must be heated while the vapor pressure increases along the line *bc* until the point *c* is reached at the temperature T. The relation between the lowering of the vapor pressure and the boiling-point raising is $ab/ac = (p_0 - p)/(T - T_0)$. But for small temperature changes, ab/ac is the slope of the dotted line, *i.e.*, it is the rate of change of the vapor pressure of the solution with the temperature. The dotted and solid lines are nearly parallel for the short distances involved in a small change of boiling point, and hence we may write dp_0/dT for ab/ac, in place of dp/dT, employing the change of vapor pressure of the pure solvent with the temperature in place of the change in vapor pressure of the solution with the temperature. Then we may write

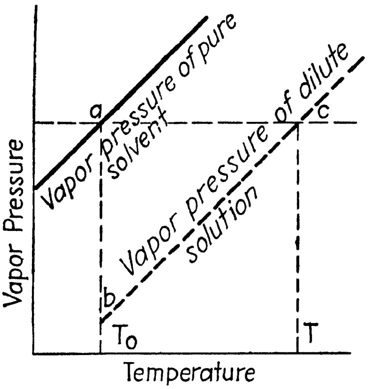

FIG 29 —Vapor-pressure relations near the boiling point.

$$\frac{p_0 - p}{T - T_0} = \frac{dp_0}{dT} = \frac{p_0 x}{T - T_0} \tag{7}$$

since $p_0 - p$ is equal to $p_0 x$ from Raoult's law. On solving the equation for the elevation of the boiling point, which is ΔT_b, we have

$$T - T_0 = \frac{p_0 x}{dp_0/dT}$$

or

$$\Delta T_b = kx \qquad (p \text{ const.}) \tag{8}$$

Since p_0 and dp_0/dT are characteristics of the solvent, the change in boiling point depends upon the mole fraction of solute but not upon its nature, provided that its vapor pressure from the solution is negligible. The relation provides a means of determining molecular weights of solutes in solvents for which k is known. The value of k will not be the same for all solvents but must be determined in one of the ways explained below. The validity of this equation is illustrated by the data of Table 32 for solutions of biphenyl in benzene.

Table 32 shows better than average conformity of a system to the ideal equation, though it is not unique. A more typical set of data, so far as usual deviations are concerned, is the following for salicylic acid in ethanol:

Molality	0.3	0.5	0.7	1.0	1.5
$\Delta T_b/x$	25.5	26.3	26.9	26.9	28.0

Wide deviations may be found when association, dissociation, solvation, or reaction of solute with solvent occurs, but these are misapplications of the equation rather than deviations. Yet variations in $\Delta T/x$ with increasing x are sometimes found when none of these factors is known to be responsible, and no explanations have yet been found

TABLE 32—BOILING POINTS OF SOLUTIONS OF BIPHENYL IN BENZENE[1]

Mole fraction solute	ΔT_b	$\frac{\Delta T_b}{x} = k$
0.0380	1.333	35.7
0.0490	1.709	35.0
0.0613	2.152	35.1
0.0718	2.521	35.0
0.0890	3.142	35.3

In laboratory practice, the composition of a solution may be expressed in terms of the moles of solute per 1000 grams of solvent, and the elevation of the boiling point produced by a

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[1] WASHBURN and READ, *J. Am. Chem. Soc.*, **41**, 729 (1919). The vapor pressures of benzene solutions of biphenyl are given very closely by Raoult's law, and therefore conformity to equation (8) is to be expected in these solutions. Data for 70° [by Gillman and Gross, *ibid.*, **60**, 1525 (1938)] are given on p. 184. Their data for 50° are

x_B	1.00	0.930	0.890	0.848	0.786
p, mm	270	249	240	228	215
$p_{0B}x_B$,		251	241	229	212

mole of solute in 1000 grams of solvent is called the *molal elevation of the boiling point, B* For example, 1000 grams of water is 1000/18, or 55.5, moles; and when a mole of solute is dissolved in 1000 grams of water its mole fraction is $x = 1/(1 + 55.5) = 0.0177$. The vapor pressure of water at its boiling point changes at the rate of 0.0357 atm per deg , and by substituting these quantities into equation (8) we find

$$\Delta T_b = \frac{0.0177}{0.0357} = 0.50°$$

for a solution of a mole of solute in 1000 grams of water. Then the boiling-point elevation of any dilute aqueous solution of a nonvolatile substance in water is

$$\Delta T_b = 0.50m = Bm \qquad (9)$$

This equation furnishes a convenient means of determining approximate molecular weights of dissolved substances, since the moles per 1000 grams of solvent is given by equation (9) from the boiling-point elevation and the grams of solute per 1000 grams of solvent is known from analysis.

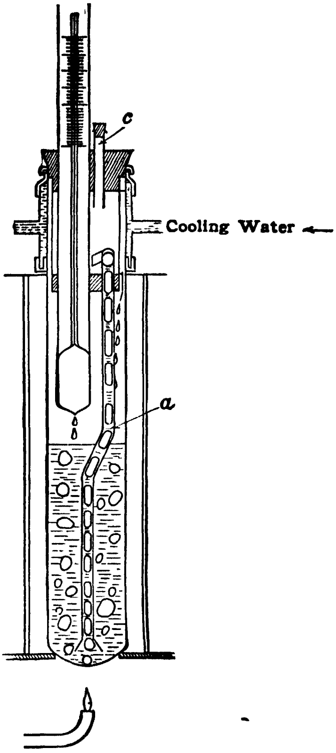

FIG. 30 —Boiling-point apparatus

The narrow tube *a* serves to pump an intimate mixture of solution and vapor over the thermometer Weighed pellets of solute are introduced through *c*, or the solution may be analyzed after a determination The condenser is so arranged that cold solvent returning to the solution from it does not touch the thermometer, but runs down the pump tube. [*Cottrell, J. Am. Chem. Soc*, **41,** 721 (1919).]

It will be noted that the boiling-point elevation has been expressed in two ways, $\Delta T_b = kx$ and $\Delta T_b = Bm$. Both these equations state the same fact, namely, that the boiling-point elevation for a dilute solution of a nonvolatile solute is proportional to the quantity of solute in a given quantity of solvent. If m is the molality of a solute and M_0 is the molecular weight of the solvent, the mole fraction of solute is

$$x = \frac{m}{m + (1000/M_0)}$$

In a dilute solution m is small compared with $1000/M_0$, and the mole fraction is nearly $m/(1000/M_0)$. Thus the mole fraction and molality are almost proportional to one another; but since $1/[1 + (1000/M_0)]$ is not a unit mole fraction when the molality is unity, it will be evident that the numerical values of k and B are not the same for any solvent or proportional to one another for different solvents. Some values of these constants are given in Table 33.

It will be recalled that the approximate Clapeyron equation expresses the change of vapor pressure in terms of the molal latent heat of evaporation. By substituting

$$\frac{dp_0}{dT} = \frac{p_0 \Delta H_m}{RT_0^2}$$

in equation (7) we have

$$\frac{dp_0}{dT} = \frac{p_0 \Delta H_m}{RT_0^2} = \frac{p_0 x}{T - T_0}$$

and on solving for ΔT_b we have

$$\Delta T_b = \frac{RT_0^2}{\Delta H_m} x = kx \qquad (p \text{ const.}) \tag{10}$$

For comparison we calculate a value of B for water from this equation. The heat of evaporation of water is 9700 cal. per mole, whence for one mole of solute per 1000 grams of water

$$\Delta T_b = \frac{1.99 \times (373)^2}{9700} \times \frac{1}{1 + 55.5} = 0.51°$$

It will be observed that k may be obtained from $RT_0^2/\Delta H_m$ as shown in equation (10), from $p_0/(dp_0/dT)$ as shown in equation (8), or directly from boiling-point measurements as shown in Table 32. Yet when all three of these procedures are used, slightly discordant values of k result, and the disagreement seems to lie outside the probable errors of the experiments even when very dilute solutions are concerned. No definite explanation of the discordance is known.

TABLE 33.—BOILING-POINT CONSTANTS

Solvent	Boiling point	k	B
Benzene	80.09	35	2.6
Carbon bisulfide	46.0	31	2.4
Carbon tetrachloride	76.5	33.4	5.05
Chloroform	61.2	32.0	3.4
Ethyl alcohol	78.26	26	1.24
Ethyl ether	34.5	30.2	2.21
Hexane	68.6	34.1	2.9
n-Octane	125.8	38.9	4.4
Water	100.0	28.9	0.51

Fractional Distillation at Constant Pressure.—Liquid mixtures of two volatile components are in equilibrium with vapors in which the mole fractions usually differ from those in the liquid phase, as we have seen in Fig. 28. In place of considering these quantities for constant temperature, we now consider the equilibrium mole fractions in the two phases at a constant pressure of 1 atm. and bring the mixture to this pressure by adjusting the temperature. When heat is applied to these mixtures, vapor is expelled and may be condensed, as in the familiar process of distillation. The *first portion* of distillate represents the composition of vapor in equilibrium with the liquid from which it was expelled, provided that the quantity of distillate is very small compared with the quantity of liquid remaining. It will be assumed that distillation is conducted so slowly as to maintain equilibrium in the distilling vessel and that condensation of the vapor is complete so that the composition of condensate is the same as that of the equilibrium vapor.

We take up first the temperature-composition diagrams for *equilibrium* between liquid and vapor at 1 atm. total pressure,[1] next the compositions of residue and distillate obtained when a *single portion of distillate* is collected from a fixed quantity of liquid by distillation over a moderate temperature range (in

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[1] These diagrams are usually applicable at any *constant* pressure near 1 atm., without correcting for geographical or climatic variations in atmospheric pressure; but, of course, the experimental data must all be taken for a single pressure. Daily variations of atmospheric pressure in a given locality may produce changes in observed boiling points of as much as 1° above or below the normal, and for precise work these observed temperatures must be corrected to 1 atm.

which the compositions of both phases change continuously as distillation progresses), and finally *complete fractionation* by which through repetition of partial distillation and partial condensation the mixture is separated into its components or into one component and a constant-boiling mixture. This third procedure will yield the pure substances when the boiling points of all mixtures lie between those of the components. If some of the mixtures boil outside of this temperature range, separation by repeated fractionation may be carried only to the formation of a maximum (or minimum) boiling mixture as a final residue (or distillate) and one pure component as a final distillate (or residue). In discussing fractional distillation, it will be important to make clear whether equilibrium compositions, single distillates, or complete fractionation is being discussed.

As is common practice, we shall designate mole fractions in the liquid mixture by x with a suitable subscript and mole fractions in the vapor or distillate by y with a suitable subscript. The partial pressure of any component will be understood to be the product of total pressure and its mole fraction in the vapor, for there is no way of measuring partial pressures directly.

a. Equilibrium Compositions.—Toluene ($C_7H_8 = 92$) and acetone ($C_3H_6O = 58$) mix in all proportions, and the boiling points of all mixtures of them lie between those of the components[1] Table 34 gives the boiling points and equilibrium mole fractions of liquid and vapor for several mixtures. These data are plotted in Fig. 31, in which liquid composition is shown by a solid line and vapor composition by a dotted line. "Tie lines" such as x_1y_1 and x_2y_2 show the equilibrium compositions for selected temperatures.

Consider a vessel closed by a movable piston, in which a mixture of 0.2 mole of acetone and 0.8 mole of toluene is heated while the pressure remains 1 atm., but no vapor escapes from the container. At 84° the solution reaches its boiling point and expels a first vapor of composition y_1. If the heating is continued, say to 87°, the liquid composition changes along the solid line from x_1 to x_2 while the vapor composition changes from y_1 to y_2 along

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[1] Other systems in which this simplicity is observed are ethanol-*n* butanol [for which data are given by Brunjes and Bogart in *Ind. Eng. Chem.*, **35**, 255 (1943)] and CCl_4-C_2Cl_4 [for which data are given by McDonald and McMillan in *Ind. Eng. Chem.*, **36**, 1175 (1944)].

the dotted line. Upon further heating the compositions change, the quantity of vapor increases, the quantity of liquid decreases until evaporation becomes complete at 104°, and in the last drop of liquid to evaporate x_A is about 0.02. This imaginary process has been described to illustrate the meaning of Fig. 31, but it would be inconvenient, since it would require a vessel of some 35 liters capacity to carry it out.

For all ranges of temperature and composition within the field below the solid line in Fig 31, a liquid phase alone results at 1 atm. pressure; for all ranges of temperature and composition above the dotted line only vapor exists at 1 atm. Between these lines a liquid phase of composition x and a vapor phase of composition y are at equilibrium, so that this is a two-phase area. For illustration, a vapor containing 60 mole per cent of acetone begins to condense at about 87° and when cooled to 70° without the escape of condensate consists of a liquid phase in which x_A is 0.48 and a vapor in which $y_A = 0.86$. Partial condensation serves to separate a vapor mixture into two portions of different composition, just as partial evaporation does.

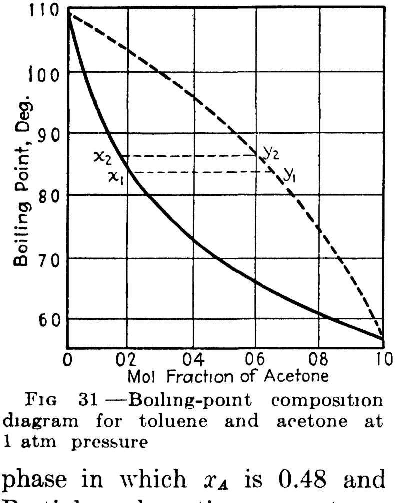

FIG 31 —Boiling-point composition diagram for toluene and acetone at 1 atm pressure

b. Fractional Distillation.—The usual procedure in distillation is to remove the vapor as fast as it forms by passing it into a condenser. If the mixture in which $x_A = 0.20$ were distilled until the boiling point rose from 84 to 87°, the vapor (or distillate) composition would vary from y_1 to y_2 (Fig. 31), say from 0.64 to 0.60, so that in the whole distillate y_A would be 0.62. The composition of the residue in the flask would be x_2, or about 0.16, and not the average of x_1 and x_2. It should be noted that $y = 0.62$ and $x = 0.16$ are not on a horizontal tie line and should not be, since the whole distillate was not in equilibrium with (or expelled from) a liquid of composition $x_A = 0.16$. By a continuation of this process, with fresh receivers under the condenser, the entire mixture could be separated into fractions passing over in 3°

Table 34—Boiling Points and Compositions of Toluene-acetone Mixtures[1]

Boiling point	Mole fraction of acetone in		$p_A = py_A$
	Liquid	Vapor	
109.4	0	0	0
93.5	0.108	0.449	341 mm.
85.0	0.187	0.636	484
72.8	0.383	0.811	616
67.0	0.572	0.883	671
64.0	0.686	0.916	696
61.2	0.790	0.941	715
59.5	0.871	0.964	732
58.0	0.938	0.981	746
56.5	1.00	1.00	760

ranges. Each succeeding distillate would be richer in toluene; the 102 to 105° distillate would have about the composition of the original mixture, for example; and the residue after one more distillation would be almost pure toluene. We shall come in a moment to a method by which the distillates are distilled again and the residues suitably combined for further distillation until substantially complete separation into the pure components is obtained for this type of mixture.

A material balance enables us to compute the weights of distillate and residue obtained in a single fraction. In the illustration given above, a mixture of 0.2 mole of acetone and 0.8 mole of toluene was distilled until a 3° fraction of distillate resulted, y_A being 0.62 in the distillate and x_A being 0.16 in the residue. If d moles of distillate resulted, $0.62d$ mole of acetone were in the distillate and $0.16(1 - d)$ mole of acetone remained in the flask. The total acetone in the original mixture was 0.2 mole, so that $0.62d + 0.16(1 - d) = 0.2$ and $d = 0.087$. The quantity of acetone in the distillate is $0.087y_A$, or 0.054 mole; the quantity of toluene is $0.087(1 - y_A)$, or 0.033 mole. These quantities are, respectively, 3.13 and 3.04 grams, or a total of 6.17 grams of distillate. The original mixture weighed 85.2 grams, this being $0.2 \times 58 + 0.8 \times 92$, and therefore 79.0 grams remained in the flask.

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[1] Rosanoff, Bacon, and White, *J. Am. Chem. Soc.*, **36**, 1803 (1914).

This 6.17 grams of distillate in which x_A is 0.62 would boil at about 66°, as shown in Fig. 31, and yield a new distillate in the first portion of which y_A would be 0.90; a 3° fraction would be about 88 mole per cent acetone and much smaller in quantity than 6.17 grams. A third distillation of this second distillate would yield a very small amount of third distillate in which y_A would be about 0.99.

c. Complete Fractionation.—In order to illustrate the *principle* of the procedure for obtaining larger quantities of nearly pure toluene and acetone from a mixture in which x_A is 0.20, for example, consider a simple (but experimentally inadequate) arrangement of four vessels containing mixtures of these substances at their boiling points, as follows:

(1)	(2)	(3)	(4)
$x_A = 0.02$	$x_A = 0.20$	$x_A = 0.50$	$x_A = 0.85$
$t = 105°$	$t = 84°$	$t = 68°$	$t = 60°$
$y_A = 0.20$	$y_A = 0.64$	$y_A = 0.86$	$y_A = 0.96$

Each vessel has a long and short exit tube so arranged that the vapor from (1) is discharged under the liquid in (2), the vapor from (2) discharges under liquid (3), etc., and finally, the vapor from (4) passes into a condenser. Vessel (1) is heated; the others are thermally insulated and not heated. (Note the location of the tie lines corresponding to these four liquids and vapors on Fig. 31 before reading the next paragraph.)

The vapor expelled from (1) at 105° is cooled to 84° in (2), causing partial condensation; the latent heat of this condensation is used to form a vapor in which y_A is 0.64, while the liquid in (2) is enriched in toluene. Vapor expelled from (2) at 84° is cooled to 68° in (3), causing some enrichment of this liquid in toluene and the formation of a vapor in which y_A is 0.86. This vapor is cooled to 60° in (4), where partial condensation yields the heat required to expel a vapor in which y_A is 0.96. As these operations continue, the liquid in (1) approaches pure toluene, since x_A is only 0.02 and y_A is 0.25. Use of one or two more vessels on the toluene side would yield a final liquid residue that is nearly pure toluene; addition of one or two more on the acetone side would yield nearly pure acetone vapor for the final condenser. If to such a plan we add means of keeping the liquid compositions constant by *flowing liquid* from (4) to (3), from

(3) to (2), from (2) to (1) and if the losses of the pure components from this multiple distilling arrangement are made up by adding more boiling liquid 20 mole per cent solution to vessel (2), a continuous yield of both components results.

Such an arrangement would, of course, be too crude for actual use. In practice, the vessels are called "plates" or trays; they are arranged one over another in a "fractionating column" with "bubble caps" to promote contact between liquid and vapor and with downtakes for the liquid to flow toward the high-boiling portion of the column, as illustrated in Fig. 32. Heat is supplied at the bottom of this fractionating column, the high-boiling component is withdrawn as a liquid at the bottom, and the low-boiling component leaves the top of the column as a vapor, which is condensed in a separate condenser. The liquid to be fractionated is heated to its boiling point and fed in on the plate of which the liquid phase has the same composition.

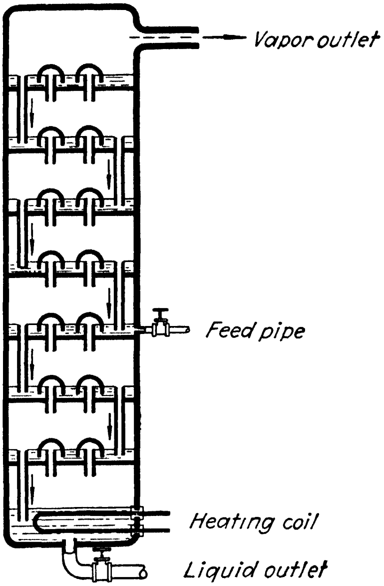

FIG. 32.—Idealized fractionating column

In the laboratory, a flask containing the boiling mixture serves as the bottom "tray," and a glass tube containing "packing" or supplied with baffles and depressions for the liquid constitutes the "column," to the top of which a condenser is attached. When the boiling points of the components to be separated differ by 5°, complete fractionation may be accomplished with as little as 20 mg. of liquid. Fractionating towers in industry may be 32 ft. or more in diameter and 60 to 115 ft. in height and may contain 30 to 80 plates with 1000 or more bubble caps to each plate. A single tower may handle as much as 100,000 barrels of oil per day.

When binary mixtures are to be separated, operation is usually at atmospheric pressure; but petroleum fractionating towers sometimes operate under pressures of 300 lb. or more, and in other industrial distillation the stills operate under reduced pressures. Side streams are sometimes withdrawn from a plate and passed through stripping towers or otherwise treated.

Mixtures of three or more components are sometimes separable by fractional distillation as well, but they require special procedures that we cannot consider here. The design of efficient fractionating columns is a complex problem for a chemical engineer, but the fundamental data that he requires for this purpose are the equilibrium mole fractions of liquid and vapor, such as are shown in Fig. 31.

Constant-boiling Mixtures (Azeotropes).—Many pairs of liquids form certain mixtures boiling higher than either component or lower than either component and of course one mixture with a maximum (or minimum) boiling point. Such mixtures are called azeotropic mixtures, and the pairs of liquids forming them are called azeotropes. The maximum (or minimum) boiling mixture cannot be further separated by fractional distillation at constant pressure. A few illustrations at 1 atm. pressure are quoted here, and thousands of others are known.

Components and boiling points		Constant-boiling mixture
Water, 100°	Ethyl alcohol, 78.26°	89.4 mole per cent alcohol, 78.15°
CCl_4, 76.5°	Ethyl alcohol, 78.26°	39.7 mole per cent alcohol, 64.95°
Water, 100°	Nitric acid, 86°	62 mole per cent water, 122°
Water, 100°	Ethyl acetate, 77.1°	24 mole per cent water, 70.4°

These constant-boiling mixtures are not compounds, for the mole ratios in them are seldom whole numbers, and they change materially when the distillations are carried out at pressures other than 1 atm. For example, the mole per cent of ethanol in the azeotropic mixture with water changes with the pressure at which the distillation is conducted, as follows:[1]

Pressure, atm.	1.0	0.50	0.25	0.125
Mole per cent ethanol	89.4	91.5	94.1	99.7

In some industrial alcohol fractionating columns the pressure is as low as 0.125 atm., at which pressure the boiling temperature

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[1] Beebe, Coulter, Lindsay, and Baker, *Ind. Eng. Chem.*, **34**, 1501 (1942).

of water is about 50°C. and the boiling temperature of the azeotrope is about 35°C., but there are important reasons other than the enriched azeotrope for conducting the distillation at such a low pressure. Azeotropes are not ordinarily "broken" by this means, since more economical methods are available.

Another example is constant-boiling hydrochloric acid, for which the azeotropic mixture boiling at 1 atm. pressure contains 20 22 per cent HCl by weight, which is very nearly the composition $HCl.8H_2O$. A solution containing more water than this mixture expels water in a higher mole ratio than 1:8 and approaches this composition; one containing less water expels more than 1HCl to $8H_2O$ and likewise approaches 20.22 per cent HCl by weight. But when the distillation is conducted at some pressure other than 1 atm., the ratio of HCl to water in the constant-boiling mixture changes, so that the evidence for compound formation is not convincing. Since the preparation of "constant-boiling hydrochloric acid" is a convenient means of obtaining a solution of accurately known composition, we quote the data applicable to climatic changes in pressure.[1]

Pressure, mm	770	760	750	740	730
Weight per cent HCl	20 197	20 221	20 245	20 269	20 293

Mimimum-boiling mixtures are somewhat more common than maximum-boiling mixtures. The only difference in their treatment is that the minimum-boiling mixture is the ultimate distillate in complete fractionation, while the maximum-boiling mixture is the ultimate residue in this process.

Systems of two components in which maximum-boiling or minimum-boiling mixtures form may be separated into portions of different compositions by fractional distillation except when the system has the composition of the azeotropic mixture. A single fraction of distillate may be collected, or repeated fraction may be performed; but this latter operation will not yield the two pure components. Equilibrium mole fractions of liquid and vapor for 1 atm. and varying temperature may be shown on diagrams such as Fig. 34, which is read in the same way as Fig. 31. Another common way of plotting the data is shown in Fig. 33,

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[1] Foulk and Hollingsworth, *J. Am. Chem. Soc.*, **45**, 1227 (1923); for other examples of azeotropic ratios changing with pressure see *J. Phys. Chem.*, **36**, 658 (1932).

which is easier to read for compositions but which does not show the boiling temperatures.

Equilibrium data for ethanol (ethyl alcohol) and water[1] at 1 atm. pressure are given in Table 35 and plotted in Fig. 34

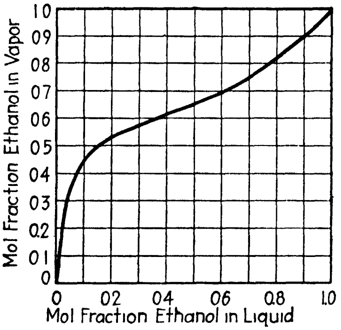

FIG. 33.—Equilibrium mole fractions in liquid and vapor at 1 atm. pressure for ethanol and water.

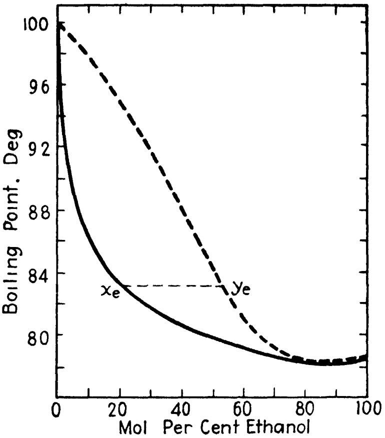

FIG. 34.—Temperature-composition diagram for water and ethanol at 1 atm. pressure.

Liquid composition is shown by a solid line and vapor composition by a dotted line, as was done in earlier diagrams.

TABLE 35.—EQUILIBRIUM MOLE FRACTIONS OF ETHANOL AND WATER

B. pt.	x_e	y_e	B. pt.	x_e	y_e
86 4	0 100	0 442	79 1	0 600	0.699
83 3	0 200	0 531	78 6	0.700	0 753
81 8	0 300	0 576	78 3	0 800	0 818
80 7	0 400	0 614	78 2	0 894	0 894
79 8	0 500	0 654	78 3	1.000	1 000

A solution of 20 mole per cent ethanol would boil at 83.3° and yield a first vapor in which y_e was 0.53; a fraction collected between 83.3° and 84.3° would be about 50 mole per cent ethanol.

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[1] From Cornell and Montonna, *Ind. Eng. Chem.*, **25**, 1331 (1933); data for methanol and water, and for acetic acid and water are given in the same paper. Data for ethanol and water in substantial agreement with those above are given by Baker, Hubbard, Huguet, and Michalowski, *ibid.*, **31**, 1260 (1939).

The first vapor from redistillation of this small distillate would be about 65 mole per cent ethanol. Repeated fractionation in a column such as that shown in Fig. 32 would separate the mixture into a final residue of pure water, and a final distillate containing 89 mole per cent (or 96 weight per cent) ethanol, the minimum-boiling mixture. This would be true of any mixture containing less than 89 mole per cent of ethanol. Although it is true that azeotropic compositions change with the pressure under which distillation is conducted, it is usually not practical to apply this fact to the further enrichment of the distillate, since other means better suited to the preparation of anhydrous ethanol from the 89 mole per cent mixture are known. Any mixture containing more than 89 mole per cent ethanol would also yield the azeotropic mixture as a final distillate upon complete fractionation and pure ethanol as a final residue.

Similar statements would apply to any system in which one mixture has a minimum boiling point; this mixture would be the final distillate upon complete fractionation, and the final residue would be whichever pure component has to be removed to produce this composition. Maximum-boiling mixtures form the final *residue* upon complete fractionation, and one pure component forms the final distillate. Through the use of material balances the quantities of distillate and residue may be computed, as was done in an earlier section. For example, 1000 grams of 20 mole per cent ethanol is 8.48 moles of ethanol and 33.92 moles of water; the distillate resulting from complete fractionation would contain all the ethanol, making 8.48/0.89 = 9.53 moles of distillate, 1.05 moles of water, and 8.48 moles of ethanol. The residue would be pure water, 33.92 − 1.05 = 32.87 moles, or 592 grams of water.

While it is true, as suggested above, that azeotropes may not be separated by fractional distillation in a two-component system at constant pressure and that their separation by changing the pressure is tedious or at least uneconomical, it is not true that such mixtures are incapable of separation by distillation, for they are "broken" industrially in many processes. The usual expedient is to add a third substance called an "entrainer," which may or may not form an azeotrope with one or the other component of the original mixture, and to fractionate the three-component system. The addition agent, or "entrainer," cycles through the process with little loss, and the end products are the two components of the original azeotrope. A common entrainer is benzene for the preparation of anhydrous alcohol from the azeotrope with water, and many others are known.[1]

Distillation of Insoluble Liquids with Steam.—If two liquids are mutually insoluble, neither one lowers the vapor pressure of the other and the total vapor pressure of a mixture of them is the sum of their vapor pressures. When such a mixture is heated in a distilling flask until this sum reaches atmospheric pressure, the mixture boils and the substances pass out of the flask in the mole ratio of their vapor pressures. Liquids insoluble in water may thus be distilled with steam at temperatures that are not only below the boiling points of the liquids, but below the boiling point of water as well. For substances of high boiling point that do not react with water, steam distillation is a convenient expedient for effecting distillation at low partial pressures without the use of vacuum equipment.

Consider, for example, a mixture of water with terpinene ($C_{10}H_{16}$, boiling point 182°), whose vapor pressures are

t	90°	95°	100°
p, mm for terpinene	91	110	131
p, mm for water	526	634	760

The liquids are substantially insoluble in one another; the total vapor pressure is 744 mm at 95° and 891 mm. at 100°. While the vapor-pressure curves are not quite linear functions of the temperature over a range of 5°, it will be evident that at about 95 5° the total vapor pressure will be 1 atm. from this mixture (Actually dp/dT is 24 mm. per deg. for water at 95° and 4 mm. per deg. for terpinene, or 28 mm. for the two together, and $^{16}\!/_{28}°$ is sufficiently near to 0.5°.) In the vapor expelled from the flask, p_w will be 648 mm., p_t will be 112 mm., and the mole ratio in the distillate will be the ratio of these pressures. Each mole of distillate will thus contain 0.147 mole of terpinene and 0.853 mole of water, or 57 per cent terpinene by weight; and distillation will take place 87° below the boiling point of pure terpinene.

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[1] For a discussion of azeotropic distillation, see Ewell, Harrison, and Berg, *ibid.*, **36**, 871 (1944).

Substances of higher boiling point will have lower vapor pressures near 100°, and thus the yield in moles per mole of distillate will be smaller; but against the small yield must be set the advantage of convenient distillation at low partial pressures.

So long as both substances are present at equilibrium in the distilling flask, the temperature will remain constant and the composition of distillate will be independent of the relative quantities in the flask, since each substance exerts a vapor pressure dependent upon temperature alone and independent of the quantity of liquid present.

An accurate measurement of the temperature of a steam distillation and of the weight composition of the distillate serves to determine the molecular weight of the vapor of an insoluble substance, as well as its vapor pressure at this temperature. For illustration,. suppose a substance A distills with steam at 99.0° under an observed barometric pressure of 752.2 mm., yielding a distillate that is 25 per cent A by weight. The vapor pressure of water at 99° is 733.2 mm., and that of the substance A is thus 19.0 mm. The mole ratio in the distillate is 733.2/752.2 to 19/752.2, or 0.975 mole of water to 0.0252 mole of A. In 100 grams of distillate there are $^{75}\!/_{18} = 4.17$ moles of water to $25/M$ moles of A, and these quantities must be in the ratio of the partial pressures. Then $0.975 : 0.0252 = 4.17 : (25/M)$, whence $M = 232$ for the substance.

Liquids which are slightly soluble in water and in which water is slightly soluble may also be distilled with steam, but the mole ratio in the distillate is not to be computed from the vapor pressures of the pure substances or from them and Raoult's law, for such solutions are far from ideal. For illustration, when aniline (C_6H_7N) and water are shaken to equilibrium at 100°, there are two phases, containing 7.2 and 89.7 per cent aniline by weight, respectively. In these mutually saturated solutions the mole fractions of aniline are 0.015 and 0.63; but since the solutions are in equilibrium with one another, they are both in equilibrium with the same vapor. The value of y_A in this vapor is about 0.045, as determined by analysis of the distillate, and this value could not be obtained from calculations assuming either layer to be an ideal solution. The vapor pressure of aniline at 100° is 0.060 atm.; and from Raoult's law p_A would be 0.63×0.060, or 0.038, and p_{H_2O} would be 0.985, whence y_A is calculated to be 0.037

in place of 0.045 found by experiment It will always be true that the calculated partial pressures are below the observed ones for liquids of limited solubility.

Freezing Points of Solutions.—The freezing point of a solution is defined as the temperature at which the solution is in equilibrium with the pure crystalline solvent. Since solutions when cooled usually deposit one component as a solid before the other, the freezing point of a solution is not the temperature at which the solution as a whole becomes solid but the temperature at which it *begins* to deposit solid solvent if cooled so slowly that equilibrium is maintained. Equilibrium is more readily attained when the cooled solution is poured over a liberal excess of crystalline solvent; the composition of the solution may be determined by analyzing a portion of it withdrawn after the equilibrium temperature has been measured.

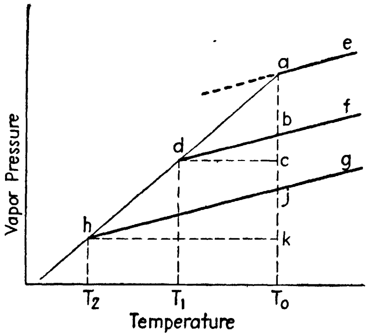

FIG 35—Vapor-pressure relations near the freezing point

Addition of a solute will lower the equilibrium pressure of solvent vapor at any given temperature, and for ideal solutions the decrease in solvent vapor pressure is shown by Raoult's law. At T_0, the freezing point of the pure solvent, the vapor pressures of the solid and liquid phases are equal, but at this temperature the vapor pressures of crystalline solvent and a solution will not be equal. Since the vapor pressure of the solid decreases with falling temperature more rapidly than does the vapor pressure of the solution, cooling will bring the two vapor pressures to equality at the freezing point of the solution.

A diagram of these conditions is given in Fig. 35, in which *ae* shows the change in vapor pressure of liquid solvent with temperature, *hda* this change for solid solvent, and *dbf* the change of solvent vapor pressure for a solution in which x_1 is the mole fraction of solute. Since *hda* and *dbf* intersect at *d*, T_1 is the freezing point of this solution and *cd* or $T_0 - T_1$ is the freezing-point depression ΔT_f. The relation between *cd* and the mole fraction of solute x_1 is desired. It will be seen from the figure that *ab* is $p_0 - p$, which is connected through Raoult's law with x_1. From the relations in Fig. 35 it will be evident that

$$\frac{ab}{cd} = \frac{ac}{cd} - \frac{bc}{cd}$$

For small temperature intervals such as are involved in freezing-point changes in *dilute* solutions, *ac*/*cd* is substantially the slope of the vapor-pressure curve for the solid solvent at the freezing point; and *bc*/*cd*, which is the slope of the vapor-pressure curve for the solution, is substantially equal to the slope of the vapor-pressure curve for the pure solvent at the freezing point.

These slopes are given by the approximate form of the Clapeyron equation as

$$\frac{ac}{cd} = \frac{dp_{\text{subl}}}{dT} = \frac{p_0\,\Delta H_{\text{subl}}}{RT_0^2} \quad \text{and} \quad \frac{bc}{cd} = \frac{dp_0}{dT} = \frac{p_0\,\Delta H_{\text{evap}}}{RT_0^2} \tag{11}$$

Upon subtracting the second of these relations from the first, (noting that $\Delta H_{\text{subl}} - \Delta H_{\text{evap}} = \Delta H_{\text{fusion}}$ for a mole of solvent at the freezing point), we obtain the relation between *ab* and *cd*, which is

$$\frac{ab}{cd} = \frac{\Delta H_{\text{fusion}} p_0}{RT_0^2} = \frac{p_0 - p}{T_0 - T_1}$$

Upon rearranging and putting x_1 for $(p_0 - p)/p_0$ from Raoult's law, we obtain the freezing-point equation

$$T_0 - T_1 = \frac{RT_0^2}{\Delta H_f} x_1$$

Since the triangles *abd* and *ajh* in Fig. 35 are similar, the relation between *aj* and *hk* is

$$T_0 - T_2 = \frac{RT_0^2}{\Delta H_f} x_2$$

These equations show that the freezing-point depression, which we shall write ΔT_f, is proportional to the mole fraction of solute and that the proportionality constant is $RT_0^2/\Delta H_f$, which may be calculated from the properties of the pure solvent. For a dilute solution the relation stands

$$\Delta T_f = \frac{RT_0^2}{\Delta H_f} = Kx \tag{12}$$

The proportionality constant K is the factor by which the mole fraction of the solute in a dilute solution must be multiplied to give the freezing-point depression. This quantity is 104° for water, but there is no aqueous solution that freezes at $-104°$; even if the mole fraction of solute were 0.10, it would not follow that ΔT_f is 10.4° except by accidental compensation, for such a solution does not meet the assumptions made in deriving the equation.

Since this equation closely resembles equation (8) for the boiling-point elevation, we should note that the same approximations regarding slopes were made in deriving both equations, and hence each one is valid only so long as these approximations are justified.[1] For solutions in which ionization or polymerization of the solute does not occur, the equation will give ΔT_f in substantial agreement with experiment when the mole fraction of solute is not greater than 0.02. It should be noted that this equation does not require the solute to be nonvolatile. The curves *adh* and *dbf* of Fig. 35 intersect when the solvent vapor pressure is the same above the pure solid solvent and the solution, whether or not the solute has a vapor pressure.

Climatic variations in barometric pressure produce negligible changes in freezing points except when the highest precision is necessary, which is not true of the boiling-point equation[2] But the freezing-point equation does require that the crystalline phase at equilibrium be the pure solvent, just as the boiling-point equation requires that the vapor be pure solvent. We shall see in a later chapter that some solutions deposit crystalline phases that are not pure solid solvent; of course, equation (12) does not apply in these systems.

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[1] A more exact equation relating the freezing-point depression to x, the mole fraction of solute, is

$$\frac{d \ln (1 - x)}{dT} = \frac{\Delta H_f}{RT^2} \tag{13}$$

If ΔH_f is constant over the temperature interval involved, the integral of this equation between T_0 and T is

$$T_0 - T = \frac{-RTT_0}{\Delta H_f} \ln (1 - x)$$

This relation will give better agreement for high mole fractions of solute; for dilute solutions it reduces to equation (12) above

[2] If the barometer changed from 760 to 740 mm , the freezing point of an aqueous solution would rise about 0.0002°, its boiling point would fall 0.74°.

In precise work it is necessary to remove air from the solutions, since air would act as a solute with the usual effect upon the freezing point. We have already seen that the definition of centigrade zero includes a provision that ice be in equilibrium with water saturated with air at 1 atm. and that complete removal of the air raises the freezing point 0.0023°.

In dilute solutions $N_1/(N_1 + N_2)$, the mole fraction of solute, is close to N_1/N_2, and therefore the freezing-point equation may be written

$$\Delta T_f = Fm \tag{14}$$

in which F is the lowering produced per mole of solute in 1000 grams of solvent. The freezing-point depression for 1 mole of solute in 1000 grams of benzene may be calculated from equation (12), since the fusion of benzene at 5.4° absorbs 30.3 cal. per gram, as follows:

$$\Delta T_f = \frac{1.99(278.5)^2}{30.3 \times 78} \, \frac{1}{1 + 1000/78} = 4.7°$$

It should be noted that 1000 grams of benzene is 12.8 moles and that the mole fraction of solute is hence 0.072, which is scarcely a "dilute solution." If the above calculation is repeated for 0.1 mole of solute in 1000 grams of benzene, ΔT_f will be 0.51 and accordingly $F = 5.1$ is obtained. In the limit $F = K/(1000/M)$,

Table 36.—Freezing-point Constants[1]

Substance	M. Pt.	K	F	Substance	M. Pt.	K	F
Acetic acid	17	60	3.9	Ethylene bromide	10		12.5
Benzene	5.5	65	5.1	Naphthalene	80	55	7.0
Benzophenone	47.7	54	9.8	Nitrobenzene	5.7	57	7.0
Camphor	179		38	Stannic bromide	26.4		24.3
Diphenyl	69	53	8.2	Stearic acid	69.3	16	4.5
p-Dichlorbenzene	52.9	51	7.5	Water	0	104	1.86

[1] For F in other solvents see "International Critical Tables," Vol. IV, p. 183; additional values of K may be computed from the latent heats of fusion in Table 21. The recorded values of K and F are not among the most satisfactory data in physical chemistry. Values which are stated to 0.1° are frequently in error by 1° or more, and there is no simple way of sorting the good data from the poor.

where M is the molecular weight of solvent, and since K is 65 for benzene and $1000/M$ is 12.8, $F = 65/12.8 = 5.1$, which is the value given in Table 36.

These calculations have been given to show that equation (14) is a suitable approximation for dilute solutions, and not applicable to solutions of high molality. Freezing-point data are frequently recorded in tables of m and $\Delta T_f/m$, which is a useful device, but it will be found that $\Delta T_f/m$ is not constant in these tables For most calculations in which the solute concentration is high, equation (12) will be a better choice than equation (14).

Some experimental values of $F = \Delta T_f/m$ for water are given in Table 37. Values of both K and F for some common solvents are given in Table 36.

TABLE 37 —FREEZING POINTS OF SOLUTIONS OF MANNITOL IN WATER[1]

Molal concentration	Freezing-point depression	$F = \Delta T_f/m$
0 006869	0 01274	1 853
0 01006	0 01846	1 847
0 01041	0 01930	1 855
0 02039	0 03790	1 859
0 02249	0 04171	1 854
0 05061	0 09460	1 868
0 06062	0 11265	1 858
0.09574	0 1790	1 870
0 1197	0 2225	1 858

Freezing-point depressions furnish a convenient means of determining the molecular weights of solutes when such effects as ionization or polymerization or solvation of the solute are absent. For example, the molecular weight of triphenylmethane [$(C_6H_5)_3CH = 244.1$] in benzene as derived from freezing points is shown in Table 38.

By means of thermocouples it has been possible to measure very accurately the freezing points of quite dilute solutions. Usually the solution is made up somewhat stronger than needed and poured over an excess of crystalline solvent. The mixture is stirred until equilibrium is established, the freezing tempera-

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[1] FLUGEL and ROTH, *Z physik. Chem.*, **79**, 577 (1912).

ture is accurately determined, and a sample of the solution is withdrawn through a chilled filter and analyzed. This procedure is more accurate than that of chilling a solution of known concentration until solid begins to separate, for a correction must then be applied to allow for the solid that has separated. When a large quantity of solid is used, equilibrium is more readily and more certainly established, and the added labor of analyzing the solution actually at equilibrium is well justified. If a solution of known strength is cooled until solid separates, undercooling is almost unavoidable, equilibrium is established slowly, and the correction for the quantity of solid deposited is uncertain.

TABLE 38.—FREEZING POINTS OF TRIPHENYLMETHANE IN BENZENE[1]

Molality	Freezing-point depression	Molecular weight
0.000313	0.00158	244.5
0.000634	0.00322	243.5
0.000986	0.00497	245.4
0.004096	0.02082	243.5
0.0248	0.1263	243.1
0.04375	0.2214	244.6

The molal freezing-point depressions $\Delta T_f/m$ calculated for dilute solutions of inorganic salts in water will not be constant or close to 1.86°, because of ionization of the solutes. But the extent of ionization in these solutions is not to be calculated simply by assuming that $\Delta T_f/m$ divided by 1.86 gives the total number of solute moles (molecules plus ions) per formula weight of salt. This topic is discussed in the next chapter.

Molecular weights derived from freezing-point determinations in nonaqueous solvents frequently require interpretation as well, for effects such as ionization or polymerization into double molecules or solvation sometimes occur. The figures for tetrabutyl ammonium perchlorate (formula weight 341.8) in benzene[2] are an extreme example in which the interpretation is made more difficult by an appreciable conductance of the solutions. The data are shown in Table 39.

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[1] BATSON and KRAUS, *J. Am. Chem. Soc.*, **56**, 2017 (1934).

[2] ROTHROCK and KRAUS, *ibid.*, **59**, 1699 (1937).

TABLE 39.—MOLECULAR WEIGHTS

Moles per 1000 grams benzene	ΔT_f	$\frac{\Delta T_f}{\Delta T_{\text{ideal}}}$	Apparent molecular weight
0.00109	0.00184	0.333	1029
0.00434	0.00535	0.243	1404
0.00962	0.00982	0.202	1692
0.01423	0.0120	0.166	2052

Solutions of urea in water are more nearly typical of solutions in general than are the examples of close conformity to the ideal laws or the extreme deviations from them that have been quoted. They conform fairly closely at moderate concentrations, more closely at low concentrations, and deviate at high concentrations. The freezing-point depressions[1] illustrate this fact.

m	0.3241	0.646	1.521	3.360	5.285	8.083
ΔT_f	0.5953	1.170	2.673	5.490	8.082	11.414
$\Delta T_f/m$	1.837	1.811	1.757	1.660	1.529	1.412

Solutions of ethanol (ethyl alcohol) in water also conform to the ideal equation for freezing-point depression in dilute solution and deviate at higher molalities. In these solutions the ratio $\Delta T_f/m$ increases with the molality, while the same ratio decreased with increasing molality for the urea solutions above. There is no way of predicting whether the deviations will be in one way or the other. The data for ethanol are as follows:

m	0.1	1.0	2.0	4.0	6.0	7.0	10.0	15.0
$\Delta T_f/m$	1.83	1.83	1.84	1.93	2.05	2.12	2.2	2.0

Osmotic Pressure.—The molecules of a solute in a dilute solution are separated from one another by distances that are large compared with the diameters of the molecules, and they have a certain freedom of motion. This condition is similar to that of the molecules of a gas, the main difference being that the space between the molecules in a solution is filled with solvent. Early experiments showed that the pressure necessary to prevent the flow of water through an animal membrane into a solution was proportional to the concentration of solute and that this pressure increased nearly in proportion to the absolute temperature.

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[1] CHADWELL and POLITI, *ibid.*, **60**, 1291 (1938).

These facts led van't Hoff to suggest that the solute exerts an "osmotic pressure" corresponding to the pressure that it would exert in the form of gas in the same volume if the solvent were removed. To test this supposition it would be necessary to devise a membrane that was impermeable to solute molecules and allowed free passage of solvent.

Consider a cylinder closed at one end by such a membrane, filled with a solution, fitted with a movable piston, and immersed in pure solvent. If the pressure exerted by the piston exceeds the osmotic pressure, solvent will be forced out of the solution through the membrane; if the pressure is less than the osmotic pressure, solvent will enter the solution through the membrane; and when the pressure on the piston is equal to the osmotic pressure, no solvent will pass through the membrane in either direction. To the extent that this conception of osmotic pressure is correct, the osmotic pressure in a dilute solution will be equal to that calculated on the assumption that the solute is an ideal gas in the same volume at the same temperature.

In spite of experimental difficulties, which were many and troublesome,[1] suitable membranes have been devised, and some osmotic pressures have been obtained. They confirm the assumption that in a dilute solution an osmotic pressure exists which is given by the equation

$$\pi v = nRT \qquad \text{or} \qquad \pi = CRT \tag{15}$$

in which C is the volume concentration, R has the same value as in the ideal gas law, and π is the osmotic pressure. Osmotic pressures of sugar are shown in Table 40; a membrane of copper ferrocyanide embedded in the walls of a clay vessel was used. The columns headed "Ratio" show the ratio of the measured osmotic pressure to the pressure calculated on the assumption that the solute is an ideal gas occupying the volume of the solution. The deviations of these numbers from unity are no greater than one might expect of a gas of molecular weight 342 at these pressures and temperatures. Osmotic pressures of mannite at

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[1] See Morse, *Carnegie Inst. Wash. Pub.*, **198** (1914); Berkley and Hartley, *Phil Trans Roy. Soc* (*London*), (*A*) **209,** 177 (1909); (*A*) **218,** 295 (1919) for the method and experimental data. The pressures in Table 40 are taken from the paper by Morse.

molalities below 0.5, or at osmotic pressures below 12 atm., differ from the calculated ideal gas pressures by less than 1 per cent.

If the osmotic-pressure equation is written in the form

$$\pi v = \frac{m}{M} RT$$

it will be evident that these experiments could be used to determine molecular weights of solutes. Osmotic-pressure measurements are experimentally difficult for solutes of moderate molecular weight, chiefly because of the preparation of semipermeable membranes that will not "leak" solute; therefore, molecular weights are usually determined from freezing points or boiling points. But the recent interest in high polymers, which may have molecular weights of 100,000 or more, has directed attention to osmotic pressures as a means of studying them. A solution of 10 grams of such a substance in 1000 grams of water would have a freezing-point depression of only 0.00018°, and the presence of the slightest impurity would render the measured depression uncertain. Such a solution would have an osmotic pressure of 0.0025 atm., which is 26 mm. of water. Membranes that are impermeable to such large molecules and capable of withstanding this small pressure are *comparatively* easy to make, but deviations from the laws of ideal solutions are quite high for solutes of such high molecular weights, even at low molalities. To correct for them the common expedient is to plot the ratio of osmotic pressure to concentration, extrapolate to zero concentration, and determine the molecular weight from the limiting ratio of π to C, as was done in determining precise molecular weights of gases from densities in Chap. I.

For example, the ratio π/C for polyisobutylene in benzene[1] is nearly independent of the concentration, but the ratio π/C for the same preparation in cyclohexane changes rapidly with C. Plots of π/C against C are nearly linear for both solvents and when extrapolated to zero concentration give the same limit of π/C, as shown in Fig. 36. The extrapolated value of nearly 0.001 atm. gives for a concentration of 10 grams per liter of solution at 25°C. an *average* molecular weight of 250,000. In such preparations the presence of larger and smaller molecules is

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[1] Flory, *J. Am. Chem. Soc.*, **65**, 372 (1943).

not excluded, and indeed their presence is probable. The freezing-point depression of this solution in benzene would be about 0.0002°, and, while such a temperature difference can be measured, the presence of a slight impurity of reasonable molecular weight would render the measured freezing point uncertain.

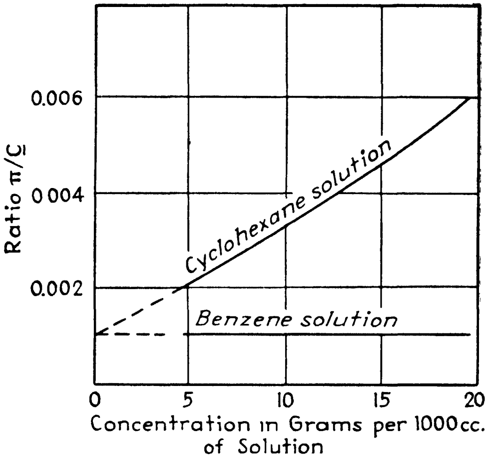

FIG. 36.—Osmotic pressures of polyisobutylene solutions at 25°.

The osmotic membranes are probably permeable to ordinary solutes, and thus they correct for the presence of these solutes and yield the average molecular weight of the polymer.

Similar wide deviations from ideal solutions are shown by other systems, for example, polymethylmethacrylates in chloroform.[1]

TABLE 40—OSMOTIC PRESSURES OF SUGAR SOLUTIONS, IN ATMOSPHERES

Molal concentration	0°		20°		40°		60°		Average ratio
	Osmotic pressure	Ratio	Osmotic pressure	Ratio	Osmotic pressure	Ratio	Osmotic pressure	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

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[1] HOFF, *Trans. Faraday Soc.*, **40**, 233 (1944).

Plots of π/C against C are nearly linear but not horizontal, and extrapolation to zero concentration gives acceptable molecular weights.

The osmotic pressure is related to p_0/p, the ratio of the vapor pressure of the pure solvent to that of the solvent from solution, by the equation

$$\pi = \frac{RT}{v_l} \ln \frac{p_0}{p} \tag{16}$$

in which v_l is the volume of a mole of liquid solvent. This equation may be derived from an isothermal reversible cycle of changes in which (1) a mole of solvent is expressed reversibly from a large quantity of solution through a semipermeable membrane, (2) the solvent is vaporized reversibly under its vapor pressure p_0, (3) the solvent vapor is expanded reversibly to p, and (4) the vapor is condensed reversibly into the solution. The work done in these steps is

$$\begin{aligned} w_1 &= -\pi v_l \\ w_2 &= p_0(v_v - v_l) = RT \\ w_3 &= RT \ln \frac{v_2}{v_1} = RT \ln \frac{p_0}{p} \\ w_4 &= p(v_l - v_v) = -RT \end{aligned}$$

TABLE 41.—CANE-SUGAR SOLUTIONS AT 30°

Molal concentration	Measured osmotic pressure[1] (atmospheres)	Calculated osmotic pressures			
		Equation (15)	Per cent error	Equation[2] (16)	Per cent error
0.10	2.47	2.47	0	2.47	0.0
1.00	27.22	24.72	9	27.0	1.0
2.00	58.37	49.40	15	58.4	0.0
3.00	95.16	74.20	23	96.2	0.0
4.00	138.96	98.90	29	138.3	0.5
5.00	187.3	123.60	33	182.5	2.5
6.00	232.3	148.30	36	230.9	0.6

[1] FRASER and MYRICK, *J. Am. Chem. Soc.*, **38**, 1907 (1916).

[2] Vapor pressures from BERKLEY, HARTLEY, and BURTON, *Phil. Trans. Roy. Soc. (London)*, **218**, 295 (1919). The data are as follows:

Molal concentration	1.00	2.00	3.00	4.00	5.00	6.00
Ratio p_0/p	1.020	1.044	1.072	1.104	1.140	1.17

According to the second law of thermodynamics the summation of work in a reversible isothermal cycle is zero, and this is such a cycle, so that

$$-\pi v_l + RT + RT \ln \frac{p_0}{p} - RT = 0$$

and, upon solving this equation for π, equation (16) results. As may be seen from Table 41, this equation gives calculated osmotic pressures that agree with experimental pressures within the error of the data, while equation (15) deviates seriously from the measured pressures.

Problems

Numerical data for some of the problems must be sought in tables in the text.

1. When the concentration of SO_2 is 1 mole per liter of $CHCl_3$ at 25°, the equilibrium pressure of SO_2 above the solution is 0 53 atm. When the total SO_2 is 1 mole per liter of water at 25°, the equilibrium pressure of SO_2 above the solution is 0 70 atm , and 13 per cent of the solute is ionized into H^+ and HSO_3^-. Sulfur dioxide is passed into a 5-liter bottle containing a liter of water and a liter of $CHCl_3$ (but no air) until the total moles of SO_2 per liter of water at equilibrium is 0 20 at 25° Under these conditions 25 per cent of the SO_2 in the water layer is ionized Henry's law applies to the nonionized portion ($SO_2 + H_2SO_3$) in water and to SO_2 in $CHCl_3$ (*a*) How many moles of SO_2 were passed into the bottle? (*b*) More SO_2 is passed into the bottle until the total quantity is 1 mole Estimate the fraction ionized in the water layer under these conditions by interpolation from the data on page 189, and calculate the moles of SO_2 in each of the three phases

2. The boiling point of methanol (CH_3OH = 32) is 65°, its molal latent heat is 8400 cal at 65° and may be assumed constant over the temperature range of this problem A solution of 0 5 mole of $CHCl_3$ in 9 5 moles of CH_3OH boils at 62.5° Calculate the total vapor pressure and the composition of the vapor in equilibrium with a solution containing 1 mole of $CHCl_3$ and 9 moles of CH_3OH at 62 5°.

3. (*a*) The ratio of the pressure of CO_2 in atmospheres to the molality of the saturated solution is p/m = 29 at 25°C. Calculate the total pressure at equilbrium in a 2-liter bottle containing 0 10 mole of CO_2 and 1000 grams of water (but no air) at 25° (*b*) The ratio p/m = 100 for CO_2 in water at 100°. Calculate the total pressure in the bottle at 100°C , neglecting small corrections (*c*) List the factors neglected in the calculation of part (*b*).

4. The latent heat of evaporation of toluene (C_7H_8 = 92) is 85 cal. per gram at 110°C (the boiling point). When toluene is distilled with steam at 1 atm. total pressure, the distillation temperature is 84°C. Toluene and water are mutually insoluble. How many grams of toluene will be in 100 grams of distillate?

5. Calculate the boiling-point constants k and B and the freezing-point constants K and F for benzene from the physical constants of benzene in Tables 16 and 21, and compare with the values in Tables 33 and 36.

6. Ethanol (C_2H_5OH) boils at 78.3°, and its molal latent heat is 9400 cal. A solution of 0.07 mole of benzene in 0.93 mole of ethanol boils at 75° and 1 atm. (*a*) Calculate the partial pressures of ethanol and benzene in the vapor. (*b*) Calculate the partial pressure of each substance above a solution of 0.1 mole of benzene and 0.9 mole of ethanol at 75°.

7. The vapor pressure of a solution of 2.38 moles of cane sugar ($C_{12}H_{22}O_{11}$) in 1000 grams of water at 30° is 94.88 per cent that of pure water. Calculate the osmotic pressure of this solution from the vapor pressure. Calculate also its osmotic pressure, assuming that it behaves as an ideal gas at this concentration. The measured osmotic pressure is 73 atm.

8. The change of vapor pressure of benzene ($C_6H_6 = 78$) with temperature is given in a footnote on page 114, and its boiling point for 1 atm. is 80.09°. (*a*) Calculate the vapor pressure at 80.09° of a solution containing 0.20 mole of nonvolatile solute in 1000 grams of benzene. (*b*) Calculate the boiling point of this solution from the vapor-pressure data. (*c*) Calculate the boiling-point constants k and B for benzene from the vapor-pressure data. (*d*) Calculate another value of k, taking $\Delta H_m = 7600$ cal for benzene.

9. Calculate the weights of ethyl alcohol, of ethylene glycol, and of glycerol required for 25 kg. of solution that would not deposit ice at 0°F (−17.8°C.).

10. Equilibrium mole fractions for ethanol-water mixtures are given in Table 35 and Fig. 34. (*a*) If 1000 grams of a mixture that boils at 83.3° are distilled until the boiling point rises to 86.4°, what weight of distillate will be obtained? (*b*) Calculate the temperature at which the original mixture would begin to deposit ice, assuming it an ideal solution. Recalculate this temperature from the data on page 220. (*c*) Calculate the weight of ice deposited per kilogram for the residue obtained in part (*a*) if this residue were cooled to the actual freezing point of the original mixture. (*d*) A *vapor* mixture of 0.4 mole of ethanol and 0.6 mole of water is cooled to 81.8° and 1 atm. without removing the condensate from the vessel. What are the equilibrium mole fractions in this system? What weight of vapor remains uncondensed?

11. Ethyl iodide is an ideal solute when dissolved in *p*-chlorotoluene (mol. wt. 126.5, m. pt. 7.80°). The freezing-point depression for this solution changes with m, the moles of solute per 1000 grams of solvent, as follows:

ΔT_f	0.263°	0.487°	0.708°	1.262°
m	0.0468	0.0875	0.128	0.227

For chloroacetic acid ($C_2H_3O_2Cl = 94.5$) in *p*-chlorotoluene, ΔT_f changes with the *grams* of solute (g) per 1000 grams of solvent as follows.

ΔT_f . .	0.27	0.42	0.52	0.62
g . .	9.2	13.6	18.0	20.8

Calculate ΔH_f and F for *p*-chlorotoluene and the molecular weight of chloroacetic acid in *p*-chlorotoluene [*J Chem Soc* (*London*), **1934,** 1971.]

12. The distribution ratio C_w/C_e for formaldehyde (HCHO) between water and ether at 25° is 9 2 for volume concentrations (*a*) How many liters of water will be required to remove in one extraction 95 per cent of the formaldehyde from a liter of ether containing one mole of formaldehyde? (*b*) How much formaldehyde would remain in a liter of ether containing initially one mole of formaldehyde after eight successive extractions with 50 ml of water?

13. The freezing-point depression for 0 05 mole of bromine in 1000 grams of water is 0 0938°, that for 0 05 mole of chlorine in 1000 grams of water is 0 157° What is the chemical explanation of the difference in $\Delta T_f/m$ for the two solutions?

14. Calculate the Bunsen coefficient α for H_2S in water at 25° and for SO_2 in water at 25°, from the data on pages 187 and 189

15. Calculate the boiling-point constant k for ethyl ether from the data in Table 14, calculate another value from Table 16, compare with the entry in Table 33

16. (*a*) Calculate the temperature at which *n*-C_8H_{18} will distill with steam at 1 atm total pressure and the composition of the distillate in per cent by weight (*b*) Repeat the calculation for a total pressure of 0 84 atm, which would prevail 1 mile above sea level (See Table 14 for data)

17. The solubility of H_2S in water at 25° is 0 102 mole per liter of solution when $p(H_2S)$ is 1 atm , and the distribution ratio between benzene (C_6H_6 = 78) and water is $C_w/C_b = 5\ 72$ for volume concentrations. The vapor pressures of the pure liquids at 25° are 0 12 atm for benzene and 0 03 atm for water Hydrogen sulfide is passed into a 5-liter bottle containing a liter of benzene and 400 ml of water (and no air) until the *total pressure* at 25° is 5 atm (*a*) Neglecting effects calculable from Raoult's law, calculate how many moles of H_2S are in each of the three phases at equilibrium (*b*) Show that the neglected pressure changes are negligible compared with the total pressure (*c*) Calculate the total pressure at equilibrium if 2 more liters of benzene are forced into the bottle and no gas escapes

18. Equilibrium mole fractions at 1 atm total pressure for nitric acid (HNO_3 = 63, b pt 86°, symbol N) and water (symbol W) change with the temperature as follows.

Temperature	110°	120°	122°	120°	115°	110°	100°
Mole per cent N in liquid	11	26	38	45	50	54	62
Mole per cent N in vapor	1	10	38	70	84	90	93

(*a*) Draw a complete temperature-composition diagram for this system. (*b*) A vapor mixture of 3N + 2W is cooled to 114°, and no condensate is withdrawn from the system What are the equilibrium compositions in the liquid and vapor phases? (*c*) A liquid mixture of 3N + 2W is completely fractionated by repeated fractional distillation. State the composition and calculate the weight of distillate and of residue obtained. (*d*) A liquid mixture of 3N + 2W is distilled until the boiling point rises 4°, and the distillate is collected in a single portion. Calculate the weight and composition of the distillate.

19. Equilibrium mole fractions at 1 atm. total pressure for carbon tetrachloride (CCl_4, mol. wt. 154, b. pt. 120.8°, symbol C) and tetrachloroethylene (C_2Cl_4, mol. wt. 166, b. pt. 76.9°, symbol T) change with temperature as shown in the following table.

t ...	108.5	100.8	93.0	89.3	86.0	83.5	81.5	79.9	77.5
x_c	0.100	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900
y_c ..	0.469	0.670	0.800	0.861	0.881	0.918	0.930	0.958	0.980

(*a*) Draw a complete temperature-composition diagram for this system. (*b*) A vapor mixture of 3C and 7T is cooled to 100.8°, the pressure remains 1 atm., and no condensate escapes from the vessel. What are the quantities of C and T in the vapor? (*c*) A liquid mixture of 3C and 7T is distilled until the boiling point rises to 100.8°, and the distillate is collected in a single portion. What are the quantities of C and T in the distillate? (*d*) This distillate is distilled until the boiling point rises 5°. Calculate the composition and weight of distillate obtained. [Data from McDonald and McMillan, *Ind. Eng. Chem.*, **36**, 1175 (1944).]

20. The steam distillation of an insoluble liquid takes place at 90°C. and 1 atm. total pressure, and the distillate contains 24 per cent by weight of water. (*a*) Calculate the molecular weight of the substance distilled. (*b*) This substance boils at 130°. Calculate its molal heat of evaporation.

21. The distribution ratio C_w/C_t for acetone between water and toluene is 2.05. The constant $C_w/p = k_1$ is 2.8 for acetone in water, when the concentrations are in moles per liter and the pressures in millimeters of mercury. (*a*) Calculate the moles of acetone extracted from 650 ml. of water containing 0.25 mole of acetone, if it is shaken three successive times with 50-ml. portions of pure toluene. (*b*) Calculate the constant $C_t/p = k_2$ for acetone dissolved in toluene.

22. (*a*) If 1 gal. of glycerol and 3 gal. of water form the solution in an automobile radiator, at what temperature will ice begin to separate out of the solution? (*b*) What weight of ice will deposit from this solution at 0°F. (= −17.8°C.)? A gallon of water weighs 3785 grams; glycerol ($C_3H_8O_3$ = 92) has a density of 1.26, the latent heat of fusion of ice is 79 cal. per gram. (*c*) Repeat the calculation of the weight of ice deposited at 0° from a solution of 1 gal. of alcohol (C_2H_5OH = 46, density 0.79) in 3 gal. of water.

23. Naphthalene ($C_{10}H_8$ = 128) is soluble in benzene and not volatile from the solution. The vapor pressure of a solution of 90 grams of naphthalene in 1000 grams of benzene (C_6H_6 = 78, b. pt. 80.1°) is 0.80 atm. at 75°, the latent heat of evaporation of benzene is 7600 cal. per mole. (*a*) Calculate the vapor pressure of pure benzene at 75°. (*b*) Calculate the boiling point of the solution.

24. Mixtures of carbon tetrachloride and ethylene dichloride are partly distilled, and the equilibrium vapor compositions are determined from the ***boiling points*** of the first portion of each distillate. The data are as follows:

Mole per cent $C_2H_4Cl_2$ in liquid	0	10	30	60	80	90	100
Boiling point of liquid	76.5	75.7	75.3	76.5	78.5	80.2	82.7
Boiling point of distillate	76.5	75.5	75.3	75.7	77.0	78.5	82.7

Sketch the distillation diagram, showing vapor composition by a dotted line. Estimate from the diagram the quantity and composition of distillate and residue resulting if 1000 grams of a liquid mixture of 70 mole per cent $C_2H_4Cl_2$ was distilled until the boiling point rose 2°.

25. Benzophenone ($C_6H_5COC_6H_5 = 182$, m. pt. 47.7°) and diphenyl ($C_{12}H_{10} = 154$, m. pt. 69°) mix in all proportions in the liquid phase. A solution containing 22.8 mole per cent diphenyl begins to deposit solid benzophenone at 35.0°, and a solution containing 78.0 mole per cent diphenyl begins to deposit solid diphenyl at 56.2°. (*a*) Calculate the freezing-point constants $RT_0^2/\Delta H_m$ for these substances. (*b*) Considering first one and then the other as the solvent, calculate the composition of a mixture of these substances that would freeze at 25.2°. The freezing-point curves are found by experiment to intersect at 39.3 mole per cent diphenyl and at 25.2°. [LEE and WARNER, *J. Am. Chem. Soc.*, **55**, 209 (1933).]

26. Nitrobenzene ($C_6H_5NO_2 = 123$) is only slightly soluble in water. At 99.3° the two solutions contain 0.12 mole per cent nitrobenzene and 91.2 mole per cent nitrobenzene, respectively. The vapor pressure of each of the solutions is 1.00 atm. at 99.3°, and at 99.3° the vapor pressure of pure nitrobenzene is 0.0275 atm. (*a*) What is the composition of the vapor in equilibrium with the solutions, in mole fraction, and in weight fraction? (*b*) Calculate the vapor pressure of water at 99.3° from the data in this problem.

27. Equilibrium mole fractions of acetone in the liquid (x_a) and vapor (y_a) for mixtures of acetone and chloroform at 1 atm. total pressure change with temperature as follows:

t°C	56°	59°	62.5°	65°	63.5°	61°
x_a	0	0.20	0.40	0.65	0.80	1.0
y_a	0	0.11	0.31	0.65	0.88	1.0

(*a*) Draw a temperature-composition diagram for this system. (*b*) A liquid mixture of 1 mole of chloroform and 4 moles of acetone is distilled until the boiling point rises to 60°, and the distillate is collected in a single portion. Calculate the weight of distillate obtained. (*c*) A mixture of 1 mole of chloroform and 4 moles of acetone is completely fractionated by repeated distillation. Calculate the weight of distillate and weight of residue obtained.

28. The atomic heat of fusion of cadmium at its melting point (596°K.) is 1460 cal., the atomic heat of fusion of bismuth at its melting point (546°K.) is 2500 cal., the liquids mix in all proportions, and both have monatomic molecules. (*a*) Calculate the temperature at which a solution containing 10 *atomic* per cent bismuth would be in equilibrium with solid cadmium and the temperature at which a solution containing 10 *atomic* per cent cadmium would be in equilibrium with solid bismuth. (*b*) Calculate the freezing point of a solution containing 40 *weight* per cent cadmium, assuming first cadmium and then bismuth to be the solvent. (Experiment shows that a solution containing 40 weight per cent cadmium is in equilibrium with both solid metals at 413°K.)

29. The ratio π/C of the osmotic pressure (in millimeters of Hg) to concentration (in grams per liter) for a solution of serum albumin in water at 25° changes with concentration C as follows.

π/C	0.430	0.385	0.335	0.315
C	73	50	30	18

(*a*) Calculate the molecular weight of the solute from the limiting π/C (*b*) Calculate the freezing-point depression for the solution containing 30 grams per liter

30. The following table gives p, the partial pressure of HCl in atmospheres, and x, the mole fraction of HCl in CCl_4 at 25°:

p	0.235	0.500	0.559	0.721	0.872
x	0.00379	0.00803	0.00922	0.01190	0.01415

(*a*) Calculate the Henry's law constant k as defined in equation (4) for this system. (*b*) From the average value of k calculate the constants k' and k''' as defined in equation (5) for this system, taking the density of CCl_4 as 1.498 at 25° (*c*) Calculate the Bunsen coefficient α as defined on page 186 for this system at 25°. [Howland, Miller, and Willard, *J Am. Chem. Soc.*, **63,** 2807 (1943)]

CHAPTER VII

SOLUTIONS OF IONIZED SOLUTES

This chapter presents some experimental facts relating to vapor pressures, freezing points, conductances, and other properties of solutions in which ions rather than molecules are the important solutes; it considers the products formed when an electric current passes between electrodes in these solutions, the changes in the quantity of solutes near the electrodes, and the interpretation of these effects in terms of the velocities and other properties of the ions. After the necessary facts have been presented, the underlying theory will be considered.

The standard methods for determining molecular weights of solutes, such as were described in the previous chapter, lead to impossible values when applied to solutions of inorganic salts in water. For example, the freezing-point depression of a solution of 30 grams of sodium chloride in 1000 grams of water is about 1 7°, which would indicate a molecular weight of 32, while 58.5 is the sum of the atomic weights of sodium and chlorine. The vapor density of hydrogen chloride agrees with the common formula HCl, but the freezing-point depression for 3.65 grams of HCl in 1000 grams of water is 0.35° in place of 0.186°, which would be expected of 0 1 mole of "ideal" solute. Similar effects are found for almost all inorganic solutes in water.

Such solutions conduct electricity to a moderate extent, while the solutions studied in the previous chapter have only negligible conductances.[1] From a study of the properties of these solutions, Arrhenius suggested that the solutes in conducting solutions are dissociated into charged particles called ions; and since

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[1] Even the best conducting *solutions* are poor conductors compared with metals. For example, the resistance of a centimeter cube of molal potassium chloride solution at 20° is about 10 ohms A copper wire of 1 sq. cm. cross section and of this resistance would be about 35 miles long. A centimeter cube of molal sugar solution would have a resistance of about 10 megohms. Thus the conductances of the three types of systems are of different orders of magnitude.

this results in the formation of two effective moles of solute ion for each formula weight of sodium chloride (for example) that ionized, a partial explanation of the small molecular weights was at hand. The anomalous molecular weights were always less than the formula weight but greater than half of it for solutes of this type, and they decreased with decreasing concentration. He therefore assumed that ionization was incomplete, that it was a dissociation equilibrium that changed with concentration, as would be true of any dissociation. The original term was "electrolytic dissociation" rather than ionization.

Experimental work upon the properties of aqueous solutions was begun about 1890 by Arrhenius, Kohlrausch, Ostwald, van't Hoff, and Hittorf and continued by many others until sufficient data were available for a fairly comprehensive theory that explained the behavior of these solutions "within the experimental error." But as experimental errors were largely eliminated, it became evident that the theory was unable to explain many of the experimental facts. For example, the "fractional ionization" as derived from mole numbers (page 237) or from the conductance ratio (page 276) did not change with concentration in the way to be expected from the laws of chemical equilibrium Moreover, the extent of ionization in a given solution as measured by the two methods was not the same. There was much discussion of the "abnormality of strong electrolytes" but no clear definition of the term "extent of ionization." If ionization meant the transfer of an electron from sodium to chlorine, ionization was complete in any solution, and we now believe that this effect attends the formation of sodium chloride from its elements. If complete ionization meant the separation of the ions by dilution to such an extent that they were "normal solutes" completely freed from influence upon one another, there was no evidence that this condition was attained in the most dilute solutions that could be studied experimentally.

Suggestions of "complete ionization" were occasionally heard before 1910, and between 1915 and 1925 most physical chemists accepted the idea that "strong" (highly ionized) electrolytes were completely ionized. Of course, this idea was not applied to "weak," or slightly ionized, solutes such as ammonium hydroxide or acetic acid, for there is no evidence that they are ionized more than a few per cent in solutions of moderate concentration. The assumption of complete ionization for "strong" electrolytes meant only that an effort would be made to explain the properties of these solutions on grounds other than a supposed fractional ionization, namely, an interionic attraction existing between the ions of opposite charge.

A large amount of experimental work on solutions is still in progress in many laboratories; extensions and revisions of theories are still under way; and while a fairly satisfactory general theory has been developed, much still remains to be done. Under these circumstances it seems best to present the bulk of the experimental evidence first, then the interpretation that is beyond question, then a summary of the older theory and its shortcomings, and finally a brief review of the newer theory.

Types of Electrolytes.—Ionizing solutes may be divided into classes according to their products upon ionization. Simple binary (or uni-univalent) electrolytes, such as hydrochloric acid, sodium nitrate, and potassium acetate, yield a single positive ion bearing a unit positive charge, or having lost 1 electron, and a single negative ion bearing a unit negative charge, or having acquired 1 electron. Solutes of this type exhibit the simplest phenomena in solution and have been more extensively studied than salts of other types. Another simple type of ionization is shown by copper sulfate and other salts; each ion bears two units of electricity, but a molecule forms only two ions. The remaining types of ionized solutes are more puzzling in their behavior and more difficult to study experimentally, because of the possibility of ionization in different ways or in different steps. Thus sulfuric acid ionizes according to the reaction

$$H_2SO_4 = H^+ + HSO_4^-$$

and the negative ion may ionize further.

$$HSO_4^- = H^+ + SO_4^{--}$$

The formation of intermediate ions of the HSO_4^- type is very common in the ionization of weak acids, which form ions such as HS^-, HCO_3^-, HSO_3^-, and HPO_4^{--}. These are the important negative ions in solutions of NaHS, $NaHCO_3$, $NaHSO_3$, and Na_2HPO_4, respectively. The presence of ions such as $ZnCl^+$ in zinc chloride solutions is also a possibility, and the evidence for ions of the composition $FeCl^{++}$ and $FeCl_2^+$ in ferric chloride solution is convincing. No satisfactory *general* methods have been devised for establishing definitely the presence or absence of these intermediate ions.[1]

Mole Numbers for Ionized Solutes.—We have defined a molal solution as one containing a mole or formula weight of solute per 1000 grams of solvent and a normal solution as one containing a chemical equivalent of solute per liter of solution. In this chapter we adhere to these definitions, of course, but we do not find by experiment that a mole of a salt produces the effect upon vapor pressure or freezing point that would be expected of a nonionized solute. For our convenience in studying the results of experiment, we define a quantity called the mole number, which van't Hoff designated by i, and which is the ratio of the moles of solute as calculated from a vapor-pressure lowering (or other change) to the moles of solute as indicated by the conventional formula weight. Thus, the vapor-pressure lowering produced by 58.5 grams of sodium chloride in 1000 grams of water at 18° is 0.475 mm , and Raoult's law indicates that 1.75 moles of ideal solute in 1000 grams of water produces this effect. Hence 1.75 is the mole number for 1m sodium chloride at 18°. The freezing-point depression of a solution of 46.8 grams of sodium chloride in 1000 grams of water is 2 705°, and the ratio 2.705/1.86 = 1.455 indicates 1.455 moles of solute per 1000 grams of water. From the weight composition of the solution,

$$46.8/58.5 = 0.80$$

mole of solute, and 1.455/0.80 = 1.82 is thus the mole number for 0.80m. NaCl at the freezing point.

It was formerly supposed that the change of i with the concentration was due to changing fractional ionization and that for an electrolyte of the A^+B^- type, $\alpha = i - 1$ measured the extent of ionization. From the fact that $i = 2.15$ for 1m. LiBr it is

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[1] Experiments in which solutions of the chlorides of Ba, Sr, Ca, Zn, Cd, Co, Mg, Ni, or Cu were shaken with ammonium permutite to equilibrium indicate that no ions of the type MCl^+ exist below normal concentrations. [Günther-Schulze, *Z Elektrochem.*, **28**, 387 (1922)] On the other hand, transference data for concentrated solutions of cadmium chloride are difficult to interpret unless $CdCl^+$ ions exist in solution, and experiments upon the behavior of sulfuric acid indicate definitely the presence of HSO_4^- ions in solution. There is also good evidence for the existence of $PbCl^+$ in lead chloride solutions and for $PbOH^+$ as the hydrolysis product for lead ion

evident that mole numbers do not measure the extent of ionization. Other univalent electrolytes also have mole numbers greater than 2 at high concentrations, though all these mole numbers fall below 2 at lower concentrations and again approach 2 at the limit of dilution.

Another quantity sometimes used in discussing freezing-point or vapor-pressure data of solutions of electrolytes is the "osmotic coefficient" φ, which is i divided by the number of ions formed by the dissociation of 1 mole Thus, $\varphi = i/2$ for NaCl or $MgSO_4$ and $\varphi = i/3$ for $MgCl_2$ or H_2SO_4.

Vapor-pressure Lowering for Ionized Solutes.—Table 42 gives the vapor pressures of some solutions of electrolytes in water at 18°. The data show that solutions of the same molality do not have the same vapor pressure, and hence i depends upon the particular solute as well as upon the ionic type. Because of the serious experimental difficulties, few precise measurements of vapor pressures below 1*m*. have been made.

TABLE 42—VAPOR PRESSURES OF AQUEOUS SOLUTIONS[1] AT 18°
(p_0 = 15 48 mm at 18°)

Molality	Vapor pressure, mm. Hg			
	LiBr	NaCl	LiCl	KCl
1 00	14 90	15 02	14 94	15 01
2 00	14 18	14 46	14 27	14 52
3 00	13 34	13 88	13 46	14 00
4 00	12 32	13 19	12 57	13 48
5 00	11 29	12 46	11 55	

Freezing Points of Ionized Solutes.—Data are available in much larger quantities for the freezing-point depressions produced by salts; the data in Table 43 may be taken as typical of modern work of high quality. One form of apparatus for such work is shown in Fig. 37. It will be noted that the mole number, which is obtained by dividing ΔT_f by 1.86*m*. in Table 43,

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[1] The data of A. Lannung, *Z. physik. Chem.*, (*A*) **170,** 139 (1934), were plotted on a large graph from which vapor pressures at these concentrations have been read. He gives data at irregular concentrations up to saturation for all of the alkali halides in aqueous solution at 18°. Other data on vapor pressures of salt solutions will be found in Table 53.

is very far from unity and that it varies with the concentration. Like the mole numbers based on vapor pressures, they are not the same for different salts at the same concentration.

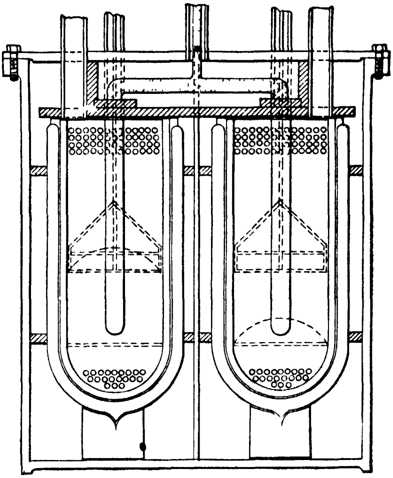

FIG. 37.—Freezing-point apparatus.

This difference is particularly noticeable when salts of different types, such as potassium nitrate and magnesium sulfate, are compared.

TABLE 43.—FREEZING POINTS OF AQUEOUS SALT SOLUTIONS[1]

Molality	Freezing-point depression			
	KNO_3	$LiNO_3$	NaCl	$MgSO_4$
0.01	0.03587	0.03607	0.03606	0.0300
0.02	0.07072	0.07159	0.07144	0.0565
0.05	0.1719	0.1769	0.1758	0.1294
0.10	0.3331	0.3762	0.3470	0.2420
0.20	0.6370	0.7015	0.6849	0.4504
0.50	1.414	1.786	1.692	1.0180
0.80	2.144	2.928	2.705	

An examination of the available data upon freezing points of salts in dilute aqueous solution shows that salts of the same type

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[1] SCATCHARD, PRENTISS, and JONES, *J. Am. Chem. Soc.*, **54**, 2690 (1932), **55**, 4335 (1933). The data for $MgSO_4$ are by Hall and Harkins, *ibid.*, **38**, 2672 (1916).

have roughly the same mole numbers at a given concentration. Thus for salts of the KCl type the maximum and minimum mole numbers for 0.1*m*. were 1.90 and 1.78. Some of the data for other salts are shown in Table 44.

TABLE 44.—MOLE NUMBERS DERIVED FROM FREEZING-POINT LOWERINGS[1]

Solute	Molal concentration								
	0.005	0.010	0.020	0.050	0.10	0.20	0.50	1.00	2.00
HCl	1.96	1.94	1.92	1.90	1.89	1.90	1.98	2.12	2.38
$AgNO_3$	...	1.94	1.90	1.84	1.79	1.72	1.59	1.42	1.17
NaCl	1.95	1.94	1.91	1.90	1.87	1.83	1.81	1.81	1.86
KCl	1.96	1.94	1.92	1.89	1.86	1.83	1.78	1.75	1.73
KNO_3	1.96	1.93	1.90	1.85	1.78	1.70	1.55	1.38	
NH_4NO_3	....	1.92	1.90	1.87	1.83	1.77	1.68	1.57	1.43
$Pb(NO_3)_2$	2.74	2.64	2.51	2.30	2.13	1.93	1.57	1.31	
$ZnCl_2$	2.84	2.77	2.71	2.66	2.66	2.67	2.70	2.80	2.95
$MgCl_2$	..	2.72	....	2.68	2.66	2.68	2.90	3.42	4.8
$MgSO_4$	1.62	1.57	....	1.30	1.21	1.13	1.07	1.09	
$CuSO_4$	1.55	1.45	....	1.22	1.12	1.03	0.93	0.92	
H_2SO_4	2.59	2.47	....	2.21	2.17	2.04	1.99	2.18	2.74

Boiling-point elevations, like freezing-point depressions, measure the change in vapor pressure of solvent caused by decreased mole fraction of solvent and thus furnish a measure of the mole number. Mole numbers change but little with temperature, and the freezing-point depressions are easier to measure precisely, so that there are few data based on boiling points. The following data for silver nitrate are typical:

Molality	0.05	0.20	0.50	1.0
Mole number	1.82	1.70	1.69	1.59

It will be evident from the mole numbers based on any of these methods that something fundamentally different in the properties of the solute is indicated. No slight deviation from the laws of ideal solutions can explain them. The fourth line of Table 44 does not mean that potassium chloride molecules deviate from the behavior of an ideal solute 96 to 73 per cent, depending upon the concentration, and it is improbable that dissociation or

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[1] Based upon freezing points from "International Critical Tables," Vol. IV, pp. 254–263.

ionization to this extent is alone responsible. We shall postpone a discussion of the mole numbers until other important experimental facts have been presented.

Conduction of Electricity.—Aqueous solutions which have the properties given in the preceding paragraphs also conduct electricity, while those which do not show these deviations from the molal properties of ideal solutions have negligible conductances. Because of this property of conducting electricity, substances that ionize in solution are often called "electrolytes." There is one fundamental difference between the conduction of these solutions and that of the metals. Metallic conduction is not accompanied by the movement of matter, while *electrolytic conduction* is always attended by chemical reactions at the electrodes, in which electricity is given to uncharged atoms (or atom groups) or is accepted from them, and by the motion of charged particles through the solution. For example, when an electric current is passed through an aqueous solution of copper chloride between chemically inert electrodes, metallic copper is plated on the negative electrode, chlorine gas is evolved at the positive electrode, and concentration changes occur near both electrodes which indicate that both cupric ions and chloride ions have taken part in carrying electricity through the solution. Corresponding effects are observed when electricity is passed through any conducting solution, though as we shall see presently it is not necessarily true that the ions which form or discharge at the electrodes during electrolysis are those which carry most of the electricity through the solution. The products of electrolysis depend on the material of the electrodes, the current density, and the concentration of solute, as well as on the nature of the solute.

The decomposition that results when electricity passes through a solution is called electrolysis; the metallic conductors through which electricity enters or leaves the solution are called the anode and cathode, or the electrodes. At the anode, or positive electrode, a chemical reaction takes place by which electrons are given to the metal and oxidation takes place. At the cathode, electrons are received from the metal, and chemical reduction takes place. During these reactions charged ions move through the solution in opposite directions at characteristic velocities and in such quantities that the sum of the equivalents of positive ion crossing any boundary in their motion toward the cathode and the equivalents of negative ion crossing this boundary in their motion toward the anode is equal to the total quantity of electricity passed through the solution. These processes occur simultaneously of course, but we shall consider the electrode reaction first and then the motion of the ions through the solution.

Faraday's law states that when electricity passes through a solution the total quantity of chemical change produced at *each electrode* is strictly proportional to the quantity of electricity and dependent on that alone and that in electrolysis chemically equivalent quantities of substances are produced or destroyed at the electrodes. The nature of these chemical changes depends on the ions in solution and the material of the electrodes, but the total quantity of chemical change, measured in equivalents, is independent of every factor except the quantity of electricity. The electromotive series or potential series, which is given in Table 99, gives the anode potentials for electrode reactions. Of all possible anode reactions, the one of highest potential tends to take place first. Electrode potentials are given for anode reactions or oxidations, and since cathode reactions are all reductions the one of lowest anode potential has the greatest tendency to act as a cathode; hence, of all possible cathode reactions, that of the lowest potential in the electromotive series tends to take place first. These potentials vary with the concentration of the solute in a way we are to consider in Chap. XIX, but in the examples considered here the differences are great enough for changing concentration not to change the order in which the reactions occur.

In order to illustrate the application of Faraday's law, suppose four vessels, each containing a solution and a pair of electrodes, to be arranged as shown in Fig. 38 and connected in series so that the different chemical effects of a fixed quantity of electricity may be observed. The anode is defined as the electrode at which electrons are given to the electrode, and therefore the left-hand electrode is the anode in each vessel; it is the electrode at which oxidation takes place. If a current is passed through these cells in the direction indicated, the products of electrolysis will appear as deposits on the electrodes, as gases evolved from solution, or as new solutes in solution near the electrodes, as follows: (*a*) chlorine is evolved from the carbon anode, hydrogen is evolved from the platinum cathode, and sodium hydroxide is formed in the solution around it; (*b*) zinc chloride is formed in solution around the zinc anode, silver chloride is reduced to silver at the cathode, and sodium chloride is formed in the solution around this electrode; (*c*) oxygen is evolved from the platinum anode, nitric acid forms in the solution around it, and silver is deposited upon the platinum cathode; (*d*) oxygen is evolved from the anode, sulfuric acid is formed in solution near it, and copper is deposited upon the cathode.

The solutions are not assumed to be of the same strength or at the same temperature or of the same resistance. The only conditions imposed are that all the electricity which passes through one cell must pass through the others and that the current density at the electrodes is such that the reacting ions reach the electrodes by migration, diffusion, or convection fast enough to produce clean chemical reactions free from "side reactions." This condition is imposed here because Faraday's law governs the *total quantity* of chemical reaction produced by a given quantity of electricity even when several reactions occur at an electrode, but it does not say what ions react. At the cathode in the copper sulfate solution, for example, if the current density is too high, both hydrogen and copper plate out, since copper ions cannot reach the electrode and discharge fast enough to carry the total current. Under these conditions Faraday's law accurately describes the total number of equivalents of hydrogen plus copper discharged, but the weight of copper deposited will not correspond to the total quantity of electricity.

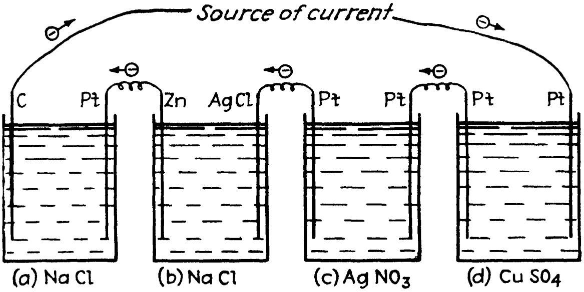

FIG 38 —Electrolysis diagram for Faraday's law

A quantitative examination of the products of electrolysis will show that the sulfuric acid formed at the anode in *d* is just sufficient to neutralize the sodium hydroxide formed at the cathode in *a*; that the chlorine evolved from the anode in *a* will convert all the silver deposited on the cathode in *c* into silver chloride or all the copper on the cathode from *d* into copper chloride; that the silver formed from silver chloride in *b* is equal in weight to that deposited in *c*; that the sodium hydroxide of *a* will precipitate all the zinc ion formed at the anode in *b* as zinc hydroxide; and that the zinc hydroxide so formed is just sufficient to react with the sulfuric acid of *d*.

All these chemical details may be summarized in the single statement that a fixed quantity of electricity passing through a solution produces chemical substances at the electrodes which are equivalent to one another. Special experimental conditions, such as control of current density and concentration, are often required to restrict each electrode reaction to a *single* chemical change, as has been said before; and when these precautions are observed, the quantity of chemical change as shown by a *single* electrode reaction is proportional to the quantity of electricity and independent of every other influence.

Since the ampere is defined as a uniform current that deposits 0 0011180 gram of silver from silver nitrate solution each second and since the atomic weight of silver is 107.880, the ratio 107 880/0.0011180 gives the number of ampere-seconds or coulombs of electricity required to deposit a chemical equivalent of silver. This quantity is 96,494 amp -sec. (usually rounded off to 96,500 except in the most precise calculations), and it is called 1 *faraday* of electricity

Faraday's law may be restated in terms of this constant as follows: The passage of 1 faraday of electricity through an electrolytic solution produces one chemical equivalent of some chemical change at *each electrode*. Faraday's law is an exact law to which there are no known exceptions; it has been confirmed by experiments upon the widest variety of solutes in water and for solutions of silver nitrate in fused potassium nitrate[1] and in pyridine[2] and other nonaqueous solutions. As

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[1] RICHARDS and STULL, *Proc. Am Acad Arts Sci* , **38,** 409 (1902). Silver was deposited from an aqueous solution of silver nitrate at 20° and in the same circuit from silver nitrate dissolved in fused sodium nitrate and potassium nitrate at 250°. The weights of silver deposited agreed within 1 part in 20,000.

[2] KAHLENBERG, *J Phys. Chem.*, **4,** 349 (1900).

the precision of the experiments is increased, the equivalence of the chemical changes becomes closer.

Calculation of Avogadro's Number.—A univalent positive ion is an atom or group of atoms that has lost an electron, and its discharge at a cathode takes place when it acquires the electron. The ratio of Faraday's constant to the electronic charge is thus the number of electrons in a faraday, which is the number of atoms in a gram atom, or Avogadro's number. In the absolute electromagnetic system of units, 1 faraday is 9649.4 absolute coulombs, and in the same units the charge of an electron is $1\,598 \times 10^{-20}$, whence Avogadro's number is

$$\frac{9649\ 4}{1\ 598 \times 10^{-20}} = 6.03 \times 10^{23}$$

It will be seen that this value is in agreement with determinations by the other methods given on pages 71 and 170. It is one of the most accurate values for Avogadro's number that we have at the present time.

Electrode Reactions.—It has been stated above that Faraday's law says nothing as to which of several possible reactions will occur at an electrode; it describes only the total quantity of chemical change produced. The electric potential determines which reaction occurs; if the current density is not too high, only the reaction of lowest required potential takes place Electrode potentials such as those listed in Table 99 are expressed in volts for changes in state by which the ions concerned are used reversibly at unit activity or formed reversibly at unit activity These potentials change with the concentrations of ion solute in a way that is explained in Chap. XIX, but we may note here that for univalent ions the potential changes about 0.06 volt for a tenfold change in ion concentration. For example, in the first cell in Fig. 38, hydrogen was evolved at the cathode and no sodium was deposited. It may be seen in Table 99 that sodium is near the top of the list of anodic potentials and thus that it would require a high opposing potential to cause the deposition of sodium at the cathode, whereas hydrogen is lower in the list and would require a smaller potential for its evolution. Quantitatively, the potential required to deposit sodium is about 3.0 volts higher than that required to discharge hydrogen ions under these conditions. As hydrogen ions are present from the slight ionization of water, these are discharged and the required potential for sodium is never reached. Similarly in *b*, the potential required to discharge chlorine at the zinc anode is 2 volts higher than that required for zinc to pass into solution. *The reaction requiring the lowest potential always takes place first.* There are, of course, hydrogen ions from water in the silver nitrate solution of *c*, but the potential required to discharge them is higher than that required for silver by about 1.2 volts; therefore, the metal deposits. In *a*, chlorine is evolved at the anode in place of oxygen from the hydroxide ions of water, for chlorine has a lower discharge potential than oxygen under these conditions.

If we denote a faraday of negative electricity, or Avogadro's number of electrons, by the symbol e^-, electrode reactions are readily described by chemical equations in which this quantity is written as if it were a reacting substance or a reaction product. Thus, the electrode reactions described on page 240 are

$$\left.\begin{aligned} &\mathrm{Cl^-} = \tfrac{1}{2}\mathrm{Cl_2} + e^- \\ &\mathrm{H_2O} + e^- = \mathrm{OH^-} + \tfrac{1}{2}\mathrm{H_2} \end{aligned}\right\} \qquad (a)$$

$$\left.\begin{aligned} &\tfrac{1}{2}\mathrm{Zn} = \tfrac{1}{2}\mathrm{Zn^{++}} + e^- \\ &\mathrm{AgCl} + e^- = \mathrm{Ag} + \mathrm{Cl^-} \end{aligned}\right\} \qquad (b)$$

$$\left.\begin{aligned} &\tfrac{1}{2}\mathrm{H_2O} = \mathrm{H^+} + \tfrac{1}{4}\mathrm{O_2} + e^- \\ &\mathrm{Ag^+} + e^- = \mathrm{Ag} \end{aligned}\right\} \qquad (c)$$

$$\left.\begin{aligned} &\tfrac{1}{2}\mathrm{H_2O} = \mathrm{H^+} + \tfrac{1}{4}\mathrm{O_2} + e^- \\ &\tfrac{1}{2}\mathrm{Cu^{++}} + e^- = \tfrac{1}{2}\mathrm{Cu} \end{aligned}\right\} \qquad (d)$$

It was stated on page 240 that the products of the anode reaction for nitrate ions on platinum and for sulfate ions on platinum are the same, and we have shown above that neither electrode reaction mentions the negative ion. In each reaction, oxygen is evolved, and hydrogen ions form in solution at the expense of decomposed water. While it is sometimes stated that the sulfate ion or nitrate ion discharges and then reacts with water to form sulfuric acid or nitric acid and oxygen, there is no experimental evidence for these statements. Even if this peculiar mechanism were true, it is a fact that no change in the number of sulfate ions finally results from the electrode reaction. The equations as written express the observed *facts*, and nothing is to be gained by combining these facts with fanciful assumptions such as the deposition of nitrate ions or sulfate ions or the plating out of sodium metal on the cathode from an aqueous solution, followed by a reaction between sodium and water to produce hydrogen and sodium hydroxide.

The common effects observed at an anode are (1) the discharge of a negative ion when it is not an oxygenated ion and when the anode metal is inert, (2) the formation of a positive ion when the metal of the electrode forms ions that do not precipitate with those of opposite charge in the solution, (3) the formation of an insoluble salt when precipitation takes place between the ion of the anode metal and the negative ion in solution, and (4) the evolution of oxygen gas. This evolution of oxygen is attended by the loss of hydroxyl ions and the formation of water in alkaline solutions, as shown by the reaction

$$OH^- = \frac{1}{2}H_2O + \frac{1}{4}O_2 + e^-$$

and by the decomposition of water with the formation of hydrogen ions when the solution is neutral or acid, as shown by the equation

$$\frac{1}{2}H_2O = H^+ + \frac{1}{4}O_2 + e^-$$

Although this is not a full list of the chemical effects observed at anodes, it will suffice for the purpose in this chapter and we shall return to the topic later.

The common effects observed at a cathode are (1) the discharge of a positive ion when the ion is below hydrogen in the electromotive series, (2) the formation of a negative ion from a reducible material such as chlorine gas, (3) the reduction of an insoluble salt with the formation of a negative ion into solution, and (4) the evolution of hydrogen gas when the positive ion lies above hydrogen in the electromotive series. In acid solutions this is attended by the loss of hydrogen ions from solution as shown by the reaction

$$H^+ + e^- = \frac{1}{2}H_2$$

and in neutral or alkaline solutions it is attended by the formation of hydroxyl ions and the decomposition of water as shown by the reaction

$$H_2O + e^- = \frac{1}{2}H_2 + OH^-$$

Measurement of the Quantity of Electricity.—The number of coulombs of electricity passing through an electric circuit is best measured through an application of Faraday's law, by weighing the silver deposited upon a platinum cathode from silver nitrate. Since this reaction is the basis of the definition of the international ampere, it has been most carefully studied to devise apparatus and procedures for limiting the cathode reaction to this single effect.

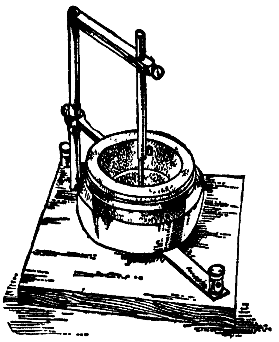

FIG. 39.—Porous-cup type of silver coulometer.

The standard coulometer in which this is done is shown in Fig 39,[1] in which a porous cup of unglazed porcelain surrounds an anode of pure silver and is suspended above a platinum dish serving as a cathode on which silver deposits Both dish and cup are filled with silver nitrate solution After electrolysis the silver deposit is carefully washed free of silver nitrate and dried and weighed.[2]

Unless precautions are taken to prevent the electrolyte around the anode from reaching the cathode, deposits are obtained that are too heavy, owing to the formation of some unknown substance at the anode (possibly colloidal charged silver), which deposits and which is not removed by washing

When commercial quantities of electricity are involved, the use of silver is out of the question, and copper is usually deposited from copper sulfate for this purpose Lead from solutions of lead silicofluoride may also be used, or the volume of hydrogen evolved from a cathode in acid solution may be measured The commercial processes of copper refining and electroplating are everyday confirmations of the law of electrolysis. It is the universal experience in such processes that the weight of metal deposited is strictly proportional to the quantity of electricity passed through the electroplating cell when the current is not allowed to cause other reactions, such as the evolution of gas from the electrodes. The character and adherence of the metal film depend on current density, the concentration of electrolyte, efficient stirring, and temperature control, but the weight of metal deposited is independent of these factors.

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[1] *Bull. U.S. Bur. Standards*, **1,** 3 (1904).

[2] Special reference should be made to the work of the U.S. Bureau of Standards and England's National Physical Laboratory. Important papers will be found in *Bull. U.S. Bur. Standards*, **1,** 1 (1904); **9,** 494 (1912); **10,** 425; **11,** 220, 555 (1914); *Sci. Paper*, **283** (1916); Richards, *Proc. Am. Acad. Arts Sci.*, **37,** 415 (1902); **44,** 91 (1908); *J. Am. Chem. Soc.*, **37,** 692 (1915); Smith, Mather, and Lowry, *Nat. Phys. Lab. Researches*, **4,** 125.

Atomic-weight Ratios from Electrolysis.—Since Faraday's law is an exact law, an electric current passing through solutions may be used to liberate or deposit chemically equivalent quantities of substances from solutions in the same circuit, whether or not the reactions take place in the same solution. It is necessary only that the chosen electrode reactions involve a single ion solute and a single product. Two electrode reactions that meet this requirement are

$$Ag^+ + e^- = Ag$$

and

$$I^- = \tfrac{1}{2}I_2 + e^-$$

Since silver iodide is an insoluble salt, these reactions may not be carried out in the same solution, but a suitable experimental arrangement is a silver coulometer in series with electrodes dipping into potassium iodide solution. Data that show the experimental results of electrolysis with this arrangement are given in Table 45. Upon dividing the weights of iodine in the second column by the corresponding weights of silver in the first column, the ratio Ag:I will be found to be 1:1.1762. A careful determination of the combining ratio of silver and iodine by gravimetric analysis[2] gave the ratio 1:1.17643, which shows that

TABLE 45.—DATA ILLUSTRATING FARADAY'S LAW[1]

Weight of silver deposited	Weight of iodine deposited	Calculated coulombs		Difference in per cent	Milligrams of iodine per coulomb	Value of the faraday (I = 126.92)
		From silver coulometer	From potential and resistance			
4 10469	4 82862	3,671 45	3,671 53	0 002	1 31518	96,504
4 09903	4 82224	3,666 39	3,666 55	0 004	1 31526	96,498
4 10523	4 82851	3,671 94	3,671 84	0 003	1 31498	96,518
4 10475	4 82860	3,671 51	3,671 61	0 003	1 31515	96,506
4 10027	4 82247	3,667 50	3,667 65	0 004	1 31492	96,523
4.10516	4 82844	3,671 88	3,671.82	0 001	1 31498	96,519

Average value of the faraday: **96,515**

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[1] BATES and VINAL, *ibid.*, **36**, 916 (1914); *Bull. U.S. Bur. Standards*, **10**, 425 (1914).

[2] BAXTER and LUNDSTEDT, *J. Am. Chem. Soc.*, **62**, 1829 (1940).

Faraday's law is accurate within 2 parts in 10,000. There is of course no implication that this small difference is due to any failure of Faraday's law, for the limit of accuracy of the experiments is about 1 part in 10,000.

In the experiments recorded in Table 45 the quantity of electricity was measured from the potential drop across a known resistance and the time of the electrolysis; thus the experiments also yielded a determination of the faraday. If 126.92 is accepted as the atomic weight of iodine, these calculated values of the faraday are shown in the last column of the table.

Resistance and Conductance.—The familiar law of Ohm that the current flowing in a conductor is equal to the applied electromotive force[1] divided by the resistance of the conductor applies also to solutions that conduct electrolytically. This law, $I = E/R$, is often used in a form in which the resistance R is replaced by its reciprocal $1/R$, which is called the conductance. Ohm's law is then

$$I = E \times \text{conductance} \tag{1}$$

The specific resistance of a substance is the resistance of a centimeter cube of it; the reciprocal of this is the *specific conductance*, L. The conductance of any substance increases with its cross section and decreases in proportion to its length. If the specific conductance is L, the conductance of a quantity of material in a form other than a centimeter cube is

$$\text{Conductance} = L\frac{q}{l} \tag{2}$$

where q is the cross section and l the length of the conductor. Conductance is expressed in reciprocal ohms; thus, if the resistance is 175 ohms, the conductance is $1/175 = 0.00572$ reciprocal ohm. The specific conductance of a given salt solution increases almost in proportion to the concentration up to about 0.1 N, and it increases almost linearly with increasing temperature; but the specific conductances of different "strong" electrolytes at the

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[1] If resistance measurements are made with direct current, the applied electromotive force must be corrected for that of the electrolytic cell formed by the products of electrolysis. Measurements of resistance are usually made with alternating current to avoid this correction. The method will be described on p. 254.

same temperature and same moderate concentration may differ from one another by fivefold or more. Exact relations of specific conductance to temperature and concentration are determined by experiment only.

Equivalent Conductance.—The equivalent conductance of a solution at a given concentration is defined as the product of its specific conductance and the volume of solution containing one equivalent of electrolyte. Thus it is the conductance of a sufficient number of centimeter cubes in parallel to contain one equivalent of solute. Denoting the equivalent conductance by the Greek letter lambda, Λ, as is the usual custom, and the concentration as C equivalents per liter of solution, the relations between these two quantities are

$$\Lambda = \frac{1000}{C} L \qquad \text{or} \qquad L = \frac{C}{1000} \Lambda \tag{3}$$

As a means of visualizing the equivalent conductance, consider two parallel electrodes of indefinite extent, 1 cm. apart, between which 1 liter of normal solution is placed. The cross section of the solution is 1000 sq. cm., and the length of the conducting column is 1 cm. Thus, from equation (3), we have

$$\Lambda = L \frac{1}{1000}$$

If this solution is diluted to some lower concentration C, the volume becomes $1000/C$ ml., which is the cross section since the length is still 1 cm. Experimentally the quantities measured are L and C, but the data commonly recorded are Λ and C, for convenient interpolation and for other purposes that will be explained later in the chapter.

Table 46 shows the change of equivalent conductance with concentration for a few electrolytes.[1] It will be noted that for salts of the same ionic type the equivalent conductance increases with decreasing concentration to about the same fractional

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[1] Data for almost all aqueous solutions will be found in "International Critical Tables," Vol. VI, pp. 230–258. Recent work is reported in the current literature of chemistry. See also Kraus, "The Properties of Electrically Conducting Systems," Chemical Catalog Company, New York, 1922, and Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," 1943.

TABLE 46.—EQUIVALENT CONDUCTANCES AT 25°

C	NaCl	KCl	HCl	LiCl	HNO_3	KNO_3	HIO_3
0.0005	124.5	147.8	422.7	113.2	416.2	142.8	386.3
0.0010	123.7	147.0	421.4	112.4	414.6	141.8	383.9
0.0020	122.7	145.8	419.2	111.1	412.9	140.5	379.9
0.0050	120.7	143.6	415.8	109.4	409.0	138.5	370.9
0.010	118.5	141.3	412.0	107.3	405.2	135.8	359.7
0.020	115.8	138.3	407.2	104.6	400.8	132.4	343.0
0.050	111.1	133.7	399.1	100.1	392.5	126.3	310.7
0.100	106.7	129.0	391.3	95.9	384.2	120.2	278.3
0.200	101.6	123.9	379.6	89.9	374.4	113.3	242.2
0.500	93.3	117.2	359.2	81.0	356.6	101.4	219.5
1.000	..	111.9	332.8	73.1	333.2		

C	NaOH	HF	$AgNO_3$	$\frac{1}{2}H_2SO_4$	$\frac{1}{2}CuSO_4$	$\frac{1}{2}BaCl_2$
0.0005	245.6	...	131.6	413.1	121.6	
0.0010	244.7	...	130.5	399.5	115.2	134.5
0.0020	. .	142	128.7	390.3	110.3	131.7
0.0050	240.8	87	127.2	364.9	94.1	127.7
0.0100	238	70	124.8	336.4	83.1	123.7
0.0200	227	56	121.4	308.0	72.2	119.2
0.0500	221	41	115.2	272.6	59.0	111.7
0.100		36	109.1	250.8	50.6	105.3
0.200	...	32	101.8	234.3	43.5	98.6
0.500	.	31		222.5	35.1	88.8
1.00	.				29.3	80.5

extent over a given concentration range. At low concentrations a plot of equivalent conductance against the square root of the equivalent concentration is almost a straight line for all "strong" electrolytes, as may be seen in Fig. 40. It will also be evident from this figure that slightly ionized solutes such as acetic acid or hydrofluoric acid change equivalent conductance with concentration in an entirely different way.

Limiting Equivalent Conductance.—The equivalent conductance continues to increase with dilution down to the lowest concentrations at which experiments are possible for all substances. For salts of the KCl type, Λ at 0.001 N is about 98 per cent of the limiting value determined in the way to be explained below. For so-called "weak" electrolytes, which are slightly ionized at moderate concentrations, the equivalent conductance is still increasing rapidly with decreasing concentration in the most dilute solution that can be measured. The data for

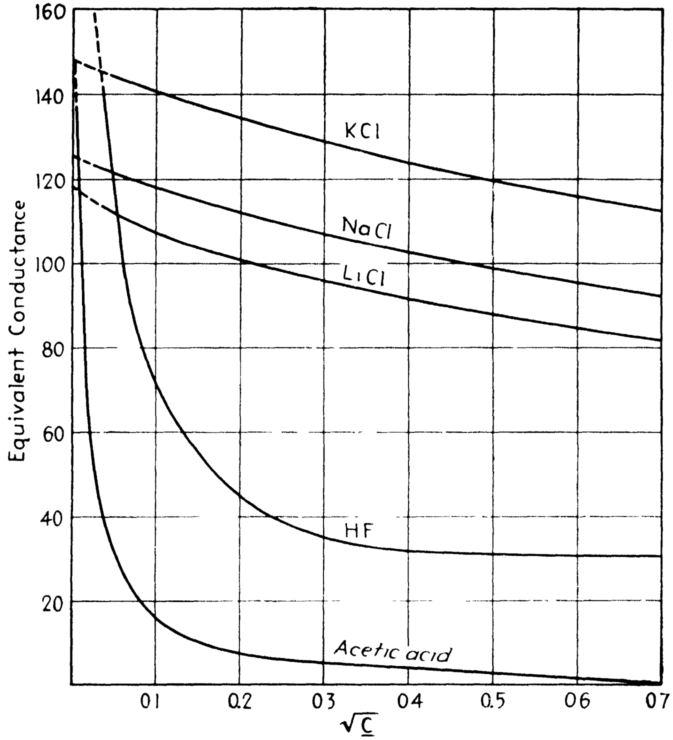

FIG. 40.—Change of equivalent conductance with concentration

very dilute acetic acid[1] and HCl at 25° will illustrate the great difference in these changes with concentration:

C . . .	0.001028	0.0001532	0.0001113	0.0000280
Λ for HCl	421.4	424.4	424.6	425.13
Λ for HAc . .	48.13	112.0	127.7	210.3

There are reasons that will appear below for expecting the equivalent conductance to reach a limit of 426.0 for HCl and a limit of 390.6 for acetic acid, but the limit 390.6 may not be determined from the data quoted above or from measurements on more dilute solutions. The data for other "weak" electrolytes

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[1] MACINNES and SHEDLOVSKY, *J. Am. Chem. Soc.*, **54**, 1429 (1932).

show similar behavior, but the ratio of the conductance at 0.001 N to that at limiting dilution for different weak electrolytes shows no regularity such as that found for strong electrolytes; it may vary a thousandfold. Thus it is evident that the small change of Λ with C for strong electrolytes may not be explained in the same way as the very large change of Λ with C for weak electrolytes. We shall see later that the change of Λ with C for salts is due mainly to decreasing attractions between the charged ions at lower concentrations, while the increase in Λ with decreasing C for weak electrolytes is due mainly to an increased fractional ionization of the solute, which produces an increase in the number of ions available for carrying electricity.

For salts and other highly ionized solutes the limiting conductance may be obtained by plotting the equivalent conductance against some function of the concentration, extrapolating the curve to zero concentration, and reading the intercept It should be understood that this limiting value of the equivalent conductance, which is written Λ_0, is not the conductance of pure water, for in these dilute solutions the slight conductance of the water is subtracted from the measured conductance of the solution to give that due to the solute.

More than 30 functions suitable for this extrapolation have been proposed[1] at one time or another Kohlrausch observed empirically that the relation

$$\Lambda = \Lambda_0 - A\sqrt{C}$$

was valid in dilute solutions of strong electrolytes, where the constant A applied only to a single solute at a single temperature. The equation of Onsager[2] is also of this form, but he is able to calculate the quantity A from the valencies of the ions, the viscosity and dielectric constant of the solvent, and other constants.

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[1] KOHLRAUSCH, *Wiss. Abhandl. phys -tech Reichsanstalt*, **3**, 219 (1900), NOYES and FALK, *J. Am Chem Soc*, **34**, 454 (1912); ONSAGER, *Physik. Z.*, **27**, 388 (1926), **28**, 277 (1927), SHEDLOVSKY, *J. Am. Chem. Soc.*, **54**, 1405 (1932); JONES and BICKFORD, *ibid*, **56**, 602 (1934)

[2] *Physik. Z*, **27**, 388 (1926); **28**, 277 (1927). A discussion of this somewhat complex equation, of the factors that are taken into account in its derivation, and of its applicability and limitations and some illustrations of its use in obtaining limiting conductances are given by MacInnes in *J Franklin Inst*, **225**, 661 (1938).

Recently the conductances of very dilute solutions have been intensively studied and measured The theory of Debye and Hückel, which will be discussed briefly later, was mainly responsible for this renewed interest, but it is beyond the scope of this book to consider the experimental technique or interpretation of the work. Students should consult references such as those below for the details.[1] The limiting conductances for salts and other highly ionized substances, as estimated by the various methods, usually agree within a few tenths of a unit

The limiting equivalent conductance for weak acids and bases may not be obtained from extrapolation of conductance data for the acid itself but is available through a simple procedure. The *difference* between the limits for HCl and NaCl is the same as the difference between the limits for HX and NaX, whatever univalent ion we denote by X, namely, the difference between Λ_0 for H^+ and Na^+. This difference at 25° is 299 7. To obtain Λ_0 for lactic acid at 25°, one need only determine the limit Λ_0 for sodium lactate and add to it 299 7. This limit for sodium lactate is 88.8, and therefore the limiting equivalent conductance of lactic acid at 25° is 388.5. Since lactic acid is a weak acid, the limit cannot be obtained by direct measurement of lactic acid, as has been said before A similar procedure serves for calculating the limiting equivalent conductance of any weak acid. For weak bases, it should be noted that the difference between the limiting equivalent conductances of NaOH and NaCl would be the same as the difference between the limits for BOH and BCl, whatever univalent positive ion we denote by B, namely, the difference between Λ_0 for OH^- and Cl^-, which is 120.7 at 25°. The limiting equivalent conductance of NH_4Cl at 25° is 149.7, and, by adding 120.7 to this quantity, we have 270.4 as the limiting equivalent conductance for NH_4OH at 25°. This limit could not be obtained by direct experiment on dilute NH_4OH. For any solute the limiting equivalent conductance is evidently the sum of the limits for its individual ions, and a method of obtaining these individual conductances is to be given on page 266.

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[1] DAVIES, "The Conductivity of Solutions," John Wiley & Sons, Inc , New York, 1933, JONES and DOLE, *J Am Chem. Soc* , **52,** 2245 (1930), **56,** 602 (1934); SHEDLOVSKY, BROWN, and MACINNES, *Trans. Electrochem Soc* , **66,** 237 (1934); KRAUS ET AL , *J. Am Chem. Soc.,* **55,** 21 (1933); and earlier papers, HARNED and OWEN, *op. cit.*

Conductance Ratio.—The ratio of the equivalent conductance of a solution at some concentration C to its limiting value at the same temperature, which is called the conductance ratio Λ_c/Λ_0, was at first assumed to measure the fractional ionization of the solute at the concentration C. This ratio would be a measure of the extent of ionization if the change in equivalent conductance with concentration were due *only* to an increasing concentration of ions of constant mobility with increasing dilution. But the experiments to be discussed on page 256 show that the ratio of the ionic velocities changes with the concentration, and hence at least one ion changes its velocity with changing concentration. Since the motions of the positive and negative ions in opposite directions through the solution would be influenced by those of opposite charge to an extent that depends on the concentration, it is improbable that the velocity of either ion under a fixed potential gradient is constant There is probably little relation between the conductance ratio and the fractional ionization of any *highly ionized* solute.

The data quoted for salts show that the equivalent conductance increases about 2 per cent below 0 001 N, while for acetic acid the increase below this concentration is about sevenfold

In 0.001 N acetic acid the ionized fraction is not much over 10 per cent; thus the ion concentration is about 0 0001 N, and at this ion concentration the ionic attractions, insofar as they interfere with the conductance, are small. Hence Λ/Λ_0 is almost a measure of the fraction ionized in solutions of *weak electrolytes*. We shall see in Chap IX that for slightly ionized solutes the fraction ionized changes with the concentration in the way to be expected from the laws of chemical equilibrium when Λ/Λ_0 is taken as a measure of this fraction. But we shall also see in the same place that Λ/Λ_0 is not a measure of the fraction ionized for strong electrolytes

Measurement of Conductance.—In laboratory practice the resistance of a solution is measured by means of a Wheatstone bridge, using an alternating current of fairly high frequency from a suitable generator E (Fig 41*a*), with a telephone receiver T, or other convenient apparatus, in place of a galvanometer. A resistance R is chosen for the box of such size that there is a point b near the middle of the bridge wire *abc* at which there is no audible sound in the telephone receiver. Then the resistance of the box is to that of the cell as the corresponding lengths of the uniform resistance wire *abc*; that is, $R_{\text{box}}:R_{\text{cell}} = ab:bc$. The reciprocal of this resistance is the conductance of the cell, and from its dimensions the specific conductance can be calculated by means of equation (2), then the equivalent conductance from equation (3).

For the purpose of reducing electrolysis effects at the electrodes to a minimum, alternating current of low potential is employed at frequencies of 1000 to 5000 cycles, the electrodes of the conductance cell are coated with "platinum black" to increase their effective surface, and the current passing through the cell is made as small as the detector permits. A convenient form of conductance cell with electrodes sealed inside a glass chamber is shown in Fig 41*b* Since the distance between electrodes in such a cell is more difficult to measure than the conductance of a solution between the electrodes, it is customary to determine the "cell constant" L/L' from L', the actual conductance of a standard solution It is more convenient to weigh the salt and the solution than to weigh salt and water, since in the former procedure some of the water may be used in effecting transfer of the salt Suitable conductances, corrected to vacuum weights for both salt and solution, and corrected for conductance of the water (about 10^{-6}), are as follows:[1]

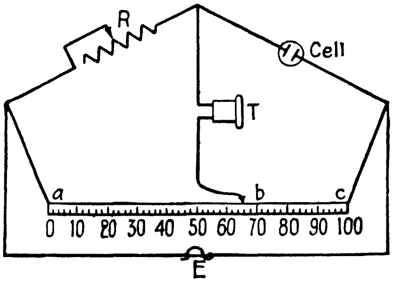

FIG. 41*a*—Arrangement of Wheatstone bridge for measuring conductivity of a solution

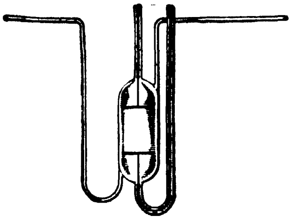

FIG. 41*b*.—Conductance cell, pipet type.

Grams KCl per 1000 grams of solution	Specific conductance		
	0°	18°	25°
71.1352	0.065176	0.097838	0.111342
7.41913	0.0071379	0.0111667	0.0128560
0.745263	0.00077364	0.00122052	0.00140877

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[1] JONES and BRADSHAW, *J. Am Chem Soc*, **55**, 1780 (1933).

Through the use of vacuum-tube generators for the alternating current, new amplifiers, and high-precision bridges, the method of measuring the conductances of solutions has been brought to a high state of perfection Some of these improvements are described by Jones and Josephs, *J Am Chem Soc*, **50,** 1049 (1928) [see also Jones and Bollinger, *ibid*, **51,** 2407 (1929), Jones and Bradshaw, *ibid*, **55,** 1780 (1933)]. A new type of cell, and a screened bridge are described by Shedlovsky, *ibid*, **52,** 1793 (1930), a simpler bridge is described by Luder, *ibid*, **62,** 89 (1940), a cathode-ray oscillograph detector is described by Jones, Mysels, and Juda in *ibid*. **62,** 2919 (1940). The preparation and storage of water of sufficient purity for accurate work on dilute solutions involve repeated distillation and elaborate precautions against contamination [see Kendall, *ibid*, **38,** 2460 (1916), **39,** 9 (1917); Weiland, *ibid*, **40,** 131 (1918)] Apparatus, procedures, errors, calibrations, and an ample bibliography are given in catalog EN-95 of the Leeds & Northrup Co (1938) The electrical characteristics of the bridge assembly are discussed by Acree, Bennett, Gray, and Goldberg in *J Phys. Chem*, **42,** 871 (1938)

Conductance of Pure Water.—As stated above, the conductance of the water used in preparing a solution is subtracted from the measured conductance in determining that due to the salt. Careful experiments have shown that water itself is ionized to a slight extent, such that at 25° the concentration of hydrogen ion (and of hydroxide ion as well) is 0.0000001 N. It is not from this source that most of the error in measuring conductivities of dilute solutions arises, but from the presence of dissolved impurities. Even after careful distillation, water may contain ammonia and carbon dioxide; and it will dissolve sodium and calcium salts from glass in a very short time. Perfectly pure water has a specific resistance of 20,000,000 ohms, ordinary distilled water a specific resistance of perhaps 100,000 ohms, and a good quality of "conductivity water" from 1,000,000 to 10,000,000 ohms. Water of a resistance greater than 1,000,000 ohms per centimeter cube can be preserved in glass for not more than a very few hours—perhaps for a day or so in quartz vessels. For this reason, conductivity water is freshly prepared for a set of measurements, first by distillation in the usual way, then by a second distillation (often directly into the conductivity apparatus) from alkaline permanganate solution, the first third of the distillate being rejected.

Change of Conductance with Temperature.—The equivalent conductance for a given salt at a given concentration increases rapidly with temperature. The data for NaCl in Table 47 are

TABLE 47.—EQUIVALENT CONDUCTANCE OF SODIUM CHLORIDE[1]

Concentration	0	0.0005	0.0010	0.0020	0.0050	0.0100
15°	101.20	99.64	99.00	98.12	96.49	94.88
25°	126.48	124.54	123.77	122.69	120.67	118.55
35°	153.85	151.43	150.47	149.14	146.64	144.03
45°	182.73	179.79	178.62	177.00	173.96	170.78

typical of the behavior of most salts. The change of Λ_0 with changing temperature almost parallels the change in fluidity of water with temperature; namely, each increases about 2 per cent of the value at 0°C for every degree rise in temperature. At moderate concentrations the fractional change in equivalent conductance is slightly less than the change for Λ_0. Since the temperature coefficient of Λ_0 for HCl[2] is less than that for NaCl and the change for NaCl is less than the temperature coefficient of fluidity, it will be evident that factors other than fluidity of the water affect the change of conductance with temperature. In order to show the relative changes, the ratios $\varphi_t/\varphi_{25^\circ}$ for water, $\Lambda_t^0/\Lambda_{25}^0$ for HCl, and $\Lambda_t^0/\Lambda_{25}^0$ for NaCl are plotted against the temperature in Fig. 42.

Transference Numbers.—Faraday's law states that the quantity of electricity passing through a solution is strictly proportional to the quantity of chemical change at each electrode, that 96,500 amp.-sec., or 1 faraday, of electricity produces or destroys one chemical equivalent of chemical substance at each electrode, and that the total changes at the electrodes may be shown by a pair of electrode reactions which add to an ordinary chemical equation. But each electrode reaction involves an equivalent of one ion and none of the opposite charge, and electrical neutrality must be maintained at all times in all parts of the solution. The loss of an equivalent of negative ion from the solution near the anode by electrolysis is partly compensated by

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[1] GUNNING and GORDON, *ibid.*, **10,** 126 (1942). Data for potassium chloride are given in the same paper.

[2] The limiting equivalent conductance of HCl at various temperatures is

t	5°	15°	25°	35°	45°	55°	65°
Λ_0	297.6	362.0	426.2	489.2	550.3	609.5	666.8

OWEN AND SWEETON, *J. Am. Chem. Soc.*, **63,** 2811 (1941).

the movement of negative ions into this portion of the solution and partly by the movement of positive ions out of this part of the solution, the sum of these effects being equal to the loss by electrolysis.

If N faradays pass through the solution and N equivalents of negative ion are lost in the anode reaction, N_c equivalents of positive ion leave the anode portion and N_a equivalents of negative ion enter it. The relation between these quantities is

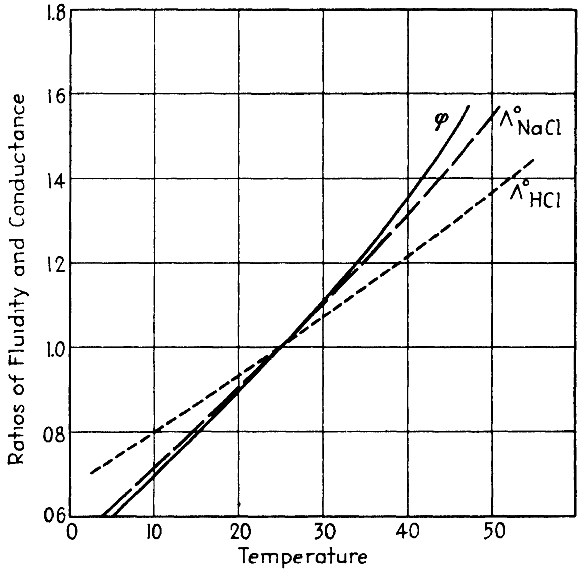

FIG 42 —Change of fluidity and limiting conductance with temperature.

$$N = N_c + N_a$$

but it does not follow that N_c and N_a are equal. In the electrolysis of HCl with a silver anode, for example, each faraday passed through the solution causes the loss of an equivalent of chloride ion by electrolysis from solution around the anode, and electrical neutrality is maintained by the loss of 0.83 equivalent of hydrogen ion from the solution near the electrode and the entry of 0.17 equivalent of chloride ion. Thus N_c is $0.83N$ and N_a is $0.17N$. In the electrolysis of sodium chloride under the same conditions there is the same loss of negative ion by electrolysis, and analysis of the solution near the anode shows the loss of 0.38

equivalent of sodium chloride. For this solution N_c is $0.38N$ and N_a is $0.62N$; the changed fractions are due to the fact that sodium ion has a much smaller velocity than hydrogen ion.

We now define a quantity called the *transference number*, which for the positive ion in a solution of a single electrolyte is given by the equation

$$T_c = \frac{N_c}{N_c + N_a}$$

and for the negative ion by the equation

$$T_a = \frac{N_a}{N_c + N_a}$$

The transference number of an ion is thus the fraction of the total electricity carried in the solution by that ion. It is the fraction of an equivalent of ion transferred across any boundary in the solution per faraday of electricity carried through the boundary. But ions move with different velocities in a solution of the same concentration under the same potential gradient, and thus these fractions are not one-half.

The actual velocities of ions in solutions of the same concentration, at the same temperature, and under the same potential gradient are characteristic properties of the ions; thus the transference number of chloride ion (for example) will depend upon the velocity of the positive ion with which it is associated. If V_c and V_a are the ionic velocities, the transference numbers may also be defined by the relations

$$T_c = \frac{V_c}{V_c + V_a} \qquad \text{and} \qquad T_a = \frac{V_a}{V_c + V_a}$$

Transference numbers may be derived from several types of experiment, of which two will be described in this chapter and another in a later one.

In the *gravimetric method* a measured quantity of electricity is passed through a solution, and separate portions of it are analyzed after the electrolysis to determine the gains and losses in the portions of the solution near the electrodes. (A description of the apparatus and the means of withdrawing the portions without mixing will be given presently.) It is an essential characteristic of these experiments that a "middle" portion of the solution be unchanged at the end of an experiment, which is accomplished by using a long tube for the electrolysis and so adjusting the experimental conditions that the changes are confined to the region near the electrodes. We shall first describe an idealized experiment in which a large tube is filled with 0.1*m*. sodium chloride and fitted at its ends with a platinum cathode and a silver anode. The tube is so fitted that after the passage of a faraday of electricity the solution may be withdrawn from the cathode region, then from two separate "middle portions" (for check analysis), and finally from an anode portion The electrode portions will have changed composition, but there must be no change in the ratio of salt to water in the middle portions

Diagrammatically this arrangement is as follows:

Silver anode	Anode portion of NaCl	Anode-middle portion of NaCl	Cathode-middle portion of NaCl	Cathode portion of NaCl	Platinum cathode

When 1 faraday of electricity is passed through the solution, the anode reaction is

$$Ag(s) + Cl^- = AgCl(s) + e^-$$

by which one equivalent of chloride ion is lost from the solution near the anode. At the same time the cathode reaction

$$H_2O + e^- = \frac{1}{2}H_2(g) + OH^-$$

forms an equivalent of negative ion at the cathode. Thus the electrical neutrality of the whole solution is maintained as the result of these reactions. To maintain the electrical neutrality of the anode portion, part of an equivalent of chloride ion moves into this portion and part of an equivalent of sodium ion moves out of it into the middle portion. To maintain electrical neutrality in the cathode portion, some chloride ions move out of it and some sodium ions move into it.

Analysis of the separate portions of the solution after passing 1 faraday through the whole cell shows that the anode portion contains 0.38 mole less sodium chloride than was associated with the amount of water in this portion before the electrolysis took place In the cathode portion there is 0.62 mole less sodium chloride than before, and 1 00 mole of sodium hydroxide. In both middle portions the ratio of salt to water is still 0 1 mole of NaCl to 1000 grams of water Sodium ions have been transferred from the anode portion through the middle portion to the cathode portion, and chloride ions have been transferred from the cathode portion through the middle portion to the anode portion

In the *anode portion*, where the electrode reaction is

$$Ag(s) + Cl^- = AgCl(s) + e^-$$

the solution has lost one equivalent of chloride ion by this electrolytic reaction, with no positive ion involved. The analytical data showed the net loss of 0 38 equivalent of Na^+ and Cl^- from this portion, and these results may be explained simply if 0.38 equivalent of Na^+ left the anode portion by transfer into the middle portion, while 0 62 equivalent of Cl^- entered the anode portion from this middle portion. Since there was no change in the ratio of salt to water in the middle portions, these effects of transfer evidently took place across the other boundaries in the solution as well. Since 38 per cent of the faraday of electricity was carried by sodium ions, the transference numbers for 0.1*m.* are

$$T_{Na} = 0.38 \qquad \text{and} \qquad T_{Cl} = 0\ 62$$

The same fractions are obtained from the results in the *cathode portion*, where the electrode reaction was

$$H_2O + e^- = \frac{1}{2}H_2(g) + OH^-$$

Electrical neutrality is maintained in this portion of the solution by the loss of 0.62 equivalent of chloride ion into the middle portion and the gain of 0.38 equivalent of sodium ion from it. These transfers to or from the middle portion are compensated by corresponding transfers from or to the anode portion, so that the total sodium chloride in the middle portion is unchanged. The transfer of electricity through this solution was by 0 38 equivalent of Na^+ and 0.62 equivalent of Cl^-, and these fractions are the transference numbers, namely, $T_{Na} = 0.38$ and $T_{Cl} = 0.62$

It will be understood, of course, that the OH^- ions formed at the cathode take part in the conductance of the solution near the cathode; these ions move toward the anode faster than do chloride ions. But it is a necessary characteristic of transference experiments such as this that the electrolysis must be interrupted before any hydroxyl ions reach the middle portion This illustration does not show what fraction of the total electricity is carried by sodium ions in a mixture of NaOH and NaCl; it shows only the relative velocities of the ions of sodium chloride in the unchanged middle portions of the solution by considering the changes in the electrode portions

The results of transference experiments may, for the sake of clearness, be summarized in gain-and-loss tables like the following:

ANODE PORTION $Ag(s) + Cl^- = AgCl(s) + e^-$			CATHODE PORTION $H_2O + e^- = \frac{1}{2}H_2(g) + OH^-$	
Gain	Loss		Gain	Loss
	$1.0\ Cl^-$	Electrolysis	$1.0\ OH^-$	
$0.62\ Cl^-$	$0.38\ Na^+$	Transference	$0.38\ Na^+$	$0.62\ Cl^-$
	$0.38\ Na^+Cl^-$	Net changes	$1.0\ Na^+OH^-$	$0.62\ Na^+Cl^-$

In order to show that the transference effects are independent of the nature of the electrodes, while the net changes in the electrode portions of solutions are not, assume this experiment to be repeated with a silver chloride cathode, but with the silver anode retained. Analysis of the anode portion still shows the net loss of 0.38 NaCl from it. The gain-and-loss tables would then be as follows.

ANODE PORTION $Ag(s) + Cl^- = AgCl(s) + e^-$			CATHODE PORTION $AgCl(s) + e^- = Ag(s) + Cl^-$	
Gain	Loss		Gain	Loss
	$1.0\ Cl^-$	Electrolysis	$1.0\ Cl^-$	
$0.62\ Cl^-$	$0.38\ Na^+$	Transference	$0.38\ Na^+$	$0.62\ Cl^-$
	$0.38\ Na^+Cl^-$	Net changes	$0.38\ Na^+Cl^-$	

The net effects have been changed, but the interpretation of them in connection with the gain or loss required by Faraday's law is still the transfer of 0.38 equivalent of sodium ion out of the anode portion and into the cathode portion per faraday of electricity passing, and thus 0.38 is transference number of sodium ion in this solution.

When the solute is changed, the transference effects are also changed. Assume the electrodes to be a silver anode and a platinum cathode, and the apparatus to be filled with 0.1 *N* HCl in place of NaCl. The results of passing a faraday through this solution are shown by new tables, as follows:

ANODE PORTION $Ag(s) + Cl^- = AgCl(s) + e^-$			CATHODE PORTION $H^+ + e^- = \frac{1}{2}H_2(g)$	
Gain	Loss		Gain	Loss
	1.0 Cl^-	Electrolysis		1.0 H^+
0.172 Cl^-	0.828 H^+	Transference	0.828 H^+	0.172 Cl^-
	0.828 H^+Cl^-	Net changes		0.172 H^+Cl^-

With the same loss by electrolysis in the anode portion the net loss from it is much higher, which is explained by the fact that hydrogen ions move faster than sodium ions and therefore carry a larger fraction of the electricity through the solution. Thus the transference number of chloride ion in 0.1*m* HCl is 0.172, while in the NaCl solution the transference number of chloride ion is 0.62.

An apparatus large enough to conduct such an experiment with a whole faraday would be cumbersome and is unnecessary. Since both electrolysis and transference are proportional to the quantity of electricity, an apparatus such as that shown in Fig. 43[1] and about 0.01 faraday are used. Two silver coulometers *S* measure the total quantity of electricity passing; *C* is a cathode; *A*, an anode. The two parts of the apparatus are joined at *D*, the whole is filled with solution, and the experiment is run with both large stopcocks open, while the apparatus is immersed in a thermostat. The stopcock keys must have a bore as large as the diameter of the tubing (about 3 cm.) to prevent local heating and

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[1] WASHBURN, *ibid.*, **31**, 332 (1909).

convection. When the experiment is finished, these stopcocks are closed to isolate the anode and cathode portions, and two or three middle portions may be withdrawn through the side tubes *a* and *c* for check analysis. The apparatus is divided at *D*, and the parts containing the anode and cathode portions are weighed and opened for analysis of the solution.

The actual data on which our first illustration of transference was based were obtained from an experiment in such a piece of apparatus and are as follows. The anode portion of solution weighed 176.15 grams and contained 0.852 gram of sodium chloride and 175.3 grams of water. The original solution put into the apparatus contained 5.485 grams of sodium chloride per 1000 grams of water, or 1.025 grams in 175.3 grams of water. Thus the loss of sodium chloride from the anode portion was 0.173 gram, or 0.00295 equivalent. The silver coulometer in series with the electrolysis apparatus to measure the quantity of electricity deposited 0.842 gram of silver, which required 0.842/107.88 = 0.00780 faraday. The middle portions must be shown to have the same ratio of sodium chloride to water at the end of the experiment as at the beginning. This condition was met in this experiment, and therefore all the changes are

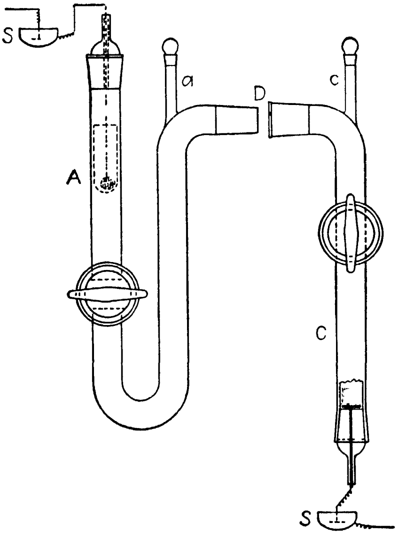

FIG. 43.—Diagram of transference apparatus and connections.

shown by the analysis of the anode portion of solution. These changes and a corresponding set of figures for the cathode portion are shown in the following table:

ANODE PORTION $Ag(s) + Cl^- = AgCl(s) + e^-$ (Basis 0.00780 faraday)			CATHODE PORTION $H_2O + e^- = \frac{1}{2}H_2(g) + OH^-$ (Basis 0.00780 faraday)	
Gain	Loss		Gain	Loss
	0.00780 Cl^-	Electrolysis	0.00780 OH^-	
0.00485 Cl^-	0.00295 Na^+	Transference	0.00295 Na^+	0.00485 Cl^-
	0.00295 Na^+Cl^-	Net change	0.00780 Na^+OH^-	0.00485 Na^+Cl^-

A loss of 0.00295 equivalent of sodium ion from the anode portion for 0.00780 faraday of electricity gives

$$T_{Na^+} = 0.00295/0.00780 = 0.38$$

as before. It is suggested that gain-and-loss tables be set up on the actual basis of the experiment in the solution of problems at the end of the chapter.

Moving Boundary Method for Transference Numbers.—We have seen on page 261 that the changes *due to transference* are independent of electrode reactions and that the ratio of the transference numbers is the ratio of the equivalents of each ion moving through the middle portion. The number of equivalents of ion passing through any cross section of solution is the product of concentration, cross section, and distance moved. Since distance and cross section are commonly expressed in centimeters and square centimeters, respectively, the concentration of ions must be in equivalents per centimeter cube, or $C/1000$ if C is the normality of the solution. For the positive and negative ions the expressions for equivalents passing are

$$N_+ = \frac{C}{1000} qd_+ \qquad \text{and} \qquad N_- = \frac{C}{1000} qd_-$$

and for a single solute C and q are common to both ions. Hence $T_+/T_- = d_+/d_-$, and any method of determining these distances moved by the ions would yield values of the transference number through the relation

$$T_+ = \frac{d_+}{d_+ + d_-}$$

An idealized diagram of the moving boundary method[1] is shown in Fig 44, which assumes a layer of sodium chloride over one of lithium chloride and beneath one of sodium acetate, with the boundaries before electrolysis shown by the solid lines. When electricity passes through the cell, the boundaries move as indicated; and since chloride ions are followed by the slower acetate ions and sodium ions by the slower lithium ions, the boundaries remain sharp and may be located by the different indexes of refraction of the solutions. After electricity has passed for a suitable length of time, the boundaries move to the positions indicated by the dotted lines, and it is found that, in 0 1m sodium chloride solution at 25°, the ratio of the distances moved is $d_{\mathrm{Na}}:d_{\mathrm{Cl}} = 38:62$, and therefore T_{Na^+} is 0.38, as was found in the gravimetric method.

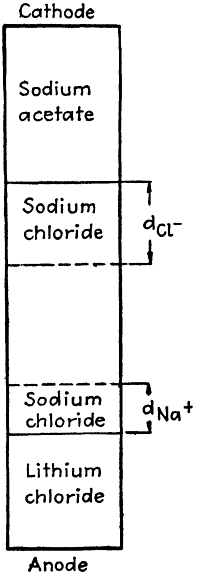

FIG. 44.

The experimental difficulties of the method, which are many, have been overcome so completely that transference numbers from this source are probably the most reliable of any now available. Agreement between this method, the gravimetric one, and a third method based on the potentials of concentration cells (to be given in Chap. XIX) is satisfactory. Some data are given in Table 48, from which it will be seen that there is a small but unmistakable change of transference number with concentration. At higher concentrations the changes are much greater.

Transference numbers also change with temperature, the general effect of rising temperature being to bring the transference

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[1] The actual apparatus and method for obtaining precise transference data from moving boundaries are given by MacInnes and Longsworth in *Chem. Rev*, **11,** 171 (1932); *J Am. Chem. Soc.*, **60,** 3070 (1938).

TABLE 48—TRANSFERENCE NUMBERS OF POSITIVE IONS[1] AT 25°

Electrolyte	Equivalent concentration				
	0.01	0.02	0.05	0.10	0.20
KCl	0.490	0.490	0.490	0.490	0.489
NaCl	0.392	0.390	0.388	0.385	0.382
LiCl	0.329	0.326	0.321	0.317	0.311
HCl	0.825	0.827	0.829	0.831	0.834
NaAc	0.554	0.555	0.557	0.559	0.561
KI	0.488	0.488	0.488	0.488	0.489
KBr	0.483	0.483	0.483	0.483	0.484
NH_4Cl	0.491	0.491	0.491	0.491	0.491
$AgNO_3$	0.465	0.465	0.466	0.468	

numbers closer to 0.5 for all ions. The slower ions thus have larger temperature coefficients of velocity than the faster ions. The following data[2] for the transference number of sodium ion in sodium chloride are typical of salts in general:

Concentration	0.001	0.010	0.100
T_{Na^+} at 15°	0.3914	0.3885	0.3820
T_{Na^+} at 25°	0.3947	0.3918	0.3853
T_{Na^+} at 35°	0.3987	0.3958	0.3892
T_{Na^+} at 45°	0.4023	0.3996	0.3932

The transference number of hydrogen ion in 0.01 N HCl changes somewhat more rapidly with temperature, as shown by the following data [3]

t°C	0°	18°	30°	50°	96°
T_{H^+}	0.846	0.833	0.822	0.801	0.748

Limiting Conductances of the Separate Ions.—It has already been explained that each salt approaches a limiting equivalent conductance as the concentration decreases. In very dilute solutions, where this limit is essentially reached, each ion is free to move almost as if no other ions were present. From the transference number obtained in dilute solutions and from the

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[1] Longsworth, *ibid.*, **57,** 1185 (1935), using the method of moving boundaries. Transference numbers by the gravimetric method are given in "International Critical Tables," Vol. VI, p. 309, for these and other electrolytes.

[2] ALLGOOD and GORDON, *J. Chem. Phys*., **10,** 124 (1942).

[3] LONGSWORTH, *Chem. Rev.*, **11,** 171 (1935).

limiting equivalent conductance, the limiting equivalent conductance of each ion in a solution may be calculated. Thus the limiting equivalent conductance for sodium chloride at 18° is 108.9 reciprocal ohms; and if this is multiplied by the transference number for sodium ion, 0.398, the result is 43.4 for the limiting equivalent conductance of the sodium ion. Since at limiting dilution the ions are substantially without influence upon one another, the Λ_0 values of the ions are additive, and 108.9 − 43.4 gives 65.5 as the limiting equivalent conductance of chloride ion.

The limiting equivalent conductance for sodium nitrate is 105.2 reciprocal ohms, 43.4 of which is due to sodium ion. Hence the limiting equivalent conductance of nitrate ion is obtained by subtraction, 105.2 − 43.4 = 61.8. For potassium nitrate the limiting value is 126.3; hence 126.3 − 61.8 = 64.5 is the equivalent conductance of potassium ion. The limiting value for potassium chloride should then be the sum of the values for potassium ion and chloride ion found above, 64.5 + 65.5 = 130. Proceeding in this way, one may calculate limiting conductances for all the ions. A few values for the common ions at a series

TABLE 49.—LIMITING CONDUCTANCES OF IONS[1]

Ion	Temperature							
	0	18	25	50	75	100	128	156
K^+	40.4	64.2	73.5	115	159	206	263	317
Na^+	26.0	43.2	50.1	82	116	155	203	249
NH_4^+	40.2	64.3	73.4	115	159	207	264	319
Ag^+	32.9	53.8	61.9	101	143	188	245	299
½Ba^{++}	33	55	63.6	104	149	200	262	322
½Ca^{++}	30	51	59.5	98	142	191	252	312
Cl^-	41.1	65.2	76.3	116	160	207	264	318
NO_3^-	40.4	61.6	71.4	104	140	178	222	263
$C_2H_3O_2^-$	20.3	34.6	40.9	67	96	130	171	211
½SO_4^{--}	41	68	79.8	125	177	234	303	370
H^+	240	315	349.8	465	565	644	722	777
OH^-	105	174	197.6	284	360	439	525	592

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[1] Some other limiting conductances at 25° are Li^+ 38.7, ½Sr^{++} 59.5, ½Mg^{++} 53.1, Br^- 78.4, I^- 76.9, and HCO_3^- 44.5. The values for 25° in the table are from MacInnes, *J. Franklin Inst.*, **225**, 661 (1938). Other data will be found in "International Critical Tables," Vol. VI, p. 230.

of temperatures are given in Table 49. Since the temperature coefficients are almost linear, values for temperatures other than those given in the table may be obtained by interpolation.

The limiting equivalent conductance for sodium lactate at 25° was given on page 252 as 88.8; and by subtracting 50.1, which is the limit for sodium ion, the limiting equivalent conductance of lactate ion is 38.7. Upon adding 349.8 for hydrogen ion to this we obtain 388.5 for the limiting equivalent conductance of lactic acid, which is in agreement with the value given on page 252.

Calculation of Conductances.—The conductance of any dilute aqueous solution of a "strong" electrolyte involving the Λ_0 values of the ions listed in the tables may be calculated from these values and an estimate of the conductance ratio. This ratio Λ/Λ_0 is about the same for all strong electrolytes of a given ionic type at the same concentration, but it is not the same for salts of different ionic types at the same concentration. Some typical values are given in Table 52 on page 276.

For illustration, we may calculate the specific conductance of 0.1 N KNO_3 at 25°. The conductance ratio at 0.1 N is 0.83 for $NaNO_3$ and $KClO_3$, so that we may take 0.83 for KNO_3, and $\Lambda_{0.1} = 0.83(73.5 + 71.4) = 120.2$, whence $L = 0.01202$ by calculation and 0.01203 by experiment. But NaCl is also of the same ionic type, and $\Lambda_{0.1}/\Lambda_0 = 0.85$ for this salt, and from this ratio the computed L for KNO_3 would have been 0.0123. It will usually be true that the calculations agree better with experiment when the conductance ratio is taken for a salt resembling as closely as possible that for which the calculation is being made. Over small ranges of concentration the equivalent conductance changes only slightly, and therefore the *specific* conductance is almost proportional to the concentration. For illustration, the specific conductance of 0.12 N KNO_3 is very close to 1.2 × 0.0120, or 1.2 times the specific conductance for 0.10 N. But the specific conductance of 0.5 N KNO_3 would not be 5 times that for 0.1 N, for in this concentration range the equivalent conductance changes 18 per cent.

Conductance of Mixtures of Electrolytes.—The specific conductance of a mixture of electrolytes of the same ionic type is almost the sum of the specific conductances of the individual salts present, calculated in the way shown above; but in calculating each one the ratio Λ/Λ_0 applicable at the *total* concentration should be used. For example, in a solution 0.05 N in HCl and 0.10 N in NaCl the ratio Λ/Λ_0 for 0.15 N should be used on both solutes, and for this ionic type the value is about 0.85 At 25°, $\Lambda_0 = 426$ for HCl and $\Lambda_0 = 127$ for NaCl. The respective specific conductances are then computed and added together to give that of the mixture, as follows:

$$L_{\text{HCl}} = \frac{0.85 \times 426 \times 0.05}{1000} = 0.0181$$

and

$$L_{\text{NaCl}} = \frac{0.85 \times 127 \times 0.10}{1000} = 0.0108$$

The calculated specific conductance of the mixture is the sum of these two quantities, or 0.0289; the measured specific conductance is 0.0291. The chief error in such calculations is of course the estimate of the conductance ratio, which differs at 0.1 N by 1 per cent for KCl and NaCl, by 3 per cent for HCl and HNO_3, and by 7 per cent for HCl and NaCl. Use of 0.88 in the above calculation in place of 0.85 would change the calculated specific conductance to 0.0299, for example.

It will be seen from these equations that the conductances are computed on the assumption that the solutes act as conductors in parallel when they are in the same solution. The actual conductance of the mixture is slightly less than would be that of the two solutions connected in parallel, since both solutes move in the same solvent and hence influence the motion of one another. This effect is taken into account by using the conductance ratio corresponding to the total concentration, since the main effect of the ions on one another arises from interaction between their charges, which is a function of the total concentration.

These equations may not be applied to mixtures such as acetic acid and sodium acetate without alteration, for the presence of acetate ions changes the fractional ionization of acetic acid in a way that cannot be estimated from the conductance ratio. (We shall see in Chap. IX how to calculate the ionization of the acid in the presence of the salt.) In mixtures of salts of different ionic type, such as NaCl and $BaCl_2$ or $CuSO_4$ and H_2SO_4, the estimate of a conductance ratio applicable to the mixture is so uncertain as to make calculated conductances of little value.

Conductimetric Titration of Acid or Base.—It will be observed that the limiting conductances of hydrogen ion and hydroxyl ion are much larger than those of other ions. During a titration of acid with a standard base the specific conductance decreases rapidly as hydrogen ion is removed from solution by neutralization and replaced by some slower positive ion; but after passing the end point the conductance increases because of the presence of rapidly moving hydroxyl ions. If the acid solution is diluted to about 0 01 N, and titration is carried out with 0.10 N NaOH, a sharp minimum will be obtained in a plot of conductance against burette readings. If a set of dipping electrodes is used, a conductimetric titration will not require much more time than the usual type, and it may be employed under some circumstances when the use of an indicator is not permissible, as in a colored or a strongly oxidizing solution

Hydration of Ions.—There is no completely decisive method for determining the quantity of water combined with solute in a solution, though much work has been done in connection with freezing-point deviations[1] and in other ways. There is, however, a method for determining whether or not the two ions of a solute carry different quantities of water, and this may be used to calculate the quantity of water combined with one ion if the other is *assumed* to carry none. Thus, suppose a transference experiment to be conducted on a solution of sodium chloride to which a little sugar has been added. Sugar is not an ionized substance and it does not move through a solution when electricity is passed; thus, if at the end of an experiment the *ratio of sugar to water* in the anode portion has changed, water must have come into this portion on the anion or have been carried out of it on the cation.

When electricity passes through a normal solution of sodium chloride, 0.76 mole of water per faraday is lost from the anode portion, as is shown by a change in the ratio of sugar to water. *Assuming* that the chloride ion does not carry any water, this 0 76 mole of water must have been carried out by 0.38 equivalent of sodium ion, this being the quantity of sodium ion leaving the

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[1] A review of hydration in general is given by Washburn, *Tech. Quart*, **21,** 360 (1908), together with a criticism of each method. More recent work on cryoscopic determination of hydration [Bourion and Rouyer, *Compt. rend.*, **196,** 1111 (1933)] seems to show that about 25 per cent of the water in molal sodium chloride solution is combined with the solute.

anode portion per faraday passed. That is, each sodium ion is associated with two molecules of water, since 0.38 equivalent carried away 0.76 mole of water. If it be *assumed* that chloride ions also carry water in these experiments, the hydration of the positive ions is correspondingly greater. For example, if a chloride ion carries four molecules of water, 0.62 equivalent of chloride ion would carry 0.62 × 4 = 2.48 moles of water into the anode portion. The net *loss* of water from the anode portion requires that 0.38 equivalent of sodium ion carry out this 2.48 moles of water and 0.76 mole in addition, making 3.24 moles of water on 0.38 equivalent of sodium ion, or a hydration of 3.24/0.38 = 8.5 moles of water per equivalent of sodium ion. This particular method gives only the difference between the hydration of one ion and another; but since the chloride ions cannot carry less than no water at all, the lower limit of hydration for the sodium ion under these conditions, and as shown by this method, is 2.0 moles per equivalent. Other "reference substances," such as resorcinol, arsenious acid, alcohol, and raffinose, in place of sugar, show the same hydrations and thus show that the effect is produced, not by the reference substance, but by actual motion of water with the ion. Some ionic hydrations by this method are given in Table 50.

TABLE 50.—HYDRATION OF IONS[1] IN NORMAL SOLUTION

Salt	Moles water carried from anode to cathode per faraday of electricity	Transference number of positive ion	Moles water on positive ion when chloride ion is assumed to have		
			0	4	10
HCl	0.24	0.844	0.3	1.0	2.1
CsCl	0.33	0.491	0.7	4.7	11.0
KCl	0.60	0.495	1.3	5.4	11.5
NaCl	0.76	0.383	2.0	8.5	18.0
LiCl	1.50	0.304	4.7	14.0	28.0

Diffusion experiments in the presence of electrolytes are said[2] to show that hydration of strong electrolytes does not change

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[1] WASHBURN and MILLARD, *J. Am. Chem. Soc.*, **37,** 694 (1915).

[2] GOTZ and PAMFIL, *Bull. sect. sci. acad. roumaine,* **8,** 266 (1923); *Chem. Abst.*, **18,** 3132 (1924).

with the concentration of the solution, which is a direct contradiction of the law of chemical equilibrium. Sugden[1] states that only cations are hydrated and that hydration is independent of the concentration of the electrolyte. If these statements are correct, the hydration of each positive ion in Table 50 is that shown under 0. Somewhat different quantities of water transported per faraday are reported by Baborovsky,[2] as follows:

HCl	KCl	NaCl	LiCl	KBr	NaBr	LiBr
0.43	0.47	0.90	1.62	0.89	1.58	2.10

Conductance in Solvents Other than Water.[3]—Inorganic solutes in solvents such as formic acid, liquid ammonia, organic amines, acetone, alcohols, dioxane, and other liquids have appreciable conductances, some of which approach those of aqueous solutions at the same temperature and concentration. For example,

TABLE 51.—CONDUCTANCE OF SODIUM IODIDE IN ACETONE[4] AND ISOAMYL ALCOHOL[5]

Equivalent concentration	Equivalent conductance in acetone			**Equivalent conductance in isoamyl alcohol at 25°**
	0°	25°	40°	
1.0000	.....	26.4	28.65	
0.5000	32.5	38.4	41.00	1.396
0.2000	44.9	52.7	56.60	1.339
0.1000	53.7	64.1	68.90	1.294
0.0500	63.1	76.1	82.70	
0.0200	77.2	95.0	103.80	1.649
0.0100	89.0	109.7	121.40	2.024
0.0050	99.0	124.5	139.40	2.560
0.0020	111.0	143.2	163.00	3.394
0.0010	118.5	155.0	178.00	4.184
0.0005	125.0	164.6	188.90	
0.0002	129.4	171.7	197.20	6.115
0.0001	129.9	173.6	199.90	6.636
0.0000	(131.4)	(176.2)	(204.00)	(7.790)

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[1] *J. Chem. Soc. London,* **129,** 174 (1926).

[2] *J. chim. phys.,* **25,** 452 (1928).

[3] The data on electrically conducting systems have been brought together in a single volume by C. A. Kraus, *op. cit.*, to which reference may be made for detailed information concerning nonaqueous solvents.

[4] McBAIN and COLEMAN, *Trans. Faraday Soc.,* **15,** 27 (1919).

[5] KEYES and WINNINGHOFF, *Proc. Nat. Acad. Sci.*, **2,** 342 (1916).

Λ_0 for NaI at 25° is 7.8 in isoamyl alcohol, 167 in acetone, 61 in pyridine, 301 in liquid ammonia, compared with 126.94 in water. The ions in these solutions are the same as in water solutions, and Faraday's law applies, though the relative velocities of the ions are not the same. Mole numbers for a given solute at a given concentration vary widely with the nature of the solvent. The conductance data in Table 51 are typical of nonaqueous solutions

Conductances of Pure Liquids.—Most common liquids have very slight electrical conductances at ordinary temperature. The specific conductance of *pure* water is 1.0×10^{-8} reciprocal ohm at 0°C., 4.5×10^{-8} at 25°, and 50×10^{-8} at 100°; and most liquids have even smaller conductances. Assuming that the conductance of water is due to H^+ and OH^- ions, we may calculate the concentration of these ions from the conductance by means of equation (3) and the data in Table 49. At 25°, for example,

$$4.5 \times 10^{-8} = \frac{C}{1000}(349.6 + 197)$$

whence $C = 1.0 \times 10^{-7}$ mole per liter of H^+ and OH^-; the concentrations at the other temperatures are found through the same relation to be 0.1×10^{-7} at 0° and 7×10^{-7} at 100°. These ionic concentrations in water have been confirmed by several other methods, some of which will be given in later chapters.

Fused salts, on the other hand, are very good conductors of electricity The conductance is undoubtedly due to ions, just as that of their aqueous solutions is due to ions; the products of electrolysis are often the same in aqueous solutions, except where these would react with water. Fused lead chloride yields, upon electrolysis, lead at the cathode and chlorine at the anode; the same products result when aqueous solutions of it are electrolyzed

Fused sodium hydroxide yields metallic sodium at the cathode and oxygen at the anode when it is electrolyzed; this same effect is produced by electrolysis of sodium hydroxide solution with a mercury cathode in which sodium can dissolve and be protected from the action of water;[1] Faraday's law describes quantitatively

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[1] When sodium hydroxide solution is electrolyzed with a platinum cathode, sodium does not deposit and then react with water to produce sodium

the yield in both cases. But since salts in the fused condition are acting as both solvent and solute, ionic velocities have not yet been determined, and transference experiments are impossible.

The industrial importance of electrolysis of fused salts is very great. Metallic sodium is produced almost entirely by electrolysis of fused sodium chloride, magnesium metal from the electrolysis of fused magnesium chloride, and aluminum from the electrolysis of a solution of aluminum oxide in fused cryolite, a fluoride of sodium and aluminum. Attempts have been made to develop the theory of fused salts,[1] but an adequate treatment of them has not yet been accomplished.

IONIC THEORY

Most of the important experimental facts that we shall need for a brief discussion of the ionic theory and for use in later work in this book have now been given To account for these facts the ionic theory has been built upon the following assumptions, about which there seems to be no serious doubt at the present time:

1 Inorganic salts and strong acids and bases dissolved in water (and some other solvents) are dissociated into two or more parts bearing charges of positive or negative electricity and called ions

2. The conduction of electricity through these solutions is due wholly to the movement of ions. Positively charged ions move toward the negative pole; negatively charged ions move toward the positive pole.

3. Ions have charges that are whole multiples of the charge of the electron. Chloride ions carry 1 electron per atom; nitrate, acetate, bicarbonate, and other univalent ions carry 1 electron

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hydroxide and hydrogen, as is sometimes stated Hydrogen is evolved at the cathode and oxygen at the anode during this electrolysis, when the applied electric potential is insufficient to cause the deposition of sodium Metallic sodium is deposited in a mercury cathode as an amalgam only upon application of a much higher potential than is required to discharge hydrogen at a platinum electrode

[1] See Kraus, *op. cit*, Chap XIII, for a discussion of these systems The data referring to fused salts are collected in Vol. III of the "International Critical Tables."

per atom group. Corresponding positive ions are atoms or atom groups that have lost one or more electrons, and thus become positively charged. The unit charge is 1 598 × 10^{-20} absolute electromagnetic unit, or 1.598 × 10^{-19} coulomb.

The older ionic theory as developed by Arrhenius and others also contained the following assumptions, which are now believed to be incorrect:

4. The dissociation of salts into ions is incomplete. Fractional ionization increases with decreasing concentration and approaches complete ionization as the concentration approaches zero The increase in equivalent conductance upon dilution is due to an increase in the number of charged ions of constant mobility.

5. Ions behave like independent *molecules of solute* as regards the properties of solutions that are determined by the mole fraction of the solute, such as vapor pressure, freezing point, boiling point, and osmotic pressure. Each of these particles exerts the same effect upon the freezing point as a whole molecule Nonionized molecules exert their usual effects.

Granting the last two assumptions for the moment, two methods become available for calculating the extent of ionization, and the agreement between the methods, faulty as it was in many solutions, was thought for many years to prove that the extent of ionization changed with the concentration. If C is the concentration and α the fractional ionization of a salt of the KCl type, $C\alpha$ gave the concentration of each ion and $C(1 - \alpha)$ the concentration of un-ionized molecules, whence $i = 1 + \alpha$ or $\alpha = i - 1$ Freezing points of aqueous solutions furnished the best means of measuring i; some values of $100(i - 1)$ from this source are given in Table 52, marked F.P.

On the assumption that the change of equivalent conductance with concentration is owing *only* to a change in the number of ions per equivalent of solute, the fraction of the solute ionized is given by $\Lambda/\Lambda_0 = \alpha$. Table 52 shows some values of $100(\Lambda/\Lambda_0)$, marked C.R.

These two quantities $i - 1$ and Λ/Λ_0 were accepted as measures of the fraction ionized long after it had been shown that their values were not the same in a given solution and that experimental error was not the cause of the variation. Moreover, the change of transference numbers with concentration showed that some of the ion mobilities were not constant, and this should have raised the question regarding the others.

The most serious objection to these "fractional ionizations" was the fact that the change with concentration did not follow that calculated from the laws of chemical equilibrium, which requires $C\alpha^2/(1 - \alpha)$ to be a constant. Thus, if KCl were 86 per cent ionized in 0.1 N solution, it should be 51 per cent ionized at 1 N, but the fractional ionization from freezing point and conductance ratio showed about 75 per cent ionization.

TABLE 52.—COMPARISON OF "PER CENT IONIZATION" FROM MOLE NUMBERS BASED ON FREEZING POINTS (F.P.)[1] AND FROM CONDUCTANCE RATIO (C.R.)[2]

Solute	Method	Equivalent concentration					
		0.01	0.05	0.1	0.5	1.0	2.0
KCl	F.P.	94.3	88.5	86.1	80.0	75.0	
	C.R.	94.1	88.9	86.0	77.9	75.8	71.3
NaCl	F.P.	93.8	89.2	87.5	81	81	85
	C.R.	93.6	88.2	85.2	74	68	59
LiCl	F.P.	93	91	89	93	104	137
	C.R.	92.5	87.4	84.3	71.8	64.3	54
$NaNO_3$	F.P.	91	86	83		62	50
	C.R.	93.3	87.0	83.1	70.5	62.7	52.1
KNO_3	F.P.	93.3	84.7	78.4	55.2	37.8	
	C.R.	93.8	87.3	83.1	70.8	63.9	54.9
HCl	F.P.	93.5	90	89.0	97.6	112	
	C.R.	97.2	94.0	92.0	85.8	79.0	66.7
HNO_3	F.P.	95.5	90.8	88.6	86	92.3	103.5
	C.R.	94.2	91.4	89.4	83.2	79.0	67.1
$MgSO_4$	F.P.	62	39	30	9.5	7.0	8.5
	C.R.	67.0	50.2	43.9	30.9	25.6	18.9

These contradictory interpretations were grouped under the inclusive heading "anomaly of strong electrolytes" rather than

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[1] *Ibid.*, Vol. IV, pp. 254*ff*.

[2] *Ibid.*, Vol. VI, pp. 230*ff*.

under a more descriptive one such as "need of revision of the theory," and the term "extent of ionization" was never clearly defined. It will not be profitable to study the early stages by which a new theory evolved and gained ground and "complete ionization" was gradually accepted; for some of the first consequences of its acceptance were mildly absurd. We turn now to some aspects of this theory based upon complete ionization as one working hypothesis

ASSUMPTION OF COMPLETE IONIZATION

In assuming complete ionization of salts in dilute aqueous solution, we assume that no neutral solute molecule such as KCl or HCl exists, but we do not assume that a mole of hydrogen chloride yields two moles of ideal solute, for this would require mole numbers of 2.0 at all concentrations, which would be contrary to experimental knowledge. We decide only that the properties of solutions of salts in water and other ionizing solvents will be considered in terms of properties other than a supposed fractional ionization. In an address in 1908, Lewis[1] pointed out that many of the properties of electrolytic solutions were additive properties of the ions up to concentrations approaching 1 *N*, in which the degree of dissociation was currently supposed to be about 75 per cent. He said of this additivity: "If it is an argument for the dissociation of electrolytes, it seems to be an argument for complete dissociation." Chemists were not at that time prepared to accept a theory of complete ionization; in the paper we have just quoted, Lewis himself makes the statement: "I believe we shall make no great error in assuming that the degree of dissociation as calculated from conductivities is in most cases substantially correct . . ."

Thus the data available over 35 years ago showed evidence for complete dissociation of strong electrolytes in aqueous solution to which the scientists were not blind and evidence of incomplete dissociation, which was then thought to be more probable. Substances such as H_2SO_3 and H_2CO_3 are certainly not completely ionized, the possibility of solutes such as TlCl or $BaCl^+$ still exists, and the ions $PbCl^+$, $FeCl^{++}$, and $FeCl_2^+$ have almost certainly been shown to exist; but the change of transference

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[1] LEWIS, "The Use and Abuse of the Ionic Theory," *Z physik Chem.*, **70**, 215 (1909) (in English).

number with concentration and the interionic attraction theory alike point to the impossibility of measuring the fractional ionization of a highly ionized solute from the conductance ratio One should not, however, lose sight of the fact that we still have no *conclusive* evidence that ionization of salts is complete; we still have the intermediate ion (such as HSO_4^- or HSO_3^- or HCO_3^-) to explain; we still have weak acids and bases that no one supposes completely ionized; we still have acids that are neither decisively "weak" acids nor yet completely ionized acids; and we still have no property of a solution of a salt or other "strong" electrolyte that is unquestionably connected with salt molecules in such a way as to demonstrate their presence at concentrations below $1m$.

In the discussion of some aspects of modern work on ionized solutes, we shall still accept the first three assumptions of the ionic theory given on page 274, but in place of those numbered (4) and (5) we shall now assume that

6. Ionization is complete in dilute aqueous solutions of salts and "strong" acids and bases, and un-ionized molecules are not present in these solutions.

7. The activity of an ionic solute, which is its effective concentration in influencing a chemical equilibrium or a potential or a reaction rate, is equal to its concentration only in extremely dilute solutions; at other concentrations the activity is $a = m\gamma$, where m is its molality and γ is the "activity coefficient." Thus the activity has the dimensions of a concentration, and the activity coefficient $\gamma = a/m$ is a number.

8. The change of equivalent conductance with concentration is due mainly to the interionic attraction between the charged ions for strong electrolytes; but the change of equivalent conductance with concentration for weak electrolytes is due mainly to increased ionization.

A brief discussion of the consequences of these assumptions will now be given.

Conductance and Ion Velocities.—If only one charged "particle" were concerned in the conduction of electricity, as is true in metallic conduction, the total quantity of electricity passing would be given by the equation

$$N = cqd \qquad (4)$$

in which N is the number of faradays passed, c is the concentration of moving particles in equivalents per centimeter cube, q the cross section of the conductor, and d the distance moved by the particles. But in electrolytic solutions all the ions present take part in the conduction in proportion to their concentrations and velocities, as is shown by transference experiments. For a single ionized solute yielding one negative and one positive ion of unit charge,

$$N = N_c + N_a$$

and the relation $N = cqd$ may be applied separately to each ion. The positive and negative ions move in opposite directions, of course, but the motion of positive charges in one direction produces the same electrical effect as the motion of negative ions in the opposite direction. In the relation $N = cqd$, the product qd is a volume and c is the quantity of material in a unit volume; thus if q is in square centimeters and d is in centimeters, c will be in equivalents per centimeter cube, which is $C/1000$ if we express concentrations in equivalents per liter of solution. Writing the equation for the positive ion only, we have

$$N_c = \frac{C}{1000} qV_ct \tag{5}$$

in which V_c is the velocity of the ion in centimeters per second and t is the time in seconds. These solutions obey Ohm's law, which requires that the velocity of the ion be proportional to the applied voltage, since C and q are constant. The mobility U of an ion may be defined as the velocity under unit potential gradient, and the quantity of electricity carried by the cation is then

$$N_c = \frac{C}{1000} qtU_c \frac{E}{l} \tag{6}$$

A similar expression containing U_a, the mobility of the negative ion, shows the quantity of negative electricity passing, and the total quantity is given by

$$N = N_c + N_a = \frac{C}{1000} qt(U_c + U_a) \frac{E}{l} \tag{7}$$

The current I is measured in coulombs per second, or NF/t, and is by Ohm's law equal to E/R, which from equations (1) and (2) is

$$I = EL\frac{q}{l} \tag{8}$$

Upon multiplying both sides of equation (7) by F/t and combining with equation (8), we have

$$I = \frac{NF}{t} = \frac{C}{1000}Fq(U_c + U_a)\frac{E}{l} = \frac{ELq}{l} \tag{9}$$

After canceling E and q/l, we obtain the relation of the specific conductance to the ion mobility, which is

$$L = \frac{C}{1000}(U_c + U_a)F \tag{10}$$

and the relation of equivalent conductance to mobility follows by combining this equation with equation (3).

$$\Lambda = (U_c + U_a)F = \Lambda_c + \Lambda_a \tag{11}$$

This relation implies that the equivalent conductance of a given ion is independent of the other with which it is associated. As a test of this implication, we may calculate the equivalent conductance of chloride ion at 25° and 0.01 N in several solutions by multiplying the equivalent conductance of the salt by the transference number of chloride ion.[1]

$$\begin{aligned}
T_{\text{Cl}}\Lambda_{\text{KCl}} &= 72.07 = \Lambda_{0.01} \text{ for Cl}^- \text{ at } 25^\circ\\
T_{\text{Cl}}\Lambda_{\text{NaCl}} &= 72.05 = \Lambda_{0.01} \text{ for Cl}^- \text{ at } 25^\circ\\
T_{\text{Cl}}\Lambda_{\text{HCl}} &= 72.06 = \Lambda_{0.01} \text{ for Cl}^- \text{ at } 25^\circ\\
T_{\text{Cl}}\Lambda_{\text{LiCl}} &\doteq 72.02 = \Lambda_{0.01} \text{ for Cl}^- \text{ at } 25^\circ
\end{aligned}$$

The corresponding figures for 0.10 N are, respectively, 65.79, 65.58, 65.98, and 65.49; and at higher concentrations the differences are somewhat larger. It seems proven that at low concentrations the ions have independent mobilities, as was first suggested by Kohlrausch many years ago. For chloride ion at 25° and 0.01 N this mobility under unit potential gradient is

$$U_{\text{Cl}^-} = \frac{72.05}{96500} = 0.000746 \text{ cm. per sec.}$$

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[1] MACINNES, *J. Franklin Institute*, **225**, 661 (1938).

Limiting mobilities may be calculated from the limiting equivalent conductances in Table 49 through the same relation; for example, the *limiting* mobility of chloride ion at 25° is

$$\frac{76\ 3}{96{,}500} = 0.00079 \text{ cm. per sec.}$$

The Activity Function.—The activity of any constituent of a solution is defined by Lewis[1] as its "effective" concentration (its effect in changing a chemical system at equilibrium). In an ideal solution the activity and the actual concentration are equal; in aqueous solutions of ions the activity and the ion concentration are not equal, but they approach equality as the concentration approaches zero.

Following the notation of Lewis and Randall,[2] the activity of a solvent is designated by a_1 and of a solute by a_2. Thus the vapor pressure of a solvent over a solution would be proportional to a_1, and for an ideal solution this could be computed from Raoult's law No simple law for calculating the activity of an ionized solute has yet been discovered. We may, however, designate by a_+ and a_- the activities of the positive and negative ions, respectively, and by a_2 the activity of the nonionized molecules. Then by definition

$$\frac{a_+a_-}{a_2} = K$$

In the absence of definite information regarding the concentration of nonionized solute in an electrolytic solution, Lewis defines K as unity so that

$$a_+a_- = a_2$$

Since at finite concentrations the two ions of a solute may not have the same activity, it is often expedient to consider the geometric mean of the two ion activities, which may be defined

$$a_\pm = \sqrt{a_+a_-}$$

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[1] *Proc. Am. Acad. Arts Sci.*, **43**, 259 (1907).

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

The Activity Coefficient.—Lewis defines the activity *coefficient* as the activity divided by the molality, *i.e.*,

$$\gamma = \frac{a_\pm}{m} \tag{12}$$

This coefficient *is not,* and should not be confused with, a fractional ionization. It is a factor, sometimes greater than unity, by which the molality must be multiplied to give the effect that a solute produces upon a chemical equilibrium or electrode potential or other property. Some of the methods by which activity coefficients are obtained will be given in the next section, and others later in the text.

Methods of Determining an Activity Coefficient.—The activity coefficients of solutes may be determined from their vapor pressures when the solute is sufficiently volatile; from freezing points of their solutions (but *not* from equating $i - 1$ to γ), or from the potentials of concentration cells in a way which will be explained in Chap. XIX. The activity of the solute may be calculated from the vapor pressure of the solvent by means of the equation

$$d \ln a_1 = -\frac{N_2}{N_1} d \ln a_2 \tag{13}$$

in which N_1 and N_2 are the moles of solvent and solute and a_1 and a_2 are the corresponding activities. For convenience in

TABLE 53.—COMPARISON OF ACTIVITY COEFFICIENTS AT 25°

m	NaCl		KCl		H_2SO_4	
	Vapor pressure[1]	Cell potential[2]	Vapor pressure[1]	Cell potential[3]	Vapor pressure[1]	Cell potential[4]
0.10	0.781	0.778	0.770	0.769	0.265	0.265
0.20	0.737	0.732	0.719	0.719	0.209	0.209
0.50	0.685	0.679	0.651	0.651	0.156	0.154
1.00	0.661	0.656	0.606	0.606	0.131	0.130
2.00	0.667	0.670	0.571	0.576	0.127	0.124
3.00	0.713	0.719	0.567	0.571	0.142	0.141

[1] SCATCHARD, HAMER, and WOOD, *J. Am. Chem. Soc.*, **60,** 3061 (1938).

[2] HARNED and NIMS, *ibid.*, **54,** 423 (1932).

[3] HARNED and COOK, *ibid.*, **59,** 1290 (1937).

[4] HARNED and HAMER, *ibid.*, **57,** 27 (1935).

integrating, the equation is often transformed into terms of molalities and activity coefficients, by methods which need not concern us here. Table 53 shows some activity coefficients for 25° at several molalities derived from vapor-pressure measurements and for comparison the coefficients derived from cell potentials.

Agreement between the two methods is as close as that among various experimenters using the same method. Activity coefficients may also be calculated from freezing-point depressions, provided that the data cover a range of molalities extending below 0 01m. In discussing the freezing points of dilute aqueous solutions, it has become common practice to use another function in place of the actual freezing-point depression, called the j function, and defined by the equation

$$j = 1 - \frac{\Delta t}{1.858\nu m} \tag{14}$$

where Δt is the freezing-point depression, m the molality of the solution, and ν the number of ions produced by a mole of salt, In terms of j, the relation between the activity $a_\pm$ of a solute, its freezing-point change Δt, and the molality m is[1]

$$d \ln \frac{a_\pm}{m} = d \ln \gamma = -dj - j\, d \ln m \tag{15}$$

Since the activity coefficients change with temperature, values derived from freezing points should not be compared with those from vapor pressures or electromotive forces of concentration cells without first correcting them to the same temperature.

Some activity coefficients for 25° are given in Table 54, and others will be found in Table 98.

The mean activity coefficient for simple electrolytes in a mixture of two salts at a total concentration of $c_1 + c_2$ is *about* the same as that for each salt when it is alone present at the concentration $c_1 + c_2$. Accurate data on the activity coefficients in mixtures have shown that this simple rule is not strictly true, but so far no accurate general law has been discovered.

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[1] Lewis and Randall, "Thermodynamics," Chap. XXVII, equation (3). Methods of integrating the equation are also discussed in Chap. XXIII of this excellent text.

TABLE 54.—MEAN ACTIVITY COEFFICIENTS OF IONS AT 25°C.

m	0.10	0.20	0.50	1.00	2.00	3.00
LiCl	0.792	0.761	0.742	0.781	0.931	1.174
NaBr	0.781	0.739	0.695	0.687	0.732	0.817
$NaNO_3$	0.758	0.702	0.615	0.548	0.481	0.438
$MgCl_2$	0.565	0.520	0.514	0.613	1.143	
$CaCl_2$	0.531	0.482	0.457	0.509	0.807	
Na_2SO_4	0.45	0.36	0.27	0.20		
$ZnSO_4$	0.15	0.11	0.065	0.045	0.036	0.04

Change of Activity Coefficient with Temperature.—Activity coefficients change somewhat with temperature, so that those based on freezing points require correction before being compared with coefficients derived from cell potentials at 25°. The following data are typical:

t	0°	10°	20°	30°	40°	50°	60°
0.1*m*. HCl	0.803	0.802	0.799	0.794	0.789	0.785	0.781
0.1*m*. NaCl	0.781	0.781	0.779	0.777	0.774	0.770	0.766
1.0*m*. HCl	0.842	0.830	0.816	0.802	0.787	0.770	0.754
1.0*m*. NaCl	0.638	0.649	0.654	0.657	0.657	0.656	0.654

INTERIONIC-ATTRACTION THEORY[1]

The most important recent event in theoretical electrochemistry is certainly the publication of papers on the interionic attraction theory of electrolytes by Debye and Hückel[2] and by Onsager.[3] Although the picture these authors give of the phenomena occurring in solutions of electrolytes has none of the engaging simplicity of the electrolytic-dissociation theory as advanced by Arrhenius, there is little doubt that the later theory, incomplete as it must be granted to be in details, is remarkably successful in organizing and predicting the results of measure-

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[1] These paragraphs are condensed from the excellent paper of Shedlovsky, Brown, and MacInnes in *Trans. Electrochem. Soc.*, **66**, 237 (1934). For an extensive bibliography and further discussion of this material, see Scatchard, *Chem Reviews*, **13**, 7, (1933), MacInnes, "Principles of Electrochemistry," Chap. VII, 1939, or Harned and Owen, *op. cit.*, 1943.

[2] DEBYE and HUCKEL, *Physik Z.*, **24**, 305 (1923), **26**, 93 (1925)

[3] ONSAGER, *ibid.*, **27**, 338 (1926), **28**, 277 (1927).

ments. In the interionic-attraction theory of electrolytes the properties of the solutions are considered to be due to the interplay of electrostatic forces and thermal vibrations The first of these tends to give the ions a definite arrangement, and the second acts to produce a random distribution.

The methods of Debye and Huckel are still the subject of discussion and occasionally of acrimonious dispute, but they have led to equations that could be tested experimentally. It appears to be a safe statement that, in dealing with the thermodynamic properties of dilute solutions of electrolytes in solvents of high dielectric constant, the more accurate the experimental data the more surely they can be fitted by equations obtained by Debye and Hückel or by extensions devised to make them mathematically more adequate.

These equations take account of the fact that the ions are not fully independent but must attract and repel each other in accordance with Coulomb's law. If these electrical forces were the only ones acting on the ions, they would tend to arrange themselves in a space-lattice, as in a salt crystal. However, the ions are also subject to thermal vibration of increasing intensity as the temperature is raised. The properties of an ionic solution are thus due largely to the interplay of these two effects. Since the electrostatic forces increase as ions approach each other, it follows that these properties must change as the concentration changes, and that the ions cannot have the same mobilities and osmotic (thermodynamic) properties in concentrated and dilute solutions, as postulated by the Arrhenius theory. It is a real triumph for the modern theory that the changes of these properties, at least in dilute solutions, are quantitatively as predicted.

It is a result of the presence of electrostatic forces that any selected ion, a positively charged one, for instance, will, on the average, have more negative ions near it than if the distribution were purely random. This is known as the "ion atmosphere" of the selected ion. This distribution gives rise to a potential around the ion that may be computed from the Debye-Hückel equation.

From the thermodynamic point of view the effect of the presence of the ionic atmosphere is to reduce the activity coefficients of the ions. The presence of the ionic atmosphere has at least two results on electrolytic conductance, both of which tend to decrease the ion mobilities with increasing ion concentration. These are known as (1) the electrophoretic effect and (2) the time of relaxation effect. Both these were considered by Debye and Huckel. However, the theory of conductance of electrolytes in its present form is to a large extent the work of Onsager.

We have space here only for the original equation of Debye and Hückel, which is

$$\ln \gamma = e^3 N^2 \sqrt{\frac{\pi}{R}} \left(- \frac{z^2 \sqrt{\Sigma c z^2}}{R(KT)^{1.5}} \right) \tag{16}$$

In this expression z is the valence of the ion, R is the gas constant, K is the dielectric constant of the solvent, T is the absolute temperature, e is the electronic charge, c is the ion concentration per centimeter cube, and N is Avogadro's number. For an aqueous solution of a salt of the KCl type at 25° this equation may be reduced to the following one in which all the constants are combined into a single term,

$$-\log \gamma = 0.50 \sqrt{m} \tag{17}$$

where m is now the molality of the solution. It will be noted that this equation contains no term which is characteristic of the solute. This relation is valid only in very dilute solutions; a better approximation is

$$\log \gamma = \frac{-0.50 \sqrt{m}}{1 + \sqrt{m}} \tag{18}$$

When ions of valence other than unity are present in solution, this relation is best given in terms of the valences z_+ and z_- of the ions and the ionic strength μ, which is defined as $\mu = \frac{1}{2}(\Sigma C z^2)$. The relation is

$$\log \gamma = \frac{-0.50 z_+ z_- \sqrt{\mu}}{1 + \sqrt{\mu}} \tag{19}$$

Comparisons of measured activity coefficients with those calculated from these equations show a remarkable agreement at low concentrations, but the agreement is much less satisfactory at moderate concentrations.[1] Among the additional effects that required consideration were the size of the ion, the variation in dielectric constant of the solvent produced by the presence of the solute, attraction between ions and solvent molecules, alteration of the forces acting between solvent molecules produced by the solute, changes in the hydration of solute ions at higher concentration, and possible ionic association. To allow for some of these effects, additional terms involving higher powers of the molality than its square root have been added to the equation above, but a consideration of the more complex equation would be out of place in an elementary text

According to the original treatment of Debye and Hückel or to the correction and extension of Onsager, the equivalent conductance decreases with increasing concentration for two reasons. The first, called the time of relaxation effect, comes from the fact that the ion atmosphere of a moving ion always lags behind; thus ahead there is always too little of the opposite charge for equilibrium, and behind there is always too much. The second, called the cataphoresis effect, arises from the fact that the ion must move through a medium bearing the opposite charge and therefore moving in the opposite direction.

As has been pointed out recently, the behavior of solutions containing "ionic atmospheres" is much more complex than any theory yet proposed assumes. When changes of hydration, Debye-Huckel electric effects, ionic association, dielectric constant of the medium, etc , unite in influencing the behavior of ions, any theory that pretends to explain the observations on the basis of one or a few of these variables cannot possibly be trusted as a sound solution of the problem. It should not be overlooked that ionized solutes exert a very marked effect also on molecules having no electric net charge.

Procedure to Be Followed in This Book.—In the present state of our knowledge the calculation of an activity coefficient is difficult and somewhat uncertain except in a dilute solution containing one salt of the simplest type. Comparatively little work has been done on the activity coefficients for ions in mixtures

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[1] An empirical extension of this equation suggested by Davies [*J. Chem. Soc* (*London*), **1938,** 2093] is obtained by subtracting 0.2μ from the one just given. It is claimed that the usual deviations from this equation are about 2 per cent in $0.1m$ solutions and proportionately less in more dilute solutions.

of salts. In the treatment of chemical equilibrium in the following chapters it would be very desirable to multiply the concentration of each ion by the appropriate activity coefficient if this were known. It is, however, unknown and we shall therefore make most of the calculations by using the ion concentration itself without an activity coefficient as a rough measure of the activity. We shall do so with the understanding that this procedure is not correct but that under present circumstances it is inexpedient for beginners to attempt exact calculations. When there is reason to believe that the solute is substantially un-ionized, we shall treat it as if it were not ionized. Problems involving solutes that are not "largely ionized" but that are not substantially un-ionized will not be treated in this text.

Problems

Numerical data for solving problems should be sought in the tables.

1. Write electrode reactions that illustrate each of the effects listed for anodes and cathodes on page 244.

2. The limiting equivalent conductance and the equivalent conductance at 0.01 *N* for potassium chloride change with temperature as follows:

t	15°	25°	35°	45°
Λ_0	121.1	149.9	180.5	212.5
$\Lambda_{0.01}$	114.3	141.3	169.9	199.7

(*a*) Plot these conductances against the temperature on a scale wide enough to allow extrapolation to 0° and 50°, and compute the conductance ratio Λ/Λ_0 for 0° and 50°. (*b*) The fluidity of water is 55.8 at 0°, 111.6 at 25°, and 182 at 50°. Recalculate Λ_0 for KCl at 0° and at 50° from the stated value for 25°, on the basis that all the change of conductance is caused by the changing fluidity of water, and draw on the same plot a line through these computed conductances and the actual conductance for 25°. [GUNNING and GORDON, *J. Chem. Phys.*, **10,** 126 (1942).]

3. Calculate the mole numbers for LiCl from the vapor-pressure data in Table 42.

4. Calculate the current required to deposit an atomic weight of chromium in 10 hr., on the assumption that the electrolyte is a solution of chromic acid and that 90 per cent of the electricity is used in the evolution of hydrogen gas at the cathode and 10 per cent is used in reducing chromic acid to chromium.

5. A transference experiment is run on a solution containing 8.00 grams of NaOH per 1000 grams of water, with a platinum anode and a silver chloride cathode, until 122 ml. of oxygen (25°, 1 atm.) is evolved. The cathode portion weighs 252.53 grams and contains 1.36 grams of NaOH. (*a*) Write the electrode reactions and complete gain-and-loss tables for the anode and cathode portions, and calculate the transference number of hydroxide ion. (*b*) Assume that the cathode portion is thoroughly mixed after its removal from the apparatus, that the conductance ratio is 0.85, and calculate its specific conductance at 25°. (*c*) The transference tube was 18 sq. cm in cross section, and the experiment ran for 4 hr. How far did the hydroxide ions in the middle portion move during the experiment?

6. The freezing-point lowerings of solutions of $MgSO_4$ at several molalities are given in Table 43. Calculate the mole number corresponding to each of the concentrations.

7. A 0 1*m*. solution of lithium iodide is electrolyzed in a transference experiment The electrodes consist of a platinum anode and a silver iodide cathode. By titration with thiosulfate solution, it was found that the anode portion contained 1 27 grams of free iodine The net gain of lithium iodine in the cathode portion is 0 445 gram. (*a*) Construct gain-and-loss tables for both anode and cathode portions (*b*) Calculate the transference number of iodide ion in LiI (*c*) Assume the experiment repeated with a solution 0 1*m* in HI in the same apparatus with the same quantity of electricity used. Write new gain-and-loss tables for the experiment, taking 0 18 as the transference number of iodide ion in HI.

8. A solution of 10.00 grams of perchloric acid per 1000 grams of water is electrolyzed at 25° in a tube of 20 sq cm. cross section between a silver anode and a platinum cathode with a current of 0 134 amp for 2 hr $AgClO_4$ is a soluble salt. The anode portion after electrolysis weighed 405 2 grams and contained 3 16 grams of $HClO_4$ (*a*) Write the electrode reactions and complete gain-and-loss tables for both portions, and calculate the transference number of perchlorate ion in the solution (*b*) Calculate the distance moved by perchlorate ions in the middle portion (*c*) Calculate the specific conductance of the anode portion. Assume that normality is equal to molality and that the conductance ratio is 0 90

9. A solution of 1 gram of HF per 1000 grams of water was electrolyzed between silver electrodes for 10 hr with a current of 0 01 amp. An anode portion weighing 480 2 grams contains 0 415 gram of HF AgF is a soluble salt Write electrode reactions and gain-and-loss tables for the anode and cathode portions of solution, and calculate the transference number of fluoride ion in HF.

10. A solution containing 3 65 grams of HCl per 1000 grams of water is electrolyzed for 10 hr at 25° with a uniform current in a tube 10 sq cm in cross section, between silver electrodes. The anode increases in weight 1.00 gram, and the anode portion after electrolysis weighs 601 3 grams and contains 0 0364 equivalent of HCl. (*a*) Write the electrode reactions, and show the gains and losses of each ion in the anode portion (*b*) What is the transference number of chloride ion in this solution? (*c*) How far did the chloride ions move in 10 hr ? (*d*) What was the current? (*e*) The limiting equivalent conductance of chloride ion at 25° is 76 reciprocal ohms. Estimate the specific conductance of the middle portion, and state within about what limits the estimate is reliable.

11. A current of 0.0193 amp. passes for 2.78 hr. through a solution of 6.3 grams of nitric acid per 1000 grams of water at 25° in a long tube fitted with a silver anode and a platinum cathode. After the electrolysis the anode portion weighs 402.75 grams and contains 2.415 grams of HNO_3. (*a*) Compute the weight of $AgNO_3$ in this portion and the change in the weight of HNO_3 in it. (*b*) Write gain-and-loss tables for the anode and cathode portions, with the electrode reactions at the head of each table, and compute the transference number of hydrogen ion in 0.1 *N* HNO_3 at 25°.

12. The resistance of a centimeter cube of 0.1 *N* HNO_3 at 25° is 26.0 ohms. A potential of 10 volts is applied to a tube of 0.1 *N* HNO_3 15 cm. long and 5 sq. cm. in cross section for 1 min. Neglect concentration changes near the electrodes, and calculate the number of faradays carried by the nitrate ion. How far did these ions move?

13. A sample of "hard water" known to contain only calcium sulfate and calcium bicarbonate in appreciable quantities is submitted for analysis. At 18° the specific conductance of the hard water is 0.00100. It is boiled (without loss of water) and cooled to 18°, when its specific conductance is found to be 0.000757. Assume that Λ/Λ_0 is 0.85 for each salt, that boiling completely changes the calcium bicarbonate to insoluble $CaCO_3$, and calculate the concentration of calcium sulfate ("permanent hardness") and of calcium bicarbonate ("temporary hardness"). Express the results as molecular weights per liter. The limiting equivalent conductances are Ca = 51, SO_4 = 68, and HCO_3 = about 35.

14. A solution of 65.60 grams of NaCl in 1000 grams of water is electrolyzed in a transference apparatus at 25° with a silver anode and a silver chloride cathode. A coulometer in the circuit deposited 5.670 grams of silver. The anode portion after the experiment weighed 120.23 grams and contained 6.409 grams of NaCl. Write the electrode reactions and complete gain-and-loss tables for both electrode portions, and calculate the transference number of sodium ion in the solution.

15. A transference experiment is made with a solution containing 7.39 grams of $AgNO_3$ per 1000 grams of water and using two silver electrodes. A coulometer in the circuit deposited 0.0780 gram of silver. At the end of the experiment the anode portion weighed 23.38 grams and contained 0.2361 gram of $AgNO_3$. (*a*) Write complete gain-and-loss tables for both electrode portions, and calculate the transference number of silver ion. (*b*) The cathode portion weighed 25.00 grams. How much silver nitrate did it contain?

16. (*a*) Show by a diagram approximately how the specific conductance would change as 0.1 *N* HCl is added to 0.1 *N* sodium acetate in the following proportion:

HCl, ml.	90	99	100	101	110
NaAc, ml.	100	100	100	100	100

Bear in mind that acetic acid is only very slightly ionized in the presence of HCl or NaAc. (*b*) Calculate the specific conductance of the solution containing 110 ml. of HCl.

17. A 10-ml. sample of commercial liquid bleach, containing sodium hydroxide, sodium chloride, and sodium hypochlorite, is diluted to about 500 ml. and titrated with 0.5 *N* hydrochloric acid, using the electrical conductance of the mixture as an indicator (since color indicators are bleached by hypochlorites.) Draw a plot roughly to scale showing burette reading against conductance, which is taken after every 1.0-ml addition of acid. Indicate how the plot should be read to determine the quantities of sodium hydroxide and sodium hypochlorite present. (A typical analysis might show about 0.5 *N* sodium hydroxide, 2 *N* sodium chloride, and "125 grams per liter available chlorine.")

18. The equivalent conductance at 25° for monoethanolammonium hydroxide changes with the concentration as follows:

10^3C	0.228	0.385	0.490	1.018	2.687	5.347
Λ	74.87	60.12	54.14	39.07	24.93	17.95

The limiting equivalent conductance of the *chloride* of this base is 118.58 at 25°. Calculate the fractional ionization of the base in these solutions. [SIVERTZ, REITMEIER, and TARTAR, *J. Am. Chem. Soc.*, **62,** 1379 (1940).]

19. A transference experiment is made at 25° with a solution containing 185.2 grams of CsCl per 1000 grams of water and with a silver anode and a silver chloride cathode. A silver coulometer in the circuit deposited 5.48 grams of silver. The cathode portion weighed 117.22 grams and contained 21.88 grams of CsCl. (*a*) Write the electrode reactions and complete gain-and-loss tables for the anode and cathode portions, and calculate the transference number of cesium ion in this solution. (*b*) Assume that the experiment was made with a platinum cathode and the same quantity of electricity and that the cathode portion after electrolysis contained the same weight of water as in part (*a*), and write a new gain-and-loss table for the cathode portion.

CHAPTER VIII

THERMOCHEMISTRY

The purpose of this chapter is to show how the recorded calorimetric data and the first law of thermodynamics may be combined with certain useful approximations to calculate the heat effects attending chemical reactions Measured heat effects are available for many reactions, and therefore calculations are not always required; but the obvious impossibility of measuring the heat effect attending every chemical reaction at every concentration and every temperature makes calculations from the available data a most important matter for chemists and engineers. The available materials for these calculations are (1) an adequate theory, (2) experimental data, and (3) useful approximations with which to supplement the data when necessary. Since the enthalpy increase attending an isothermal chemical change varies with the temperature and concentration of the reacting substances, it is necessary to specify carefully the composition of the systems involved if the enthalpy change is to have an exact meaning. Before proceeding with the actual calculations we review briefly the factors that determine the "state" of a system, we review the first law of thermodynamics, and we consider the experimental methods by which the data are obtained. It is suggested that pages 33 to 36 be read again in this connection.

Since the changes involved in this chapter are taking place either at constant volume or at constant pressure, the work done will be either zero or $p(v_2 - v_1)$. When only liquids and solids are involved, the work corresponding to changes in volume against atmospheric pressure is negligible; and for systems involving gases Δv will be substantially equal to ΔnRT, Δn being the change in the number of *moles of gas* in the chemical reaction.

For the purposes of this chapter it will be sufficient to consider a calorie as the heat required to raise the temperature of a gram of water 1° and a kilocalorie (written kcal.) as 1000 times this quantity, without specifying whether it is a "15° calorie," a "20° calorie," a "mean" calorie, or a "defined" calorie; and it will be sufficient to assume 4.18 joules per cal. We may leave until the need arises the definition that a "15° calorie" is 4.185 abs. joules and 4.1833 "international" joules or that a "20° calorie" is 4.1793 international joules. These distinctions are important for exact work but are not required for a first consideration of thermochemistry.

It should be recalled that the definition of an ideal gas is contained in *two* equations

$$pv = nRT \qquad \text{and} \qquad \left(\frac{\partial E}{\partial v}\right)_T = 0$$

The second of these relations, combined with the definition $H = E + pv$, gives

$$\left(\frac{\partial H}{\partial p}\right)_T = 0$$

which means that the enthalpy of an ideal gas at constant temperature is independent of pressure. Thus this equation and $pv = nRT$ also define the ideal gas.

Changes in the State of a System.—When the state of a system is fully specified, every property of it is uniquely determined, though, of course, it is not necessary to *specify* every property of a system in order to fix its state. We need specify only so many properties that the others are fixed; for example, if (1) quantity, (2) composition, (3) state of aggregation, (4) pressure, and (5) temperature of a system (or of each of its parts if it consists of more than one phase) are stated, all the properties are determined, and the system is in a definite "state." A change in any property of the system constitutes a change in the state of the system. It is commonly true that the properties listed above are those observed experimentally, and they are the ones we shall ordinarily use in this book, though others may be used in place of them. For example, we may specify the volume of a homogeneous system in place of the temperature or pressure In the calculations that follow, a pressure of 1 atm. is assumed to prevail unless some other pressure is specified.

It will be recalled that the energy content E and the enthalpy H are *properties of a system* in a specified state, that changes in them are dependent on the change in state and fully determined by the initial and final states of the system undergoing change without regard to the mechanism or process of the change. This is not true of the heat absorbed during a change in state or of the work done by the system during a change in state. It is for this reason that the heat effects are described by ΔE and ΔH in this chapter, as is the common custom in physical chemistry.

The "surroundings" of a system may be defined as any matter or space with which the system exchanges energy.

First Law of Thermodynamics.—The relations by which the first law of heat, or the first law of thermodynamics, are expressed were given on page 33. They are

$$\oint dE = 0 \qquad \Delta E = E_2 - E_1 \qquad \Delta E = q - w \qquad (1)$$

In these expressions E denotes the energy content of a system in a specified state, ΔE the increase in energy content attending a change in state, q the heat *absorbed by the system* in such a change of state, and w the work *done by the system.* Since the integral of dE around a complete cycle is zero, it follows that ΔE for any part of a cycle is equal to $-\Delta E$ for the remainder of the cycle. Hence, if ΔE is the increase in energy content attending a change in state by any path, ΔE for the reverse change in state *by any path* has the same numerical value and the opposite sign; for only so may the energy content of the system return to its initial value when the system returns to its initial state.

The relation in the form $\Delta E = E_2 - E_1$ emphasizes the fact that ΔE has the same value for a specified change in state by all paths. Hence, if by a series of reactions the same change in state is produced as by a single reaction, ΔE for the over-all change in state is the sum of the separate ΔE values of the individual steps. This important fact allows the calculation of ΔE for reactions that are inconvenient to measure calorimetrically but that are the sums of readily measurable steps or the differences between readily measurable steps. The fact that ΔE for a given change is equal to the sum of the ΔE values for a series of changes producing the same net effect was proved experimentally about a hundred years ago by the experiments of Hess and was long known as the *law of Hess*. This law has been of the greatest service in thermochemistry, but it is only a special statement of the first law of thermodynamics.

Another quantity called the enthalpy, which is a property of a system in a specified state, is defined by the equations

$$\begin{aligned} H &= E + pv \\ \Delta H &= \Delta E + \Delta(pv) \\ \Delta H &= H_2 - H_1 \end{aligned} \tag{2}$$

Since E, p, and v are all properties of a system, it follows that H is a property of a system, that $\oint dH = 0$, and that dH is an exact differential.

The relation $\Delta H = H_2 - H_1$ shows that ΔH for a given change in state produced in a single step is equal to the sum of the ΔH values for a series of changes which produce the same over-all change in state. This fact will be of great service in the calculations that are outlined in this chapter. Although ΔH is not restricted to changes at constant pressure or restricted in any way, it will be the convenient quantity to sum for *constant-pressure* processes, since it is then equal to q, as we shall see below. ΔE will be the convenient quantity to sum for *constant-volume* processes, since in these changes $\Delta E = q$.

For the special condition of changes in state at *constant pressure*, during which no work is done other than changes in volume against constant pressure, the ΔH relation is

$$\Delta H = q - w + p(v_2 - v_1) = q_p \tag{3}$$

and ΔH is a measure of the heat absorbed. Similarly, for changes in state at constant volume, $\Delta E = q - w = q_v$, since $w = 0$ when the volume is constant. When both pressure and volume change, the general relations

$$\Delta E = q - w \qquad \text{and} \qquad \Delta H = \Delta E + \Delta(pv)$$

may still be used, since they imply no restrictions as to the mechanism of the process. It should be noted that w is the work actually done and not the work that might have been done in a more efficient process. This work is $p(v_2 - v_1)$ when the process takes place at constant pressure. When the pressure varies as the process takes place, it is necessary to express p as a function of v before integrating $p\,dv$.

Thermochemical Equations.—Chemical equations are incomplete descriptions of changes in state, and they may be made into complete statements by specifying the pressure and temperature, together with the state of aggregation when this is not obvious. For example, the equation

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

does not constitute a complete formulation of a change in state, though it states the quantities and compositions of the substances undergoing change. In order to specify definitely the change in state we should write

$$CH_4(g,\ 25°,\ 1\ \text{atm.}) + 2O_2(g,\ 25°,\ 1\ \text{atm.}) = CO_2(g,\ 25°,\ 1\ \text{atm.}) + 2H_2O(l,\ 25°,\ 1\ \text{atm.}) \qquad \Delta H = -212.79\ \text{kcal.}$$

Since at low pressures $(\partial H/\partial p)_T$ is zero or very small for gases, this change in state may be formulated more briefly, and yet so fully as to be completely understood, as follows:

$$CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(l) \qquad \Delta H_{298} = -212.79\ \text{kcal.}$$

An example of a change in state in which no chemical change occurs is

$$H_2O(l) = H_2O(g,\ 1\ \text{atm.}) \qquad \Delta H_{373} = 9700\ \text{cal.} \qquad \Delta E_{373} = 8950\ \text{cal.}$$

The subscript attached to ΔH is always understood to mean ΔH for the isothermal change in state. Later we shall see that ΔH for any change in state is a function of the temperature and that means are available for calculating its change with changing temperature, but we may give as a simple example to show the necessity of specifying the temperature

$$H_2O(l) = H_2O(g,\ 0.1\ \text{atm.}) \qquad \Delta H_{323} = 10{,}250\ \text{cal.}$$

It must be clearly understood that the changes in state formulated are complete changes. For illustration, the expression

$$H_2(g,\ 1\ \text{atm.}) + I_2(g,\ 1\ \text{atm.}) = 2HI(g,\ 1\ \text{atm.}) \qquad \Delta H_{573} = -3070\ \text{cal.}$$

means that this increase in enthalpy attends the formation of 2 moles of HI at 573°K. It does not mean that when 1 mole of hydrogen and 1 mole of iodine vapor are brought together at 573°K. this effect will be observed; for the reaction is incomplete, and substantial quantities of both hydrogen and iodine remain at equilibrium with less than 2 moles of HI in this system.

Much confusion has been brought into thermochemistry by using the term "heat of reaction," which some writers define as the heat absorbed by a reaction and others as the heat evolved. It is partly to avoid this confusion (but chiefly because the terms depend on the change in state and are independent of the path followed) that we use ΔH and ΔE. Students should form the habit of saying "heat absorbed by a reaction" or "ΔH for a reaction," rather than using the ambiguous "heat of a reaction," which may be misunderstood. Some tables of thermochemical data record the heat *evolved* by chemical changes; others give heat *absorbed.* Data are given in small calories (usually abbreviated cal.) or in large calories (written kg.-cal. or kcal. or Cal. for 1000 cal) or in kilojoules (written kj. for 238.9 cal.). Whenever reference books are consulted, it will be necessary to give careful attention to this difference in notation and usage.

We shall not follow the older custom of writing a thermochemical equation in the form

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(l) + 68.32 \text{ kcal. at } 25°$$

in which a positive sign attached to a heat quantity signifies heat lost from the system. We shall follow the practice, which is now almost standard, of writing this same fact in the form

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(l) \qquad \Delta H_{298} = -68.32 \text{ kcal.}$$

since it is the enthalpy increase attending a change in the state of a system that is used in the thermodynamic calculations of physical chemistry, and it is best to become accustomed to this usage at the start.

Thermochemical Methods.—Heat effects attending changes in state are measured in a calorimeter, which is a reaction vessel immersed in a tank of water isolated from its surroundings. The change in temperature of the calorimeter and its heat capacity furnish the quantities for computing the heat effect for an isothermal change in state. This is equal to ΔE if the change in state takes place at constant volume and to ΔH if it occurs at constant pressure. But in the calorimetric process itself ΔE is zero and the temperature is not constant. In order to make this clear, consider the change in state

$$CO(25°, 1\ atm.) + \tfrac{1}{2}O_2(25°, 1\ atm.) = CO_2(25°, 1\ atm.)$$

for which ΔE at 25°C. is desired. Imagine a calorimeter large enough to contain $1CO + \frac{1}{2}O_2$ at 25° and 1.5 atm. total pressure. The change in state taking place in the calorimeter when these substances react is

$$\begin{array}{lcl} 1CO(p = 1\ atm.) + \tfrac{1}{2}O_2(p = \tfrac{1}{2}\ atm.) & = & 1CO_2(p\ \text{above}\ 1\ atm\ ) \\ \quad t = 25° & & \quad t = 25° + \Delta t \end{array}$$

and for this change in state $\Delta E = 0$. By removing a quantity of heat equal to Δt times the heat capacity of the calorimetric system in its final state (this system is a mole of CO_2, a quantity of water, the container, and the temperature-measuring devices), the final system is restored to 25°. If $-q$ is the heat removed from the system, then $-q$ will be the heat evolved by the *isothermal* change in state

$$1CO(25°, 1\ atm\ ) + \tfrac{1}{2}O_2(25°, \tfrac{1}{2}\ atm.) = CO_2(25°, 1\ atm.)$$

for this change is the sum of the calorimetric process for which ΔE was zero and the cooling process for which $\Delta E = -C_v\,\Delta t$. Since the volume was constant, no work was done and ΔE will be equal to the heat *absorbed* by the system, which is $+q$. The heat of mixing the gases is negligible at these pressures, and $(\partial E/\partial v)T$ is also negligible for gases at low pressures; therefore ΔE for the process occurring in the calorimeter is substantially equal to ΔE for the initial change of state formulated. We may write for this change in state

$$1CO(25°, 1\ atm\ ) + \tfrac{1}{2}O_2(25°, 1\ atm.) = 1CO_2(25°, 1\ atm.)$$
$$\Delta E_{298} = -67.64\ kcal.$$

In this book we shall express the quantities ΔH and ΔE in small calories when they are small and usually in kilogram-calories when they are large, and ΔH will be positive when heat is absorbed by the system at constant pressure. Likewise ΔE will be positive when heat is absorbed by the system at constant volume.

In order to prevent any loss of heat by exchange between the calorimeter and its surroundings, the latter are often maintained at the same temperature as the calorimeter itself As the temperature of the calorimeter rises during a reaction produced in it, a parallel rise is produced in the surroundings, usually by adding sulfuric acid to a solution of sodium hydroxide or by electric heating A diagram of such a piece of apparatus[1] is shown in Fig 45, which shows the bomb type of calorimeter arranged for burning a volatile liquid.

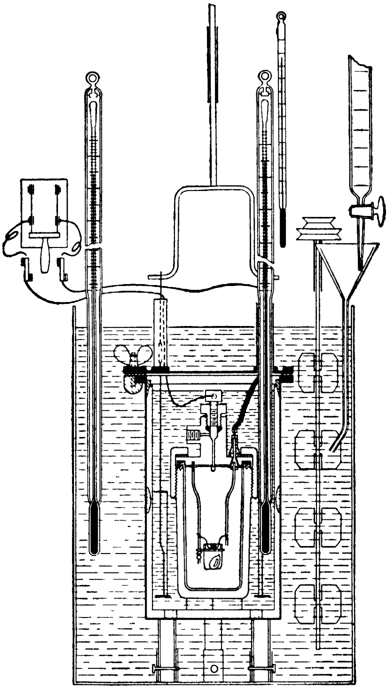

FIG 45 —Calorimeter, arranged for combustion of a volatile liquid

The material to be burned is placed in a glass receptacle of very thin walls in a platinum crucible suspended in a heavy steel bomb lined with gold, which is then filled with oxygen under considerable pressure The bomb is placed in the calorimeter (the inner vessel of water), and the substance is burned completely by means of the excess oxygen present. The heat liberated causes a rise in temperature that is indicated on the thermometer reaching to the inner vessel, and a parallel rise in temperature of the outside vessel of sodium hydroxide solution is produced by adding strong sulfuric acid from a burette at the required rate. Since the outer bath is always kept at the same temperature as the calorimeter within it, there is

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[1] RICHARDS and BARRY, *J. Am. Chem. Soc*, **37**, 993 (1915).

no exchange of heat between them, and all the heat of reaction is used to change the temperature of the calorimeter itself The total heat evolved by an isothermal change is then the product of temperature change and heat capacity of the calorimeter system A convenient means of measuring the heat capacity of a combustion bomb, the water surrounding it, and its container is by burning benzoic acid, which evolves 6324 cal per gram (weighed in air or 6319 cal per gram weighed *in vacuo*) in the same vessel. Thus all the data needed for the calculation are at hand The heat evolved per gram of unknown substance is to 6324 cal as the temperature change produced per gram of unknown is to the temperature change produced per gram of benzoic acid in the same apparatus

An outline of the computation and of the necessary corrections (for incompletely condensed water in the bomb, the formation of traces of nitric acid, heat of combustion of the ignition wire, etc) to the observed temperature rise in a calorimeter is given by Washburn.[1]

Heat effects for reactions taking place in solutions may be determined in the same way, a thin platinum vessel containing one solution being substituted for the bomb The other solution is discharged into this vessel from a pipette immersed in the calorimeter, in order that the solutions may be at the same temperature when they are mixed for the reaction.

Heat Capacity and Specific Heat.—The heat absorbed by a substance during a change in temperature is a quantity that must frequently be calculated. While it is true in general that a heat capacity is defined by the relation $c = dq/dT$, it is necessary to specify the conditions under which the heating occurs before this relation has an exact meaning. We define the heat capacity at constant volume by the relation

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v$$

and the heat capacity at constant pressure by the relation

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial E}{\partial T}\right)_p + p\left(\frac{\partial v}{\partial T}\right)_p$$

The *specific heat* is defined as the quantity of heat absorbed per gram per degree, and the heat capacity of any quantity other than a gram is the product of specific heat and mass. All the data given in this chapter, and in general in the chemical literature, refer to atomic heat capacity or molal heat capacity. Since ΔH for a change in state which involves heating a system at constant pressure through a range of temperature is $\int C_p\, dT$

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[1] *J. Research Nat. Bur. Standards*, **10**, 525–558 (1933).

between the initial and final temperatures, it is necessary to express C_p as a function of temperature before performing the integration except for the comparatively few substances of which the heat capacities do not change with temperature. For *monatomic gases* we have already seen on page 81 that the molal heat capacities are $C_v = \frac{3}{2}R$ and $C_p = \frac{5}{2}R$, both independent of temperature For any gas that conforms to the ideal gas law $pv_m = RT$, the relation

$$C_p - C_v = R$$

gives the difference between the molal heat capacities, whether the molecule has one or several atoms.

The molal heat capacities of *diatomic gases* are higher than those of monatomic gases, and they increase with rising temperature As a sufficient approximation for the solution of problems at the end of the chapter we may take the molal heat capacity as

$$C_p = 6.5 + 0.001T$$

for O_2, N_2, H_2, CO, HCl, HBr, HI, NO, and any diatomic gas or mixture of diatomic gases (except the halogens) at any moderate pressure and in the temperature range 300 to 2000°K. This equation will give the heat absorbed within 2 or 3 per cent; more accurate heat-capacity equations are given in Table 56.

Some other convenient approximations for use in the problems, which are intended to illustrate the methods rather than to provide precise answers, are $C_p = 8.5$ cal. per mole per deg. for water vapor below 800°K., $C_p = 2.0 + 0.005T$ for carbon (300 to 1000°K), $C_p = 7.0 + 0.007T$ for CO_2 or SO_2 in the same temperature range.

The entries in Table 55 will be useful in calculating the heat absorbed by some common gases when heated. They show the heat absorbed upon heating a mole of gas through 100° intervals. For example, the integral of Bryant's equation for C_p of carbon dioxide between 273 and 373°K. is 935 cal., the integral between 273 and 473°K. is 1936 cal., and these are the first two entries in the column headed $H - H_{273}$ for CO_2 in Table 55. The difference between these quantities is given under Δ and is obviously ΔH for the interval 373 to 473°K. Linear interpolation is of course permitted, and the heat absorbed in the interval 273 to

TABLE 55.—INTEGRALS OF HEAT-CAPACITY EQUATIONS FOR GASES[1]
(In calories per mole from 273°K. at constant pressure)

Temp., °K.	H_2		O_2		CO		CO_2		H_2O	
	$H - H_{273}$	Δ	$H - H_{273}$	Δ	$H - H_{273}$	Δ	$H - H_{273}$	Δ	$H - H_{273}$	Δ
273	0		0		0		0		0	
		693		707		688		935		791
373	693		707		688		935		791	
		695		728		705		1001		822
473	1388		1435		1393		1936		1613	
		700		749		722		1064		852
573	2088		2184		2115		3000		2465	
		703		767		737		1120		880
673	2791		2951		2852		4120		3345	
		707		784		752		1172		908
773	3498		3735		3604		5292		4253	
		712		800		766		1220		936
873	4210		4535		4370		6512		5189	
		718		814		779		1261		963
973	4928		5349		5149		7773		6152	
		724		826		791		1299		989
1073	5652		6175		5940		9072		7141	
		731		837		802		1331		1014
1173	6383		7012		6742		10403		8155	
		738		847		812		1358		1039
1273	7121		7859		7554		11761		9194	
		745		854		821		1381		1064
1373	7866		8713		8375		13142		10258	
		754		861		830		1397		1086
1473	8620		9574		9205		14539		11344	
		763		865		836		1411		1109
1573	9383		10439		10041		15950		12453	
		772		869		844		1418		1132
1673	10155		11308		10885		17368		13585	
		782		870		849		1420		1153
1773	10937		12178		11734		18788		14738	
		793		871		854		1418		1173
1873	11730		13049		12588		20206		15911	
		804		869		857		1410		1194
1973	12534		13918		13445		21616		17105	
		815		867		860		1399		1213
2073	13349		14785		14305		23015		18318	
		828		861		862		1380		1231
2173	14177		15646		15167		24395		19549	

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[1] G. B TAYLOR, *Ind. Eng. Chem.*, **26**, 470 (1934), based on the heat-capacity equations of Bryant, *ibid*, **25**, 820 (1933).

873° will differ but little from the heat absorbed in the interval 293 to 893°. These data may of course be used in the solution of problems. The column headed CO may also be used for N_2, the column headed H_2O may also be used for H_2S, and the column headed CO_2 may also be used for SO_2.

One should not conclude too hastily that apparently different heat-capacity equations for a given substance are discrepant when the constants in them are not the same. As a single illustration, we quote four equations for the heat capacity of carbon dioxide at constant pressure and give after each one its integral between 400 and 500°K., which is the calculated heat absorption when a mole of CO_2 is heated through this range:[1]

$$
\begin{aligned}
&(1)\ C_p = 10.34 + 0\ 00274T - 1.955 \times 10^5/T^2 && \Delta H = 1060 \text{ cal.}\\
&(2)\ C_p = 6\ 85 + 0.00853T - 0.00000247T^2 && \Delta H = 1030 \text{ cal.}\\
&(3)\ C_p = 6\ 37 + 0.0101T - 0.0000034T^2 && \Delta H = 1020 \text{ cal.}\\
&(4)\ C_p = 5.17 + 0.0152T - 0.00000958T^2 && \\
&\qquad\qquad + 2.26 \times 10^{-9}T^3 && \Delta H = 1030 \text{ cal.}
\end{aligned}
$$

But one must also be prepared to find heat-capacity equations which do not give the same heat absorption and between which it is difficult to choose For example, the integral of another heat-capacity equation for CO_2,

$$C_p = 7\ 7 + 0.0053T - 0.00000083T^2$$

from 400 to 500°K., is 900 cal ; yet this equation at temperatures above 1200°K. gives the heat absorption for CO_2 as well as any and is probably the best one for high temperatures.[2]

The data quoted have been for heating at constant pressure. Since $(\partial H/\partial p)_T$ is zero for ideal gases and very small for real gases at low pressures, these equations may be used at any constant pressure below 3 to 5 atm. unless high precision is required. Under these conditions $pv = nRT$ will also apply, and hence heat capacities of gases at constant volume may be obtained by subtracting R cal. per mole from the constant-

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[1] The equations are from (1) Gordon and Barnes in Kelley's compilation, *U.S. Bur. Mines Bull*, **371,** 18 (1934), (2) Bryant, *Ind. Eng. Chem* , **25,** 820 (1933), (3) and (4) Spencer and Flannagan, *J. Am. Chem. Soc.*, **64,** 2511 (1942).

[2] EASTMAN, *U.S. Bur. Mines Tech. Paper,* **445** (1929).

TABLE 56.—SOME HEAT CAPACITIES AT CONSTANT PRESSURE[1]

Substance	Molal heat capacity at constant pressure	Per cent error	Temperature range
H_2	$6.85 + 0.00028T + 0.22 \times 10^{-6}T^2$	1.5	300–2500
O_2, N_2	$6.76 + 0.000606T + 0.13 \times 10^{-6}T^2$	1.5	300–2500
CO_2	$7.70 + 0.0053T - 0.83 \times 10^{-6}T^2$	2.5	300–2500
NH_3	$6.7 + 0.0063T$	1.5	300– 800
H_2O	$8.22 + 0.00015T + 1.34 \times 10^{-6}T^2$	1.5	300–2500
H_2S	$7.2 + 0.0036T$	5–10	300– 600
SO_2	$7.70 + 0.0053T - 0.83 \times 10^{-6}T^2$	2.5	300–2500
Cl_2	$8.28 + 0.00056T$	1.5	273–2000
C	$2.673 + 0.00262T - 1.17 \times 10^5/T^2$	2	273–1373
HCl	$6.70 + 0.00084T$	1.5	273–2000
HBr	$6.80 + 0.00084T$	2	273–2000

pressure equations; for example, $C_v = 4.5 + 0.001T$ is a suitable approximation for the diatomic gases.

No general expressions are known for the heat capacities of *liquids;* they are usually larger than those for the corresponding solids.

The heat capacities of most of the *solid elements* approach about 6 cal. per atomic weight per degree near room temperature; they fall off rapidly at lower temperatures in a way that is not expressible by a simple equation such as that used for gases, as shown in Fig. 15 on page 152. Above ordinary temperatures the atomic heats of most solid elements increase slightly.

The heat capacities of solid compounds are *roughly* equal to the sum of the heat capacities of the elements in them (Kopp's law). Thus the molecular heat capacity of lead iodide is about equal to that of an atomic weight of lead plus that of two atomic weights of iodine, or about 18.6 cal. per mole per deg.; but large deviations from this "law" are so common as to make it of little value except as a rough guide when data are unavailable.

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[1] From Kelly, *U.S. Bur. Mines Bull.*, **371** (1934), who gives a critical review of the heat capacities of inorganic substances together with equations expressing the "best values" as functions of the temperature. These equations are in the conventional form $C_p = a + bT + cT^2$ and also in the form $C_p = a + bT - c/T^2$ for some hundreds of substances. Equations for 59 gases, in both these forms, are given by Spencer and Flannagan in *J. Am. Chem. Soc.*, **64,** 2511 (1942).

An *aqueous solution* usually has a heat capacity less than that to be expected from a mixture rule, and for calculations involving temperature changes in solutions it is necessary to measure heat capacities experimentally.[1] In approximate calculations a fair assumption is that the heat capacity of a solution is equal to that of the water it contains. For example, one may assume that a 10 per cent aqueous solution has a heat capacity of 0.90 cal. per gram per deg., a 20 per cent solution 0.8 cal. per gram per deg., etc. In general, the actual heat capacities are even less than such estimates; for example, the heat capacity of a 10 per cent solution of $MgBr_2$ is 0.79 cal. per gram per deg. The *effective* heat capacity of dissolved KCl is shown in the following table, in which m is the moles of KCl added to 1000 grams of water and C_p is the heat capacity of the resulting solution. It will be seen that the heat capacities of solutions must be measured rather than estimated, since the addition of KCl to water decreases the heat capacity of the solution to less than that of the water alone.[2]

m	0.55	1.11	2.22	3.33	4.44
C_p	986	975	968	968	966
$\Delta C/m$	−26	−23	−15	−10	−8

Changes in State of Aggregation.—Heats of evaporation have already been considered in Chap. IV. The heat absorbed in small calories per mole of liquid evaporated at constant pressure is approximately 22 times the absolute boiling point (Trouton's rule) for many liquids, but large deviations from this rule are often found, and recourse to experiment is necessary when reliable data are required. Some latent heats of evaporation at atmospheric pressure are given in Table 16.

No general rule similar to Trouton's rule is applicable to latent heats of fusion. The ratio $\Delta H_f/T$ for a mole of substance varies

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[1] Data are recorded in the "International Critical Tables," Vol. V, p. 122, and by Rossini in *J. Research Nat. Bur. Standards*, **4,** 313 (1930).

[2] In more dilute solutions the "partial molal heat capacity" approaches a definite limit. The heat capacities, in calories per gram of solution at 25°, for KCl and NaCl are given by Hess and Gramkee in *J. Phys. Chem.*, **44,** 483 (1940), as follows:

m	0.010	0.050	0.070	0.100	0.300	0.700	1.03
c_p(KCl)	0.9968	0.9929	0.9908	0.9881	0.9695	0.9342	0.9090
c_p(NaCl) . . .	0.9971	0.9943	0.9928	0.9903	0.9762	0.9501	0.9319

from 1.6 to 18.2; it has no constant value that may be used in estimating heats of fusion. Some molal latent heats of fusion are given in Table 21.[1] Many of the heats of fusion given in tables are derived from freezing points of solutions through the equations on page 215, which is permissible, of course, if the data are reliable. Unfortunately, not all the freezing-point data represent true equilibrium between a solution and the crystalline solvent, and therefore not all the recorded heats of fusion from this source are reliable. For example, the molal heat of fusion of bromine is 2580 cal. by direct calorimetry; and two values said to be based on the freezing-point constant are 2380 and 2780. Even wider variations are not uncommon.

Transitions from one crystalline form to another also absorb small quantities of heat, for example, $S_{\text{rhom}} = S_{\text{monocl}}$; $\Delta H_{368} = 95$ cal. and $C_{\text{diam}} = C_{\text{graph}}$; $\Delta H_{298} = -454$ cal , of which the first has been measured both directly and by several indirect methods and the second is the difference between the heats absorbed by the combustion of diamond and β-graphite.

Heat Absorbed by Reactions at Constant Pressure and at Constant Volume.—Two methods of procedure are followed in calorimetric work, and it is convenient to correct the values obtained by one procedure to those which would have been obtained had the other procedure been employed. Thus when iron is dissolved in acid in an open vessel, the hydrogen formed must force back the atmosphere to make room for itself, thus doing work. If the reaction had been carried out in a closed bomb, a pressure of hydrogen would have been built up and no work would have been performed. The work done is $p(v_2 - v_1)$ in the first process in which hydrogen was evolved at 1 atm. and is zero for the constant-volume process. An amount of heat equivalent to this work is absorbed in the constant-pressure process but not in the constant-volume process. The heat absorbed during the reaction at 1 *atm. pressure* is ΔH; but since no work is done by the reaction that takes place at *constant volume*, the heat absorbed is ΔE. By definition these quantities differ from one another by $\Delta(pv)$, that is,

$$\Delta H = \Delta E + p(v_2 - v_1) \tag{4}$$

---

[1] For the best compilation of heats of fusion, see Kelley, *U S. Bur. Mines Bull*, **393** (1936).

In this expression v_2 is the volume of a mole of hydrogen plus that of a mole of dissolved ferrous chloride, and v_1 is the volume of the iron and acid from which it was formed. There is only a slight change in the volume of the solution, and the volume of the iron may be neglected in comparison with that of the gas. The work term then becomes practically pv_2, which from the ideal gas equation is RT. Since the value of R is 1.99 cal., the correction term is at once available in calories, and the difference between ΔH and ΔE for this reaction at 20° is $1.99 \times 293 = 586$ cal. of heat absorbed per mole of gas generated. This should be rounded to 600 cal , since otherwise upon addition we should write down a larger number of significant figures than the experimental work justifies.

For reactions involving only solids and liquids, the difference between heats of reaction at constant volume and at constant pressure usually need not be taken into account. For reactions in which gases are involved, the increase in volume is due to the *increase* in the number of *moles of gas* during the reaction. In general,

$$\Delta H = \Delta E + \Delta nRT \tag{5}$$

where Δn is the increase that takes place in the number of *moles of gas* when the reaction occurs. For the combustion of methane at 20°, for example, the change in state may be written

$$CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(l)$$
$$\Delta H_{291} = -212.79 \text{ kcal}$$

Since $\Delta n = -2$, $\Delta nRT = -1.17$ kcal., and ΔE for this change in state is -211.62 kcal.

All the data quoted in this chapter are for constant pressure.

Molal Enthalpy of Combustion (Heat of Combustion).—Enthalpy increases for combustion have been determined precisely for almost all combustible substances, and they are used to calculate enthalpies of formation, as will be explained in the next section. Some illustrations are quoted in Table 57, and many others are known.[1]

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[1] Data for about 1500 substances are given by Kharasch in *J. Research Nat Bur. Standards*, **2**, 359 (1929); see also "International Critical Tables," Vol. V, pp. 163–169.

The combustion of organic compounds severs C—C, C—H, C═C, and C≡C bonds and changes C—O to C═O, and to each of these changes a fixed enthalpy increase may be assigned. These assigned quantities enable one to estimate the enthalpy of combustion when data are lacking and are hence useful approximations. The assigned enthalpies of combustion are[1] −52.25 kcal. for each C—H bond, −53.72 for each C—C, −121.8 for each C═C, −203.2 for each C≡C, and −15.0 for each C—O bond in the compound. For illustration, ethane contains six C—H bonds and one C—C bond, whence ΔH for its combustion is estimated to be −367.3 kcal., compared with −372.81 by experiment. For saturated hydrocarbons[2] above C_5H_{12} the addition of each CH_2 group increases the molal ΔH of combustion by −157.0 kcal. For all *saturated* hydrocarbons the molal enthalpy of combustion is almost −52.7 kcal. for each atomic weight of oxygen used;[3] this approximation gives −368.9 kcal. for ethane. As is always true, experimental data are better than approximations, but data are not always available.

TABLE 57.—MOLAL ENTHALPY OF COMBUSTION

[In kilogram-calories absorbed per mole of substance oxidized to $CO_2(g)$ and $H_2O(l)$ at 25° and constant pressure]

Substance	ΔH_{298}	Substance	ΔH_{298}
Methane (*g*)	−212.79	Methyl alcohol (*l*)	−173.64
Ethane (*g*)	−372.81	Ethyl alcohol (*l*)	−326.66
Propane (*g*)	−530.57	*n*-Propyl alcohol (*l*)	−482.15
n-Butane (*g*)	−687.94	*n*-Butyl alcohol (*l*)	−638.10
n-Pentane (*g*)	−845.3	iso-Butyl alcohol (*l*)	−638.2
Acetylene (*g*)	−310.5	Benzoic acid (*s*)	−771.85
Ethylene (*g*)	−337.3	Salicylic acid (*s*)	−722.0
Naphthalene (*s*)	−1231.0	Formic acid (*l*)	−63.0
Benzene (*l*)	−781.0	Acetic acid (*l*)	−206.7
Toluene (*l*)	−934.6	Sucrose (*s*)	−1349.6

Molal Enthalpy of Formation (Heat of Formation).—The enthalpy increase for the formation of compounds that may be synthesized in pure form from the elements is determined directly in a calorimeter. For example,

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[1] SWIETOSLAWSKI, *J. Am. Chem. Soc.*, **24,** 1312 (1920).

[2] ROSSINI, *Ind Eng. Chem.*, **12,** 1424 (1937).

[3] THORNTON, *Phil. Mag.*, **33,** 196 (1917).

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) = HCl(g) \qquad \Delta H_{298} = -22.06 \text{ kcal.}$$
$$S(s) + O_2(g) = SO_2(g) \qquad \Delta H_{298} = -70.94 \text{ kcal.}$$

Data for compounds that are not readily formed in a calorimeter may be obtained through the fact that ΔH for a specified change in state is the same by all paths. It is necessary only to devise paths by which the desired change may be brought about, one of which includes the reaction whose enthalpy increase is desired. As an illustration, suppose ΔH were required for the synthesis of benzoic acid, which may not be made directly from the elements by procedures adapted to calorimetry. One path, by which benzoic acid is formed and then burned to CO_2 and H_2O, is shown by the equations

$$7C(s) + 3H_2(g) + O_2(g) = C_6H_5COOH(s) \qquad \Delta H_{291} = x \text{ kcal.}$$
$$C_6H_5COOH(s) + 7\tfrac{1}{2}O_2(g) = 7CO_2(g) + 3H_2O(l)$$
$$\Delta H_{291} = -771.85 \text{ kcal.}$$

The sum of these equations gives another path by which $7CO_2$ and $3H_2O$ may form from the elements,

$$3H_2(g) + 7C(s) + 8\tfrac{1}{2}O_2(g) = 7CO_2(g) + 3H_2O(l)$$
$$\Delta H_{291} = -863.17 \text{ kcal.}$$

and for which ΔH is $7(-94.03) + 3(-68.32) = -863.17$ kcal., from Table 58. Since the enthalpy increase $-771.85 + x$ must be equal to -863.17, it follows that ΔH_{291} is -91.32 kcal. for the formation of solid benzoic acid from its elements.

The enthalpy of benzoic acid determined in the preceding paragraph is probably reliable to within ± 0.5 kcal., for its heat of combustion is a calorimetric standard that has been measured with care. Less reliable data and smaller differences between large quantities often yield small enthalpies of high percentage error. For example, the enthalpy of liquid toluene may be calculated from the following equations:

$$7C(s) + 4H_2(g) = C_6H_5CH_3(l) \qquad \Delta H = x \text{ cal.}$$
$$C_6H_5CH_3(l) + 9O_2(g) = 7CO_2(g) + 4H_2O(l)$$
$$\Delta H = -934.6 \text{ kcal.}$$

$$7C(s) + 4H_2(g) + 9O_2(g) = 7CO_2(g) + 4H_2O(l)$$
$$\Delta H = -931.5 \text{ kcal.}$$

Thus the enthalpy of liquid toluene is 3.1 ± 0.5 kcal., since at least this error is possible in the heat of combustion (though not in the data for CO_2 and H_2O) and a larger error is not excluded. Since the heat of evaporation of toluene is 8.0 kcal., the enthalpy of $C_6H_5CH_3(g)$ is 11.1 kcal., and this may be used to calculate ΔH for a reaction such as

$$n\text{-}C_7H_{16}(g) = C_6H_5CH_3(g) + 4H_2(g)$$

to be 59.4 kcal. with an uncertainty of less than 1 kcal. by a method that is explained in the next section.

Molal Enthalpy of Compounds (Molal Heat Contents).—It has become customary to define the molal enthalpy of an *elementary* substance in its stable state at 1 atm. pressure and a standard temperature as zero. Under this convention the enthalpy increase for the formation of a compound from its elements becomes its molal enthalpy. For example, the formation of Na_2S from its elements at 18° is shown by the equation

$$2Na(s) + S(s) = Na_2S(s) \qquad \Delta H_{291} = -89.8 \text{ kcal.}$$

and since the enthalpies of the elements are defined as zero, the molal enthalpy, or molal heat content, of Na_2S is -89.8 kcal.

This definition of enthalpies of elements as zero is an arbitrary one, and thus the enthalpies of the compounds are relative to this standard. If the enthalpy of solid sodium is taken as zero at 18°, its enthalpy at 25° is obviously not zero *relative to this standard.* The point is that, if sodium and sulfur are zero at 18°, Na_2S is -89.8 kcal. at 18°; if sodium and sulfur are zero at 25°, Na_2S is -89.8 at 25°. (The change in heat capacity attending the reaction, which is neglected in this calculation and which we shall consider later in the chapter, would influence the third figure *after* the decimal point in this calculation and is outside of the precision of the data.)

Enthalpy tables sometimes contain entries such as

$$Br_2(g) = 7.4 \text{ kcal.}$$

If the enthalpy of liquid bromine is zero at 25° and the latent heat of evaporation to form saturated vapor at 25° and 0.28 atm. is 7.4 kcal., the enthalpy of the vapor is thus 7.4 kcal. at 25° and 0.28 atm. For the imaginary state of bromine vapor at 25° and 1 atm. the same figure is used, since $(dH/dp)_T$ is substantially zero for gases at moderate pressures. The value $I_2(g) = 14.88$ kcal. is similarly obtained from the heat of sublimation of the solid.

If we denote the enthalpy of any chemical system in state 1 by H_1, which is the sum of the enthalpies of all the substances in the system, and the enthalpy of the system in state 2 by H_2, the change in enthalpy attending the change from state 1 to state 2 is the difference between H_1 and H_2, which may be written

$$H_1 + \Delta H = H_2 \qquad \text{or} \qquad H_1 = H_2 - \Delta H \tag{6}$$

We may thus calculate ΔH for any isothermal chemical reaction when the molal enthalpies of the reacting substances and reaction products are known, whether or not the reaction is adapted to calorimetry. The recorded enthalpies are for the formation of compounds at 1 atm. in their stable states at the standard temperature from the elements in their stable states at 1 atm. and the standard temperature.

Unfortunately the standard temperature selected by various writers is not the same,[1] but it is usually 18° or 25°. When the enthalpies of compounds at 18° are referred to the elements at 18°, the quantities are almost equal to those for compounds at 25° referred to the elements at 25°; and the differences are usually less than the experimental errors in the fundamental data. An exception to this statement is required for reactions involving the formation or use of ions; for in these reactions ΔH is often small, and the change with temperature is usually large. The actual calculation, with the underlying theory, will be given later in the chapter, but we may note here for illustration

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[1] Bichowsky and Rossini use 18° in their "Thermochemistry of Chemical Substances," and record Qf, which is our $-\Delta H$, for the formation, transition, fusion, and evaporation of all substances for which data exist (5840 values of Qf for formation) except for organic compounds containing more than two atoms of carbon. The data in "International Critical Tables," Vol. V, are for 18°. Lewis and Randall choose 25° as the standard temperature in their "Thermodynamics," McGraw-Hill Book Company, Inc., New York, 1923. They record also molal free energies at this temperature, since it is desirable to have both quantities at the same temperature to avoid laborious corrections. Latimer's extensive compilation of data in "Oxidation Potentials," Prentice-Hall, Inc., New York, 1938, also uses 25° as the standard temperature for molal enthalpies and molal free energies.

$$NH_4OH.Aq = NH_4^+.Aq + OH^-.Aq \qquad \Delta H_{293} = 1070 \text{ cal.}$$
$$NH_4OH.Aq = NH_4^+.Aq + OH^-.Aq \qquad \Delta H_{298} = 865 \text{ cal.}$$

The data for formic acid give an even more striking illustration.

$$HCOOH.Aq = H^+.Aq + COOH^-.Aq \qquad \Delta H_{293} = +192 \text{ cal.}$$
$$HCOOH.Aq = H^+.Aq + COOH^-.Aq \qquad \Delta H_{298} = -\ 13 \text{ cal.}$$

With the exception of such reactions, the enthalpy data for 18° may be used at 18°, 20°, 25°, or 27° (= 300°K.) without introducing errors that exceed the discrepancies in the available data. Some molal enthalpies are given in Table 58 for use in the problems at the end of the chapter. We may illustrate the use of such data by calculating ΔH for the reaction at 25°.

$$Na_2S(s) + 2HCl(g) = 2NaCl(s) + H_2S(g)$$

The enthalpy of the system in its first state is $-89.8 + 2(-22.06)$ kcal., whence $H_1 = -133.92$ kcal.; and H_2 is $2(-98.36) - 4.8$, or -201.52. Since $\Delta H = H_2 - H_1$, its value for the reaction is $\Delta H_{298} = -67.60$ kcal. A simple procedure for carrying out such a calculation, applicable to any reaction, is to write under each chemical formula in an equation the molal enthalpy of that substance, multiplied by the coefficient for the substance in the equation, as follows:

$$\begin{array}{lclc}
Na_2S(s) + 2HCl(g) & = & 2NaCl(s) + H_2S(g) & \\
-89.8 + 2(-22.06) & = & 2(-98.36) + -4.8 & -\Delta H \\
H_1 & = & H_2 & -\Delta H
\end{array}$$

It will be seen that we may substitute the molal enthalpy of a chemical substance for its formula in a chemical equation and by adding $-\Delta H$ as a term at the end of the equation obtain an equation which is readily solved for ΔH. Thus the sign of the quantity and its numerical value are obtained by a procedure that is not likely to cause an error.

This same result might have been obtained, somewhat more laboriously, by adding together in an appropriate way the expressions for the individual molal enthalpies, as follows:

$$\begin{array}{lcll}
Na_2S & = & 2Na + S & \Delta H = 89.8 \text{ kcal.} \\
2HCl & = & H_2 + Cl_2 & \Delta H = 44.12 \text{ kcal.} \\
2Na + Cl_2 & = & 2NaCl & \Delta H = -196.72 \text{ kcal.} \\
H_2 + S & = & H_2S & \Delta H = -4.8 \text{ kcal.} \\
\hline
Na_2S + 2HCl & = & H_2S + 2NaCl & \Delta H = -67.60 \text{ kcal.}
\end{array}$$

This calculation has been made for a change in state involving only the solids and gases. Since all these substances dissolve in water with appreciable enthalpy changes, ΔH for this reaction in water would not be -67.60 kcal., but another value. In order to calculate ΔH for the reaction in solution we require the molal enthalpies of the substances as solutes. This calculation will be given later in the chapter, after we have discussed enthalpy changes attending solution in water.

A word of explanation regarding quantities such as

$$H_2O(g) = -57.82$$

and $NH_3.Aq$ or $NH_4OH.Aq$ may be helpful. The enthalpy for water vapor comes from $-68\ 32$, which is the enthalpy of liquid water at 25° and 1 atm. referred to hydrogen and oxygen, and from $\Delta H = 10.50$ kcal. for the evaporation of water to form saturated vapor at 25° and 0.03 atm., which would give -57.82 kcal for the enthalpy of water vapor at 0.03 atm. For the compression to the unstable condition of vapor at 25° and 1 atm we assume $\Delta H = 0$, since $(\partial H/\partial p)_T = 0$ for the compression of an ideal gas. There is no implication that water vapor has been observed at 25° and 1 atm. pressure; we accept the value as a convenience in making calculations that involve water vapor Since ΔH is independent of path, the same result is obtained with less labor than is required for calculations along the actual path. This will be clear if the student will calculate ΔH for the two following paths, which accomplish the same net change in state:

$$(1)\ H_2O(l,\ 25°,\ 1\ \text{atm.}) = H_2O(l,\ 100°,\ 1\ \text{atm.}) = H_2O(g,\ 100°,\ 1\ \text{atm.})$$

and .

$$(2)\ H_2O(l,\ 25°,\ 1\ \text{atm.}) = H_2O(g,\ 25°,\ 0.03\ \text{atm.}) = H_2O(g,\ 100°,\ 0.03\ \text{atm.}) = H_2O(g,\ 100°,\ 1\ \text{atm.})$$

The difference between $NH_3.Aq$ and $NH_4OH.Aq$ will of course be -68.32 kcal., which is the standard enthalpy of a mole of liquid water. We have no information as to what fraction of the dissolved ammonia is NH_3 and what fraction is hydrated ammonia (NH_4OH); and since ΔH must be the same quantity whether a neutralization equation, for example, is written

$$NH_3.Aq + H^+.Aq = NH_4^+.Aq$$

or

$$NH_4OH.Aq + H^+.Aq = NH_4^+.Aq + H_2O(l)$$

it is evident that −68.32 kcal. must be the difference between $NH_3.Aq$ and $NH_4OH.Aq$. The same statement applies, of course, to $CO_2.Aq$ and $H_2CO_3.Aq$ or to $SO_2.Aq$ and $H_2SO_3.Aq$. Since these differences are conventional ones to serve the purpose illustrated, it will be evident that the quantities may not be used to show that $\Delta H = 0$ for "reactions" such as $NH_3.Aq + H_2O(l) = NH_4OH.Aq$, for we have no evidence that this is a reaction.

Enthalpy of Solution (Heat of Solution).—A few substances dissolve in water with the absorption of heat, but the majority of solids, liquids, and gases dissolve with the evolution of heat. The molal enthalpy change upon solution varies with the temperature and the quantity of solvent per mole of solute, up to a certain limit characteristic of the solute. For example, ΔH for the solution of 1 $HCl(g)$ in water at 18° varies with N, the moles of solvent water as follows:[1]

NAq	1	2	3	5	10	20
ΔH, kcal	−6.24	−11.5	−13.37	−15.00	−16.29	−16.86
NAq	50	100	200	500	1000	Limit
ΔH, kcal	−17.20	−17.32	−17.41	−17.50	−17.52	−17.63

We should thus write −22.06 − 11.5, or −33.56, kcal. for the molal enthalpy of $HCl.2Aq$ and −39.26 for $HCl.50Aq$ or HCl (1*m*.). A solution of a mole of HCl in so much water that the addition of more water caused no appreciable heat effect will be written $HCl.Aq$ in thermochemical equations to indicate indefinite dilution. This is sometimes written $HCl.\infty Aq$, but the notation $HCl.Aq$ is preferred, since there are many properties of HCl that change at lower concentrations and therefore the solution is not "infinitely" dilute except in the thermochemical sense. We use the symbol Aq, as in $HCl.25Aq$, to denote 25 moles of solvent water and reserve the formula H_2O

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[1] Data for the dilution of HCl at lower molalities are given by Sturtevant, *J. Am. Chem. Soc.*, **62**, 584 (1940). His heats of dilution are in agreement with those above.

TABLE 58—MOLAL ENTHALPIES OF COMPOUNDS[1] AT 298°K.

Substance	ΔH_{298}	Substance	ΔH_{298}	Substance	ΔH_{298}
$HCl(g)$	− 22 06	$NOCl(g)$	12 8	$KClO_3(s)$	− 91.33
$HBr(g)$	− 8 65	$NOBr(g)$	17 7	$KClO_4(s)$	−112 71
$HI(g)$	5 91	$SO_2(g)$	− 70 94	$AgCl(s)$	− 30 40
$H_2O(g)$	− 57 82	$SO_2\ Aq$	− 77 20	$AgBr(s)$	− 23 81
$H_2O(l)$	− 68 32	$SO_3(s)$	− 105 2	$AgI(s)$	− 15 17
$H_2S(g)$	− 4 80	$S_2Cl_2(l)$	− 14 3	$CuCl(s)$	− 34 3
$H_2S\ Aq$	− 9 27	$Ag_2O(s)$	− 7 30	$CuCl_2(s)$	− 53 4
$H_2SO_4(l)$	−193 75	$CaO(s)$	− 152 2	$NH_4Cl(s)$	− 75 20
$HNO_3(l)$	− 41 66	$PbO(s)$	− 52 4	$Hg_2Cl_2(s)$	− 63 15
$CS_2(l)$	15 4	$PbO_2(s)$	− 65 9	$PbCl_2(s)$	− 85 71
$CCl_4(l)$	− 33 8	$HgO(s)$	− 21 6	$AlCl_3(s)$	−166 8
$CH_4(g)$	− 17 87	$Cu_2O(s)$	− 42 5	$MgO(s)$	−143 84
$C_2H_2(g)$	54 23	$CuO(s)$	− 38 5	$Mg(OH)_2(s)$	−221 48
$C_2H_4(g)$	12 56	$ZnO(s)$	− 83 17	$MgCO_3(s)$	−265 4
$C_2H_6(g)$	− 20 19	$Al_2O_3(s)$	− 399 0	$H^+\ Aq$	0
$C_3H_6(g)$	4 96	$Ca(OH_2)(s)$	− 236 1	$Na^+\ Aq$	− 57 48
$C_3H_8(g)$	− 24 75	$CaCO_3(s)$	− 288 6	$K^+\ Aq$	− 60.10
$CO(g)$	− 26 39	$NaCl(s)$	− 98 36	$NH_4^+\ Aq$	− 31 71
$CO_2(g)$	− 94 03	$NaOH(s)$	− 101 96	$Ag^+\ Aq$	+ 25 29
$CH_3OH(l)$	− 57 45	$Na_2S(s)$	− 89 8	$Ca^{++}\ Aq$	−129 87
$C_2H_5OH(g)$	− 56 95	$Na_2SO_4(s)$	− 330 20	$Mg^{++}\ Aq$	−111 52
$C_2H_5OH(l)$	− 67 14	Na_2SO_4-		$Zn^{++}.Aq$	− 36 43
$C_2H_5OH\ Aq$	− 69 82	$10H_2O(s)$	−1032 78	$Cl^-\ Aq$	− 39 94
$CH_3COOH(l)$	−117 7	$NaNO_3(s)$	− 111 60	$Br^-.Aq$	− 28 83
$CH_3COOH.Aq$	−118 06	$Na_2CO_3(s)$	− 270 97	$I^-\ Aq$	− 13 61
$H_2CO_3\ Aq$	−167 06	$NaHCO_3(s)$	− 226 97	$OH^-.Aq$	− 54 95
$NH_3(g)$	− 10 93	$KCl(s)$	− 104 19	$HCO_3^-.Aq$	−165 22
$NH_4OH.Aq$	− 87 53	$KOH(s)$	− 102 02	$NO_2^-.Aq$	− 25 60
$NO(g)$	21 53	$KI(s)$	− 78 87	$NO_3^-\ Aq$	− 49 32
$NO_2(g)$	7 96	$K_2S(s)$	− 121 5	$SO_4^{--}\ Aq$	−215 8
$N_2O_5(g)$	0 6	$K_2SO_4(s)$	− 341 68	$CO_3^{--}\ Aq$	−161 72

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[1] Additional data, in kilogram-calories *evolved* per mole of substance at 18°, will be found in Bichowsky and Rossini, "Thermochemistry of Chemical Substances," where over 5000 entries are given. g = gas, l = liquid, s = solid, and Aq = dilute solution Ionic enthalpies are all based on the arbitrary assignment of zero to $H^+\ Aq$, and therefore $Cl^-\ Aq$ has the same assigned enthalpy as $H^+Cl^-.Aq$ We shall see in later chapters that hydrogen ion has other assigned values of zero, such as its free energy. Since in all calculations it is the *difference* in enthalpy between products and reacting substances that is useful, zero for H^+ is as good as any other quantity.

for water that is a reacting substance or reaction product, as in the thermochemical equation

$$H^+Cl^-.25Aq + Na^+OH^-.25Aq = Na^+Cl^-.50Aq + H_2O$$
$$\Delta H_{298} = -14.00 \text{ kcal.}$$

As enthalpy equations, solution and dilution may be written

$$HCl(g) + 5Aq = HCl.5Aq \qquad \Delta H_{291} = -15.0 \text{ kcal.}$$
$$HCl(g) + Aq = HCl.Aq \qquad \Delta H_{291} = -17.63 \text{ kcal.}$$

The difference between these two equations is obviously the enthalpy of dilution of HCl.5Aq to its limit, and it would be written

$$HCl.5Aq + Aq = HCl.Aq \qquad \Delta H_{291} = -2630 \text{ cal.}$$

Since the symbol Aq without a figure attached means so large an amount of solvent water that the addition of more water produces no heat effect, this last equation and that on page 314 for neutralization are "balanced," even though there appears to be an excess of water on the left side. The solution indicated by HCl.Aq is "indefinitely" dilute rather than "infinitely" dilute. For dilutions with smaller quantities of water, the equations may be written

$$HCl.20Aq + 80Aq = HCl.100Aq \qquad \Delta H_{291} = -460 \text{ cal}$$

Partial Molal Enthalpy of Solution or Dilution.—By plotting ΔH per mole of solute against the moles of water added to 1 mole of a solute S, one obtains curves that usually rise steeply at first and become horizontal for such large quantities of water that the heat of further dilution is negligible. The tangent to such a curve at $N = 5$ moles of water, for example, is the "partial molal ΔH of dilution" of a solution of composition S.5Aq. It is the heat absorbed upon adding a mole of *water* to so large a quantity of solution that there is a negligible change in composition of the solution, and it is usually written $\partial H/\partial N_{Aq}$. There is also a partial molal enthalpy for solution of the *solute* in a solution, which is the heat absorption attending the solution of a mole of *solute* in so large a quantity of S.5Aq that the change in composition of the solution is negligible. These partial molal heat quantities are important ones in many chemical calculations, such as the temperature coefficients of electromotive force in cells that form a solute into a solution, which we shall consider in Chap. XIX.

The relation of one to the other is shown by the following two procedures for introducing 1 mole of S and 5 moles of water into a large amount of solution of composition S.5*Aq.*:

1. Mix 1S with 5*Aq*, cool (or heat) to the original temperature, and add this solution of S.5*Aq* to the main body of S.5*Aq*. The enthalpy increase for the first step is the "integral heat of solution"

$$S + 5Aq = S.5Aq \qquad \Delta H = a \text{ cal}$$

For the second step, by which a solution is mixed with more solution of the same composition, $\Delta H = 0$.

2. Add a mole of S to the main quantity of solution; then add 5*Aq* to this solution, for which the enthalpy increases are $(\partial H/\partial N_S)$ and $5(\partial H/\partial N_{Aq})$, respectively. Since the sum of these steps produces the same net change as those in the first procedure, the relation between the quantities is

$$\left(\frac{\partial H}{\partial N_S}\right) + 5\left(\frac{\partial H}{\partial N_{Aq}}\right) = a$$

For example, when 1HCl is added to 5*Aq* at 18°, ΔH is $-15{,}000$ cal., but the heat effect upon adding 1HCl to a large quantity of HCl.5*Aq* has another value. The slope of the curve obtained by plotting the data for the dilution of HCl on page 314 is $(\partial H)/(\partial N_{H_2O}) = -440$ cal. at $N = 5$. The partial molal heat of solution of HCl is then obtained through the above equation from these quantities, since

$$\left(\frac{\partial H}{\partial N_{HCl}}\right) + 5(-440) = -15{,}000$$

and $(\partial H)/(\partial N_{HCl})$ is $-12{,}800$ cal. At $N = 40Aq$, $(\partial H/\partial N_{Aq})$ is only -9 cal., and $(\partial H/\partial N_{HCl})$ is $-16{,}780$, since the integral heat of solution, which is *a* in the above equation, is $-17{,}140$ cal. when HCl dissolves in 40*Aq*

Reactions in Solution.—The method of calculating ΔH for reactions in solution is the same as that for other reactions; one writes the chemical reaction and under each chemical formula the enthalpy of the solute ion or molecule or liquid or solid, then uses the relation $H_1 = H_2 - \Delta H$ as before. As an illustration we may calculate ΔH for the reaction of sodium sulfide with dilute hydrochloric acid, using the data in Table 58

$$\begin{array}{lcl} Na_2S(s) + 2H^+Cl^-.Aq & = & 2Na^+Cl^-.Aq + H_2S.Aq \\ -89.8 \quad + 2(-39.94) & = & 2(-97.42) \quad - 9.27 - \Delta H \\ H_1 & = & H_2 \quad -\Delta H \end{array}$$

whence $\Delta H = -34.43$ kcal. It will be recalled that for the reaction involving only gases and solids (page 312) ΔH was -67.60 kcal.

Enthalpy of Neutralization (Heat of Neutralization).—Neutralization of a "dilute" highly ionized acid by a "dilute" highly ionized base causes an enthalpy increase of −13,610 cal. at 20°, almost independent of the nature of the acid and base. The chemical effect common to all such neutralizations, which is substantially the only change responsible for the heat effect observed, is the union of hydrogen ion and hydroxyl ion to form water. This effect in a "dilute" solution may be shown by thermochemical equations of the usual form:[1]

$$\begin{array}{ll} H^+.Aq + OH^-.Aq = H_2O & \Delta H_{293} = -13{,}610 \text{ cal.} \\ H^+.Aq + OH^-.Aq = H_2O & \Delta H_{298} = -13{,}360 \text{ cal.} \end{array}$$

These values apply only for dilute solutions of acid and base and only when both acid and base are highly ionized in solution. Because of the different heats of dilution of acid, base, and salt, ΔH for neutralization will have a different value for each molality of salt formed when the concentrations are moderate or high. For illustration, we quote the variation of ΔH_{298} for the neutralization of sodium hydroxide with hydrochloric acid of equal strength as a function of the molality of the salt solution formed:[2]

m(NaCl)	0.5	1.0	2.0	3.0	4.0	5.0	6.0
$-\Delta H$..	13,750	14,000	14,600	15,500	16,500	17,700	18,950

When moderately dilute solutions of *slightly ionized* acids are neutralized by dilute highly ionized bases (or when the acid is highly ionized and the base slightly ionized), enthalpy increases are observed that differ materially from −13,610 cal. per mole of acid at 20° or −13,360 cal. at 25°, since under these circum-

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[1] The data in this section are quoted from Pitzer, *ibid.*, **59**, 2365 (1937).

[2] Kegles, *ibid.*, **62**, 3230 (1940).

stances the formation of water from its ions is not the only thermal process attending neutralization. For example, the neutralization of boric acid may be imagined to take place in two steps as follows:

$$\mathrm{HBO_2}.Aq = \mathrm{H^+}.Aq + \mathrm{BO_2^-}.Aq \qquad \Delta H_{298} = 3360 \text{ cal.}$$

$$\mathrm{H^+}.Aq + \mathrm{OH^-}.Aq = \mathrm{H_2O} \qquad \Delta H_{298} = -13{,}360 \text{ cal.}$$

$$\mathrm{HBO_2}.Aq + \mathrm{Na^+OH^-}.Aq = \mathrm{Na^+BO_2^-}.Aq + \mathrm{H_2O} \qquad \Delta H_{298} = -10{,}000 \text{ cal.}$$

The experimentally determined quantities are −10,000 cal. for neutralizing boric acid and −13,360 cal. for the union of hydrogen and hydrogen ions; and since ΔH is independent of path, the heat absorbed by ionization is determined by difference. This could not be determined by dilution of the acid solution with water, since ionization is far from complete at any dilution for which calorimetry is possible.

Enthalpy of Ionization.—Neutralization experiments such as the one just given are not the best method of determining enthalpies of ionization, since they are the differences between comparatively large quantities. An attempt to determine ΔH by this method for the reaction

$$\mathrm{CH_3COOH}.Aq = \mathrm{H^+}\ Aq + \mathrm{CH_3COO^-}.Aq \qquad \Delta H_{298} = -112 \text{ cal.}$$

would yield a value of little precision, and therefore ΔH for the *union* of the ions is measured instead. When a dilute solution of sodium acetate is mixed with a slight excess of dilute hydrochloric acid, the reaction is

$$\mathrm{Na^+Ac^-}.Aq + \mathrm{H^+Cl^-}.Aq = \mathrm{Na^+Cl^-}.Aq + \mathrm{HAc}.Aq$$
$$\Delta H = 112 \text{ cal.}$$

and thus ΔH for the ionization has the same value and the opposite sign. Some other enthalpies of ionization at 25° are −691 cal. for butyric acid, 2075 cal. for carbonic acid, 3600 for bicarbonate ion, −13 cal. for formic acid, −168 cal. for propionic acid, and 4000 cal. for sulfurous acid.[1]

The quantities $\Delta H_{293} = -13{,}610$ cal. and $\Delta H_{298} = -13{,}360$ cal. do not apply to the formation of water from its ions at other

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[1] PITZER, *ibid.*, **59**, 2365 (1937).

temperatures, for the change of ΔH with temperature is exceptionally high for this reaction. The general method of calculating ΔH as a function of the temperature is given later in this chapter, but we give here the final result,

$$H^+.Aq + OH^-.Aq = H_2O \qquad \Delta H = -28{,}260 + 50T$$

This equation is valid only in the range 273 to 313°K., since the data from which it was derived lie in this range. Substituting $T = 373$ into the equation, one obtains $\Delta H_{373} = 9610$ cal., but the result is unreliable and should at most be accepted as an indication that ΔH is about 9 or 10 kcal. at 373°K.

Change of Enthalpy with Temperature.—When ΔH is required at some single temperature other than that for which standard enthalpy tables are available, it may be calculated by specifying two paths for producing the same change in state and equating the summation of ΔH for the two paths, selecting one of them so that it involves the desired isothermal change at the desired temperature. A convenient procedure is to combine two isothermal steps for producing the *chemical* change with two constant-composition steps involving the *temperature* change, as illustrated in the following diagram:

$$\begin{tikzcd}
CO(g) + \frac{1}{2}O_2(g)\ 1473^\circ K. \arrow[r, "\Delta H_4 = \Delta H_1 + \Delta H_2 - \Delta H_3"] & CO_2(g)\ 1473^\circ K. \\
CO(g) + \frac{1}{2}O_2(g)\ 298^\circ K. \arrow[u, "\Delta H_3 = 13{,}780\ \text{cal.}"] \arrow[r, "\Delta H_1 = -67{,}640\ \text{cal.}"] & CO_2(g)\ 298^\circ K \arrow[u, "\Delta H_2 = 14{,}350\ \text{cal}"']
\end{tikzcd}$$

In this scheme the value of ΔH_1 is obtained from Table 58, and ΔH_2 and ΔH_3 have been obtained from Table 55, though they could also have been calculated by integrating the heat-capacity equations through the temperature range. Upon making the summation indicated for ΔH_{1473}, we find $-67{,}070$ cal. from these data. The final ΔH should be rounded to $\Delta H_{1473} = -67.0$ kcal., since the uncertainties in the basic data may exceed 0.1 kcal. in almost any such calculation.

When it is desired to express ΔH as a function of T for use in some other equation or when many calculations are to be made on the same change in state, a more general procedure is convenient. Consider any change in state in a homogeneous system for which the enthalpy increase is ΔH at T and $\Delta H + d\,\Delta H$ at $T + dT$. The enthalpy increase may be obtained as a function of the temperature by equating $\Sigma\,\Delta H$ for two paths by which the system passes from state 1 at T to a second state 2 at $T + dT$ If the change in state occurs isothermally at T and the products of the reaction are heated to $T + dT$ at constant pressure, the enthalpy increase is ΔH for the first step and $C_{p_2}\,dT$ for the second step, where C_{p_2} is the heat capacity of the system in state 2. If the reacting substances are heated to $T + dT$ and the change in state then occurs isothermally at this temperature, the enthalpy change is $C_{p_1}\,dT + (\Delta H + d\,\Delta H)$, where C_{p_1} is the heat capacity of the system in state 1. Upon equating the enthalpy changes for these two paths producing the same net change in state, we have

$$\Delta H + C_{p_2}\,dT = C_{p_1}\,dT + \Delta H + d\,\Delta H$$

or

$$d\,\Delta H = (C_{p_2} - C_{p_1})dT = \Delta C_p\,dT \qquad (7)$$

Since heat capacities are usually functions of the temperature, it is necessary to express them in powers of T before integrating equation (7).

We may illustrate the use of this general equation by the combustion of carbon monoxide,

$$CO(g) + \tfrac{1}{2}O_2(g) = CO_2(g) \qquad \Delta H_{298} = -67{,}640 \text{ cal.}$$

The heat capacity of a mole of CO and 0.5 mole of oxygen at constant pressure is found from Table 56, namely,

$$C_{p_1} = 10.14 + 0.0009T + 0.19 \times 10^{-6}T^2$$

and the heat capacity of a mole of CO_2 at constant pressure is

$$C_{p_2} = 7.70 + 0.0053T - 0.83 \times 10^{-6}T^2$$

whence ΔC_p for this reaction is obtained by subtracting the first of these equations from the second. Then we have

$$d\,\Delta H = (-2.44 + 0.0044T - 1.02 \times 10^{-6}T^2)dT$$
$$\Delta H = -2.44T + 0.0022T^2 - 0.34 \times 10^{-6}T^3 + \Delta H_0$$

The integration constant, which is usually written ΔH_0, is shown to be $-67{,}100$ cal. from the ΔH_{298} value given above; therefore, the complete expression is

$$\Delta H = -67{,}100 - 2.44T + 0.0022T^2 - 0.34 \times 10^{-6}T^3$$

The equation may, of course, be integrated between limits when only a single new value of ΔH is desired. For example, if only ΔH_{1473} is desired, integration between limits gives

$$\Delta H_{1473} - \Delta H_{298} = 600 \text{ cal.}$$

Whence $\Delta H_{1473} = -67{,}040$ cal. for this change in state, in agreement with the value of page 320.

The integration constant ΔH_0 is only an integration constant; we do not imply that it is ΔH for the change in state at absolute zero. The heat-capacity equations are valid in certain temperature ranges only, and ΔH_0 is a valid integration constant only in these ranges as well.

When any substance in a system undergoes phase transition (change of crystal form, fusion, or evaporation) in the temperature interval involved in a calculation, ΔH may not be expressed as a function of temperature by the relation

$$d\,\Delta H = \Delta C_p\,dT$$

for phase changes involve heat absorption at constant temperature that cannot be included in heat-capacity equations. The general method first given is of course applicable in these circumstances. For example, if liquid water is formed at the lower temperature and water vapor at the higher one, there is a large absorption of heat when evaporation takes place, with no attendant change of temperature, and the temperature function for C_p changes abruptly with the change in state of aggregation. A calculation for the union of hydrogen and oxygen to form water vapor at 150° will illustrate this point.

$$\begin{tikzcd}
\begin{matrix}2H_2 + O_2\\ 150^\circ,\ 1\text{ atm.}\end{matrix} \arrow[rrr, "\Delta H_2"] & & & \begin{matrix}2H_2O(g)\\ 150^\circ,\ 1\text{ atm.}\end{matrix} \\
\begin{matrix}2H_2 + O_2\\ 25^\circ,\ 1\text{ atm.}\end{matrix} \arrow[u, "\Delta H_3"] \arrow[rrr, "\Delta H_1"] & & & \begin{matrix}2H_2O(l)\\ 25^\circ,\ 1\text{ atm.}\end{matrix} \arrow[u, "\Delta H_4"']
\end{tikzcd}$$

As before, $\Delta H_1 + \Delta H_4$ must be equal to $\Delta H_3 + \Delta H_2$, and ΔH_1 is $-136{,}640$ cal. from Table 58. ΔH_4 is the sum of three steps by which liquid water at 25° is changed to water vapor at 150° through paths involving known data: First heat 36 grams of water from 25° to 100°, absorbing $36 \times 75 = 2700$ cal.; then evaporate the water, absorbing $2 \times 9700 = 19{,}400$ cal.; then heat 2 moles of water vapor to 150°, absorbing 820 cal. The sum of these quantities gives $\Delta H_4 = 22{,}920$ cal., and ΔH_3 is 2710 cal. from Table 55. Thus

$$2710 + \Delta H_2 = -136{,}640 + 22{,}920 \qquad \Delta H_2 = -116.43 \text{ kcal.}$$

The heat absorbed per mole of water vapor formed at 150°C. is -58.2 kcal. Final results of calculations should be rounded off in this way, since writing -58.215 kcal. indicates a more exact result than the data justify.

When enthalpies such as $H_2O(g) = -57.82$ kcal. at 298°K. are available, the change in state may be set up in terms of water vapor at both temperatures, the value of ΔH_4 taken from Table 55, and the calculation involving two heat capacities and ΔH for the phase change avoided. But there are many reactions for which such entries are not available and which require the longer procedure. All reactions involving solid-solid transitions or chemical decompositions necessarily fall into this class.

Application of the equation $d(\Delta H)/dT = \Delta C_p$ to the data for the union of hydrogen and hydroxyl ions leads to the surprising value $\Delta C_p = 50$ cal., as will be evident from the equation $\Delta H = -28{,}260 + 50T$ given on page 320. Since the heat capacity of water is 18 cal. per mole, this means that the *apparent* heat capacity of the ions is negative, −32 cal. for the sum of the apparent molal heat capacities of H^+ and OH^- in a dilute solution. Other ions also have this strange property; for example, the apparent ionic heat capacities in dilute solution are[1] −14 cal. for K^+, −14 for Cl^-, −7.5 for Na^+, −16.1 for OH^-, and −15.9 for H^+. At higher molalities these heat capacities change in value but are still negative, for example, −18 cal per mole for KCl at unit molality. This means that the addition of 74.5 grams of KCl to a large quantity of 1*m*. KCl solution decreases the heat capacity of the system 18 cal. The quantities are thus partial molal heat capacities, so that, at 1*m*., $dC_p/dN_{\text{KCl}} = -18$ cal and, in a very dilute solution, $dC_p/dN_{\text{KCl}} = -28$ cal

Heats of ionization for weak electrolytes are commonly small, with large changes in heat capacity, so that ΔH often changes sign within a moderate temperature range. For example, ΔH for the ionization of lactic acid is 768 cal. at 0°C., zero at 22 5°C., and −1313 cal. at 50°C., and the equation that expresses ΔH as a function of the temperature *within this range* is

$$\Delta H = 0.1355T^2 - 4.58 \times 10^{-4}T^3$$

For the first ionization of carbonic acid,

$$\Delta H = 78{,}011 - 427.6T + 0.58T^2$$

in the range 273 to 323°K.; and in the smaller range 273 to 298°K it is approximately $27{,}400 - 85T$. As one other illustration, for the ionization of bicarbonate ion, $\Delta H = 13{,}278 - 0.10884T^2$ in the range 273 to 323°K. and from 273 to 298°K. it is approximately $20{,}500 - 57T$. We shall return to a consideration of these equations near the end of the next chapter.

All these examples are only illustrations of the fact that ΔH for a given change is the same by all paths, and there is of course no implied limitation of the calculations to two isothermal paths and two constant-composition paths. In all commercial combustions air and fuel enter at about 20°, and stack gases and ashes emerge at higher temperatures; and for such processes the net heat available is ΔH for an assumed isothermal combustion less the heat required to raise the products of combustion to their emergent temperatures. For illustration, we may calculate the

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[1] Pitzer, *ibid.*, **59**, 2365 (1937).

theoretical maximum temperature attainable by burning carbon monoxide with air for which we assume $\Delta H = 0$. Since this calculation assumes no loss of heat to the surroundings, which would be impossible with the temperature differences involved, a rough calculation will suffice. We have for the basis of the calculation

$$CO + \tfrac{1}{2}O_2 + 2N_2 = CO_2 + 2N_2 \qquad \Delta H_{300} = -67.6 \text{ kcal.}$$

and this quantity of heat is available for heating 1 mole of CO_2 and 2 moles of nitrogen to the maximum temperature T. We may assume $C_p = 7 + 0.007T$ for CO_2 and $C_p = 6.5 + 0.001T$ per mole of N_2, which gives $20 + 0.009T$ for the heat capacity of the system. Then

$$+67{,}600 = \int_{300}^{T} (20 + 0.009T)dT$$

and, upon integrating between T and 300° and rearranging the equation, we have

$$74{,}000 = 20T + 0.0045T^2$$

Solution of this *equation* yields an absolute temperature higher than 2500°K But since at any such temperature some heat would be lost to the surroundings and some heat would be absorbed by the appreciable dissociation of CO_2, it is evident that this temperature would not be reached. By expressing the extent of dissociation of CO_2 as a function of the temperature, one may obtain a more complex equation allowing for the dissociation and thus may calculate the theoretical maximum temperature to a closer approximation By employing well-insulated furnaces one may almost reach this theoretical maximum temperature, which is about 2100°K. for the reaction we have been considering.

Heat balances for flow processes, whether isothermal or not, may be computed from enthalpy data and heat-capacity data in the same way. For example, if equal volumes of 2*m*. NaOH and 2*m*. HCl enter a flow calorimeter at 298°K., ΔH_{298} will be -14.00 kcal. for each mole of water formed isothermally; and since ΔH within the calorimetric system is always zero, 14.00 kcal. is available to heat the resulting sodium chloride solution, which will be 1018 grams of water containing 58.5 grams of sodium chloride. The specific heat capacity of the solution is

0.932 cal. per gram, or the heat capacity of the solution to be heated is 0.932(1018 + 58.5) = 989.7 cal. per deg. Hence the temperature of the effluent will be 14,000/989.7 = 14.15° above that of the entering solutions.

Acetaldehyde may be made industrially by passing acetylene into dilute sulfuric acid containing mercuric sulfate as a catalyzer for the reaction. The over-all change in state in the reaction vessel is

$$C_2H_2(g) + H_2O(l) = CH_3CHO(g) \qquad \Delta H_{298} = -29.5 \text{ kcal.}$$

In order to keep the temperature in the reaction vessel constant, cooling water is passed through a coil immersed in it. If this water enters at 10°C. and emerges at 25°C., substantially 2000 grams of water will thus be required for each 44 grams of acetaldehyde vapor formed.

In discussing the temperature coefficients of the heat effects attending reactions we have assumed a constant pressure, summed ΔH values, and used heat capacities at constant pressure. But the corresponding calculations for constant-volume processes are carried out in the same way; one sums ΔE values and uses heat capacities at constant volume for two paths for a change from an initial state at T_1 to a final state at T_2. We have already seen that for gases at moderate pressures the difference in molal heat capacity is $C_p - C_v = R$; for liquids and solids at moderate pressures the difference between C_p and C_v may usually be neglected.[1]

Problems

Numerical data for the problems should be sought in tables in the text.

1. Calculate ΔH for each of the following changes in state, given $C_p = 30$ cal per mole for liquid C_6H_6, $C_p = 6.5 + 0.052T$ for $C_6H_6(g)$, and the latent heat of evaporation of C_6H_6 is 7600 cal per mole at 353°K.:

(*a*) $C_6H_6(l, 293°K.) = C_6H_6(l, 353°K.)$

(*b*) $C_6H_6(l, 353°K.) = C_6H_6(g, 353°K) = C_6H_6(g, 453°K.)$, all at 1 atm.

(*c*) $C_6H_6(g, 453°K., 1 atm.) = C_6H_6(g, 453°K, 0.1 atm.)$

(*d*) $C_6H_6(l, 293°K., 1 atm.) = C_6H_6(g, 453°K., 0.1 atm.)$

2. Calculate the heat absorbed per mole of ethane formed when a mixture of ethylene and hydrogen is passed at 25° over a suitable catalyst.

3. Calculate ΔH for the reaction $CaCO_3(s) = CaO(s) + CO_2(g)$ at 1100°K., taking $C_p = 12.0$ for CaO and 23.5 for $CaCO_3$.

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[1] The difference is $C_p - C_v = \alpha^2 vT/\beta$, in which $\alpha = (1/v)(\partial v/\partial T)_p$ and $\beta = -(1/v)(\partial v/\partial p)_T$.

4. Calculate ΔH at 385°K. for the change in state

$$2NaHCO_3(s) = Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

taking 29 as the molal C_p for $NaHCO_3$ and 30 for Na_2CO.

5. For the solution of aluminum in HCl $200Aq$, $\Delta H_{291} = -127$ kcal. per atomic weight; for solution in HCl $20Aq$, $\Delta H_{291} = -126$ kcal Refer to page 314, and calculate ΔH_{291} for the dilution of $AlCl_3.60Aq$ to $AlCl_3\ 600Aq$.

6. ΔH_{291} for the solution of magnesium in $HCl.200Aq$ is -110.2 kcal. per atomic weight. Calculate ΔH_{291} for the reaction

$$3Mg + 2AlCl_3.Aq = 2Al + 3MgCl_2\,Aq$$

7. (*a*) Calculate ΔH, ΔE, $\Delta(pv)$, q, and w for the evaporation of a gram of water at 100° and constant pressure. (*b*) Calculate these quantities for the evaporation of a gram of water at 100° into an exhausted space of such volume that the final pressure of the resulting vapor is 1 0 atm

8. Calculate ΔH for the evaporation of a mole of water at 150°, at this temperature the vapor pressure of water is 4.69 atm. Takes $\Delta H = 135$ cal. at 150° for $H_2O(g,\ 4\ 69\ \text{atm}) \rightarrow H_2O(g,\ 1\ \text{atm.})$.

9. (*a*) Given the heat of sublimation of SO_3 is 10,800 cal per mole at 25°, calculate ΔH for the change in state at 25°: $SO_3(g) + H_2O(l) = H_2SO_4(l)$. (*b*) A gas mixture containing 5 moles of air and 1 mole of SO_2 enters a catalytic chamber, where practically all the SO_2 is converted into $SO_3(g)$ The resulting gas mixture is cooled to 200°C and then enters a tank containing 100 per cent H_2SO_4 at 25°C. and atmospheric pressure Sufficient water at 25°C is introduced into the tank to maintain the concentration of H_2SO_4 constant. Formulate the change in state taking place in the tank, and calculate the amount of heat that must be removed from the tank for each 5.5 moles of entering gas mixture so that the temperature in the tank will remain constant at 25°C. C_p for $SO_3(g) = 14$

10. (*a*) Formulate carefully the change in state that occurs when a mixture of $1C_2H_6(g) + 5O_2(g)$ in a 25-liter vessel at 25° is exploded and the vessel is brought back to 25° by the removal of heat. (Note that 0 032 mole of water vapor remains uncondensed.) (*b*) Calculate ΔH, ΔE, q, and w for this process. (*c*) Calculate ΔH, ΔE, q, and w for the ideal combustion process at constant pressure, $C_2H_6(g) + 3\frac{1}{2}O_2(g) = 2CO_2(g) + 3H_2O(l)$, and compare them with the corresponding quantities for the actual process described in part (*a*).

11. Calculate ΔH for the change in state

$$SO_2(g,\ 1\ \text{atm.},\ 400°\text{K.}) = SO_2(g,\ 1\ \text{atm.},\ 500°\text{K.})$$

from the heat-capacity equation in Table 56 and from

$$C_p = 11.9 + 0.0011T - 2.64 \times 10^5/T^2.$$

[SPENCER and FLANNAGAN, *J. Am. Chem. Soc.*, **64**, 2511 (1942).]

12. Calculate ΔH for the reaction $ZnO(s) + C(s) = Zn(g) + CO(g)$ at 1193°K. The atomic heat of fusion of Zn at 693°K. is 1.58 kcal., its heat of evaporation at 1193°K. is 31.1 kcal., C_p is 10 cal per atomic weight of Zn(*l*) and 13 cal per mole of ZnO(*s*).

13. The latent heat of evaporation of toluene ($C_7H_8 = 92$) is 85 cal per gram at 110°C. (the boiling point) when evaporation takes place against the atmosphere, and the vapor pressure of toluene is 0.44 atm at 84°C. Assume ΔH independent of the temperature and that toluene vapor is an ideal gas. A small flask of such volume that it is filled by 0.10 mole of liquid toluene at 84° and 0.44 atm is connected through a stopcock to a 3-liter evacuated flask. The stopcock is opened, and heat is added until the temperature returns to 84°. (*a*) Formulate *completely* the change in state that occurs. (*b*) What weight of toluene evaporates? (*c*) Calculate ΔH, ΔE, q, and w for this process.

14. The steam distillation of toluene occurs at 84°C and 1 atm total pressure. At 84°C the vapor pressure of water is 0.56 atm., and the liquids are mutually insoluble. See Problem 13 for data on toluene. (*a*) How many grams of toluene will be in the first 100 grams of total distillate if steam at 100° and 1 atm is passed into a flask containing a mixture of toluene and water at 84°? (*b*) How many grams of steam must be passed into the flask to yield this 100 grams of distillate? (Assume the flask to be thermally insulated and that steam entering at 100° is the only source of heat.)

15. Carbon monoxide may be manufactured by passing a mixture of oxygen and carbon dioxide over hot carbon. Since the oxidation of carbon evolves heat and the reduction of carbon dioxide by carbon absorbs heat, there is a mixture of oxygen and CO_2 that can be passed over carbon at 1200°K., where it will be changed to practically pure carbon monoxide without changing the temperature of the carbon bed. (*a*) Calculate ΔH for each reaction at 1200°K., and the moles of oxygen per mole of CO_2 in a mixture that would cause no change in the temperature of the carbon bed, assuming that the gases enter at 1200°K. and leave at 1200°K. (*b*) Recalculate this ratio, assuming that the reacting substances enter at 300°K. and leave at 1200°K.

16. Calculate the heat absorbed by the reaction $H_2(g) + I_2(g) = 2HI(g)$ at 600°K.

17. Estimate the heat of formation of HBr from its elements at 700°K., using the data in Problem 22.

18. Calculate ΔH for adding a mole of calcium oxide to a large quantity of HI.100.*Aq*.

19. When a mole of 0.1*m* H_3PO_4 is neutralized with a mole of sodium hydroxide in dilute solution, $\Delta H_{298} = -14{,}800$ cal. Phosphoric acid at 0.1*m*. is about 30 per cent ionized into H^+ and $H_2PO_4^-$. Calculate the heat absorbed per mole of H_3PO_4 ionized into H^+ and $H_2PO_4^-$.

20. (*a*) Calculate ΔH for the reaction

$$C_{12}H_{22}O_{11}(s) + H_2O(l) = 4C_2H_5OH(l) + 4CO_2(g)$$

at 25°C. (*b*) What additional data would be required for calculating ΔH for the production of dilute alcohol from sugar solution?

21. Calculate ΔH for the gaseous reaction $CO_2 + H_2 = CO + H_2O$ at 1100°K.

22. The formation of iodine bromide is shown by the equation

$$I_2(s) + Br_2(l) = 2IBr(g), \quad \Delta H_{298} = +19{,}720 \text{ cal}$$

The molal heat capacities may be taken as 13 3 for $I_2(s)$, 17 2 for $Br_2(l)$, and 9 0 for $I_2(g)$, $Br_2(g)$, and $IBr(g)$, the molal heat of evaporation of bromine is 7400 cal at 332°K, the molal heat of sublimation of iodine is 14,900 cal at 387°K (*a*) Calculate ΔH at 387°K for the reaction

$$I_2(g) + Br_2(g) = 2IBr(g)$$

(*b*) Calculate ΔH_{487} for this reaction

23. Calculate the ratio of air to steam in a mixture that can be blown through a fuel bed at 1000°K if the temperature of the fuel is to remain constant Assume (*a*) that no water or oxygen passes through unchanged, (*b*) that air is $4N_2 + O_2$, (*c*) that the gases enter and leave the fuel bed at 1000°K through the use of a suitable heat interchanger, and (*d*) that there is no CO_2 in the emerging gas

24. (*a*) Calculate ΔH_{298} for the reaction

$$Al_2O_3(s) + 3C(s) + 3Cl_2(g) = Al_2Cl_6(s) + 3CO(g)$$

(*b*) Calculate ΔH for the change in state $Al_2O_3(s) + 3C(s) + 3Cl_2(g)$ at 298°K $= Al_2Cl_6(g) + 3CO(g)$ at 435°K The (calculated) ΔH of sublimation of Al_2Cl_6 at 298°K is 28 85 kcal, and C_p for $Al_2Cl_6(g)$ is 34 cal per mole

25. The steam distillation of chlorobenzene takes place at 90°C under a total pressure of 1 atm, and the liquids are substantially insoluble in one another Calculate the weight of chlorobenzene in the distillate and the weight of condensed water in the flask after 100 grams of steam at 100° and 1 atm is passed into a thermally insulated flask containing 1120 grams of chlorobenzene (=10 moles of C_6H_5Cl) at 20° Neglect the heat capacity of the flask, and use the following molal quantities. C_p for liquid $C_6H_5Cl = 34$, and ΔH for evaporation of C_6H_5Cl is 8800 cal at 90°

26. When 0 0340 mole of NaOH in 35 grams of water is added to 950 grams of 0 050*m* NH_4Cl at 25°, there is a heat absorption of −29.4 cal. Calculate ΔH for the ionization

$$NH_4OH\,Aq = NH_4^+\,Aq + OH^-\,Aq$$

assuming the heats of dilution are negligible and neglecting the small ionization of NH_4OH in the final solution

27. (*a*) Calculate ΔH at 25° for the complete change in state

$$HBO_2.Aq + NH_4OH.Aq = NH_4^+BO_2^-.Aq + H_2O$$

(*b*) When 0 1 mole of HBO_2 in 1000 grams of water is added to 0 1 mole of NH_4OH in 1000 grams of water at 25°, there is a heat absorption of −600 cal. What fraction of the base has combined?

28. When a mixture of 1 mole of HCl and 5 moles of air ($O_2 + 4N_2$) passes over a catalyzer at 386°, 80 per cent of the HCl is oxidized to chlorine. (*a*) Assuming that the gases enter the reaction vessel at 20° and 1 atm, total pressure and leave it at 386° and 1 atm , formulate the change in state taking place in the vessel (*b*) What quantity of heat must be removed from, or added to, the vessel to keep its temperature 386°?

29. An important reaction for the recovery of sulfur from H_2S is

$$2H_2S(g) + SO_2(g) = 2H_2O(g) + 3S(s)$$

Calculate ΔH for this reaction at 100°C.

30. One step in the manufacture of CCl_4 involves the reaction

$$CS_2(l) + 3Cl_2(g) = CCl_4(l) + S_2Cl_2(l)$$

which takes place in a water-cooled reaction vessel at 25°. How many kilograms of cooling water at 10° must pass through coils in the reaction vessel for each kilogram of chlorine reacting to keep the temperature at 25°?

31. (*a*) Calculate ΔH at 20° for the reaction

$$4NH_3(g) + 5O_2(g) + 20N_2(g) = 4NO(g) + 6H_2O(g) + 20N_2(g)$$

(*b*) Make the additional assumptions that (1) this mixture of $4NH_3 + 5O_2 + 20N_2$ enters a vessel at 20° in which complete oxidation of the NH_3 takes place upon a suitable catalyst, (2) constant pressure of 1 atm prevails, (3) the mixture emerges at 200°, and (4) cooling water enters a coil in the reaction vessel at 20° and leaves at 70° Calculate the kilograms of water passing through the coil for each 29 moles of entering gas

32. In a flow type of water heater a flame of methane burns on a coil through which water passes Assume that (1) 30 moles of methane and 300 moles of air ($60O_2 + 240N_2$) are used each minute, (2) complete oxidation to CO_2 and water vapor, (3) the gases enter the heater at 20° and leave at 220°, and (4) the water enters at 15° and leaves at 65°. (*a*) How many liters of water flow through the coil each minute if heat interchange is complete? (*b*) What is the "dew point" of the stack gas?

33. (*a*) Calculate ΔH_{298} for the reaction $Ca(s) + 2C(s) = CaC_2(s)$, given $\Delta H_{298} = -31.3$ kcal for $CaC_2(s) + 2H_2O(l) = Ca(OH)_2(s) + C_2H_2(g)$. (*b*) Calculate ΔH_{298} for the reaction $3C(s) + CaO(s) = CaC_2(s) + CO(g)$

34. In the manufacture of hydrochloric acid, HCl gas at 100°C and water at 10°C flow countercurrent through a vessel, and a solution of the composition $HCl\ 5H_2O$ leaves the vessel at 50°. Cooling water enters a coil in the vessel at 10° and leaves at 50°. How many kilograms of water must flow through the coil for each kilogram of $HCl.5H_2O$ leaving it? [The molal heat capacity of $HCl.5H_2O$ is 85 cal per deg., and that of $HCl(g)$ may be taken as 7.0 cal. per deg.]

35. Derive an expression for ΔH as a function of temperature for the reaction $C_2H_4(g) + H_2O(g) = C_2H_5OH(g)$ that will be valid in the range 290 to 500°K. In this range the following heat-capacity equations at constant pressure are valid: $C_p = 6.0 + 0.015T$ for $C_2H_4(g)$, $4.5 + 0.038T$ for $C_2H_5OH(g)$, and $7.0 + 0.003T$ for $H_2O(g)$. [The first two heat-capacity equations are from Pardee and Dodge, *Ind. Eng. Chem.*, **35**, 273 (1943).]

36. Plot ΔH against N from the table of heats of solution of HCl on page 314, and draw tangents to the curve at $N = 5.55$ (corresponding to 10*m*. HCl) and $N = 13.9$ (corresponding to 4*m*. HCl) Determine for each molality $(\partial H/\partial N_{H_2O})$, and from this slope compute $(\partial H/\partial N_{HCl})$, the partial molal heat of solution of HCl(*g*) in 4*m* and 10*m*. HCl

37. (*a*) Calculate ΔH_{298} for the dehydrogenation of *n*-heptane to toluene as shown by the chemical equation $n\text{-}C_7H_{16}(l) = C_6H_5CH_3(l) + 4H_2(g)$, using the data below and other data from the text. (*b*) Calculate ΔH for the change in state $n\text{-}C_7H_{16}(l)$, 298°K. $= C_6H_5CH_3(g) + 4H_2(g)$ at 573°K (*c*) Calculate ΔH for the reaction at 573°K : $n\text{-}C_7H_{16}(g) = C_6H_5CH_3(g) + 4H_2(g)$. Data for *n*-heptane: ΔH_{298} (combustion) $= -1149.9$ kcal per mole, ΔH_{371} (evap.) $= 12.5$ kcal. per mole, $C_p(l) = 53$ cal per mole, $C_p(g) = 6.4 + 0.095T$. Data for toluene: ΔH_{383} (evap.) $= 8.09$ kcal. per mole, $C_p(l) = 36$ cal. per mole, $C_p(g) = 5.0 + 0.070T$.

CHAPTER IX

EQUILIBRIUM IN HOMOGENEOUS SYSTEMS

One of the most important problems of physical chemistry is the extent to which chemical reactions take place. Most of the familiar reactions of inorganic chemistry, especially those of analytical chemistry, go forward until one of the reacting substances (the "limiting reagent") is exhausted. In addition to such complete reactions, there are many others in which substantial fractions of all the reacting substances remain unchanged, even when a "stationary"[1] state is reached. These fractions vary with the proportions in which the reacting substances are put together (though the proportions in which they *react* are governed by the chemical equation) and with the pressure and temperature

Equilibrium in gaseous mixtures at constant temperature and moderate pressures will be considered first, then equilibrium in dilute aqueous solutions at constant temperature, and finally the effect of changing temperature upon equilibrium conditions. Occasionally we shall use an excess of a liquid phase or a solid phase of constant vapor pressure to control one partial pressure in a gaseous mixture, or the partial pressure of a gas to control its molality in a solution, or an excess of a solid phase to keep its molality constant in a solution; but the main topic of this chapter is chemical equilibrium in a single phase Equilibrium in systems of more than one phase will be presented in the next chapter. In gaseous systems at moderate pressures, the experimental data will be combined with the ideal gas law, Dalton's law of partial pressures, and other general principles in order to calculate the partial pressures in equilibrium mixtures. Gaseous systems at such high pressures as to render the ideal gas law invalid require

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[1] At equilibrium, or an *apparently* stationary state, the initial reaction and the reverse reaction are proceeding at equal rates in the opposite directions. The relation of these rates to the equilibrium concentration is discussed in Chap. XII.

special methods of treatment, to which we shall refer briefly after the simpler systems have been studied.

The law of chemical equilibrium applying to a gaseous system may be expressed in terms of molal concentrations or in terms of the partial pressures of the substances. Partial pressures are more commonly used, and their use leads to simpler calculations in constant-pressure processes. But partial pressures are not directly measurable quantities; they may be calculated from the chemical composition of the equilibrium system and the total pressure through Dalton's law when the ideal gas law applies. They may be calculated in a system of nearly ideal gases at constant volume from the difference between the observed total equilibrium pressure and the initial pressure of the system before reaction through the stoichiometry involved.

Since the composition of an equilibrium mixture changes with temperature and pressure, it is usually not permissible to withdraw a sample and cool it for analysis. Physical measurements, such as density, pressure, color, volume change, heat evolution, electrical conductance, spectrographic analysis, or the control of a partial pressure through the presence of a liquid or solid phase, must be applied to the system *at equilibrium*.

General Law of Chemical Equilibrium.—This law may be stated as follows: At equilibrium the product of the partial pressures of the substances formed in a reaction, each raised to a power that is the coefficient of its formula in the balanced chemical equation, divided by the product of the partial pressures of the reacting substances, each raised to a power that is the coefficient of its formula in the chemical equation, is a constant for a given temperature. Thus for the general reaction

$$aA + bB + \cdots = dD + eE + \cdots$$

the condition of equilibrium at any specified temperature is

$$\frac{p_D{}^d p_E{}^e \cdots}{p_A{}^a p_B{}^b \cdots} = K_p \qquad (t \text{ const.}) \qquad (1)$$

Partial pressures are usually, though not always, expressed in atmospheres, and it should be noted that the numerical value of K will depend on the units used unless

$$a + b + \cdots = d + e + \cdots$$

that is, K will depend on the units in which pressures are expressed for every reaction in which there is a change in the number of molecules as the reaction proceeds. The equation may be derived from the laws of thermodynamics for a system of ideal gases.[1]

If the equilibrium expression is written in terms of the molal concentrations of the substances involved, the relation becomes

$$\frac{C_D{}^d C_E{}^b \cdot \cdot \cdot}{C_A{}^a C_B{}^b \cdot \cdot \cdot} = K_c \qquad (t \text{ const.}) \qquad (2)$$

These equilibrium constants both express the fundamental relation applying to a selected system at a definite temperature, but the numerical values of K_p and K_c are not the same. If we write the ideal gas law as applying to constituent A, for example, $p_A = (n_A/v)RT = C_ART$, and a similar expression for the other constituents, substitution of CRT for these partial pressures in equation (1) shows that $K_p = K_c(RT)^{\Delta n}$, where

$$\Delta n = d + e - a - b$$

is the increase in the number of moles of gas attending the complete chemical reaction, p_A is the partial pressure in atmospheres, and R has the value 0.082 liter-atm./mole-°K.

In writing the equilibrium expressions above, we have observed a custom to which we shall adhere throughout the book and which is standard practice in physical chemistry, namely, that of writing the partial pressures or concentrations of the *reaction products* in the *numerator* of the equilibrium expression. These relations are independent of the mechanism by which equilibrium is reached; and, of course, one may write the chemical reaction in any desired way. But the equilibrium expression should always be written with the products of the chemical reaction *as written* in the numerator. For illustration, all the following expressions are equally satisfactory representations of the equilibrium between SO_3, SO_2, and O_2 at a given temperature:

(1) $SO_2 + \frac{1}{2}O_2 = SO_3 \qquad K_1 = \frac{p_{SO_3}}{p_{SO_2}p_{O_2}{}^{\frac{1}{2}}} = 1.85$ at 1000°K.

(2) $2SO_2 + O_2 = 2SO_3 \qquad K_2 = \frac{p_{SO_3}{}^2}{p_{SO_2}{}^2 p_{O_2}} = 3.42$ at 1000°K.

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[1] LEWIS, *Proc. Am. Acad. Arts Sci.*, **43**, 259 (1907)

$$(3)\quad SO_3 = SO_2 + \tfrac{1}{2}O_2 \qquad K_3 = \frac{p_{SO_2}p_{O_2}^{1/2}}{p_{SO_3}} = 0.540 \text{ at } 1000°K.$$

$$(4)\quad 2SO_3 = 2SO_2 + O_2 \qquad K_4 = \frac{p_{SO_2}^{2}p_{O_2}}{p_{SO_3}^{2}} = 0.282 \text{ at } 1000°K.$$

The partial pressures are in atmospheres for the values of K given. In each equilibrium expression the partial pressures in the numerator are those of reaction products for the corresponding chemical reaction; in each the pressure is raised to the power that is the coefficient of its formula in the equation as written. It will be clear that it is often necessary and always desirable to write the chemical reaction for which an equilibrium constant is evaluated, to state the units in which the quantities are expressed, and to state the temperature. K_3 and K_4, for example, are both "dissociation constants" for SO_3, but K_4 is the square of K_3, and without the attending chemical equation it would be uncertain which one was meant.

Another fact about equilibrium constants is of the greatest importance, namely, that they give the relation among the partial pressures involved regardless of the quantities of the substances present, regardless of the direction from which equilibrium is approached, and regardless of the presence of other gases. In systems consisting of 1 mole of SO_2 and 2.3 of oxygen, or $SO_2 + 2SO_3$, or $0.41SO_2$ and 0.21 oxygen and 0.79 nitrogen, or in the flue gas from sulfur-bearing fuel, the equilibrium expressions give the relation of the partial pressures of SO_3, SO_2, and O_2 at equilibrium. Of course, the sum of these three partial pressures is not the total pressure in two of these systems; and, in computing x_{SO_2} from the composition of the equilibrium mixture, the moles of SO_2 divided by the total moles of *all substances* present gives the mole fraction.

The law of chemical equilibrium has been tested and confirmed by experiments on a large number of chemical systems of the most varied kind. Deviations from its predictions are no greater than those found between the measured and ideal properties of solutions or gases already considered. It is probably the most important law of physical chemistry; its proper application will show what procedure is necessary to increase the yield of a desired product in a chemical reaction or what should be done to decrease the yield of an undesirable product. It indicates the precautions to be observed in analytical chemistry;

it enables us to calculate the extent to which a reaction will take place in solutions, the fraction of a substance hydrolyzed, the quantity of reagent necessary to convert one solid completely into another, and many other similar quantities.

The formulation of equilibrium expressions requires complete knowledge of the chemistry of the reacting systems. The chemical substances involved in a single equilibrium expression must be those, and only those, shown in the chemical equation. This is not to say that the methods are inapplicable in systems in which more than one chemical reaction is taking place, for we shall encounter many such systems and apply the laws of chemical equilibrium to them. In treating them we shall write a sufficient number of equations to describe all the reactions taking place, and we shall formulate a corresponding number of equilibrium expressions. Through stoichiometry, material balances, energy balances, a sufficient number of measured quantities, and suitable approximations, we shall be able to calculate the pressures or concentrations of all the substances present at equilibrium. When the pressure of a given substance appears in more than one equilibrium expression, it will be understood that it has the same value in every one, for there can be only *one equilibrium pressure* of a given substance in a given system.

In gaseous systems for which the ideal gas law and Dalton's law of partial pressures are inadequate approximations, the equilibrium law is expressed in terms of the fugacities of the substances. For the general reaction above, the equilibrium law is

$$\frac{f_D{}^d f_E{}^e}{f_A{}^a f_B{}^b} = K_f \qquad (t \text{ const.}) \qquad (3)$$

This expression is constant by definition, since the fugacity of a substance is a quantity with the dimensions of a partial pressure that represents its actual effect in a chemical system In a system of ideal gases, the fugacities are equal to the partial pressures; in any other system, they must be evaluated from the equation of state for the gas. Since these calculations are somewhat difficult for beginners, they are best reserved for more advanced courses.[1] In this brief treatment we shall confine our

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[1] See Lewis and Randall, "Thermodynamics," pp. 190–201, for the methods and some illustrations.

discussion to systems at such moderate pressures that $p_A = p_{total}x_A$ is an adequate measure of the fugacity f_A.

It cannot be emphasized too strongly that equilibrium expressions do not apply to systems that are not at equilibrium. In experimental work it is necessary to show that equilibrium has been reached through the use of suitable methods. Chemical systems react toward equilibrium at rates that decrease as equilibrium is approached; and in some systems the rates are very slow. One common procedure is to approach equilibrium from both sides, by mixing A and B in one series of experiments and by mixing D and E in another. If the same relation among the partial pressures is obtained in both series, the system has reached equilibrium. If different relations are found, the system is not at equilibrium and more time must be allowed or means of accelerating the reaction must be found. Another common test consists in heating one chemical system up to the desired temperature and in cooling another system to this temperature after it has been kept at a higher temperature for a sufficient time. Since equilibrium conditions change with the temperature, this is another means of approaching equilibrium from both sides These or other proofs of an equilibrium state are absolutely essential in experimental work and are routinely carried out by competent workers. We turn now to the application of these principles to some chemical systems.

1. Formation of Sulfur Trioxide.—When a mixture of 1 mole of sulfur dioxide and ½ mole of oxygen is heated to 1000°K. in the presence of a suitable accelerator for the reaction, 46 per cent of the sulfur dioxide is converted to sulfur trioxide when the equilibrium total pressure is 1 atm. The chemical reaction and its equilibrium expression are

$$SO_2(g) + \tfrac{1}{2}O_2(g) = SO_3(g)$$

$$K_p = \frac{p_{SO_3}}{p_{SO_2}p_{O_2}^{1/2}} \qquad (t \text{ const.}) \qquad (4)$$

With $1SO_2 + \tfrac{1}{2}O_2$ as a working basis or a material basis for the calculation, we see from the chemical reaction that 0.46 mole of SO_3 requires 0.23 mole of O_2 for its oxidation, leaving 0.54 mole of SO_2 and 0.27 mole of O_2 in equilibrium with 0.46 mole of SO_3. The equilibrium system has the composition, at 1000°K, and 1 atm. total pressure,

$$\begin{array}{l} 0.46 \text{ mole } SO_3 \\ 0.54 \text{ mole } SO_2 \\ \underline{0.27 \text{ mole } O_2\quad} \\ 1.27 \text{ total moles} \end{array}$$

The partial pressures are $0.46/1.27 = 0.362$ atm. for SO_3, $0.54/1.27 = 0.425$ atm. for SO_2, and $0.27/1.27 = 0.213$ atm. for O_2; and, upon substituting these quantities in the equilibrium expression, we have

$$K_p = \frac{0.362}{0.425(0.213)^{1/2}} = 1.85 \text{ at } 1000°\text{K.}$$

In the use of recorded equilibrium constants from the chemical literature, attention must be paid to the conventions used and to the units in which the equilibrium compositions are expressed. For example, in the original paper from which these figures come,[1] equilibrium compositions are given in moles of gas per liter, partial pressures are given in millimeters of mercury, and the equilibrium constant is $K_c = 3.54 \times 10^{-3}$ for the *dissociation* of 2 moles of SO_3 with concentrations in moles per liter. One procedure is as good as any other so far as equilibrium is concerned; we have used K_p for the formation of SO_3 to simplify calculations that are to be made in later chapters, and in conformity with the conventions used in tabulating free energies. If K_p were given for partial pressures in millimeters of mercury for the formation of $1SO_3$, its numerical value would be $1.85/\sqrt{760} = 0.067$.

As has been said before, the relation among the partial pressures given in equation (4) applies at 1000°K. to any mixture containing SO_2, O_2, and SO_3 at equilibrium, at any moderate pressure, in any proportions, and in the presence of other substances. Some illustrations may not be out of place. Let the original mixture of $1SO_2 + \frac{1}{2}O_2$ be compressed until the total pressure at equilibrium is 2 atm., and let

$$\begin{array}{r} x = \text{moles } SO_3 \\ 1 - x = \text{moles } SO_2 \\ \underline{0.5 - 0.5x = \text{moles } O_2} \\ 1.5 - 0.5x \text{ total moles} \end{array}$$

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[1] Bodenstein and Pohl, *Z. Elektrochem.*, **11**, 373 (1905).

Upon substituting the product of total pressure and mole fraction in terms of x into equation (4) we have

$$1.85 = \frac{2[x/(1.5 - 0.5x)]}{2[(1 - x)/(1.5 - 0\ 5x)]\sqrt{2[(0.5 - 0.5x)/(1.5 - 0.5x)]}}$$

While this equation is a cubic in x, the complete algebraic solution of a cubic equation is not required for practical purposes. There is only one real root, it must be positive, the chemical composition of the system places its value between 0 and 1.0, and the equilibrium data above restrict it to still narrower limits. Any compressed system reacts in the direction that relieves the compression, and this particular system must react to form more SO_3 in order to reach equilibrium under a higher total pressure. The momentary effect of doubling the total pressure would be to double each partial pressure and so bring the relation $p_{SO_3}/p_{SO_2}p_{O_2}^{1/2}$ to a lower value than 1.85 which is required for equilibrium. In order to restore the required relation among the partial pressures, p_{SO_3} must increase, and both p_{SO_2} and p_{O_2} must decrease, which requires the formation of SO_3 by the chemical reaction. The value of x in the new system at equilibrium is thus greater than 0.46, less than 1, and nearer the former value than the latter. Successive trials of 0.7, 0.6, 0.55, and 0.53 for x will show that 0.53 satisfies the equation and hence that 0.53 mole of SO_3 exists in this system when equilibrium is reached at 1000°K. and 2 atm. total pressure.

The equilibrium mixture of $0.46SO_3$, $0.54SO_2$, and $0.27O_2$ had a volume of 104 liters at 1000°K. and 1 atm. total pressure, as shown by the equation $pv = 1.27RT$.

Suppose this mixture to be expanded to 208 liters, and, as before, let

$$\begin{aligned} x &= \text{moles } SO_3 \\ 1 - x &= \text{moles } SO_2 \\ 0.5 - 0.5x &= \text{moles } O_2 \\ \hline 1.5 - 0.5x &\ \text{total moles} \end{aligned}$$

Since expansion at constant temperature is attended by the decomposition of SO_3, the new equilibrium pressure when the volume is doubled will not be 0.5 atm., but a higher value, namely, one that satisfies the ideal gas law in the form

$$p208 = (1.5 - 0.5x)RT$$

or $p = 0.395(1.5 - 0.5x)$. Upon substituting the product of each mole fraction times this total pressure into equation (4) and simplifying, we have

$$1.85 = \frac{x}{(1 - x)\sqrt{0.395(0.5 - 0\ 5x)}}$$

Again solving by trial, observing that x is positive and must be less than 0.46, we find $x = 0.39$ and

$$p = 0\ 395(1.5 - 0.5x) = 0.52 \text{ atm.}$$

Returning to the mixture of $0.46SO_3$, $0\ 54SO_2$, and $0.27O_2$ in 104 liters at 1000°K. and 1 atm pressure, suppose oxygen were added to the mixture at constant volume until the total pressure becomes 2 atm. at equilibrium. The ideal gas law shows 2 54 total moles of gas, a sulfur balance shows 1 mole of $SO_2 + SO_3$, and therefore the moles of oxygen at equilibrium is 1.54 moles. (This is not the quantity of oxygen *added* to the system, as we shall see in a moment.) Let

$$\begin{aligned} x &= \text{moles } SO_3 \\ 1 - x &= \text{moles } SO_2 \\ 1.54 &= \text{moles } O_2 \\ \hline 2\ 54 & \text{ total moles} \end{aligned}$$

Upon substituting partial pressures based on these values into equation (4), we have

$$\frac{2(x/2\ 54)}{2[(1 - x)/2.54][2(1.54/2.54)]^{1/2}} = \frac{x}{1.10(1 - x)} = 1.85$$

whence $x = 0.68$ mole of SO_3. The formation of this quantity of SO_3 required 0.68 mole of SO_2 and 0.34 mole of O_2; and since the oxygen present at equilibrium was 1.54 moles, the total oxygen in the system (other than that in the original SO_2) is $1.54 + 0.34$, or 1.88 moles. The original system contained 0.50 mole of oxygen and thus the oxygen *added* to bring the equilibrium pressure to 2 atm. was $1.88 - 0.50 = 1.38$ moles.

A balance for *total* oxygen gives the same result, namely, $1.5 \times 0.68 = 1.02$ moles of oxygen in SO_3, 0.32 mole of oxygen in 0.32 mole of SO_2, and 1.54 moles of oxygen uncombined, total 2.88 moles. Of this oxygen 1 mole was in the original SO_2, and

0.50 mole as free oxygen in the original mixture, which leaves 1.38 moles of added oxygen to make up the total.

As one more illustration, consider an initial mixture of a mole of SO_2 and 4 moles of air at 1000°K. and 1 atm. total pressure, that is, $1SO_2 + 0.84O_2 + 3.16N_2$, and let the composition after equilibrium is established be

$$\begin{array}{r@{\;=\;}l}
x & \text{moles } SO_3 \\
1 - x & \text{moles } SO_2 \\
0.84 - 0.5x & \text{moles } O_2 \\
3.16 & \text{moles } N_2 \\
\hline
\multicolumn{2}{c}{5 - 0.5x \text{ total moles}}
\end{array}$$

One may substitute mole fractions based on this table in equation (4) and find $x = 0.41$ mole of SO_3 at equilibrium in this mixture at 1000°K. and 1 atm. total pressure.

It should be clearly understood that, while the equilibrium *relations* which we have been discussing apply at any temperature in any mixture containing these substances, the *constant* 1.85 applies only at 1000°K. At some other temperature a different constant applies; for in this system and in every system the equilibrium constant is for a given temperature. In this system K_p changes with the Kelvin temperature T as follows:

K_p . . .	31.3	13.7	6.56	3.24	1.85	0.95	0.63	0.36
T . . .	801	852	900	953	1000	1062	1105	1170

Further discussion of these constants will be found at the end of the chapter, where the equation governing the change of K_p with temperature will be given.

The procedure that has been followed above is of such general application in chemical equilibrium that it is worth while to summarize the steps as routine for problem work. They are

1. Write a balanced chemical equation describing the chemical change involved. This step should never be omitted, no matter how simple or familiar the equation may be.

2. State the *working basis* of the calculation, the quantity of each substance at the start, and the pressure, volume, and temperature to be used in the problem.

3. Formulate the equilibrium expression in the standard way, and note that the pressures of reaction products always appear

in the numerator of the equilibrium expression. When sufficient data are at hand for evaluating K, insert its value and note the units employed in expressing it.

4. Set up a "mole table" describing the quantity of each substance in the equilibrium mixture in terms of a suitable unknown. The use of two or more unknowns is not excluded, but it will usually be advantageous to restrict the number of unknowns to one. Care in the choice of the unknown often yields a simpler solution of the problem.

5. Solve for this unknown by appropriate use of the data. This may be through a material balance, or an expression for total moles of gas from the ideal gas law, or a density expression in terms of the fraction reacting, or direct substitution into K_p, or any other procedure for which data are available.

2. The Synthesis of Ammonia.—As our second example of equilibrium in gaseous systems we consider the data on synthetic ammonia in a range of pressures in which deviations from the ideal gas law become important. Table 59 shows how the mole per cent of ammonia in equilibrium with a mixture of $N_2 + 3H_2$ varies with temperature and pressure. If we base our calculations upon the equation

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) = NH_3(g)$$

and formulate the equilibrium constant in the standard way, with the product of total pressure and mole fraction taken as the partial pressure for each constituent, we have

TABLE 59.—MOLE PER CENT NH_3 IN EQUILIBRIUM WITH $N_2 + 3H_2$[1]

Temperature		Total pressure, atm.			
°K.	°C.	10	30	50	100
623	350	7.35	17.80	25.11	
648	375	5.25	13.35	19.44	30.95
673	400	3.85	10.09	15.11	24.91
698	425	2.80	7.59	11.71	20.23
723	450	2.04	5.80	9.17	16.36
748	475	1.61	4.53	7.13	12.98
773	500	1.20	3.48	5.58	10.40

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[1] LARSON and DODGE, *J. Am. Chem. Soc.*, **46**, 367 (1924).

$$K_p = \frac{px_{NH_3}}{(px_{N_2})^{1/2}(px_{H_2})^{3/2}} \qquad (t \text{ const.}) \qquad (5)$$

Of course, the chemical equation might have been written as a dissociation rather than for synthesis or for 2 moles of NH_3 rather than 1. But K_p for the reaction $2NH_3 = N_2 + 3H_2$ would be the square of the reciprocal of the K_p in equation (5).

The data of Table 59 yield at once the quantities required in this expression, since one quarter of the difference between 100 and the mole per cent of NH_3 is the mole per cent of nitrogen and three quarters of this difference is the mole per cent of hydrogen in the equilibrium mixture. If the ideal gas law were valid in the equilibrium mixtures up to 100 atm. total pressure, all the K_p values for a single temperature should be the same, but Table 60, which records the value of this $K_p \times 1000$ for partial pressures in atmospheres, as calculated from the compositions given in Table 59, shows that K_p changes with the total pressure.

TABLE 60—CALCULATED $1000K_p$, IN ATM FOR $\frac{1}{2}N_2 + \frac{3}{2}H_2 = NH_3$

Temperature		Equilibrium pressure, atm.			
°K	°C	10	30	50	100
623	350	26 59	27 34	27 94	
648	375	18 15	18 43	18 66	20 30
673	400	12 92	12 93	13 05	13 78
698	425	9 20	9 20	9 34	9 90
723	450	6 60	6 76	6 91	7 27
748	475	5 16	5 14	5 13	5 33
773	500	3 81	3 86	3 89	4 03

The K_p values in Table 60 for pressures of 10 atm. may be used to calculate the composition of any equilibrium system containing nitrogen, hydrogen, and ammonia in any proportions for pressures near or below 10 atm. without large error. Consider, for example, a mixture of 1 mole of nitrogen and 2 moles of hydrogen that reacts to equilibrium at 623°K. and a total pressure of 5 atm. If we let x be the moles of ammonia at equilibrium, the "mole table" through which we express the equilibrium composition becomes

$$
\begin{aligned}
x &= \text{moles } NH_3 \\
1 - 0.5x &= \text{moles } N_2 \\
2 - 1.5x &= \text{moles } H_2 \\
\hline
3 - x &= \text{total moles}
\end{aligned}
$$

At equilibrium the partial pressures are $5x/(3 - x)$ for NH_3, $5(1 - 0.5x)/(3 - x)$ for N_2, and $5(2 - 1.5x)/(3 - x)$ for H_2. Substituting these partial pressures into equation (5) and taking K_p for 623°K. from Table 60, one may solve by trial for the moles of ammonia at equilibrium.

The values of K_p in Table 60 for higher pressures may also be used for approximate calculations, by taking a value of K_p adjusted for total pressure. But exact calculations, which are required for ammonia synthesis in industry, are too difficult for beginners.[1]

3. Dissociation of Nitrogen Tetroxide.—The experimental method applied to this system consisted in measuring the total pressure at equilibrium in a flask of known volume containing a known weight of N_2O_4. If we denote by m the initial weight of N_2O_4 added to a liter flask and by p the equilibrium total pressure, the data for a series of experiments[2] at 35°C. (= 308°K) are

m, grams,	0.578	0.933	1.16	1.31	1.99
p, atm	0.238	0.365	0.439	0.487	0.706
K_p	0.317	0.316	0.300	0.287	0.264

The only *important* chemical reaction at this temperature is

$$N_2O_4(g) = 2NO_2(g)$$

for which the equilibrium expression is

$$K_p = \frac{p_{NO_2}{}^2}{p_{N_2O_4}}$$

If we determine the total moles present at equilibrium from $pv = nRT$ and the moles of N_2O_4 before dissociation by $m/92$, we may set up a mole table, calculate partial pressures, substitute

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[1] For an exact treatment of the system $N_2 + 3H_2$ up to 1000 atm., see Gillespie and Beattie, *Phys. Rev.*, **36**, 743, (1930); *J. Am. Chem. Soc.*, **52**, 4239 (1930)

[2] VERHOEK and DANIELS, *ibid.*, **53**, 1250 (1931). The derived values when K_p is plotted against the pressure and extrapolated to zero pressure are 0.14 at 25°, 0.32 at 35°, and 0.68 at 45°

them in the equilibrium expression, and calculate the equilibrium constant for this temperature. The results of this calculation, for partial pressures in atmospheres, are given in the table above. The "drift" in a quantity supposedly constant probably indicates increasing deviation from ideal gas behavior on the part of some component, and it should be noted that the mixture of N_2O_4 and NO_2 condenses to a liquid at about 21°C. for a total pressure of 1 atm. The common expedient is to plot the derived K_p against the total pressure and extrapolate the curve to zero pressure to determine the constant applicable to the state of an ideal gas.

Some attention should be given to the qualifying statement that at 35°C the only *important* chemical reaction is the dissociation of N_2O_4, for at higher temperatures another dissociation becomes important, namely, $2NO_2 = 2NO + O_2$. The experimental study of these systems would have been more difficult if the second dissociation became appreciable before the first one was substantially complete. From a study of the dissociation of NO_2 at higher temperatures (500 to 900°K.) we may calculate the extent of its dissociation at 308°K. through a relation to be given later in this chapter. Such a calculation shows that the partial pressures of NO and O_2 are inappreciable in comparison with the pressures of NO_2 and N_2O_4 at 308°K. They are below 0.0001 atm. in the systems given in the above table and thus could not be detected experimentally by the method used in studying the dissociation of N_2O_4. At temperatures higher than about 425°K. the dissociation of N_2O_4 into NO_2 is substantially complete, and the only important chemical reaction in the system is $2NO_2 = 2NO + O_2$. Table 61 shows, for a total pressure of 1 atm., how the various partial pressures at equilibrium change with the Kelvin temperature.

4. The "Water Gas" Equilibrium.—In some reactions involving hydrogen gas at high temperatures, advantage may be taken of the fact that platinum is permeable to this gas and not to other gases. Thus a platinum tube inserted into a reaction chamber allows free penetration of hydrogen, and its partial pressure is measured by a manometer attached to the platinum tube. This method has been applied to the equilibrium

$$CO_2 + H_2 = CO + H_2O$$

at high temperatures.[1] A gaseous mixture containing known proportions of carbon dioxide and hydrogen was brought to equilibrium at a total pressure of 1 atm. As the total number of moles of gas does not change during the chemical reaction, no change of pressure is observed. But a decrease in hydrogen pressure takes place when water is formed; hence the difference between the starting pressure of hydrogen (calculated from its mole fraction in the original mixture) and the equilibrium pressure of hydrogen represents water-vapor pressure From the chemical reaction it follows that there is a mole of carbon monoxide formed for each mole of hydrogen used, i.e., for each mole of water formed, and that a mole of carbon dioxide is used for every mole of carbon monoxide formed. Thus a measurement of hydrogen pressure gives (1) the partial pressure of hydrogen, (2) the partial pressure of carbon monoxide, (3) the partial pressure of water vapor (each of these last two being equal to the decrease in hydrogen pressure during reaction), and by difference (4) the pressure of carbon dioxide. Table 62 shows the mole per cent of each substance in experiments at 1259°K., together with values of the constant

TABLE 61 —PARTIAL PRESSURES IN AN EQUILIBRIUM MIXTURE

T, °K	$p_{N_2O_4}$	p_{NO_2}	p_{NO}	p_{O_2}
300	0 330	0 670	0 000	0 000
350	0 175	0 825	0 000	0 000
400	0 020	0 980	0 000	0 000
450	0 000	0 976	0 016	0 008
500		0 928	0 048	0 024
550		0 844	0 104	0 052
600		0 718	0 188	0 094
700		0 412	0 392	0 196
800		0 191	0 540	0 270
900		0 085	0 610	0 305

$$\frac{p_{CO}p_{H_2O}}{p_{H_2}p_{CO_2}} = K_p \tag{6}$$

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[1] HAHN, *Z. physik. Chem*, **44**, 513 (1903), NEUMANN and KOHLER, *Z. Elektrochem.*, **34**, 281 (1928). BRYANT, *Ind Eng. Chem* , **23**, 1019 (1931), **24**, 592 (1932), and KASSEL, *J Am. Chem Soc* , **56**, 1841 (1934), have studied this equilibrium system by quite different experimental methods and have obtained results in substantial agreement with those reported in Table 62.

TABLE 62.—EQUILIBRIUM DATA FOR $CO_2 + H_2 = CO + H_2O$ AT 1259°K.

Original mixture		Equilibrium mixture			
Mole per cent CO_2	Mole per cent H_2	Mole per cent CO_2	Mole per cent $CO = H_2O$	Mole per cent H_2	K_p
10.1	89.9	0.69	9.4	80.5	1.60
30.1	69.9	7.15	22.96	46.93	1.58
49.1	51.9	21.22	27.90	22.95	1.60
60.9	39.1	34.43	26.45	12.67	1.60
70.3	29.7	47.50	22.82	6.85	1.60
			Average		1.60

As has been said before, equilibrium conditions change materially with the temperature. Thus, the constant, which is 1.60 at 1259°K., changes with the temperature as follows.[1]

K_p	0.219	0.412	0.675	0.999	1.37	2.21	3.11
T, °K	800	900	1000	1100	1200	1400	1600

It is a matter of the first importance to bear this in mind when comparing data from different sources.

An interesting feature of this equilibrium is the calculation of dissociation constants from it. So far nothing has been said about the presence of oxygen in this mixture, and there is in fact only an insignificant quantity present. Its partial pressure would have no effect upon the total pressure that could be detected by experimental means. (From relations to be given later in the chapter we may *calculate* the partial pressure of oxygen in the equilibrium mixtures at 1259°K. to be about 10^{-14} atm., but there are no experimental means of finding such pressures.) But the small quantity of O_2 present must satisfy the dissociations

$$2H_2O = 2H_2 + O_2 \qquad \text{and} \qquad 2CO_2 = 2CO + O_2$$

for which the equilibrium equations are

$$\frac{p_{H_2}{}^2 p_{O_2}}{p_{H_2O}{}^2} = K_{H_2O} \qquad \text{and} \qquad \frac{p_{CO}{}^2 p_{O_2}}{p_{CO_2}{}^2} = K_{CO_2}$$

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[1] BRYANT, *Ind. Eng. Chem.*, **24,** 592 (1932). These data were not obtained by measuring the partial pressure of hydrogen through platinum, but by another procedure which is given in the next chapter.

Upon dividing the second of these dissociation expressions by the first and extracting the square root, we obtain

$$\frac{p_{CO}p_{H_2O}}{p_{H_2}p_{CO_2}} = \sqrt{\frac{K_{CO_2}}{K_{H_2O}}} = K_p \tag{7}$$

which is the equilibrium expression of equation (6) for the reaction $CO_2 + H_2 = CO + H_2O$. This furnishes a means of calculating equilibrium constants from dissociation constants or of calculating dissociation constants from measurements of equilibriums. It is an expedient that we shall often use.

5. Synthesis of Iodine Chloride.—For chemical reactions in which no change in total moles attends the reaction, such as

$$\tfrac{1}{2}I_2(g) + \tfrac{1}{2}Cl_2(g) = ICl(g)$$

pressure or density measurements afford no information, and another expedient must be used. For this reaction we take advantage of the fact that the chemical reaction

$$BaPtCl_6(s) = BaCl_2(s) + Pt(s) + 2Cl_2(g)$$

maintains a constant pressure of chlorine at a given temperature so long as all three of the solid phases are present Thus, the use of a sufficient excess of solid $BaPtCl_6$ serves to control the partial pressure of one of the substances involved in the first reaction. At 736.5°K. the equilibrium pressure of chlorine is 9.5 mm. Consider a vessel containing an excess of $BaPtCl_6$ at 736.5°K., and into which enough iodine is introduced to give an *initial* pressure of 174.7 mm. of iodine vapor. At equilibrium the total pressure was found to be 342.3 mm., and therefore $342.3 - 9.5 = p_{I_2} + p_{ICl}$. It may be seen from the chemical reaction that each ICl requires $\tfrac{1}{2}I_2$, whence the pressure of ICl is twice the decrease in iodine pressure. This gives an equation

$$342.3 - 9.5 = 2(174.7 - p_{I_2}) + p_{I_2}$$

from which $p_{I_2} = 16.6$ mm. and $p_{ICl} = 316.2$ mm. Thus all the partial pressures are known, and

$$K_p = \frac{p_{ICl}}{p_{I_2}^{1/2}p_{Cl_2}^{1/2}} = \frac{316.2}{\sqrt{16.6}\,\sqrt{9.5}} = 25.4 \text{ at } 736.5°\text{K.}$$

It is, of course, permitted to write the chemical reaction

$$I_2(g) + Cl_2(g) = 2ICl(g)$$

provided that the equilibrium constant is written

$$K_p = \frac{p_{\mathrm{ICl}}{}^2}{p_{\mathrm{I_2}} p_{\mathrm{Cl_2}}} = 640 \text{ at } 736.5^\circ\mathrm{K}.$$

6. Dissociation of Nitrosyl Bromide.—Equilibrium between nitric oxide, bromine, and nitrosyl bromide has been studied[1] through the change in total pressure that attends the reaction

$$2\mathrm{NO}(g) + \mathrm{Br_2}(g) = 2\mathrm{NOBr}(g)$$

at constant volume. The equilibrium expression in terms of partial pressures, formulated in the standard way, is

$$K_p = \frac{p_{\mathrm{NOBr}}{}^2}{p_{\mathrm{NO}}{}^2 p_{\mathrm{Br_2}}} \tag{8}$$

In one series of experiments a glass bulb of 1055 ml. volume contained 0 0103 mole of NO and 0.0044 mole of Br_2. The equilibrium pressure (in atmospheres) changed with the absolute temperature as follows:

T	273	290	324	350	373	442	477
p	0 232	0 254	0 304	0 345	0 384	0 481	0 528

We may use the pressure at 350°K. to calculate the equilibrium constant for this temperature. By substituting the observed pressure, volume, and temperature in the ideal gas equation, we find 0.0127 total mole present at equilibrium. In order to express the composition of the equilibrium mixture in terms of a single unknown, we may set up a "mole table" in terms of the original quantities present, taking x as the number of moles of bromine reacting. Then $0.0044 - x$ moles of bromine remain, and $2x$ moles of NOBr have formed at the expense of $2x$ moles of NO, as may be seen from the chemical equation. Thus the "mole table" becomes

$$\begin{array}{rl}
0.0044 - x = & \text{moles Br}_2 \text{ at equilibrium} \\
2x = & \text{moles NOBr at equilibrium} \\
0.0103 - 2x = & \text{moles NO at equilibrium} \\
\hline
0.0147 - x = & \text{total moles at equilibrium}
\end{array}$$

Since this total is 0.0127, $x = 0.0020$ and the mixture consists of 0.0040 mole of NOBr, 0.0024 mole of Br_2, and 0.0063 mole of NO.

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[1] Blair, Brass, and Yost, *ibid.*, **56**, 1916 (1934).

We divide each of these quantities by 0.0127 to obtain the respective mole fractions; multiply each one by 0.345 to obtain partial pressures; and insert them in the equilibrium expression:

$$K_p = \frac{p_{\mathrm{NOBr}}{}^2}{p_{\mathrm{NO}}{}^2 p_{\mathrm{Br_2}}} = \frac{(0.110)^2}{(0.170)^2(0.065)} = 6.4 \text{ at } 350°\mathrm{K}$$

The same data may be used in a slightly different way to obtain the equilibrium constant for this system, though this procedure is applicable only in systems reacting at *constant volume* and constant temperature From the quantities of NO and bromine present we may calculate that the initial pressures would have been $p_0 = 0.280$ atm. for NO and $p_0 = 0\ 120$ atm for Br_2 at 350°K. if no reaction took place. It will be seen from the chemical equation that each mole of NO which reacts forms a mole of NOBr, and hence the sum of the partial pressures $p_{\mathrm{NO}} + p_{\mathrm{NOBr}}$ will remain constant at 0.280 atm But each mole of NOBr formed required $\frac{1}{2}$ mole of Br_2, and the progress of the reaction is attended by a decrease in pressure that measures the bromine reacting. The difference between the sum of the initial pressures (0.280 + 0 120 atm) and the equilibrium pressure (0.345 atm) is 0.055 atm., which is the decrease in the bromine pressure. Since each Br_2 yields 2NOBr, 2×0.055 is the equilibrium pressure of NOBr; $0.280 - 0.110 = 0.170$ is the partial pressure of the remaining NO, and $0.120 - 0.055 = 0.065$ is the partial pressure of the remaining Br_2 These are the partial pressures that appear in the equilibrium constant K_p given above.

The equilibrium relation among the partial pressures is valid in any chemical system containing these substances in any proportions, and in the presence of other gases, so long as the equilibrium pressure is low enough for reasonable conformity to the ideal gas laws. For example, 0.0550 mole of NO and 0.0816 mole of Br_2 in a 10-liter space at 350°K. will react to produce at equilibrium a total pressure of 0.350 atm., and treatment of these data in the way outlined above will yield a value of K_p in substantial agreement with that given above, namely, 6.4 for partial pressures in atmospheres.

If the chemical reaction is written for the *dissociation* of nitrosyl bromide,

$$2\mathrm{NOBr}(g) = 2\mathrm{NO}(g) + \mathrm{Br_2}(g)$$

the equilibrium relation is written as the reciprocal of the one given above, and K_p is 0.16 for partial pressures in atmospheres.

Equilibrium in Aqueous Solutions.—The general law of equilibrium that we have been considering in gaseous systems is applicable in aqueous or other solutions. In dilute solutions of nonionized solutes the law may be used for solutions in the approximate form already given as equation (2),

$$\frac{C_{\text{D}}{}^{d}C_{\text{E}}{}^{e}}{C_{\text{A}}{}^{a}C_{\text{B}}{}^{b}} = K_c \qquad (t \text{ const.})$$

The exact law for equilibrium in solutions is stated in terms of activities, corresponding to the exact equilibrium law for gases in terms of fugacities. It will be recalled that the activity a of a solute is a quantity with the dimensions of concentration, so defined that it is a measure of the "effective concentration," which is the effect of a solute upon the equilibrium. The equilibrium expression in terms of activities is

$$\frac{a_{\text{D}}{}^{d}a_{\text{E}}{}^{e}}{a_{\text{A}}{}^{a}a_{\text{B}}{}^{b}} = K_a \qquad (t \text{ const.}) \qquad (9)$$

and this expression is constant by definition

An activity *coefficient* is a factor by which the molality or the concentration must be multiplied in order to give the activity of a solute. Since molality (moles of solute per 1000 grams of solvent) and molal concentration (moles per liter of solution) are somewhat different in aqueous solutions and largely different in nonaqueous solutions, it will be evident that an activity is defined in two different ways. The product of *molality* and activity coefficient γ gives an activity $a = m\gamma$ in moles per 1000 grams of solvent, and the product of *molal concentration* and activity coefficient γ gives an activity $C\gamma$ in moles per liter of solution. In this brief treatment of chemical equilibrium we shall consider only dilute aqueous solutions, in which the difference between molality and concentration is slight, and we shall use $m\gamma$ and $C\gamma$ interchangeably for an activity. In more concentrated solutions this difference must be considered, of course.

In ideal solutions γ is unity at all molalities, in any solution γ approaches unity as the molality approaches zero, and in dilute solutions of nonionized solutes γ is very nearly unity and will be assumed unity in this book. In aqueous solutions containing ions the activity coefficient γ is a function of the molality, the valences of the ions, the effective "diameter" of the ions, and some other quantities. It is so defined that it approaches unity as the molality approaches zero, but in moderately dilute solutions of ionized solutes γ differs materially from unity. Some activity coefficients at 25° are quoted for illustration, and others are given in Tables 53, 54, and 98.

m	0 001	0 002	0 005	0 010	0 020	0 050
γ for HCl	0 966	0 952	0 928	0 904	0 875	0 830
γ for KCl	0 965	0 952	0 927	0 901	0 870	0 815

(The general equations showing the relation of m to γ are given on page 282.)

Upon substituting $a = C\gamma$ in equation (9) and rearranging, we obtain the equation

$$\frac{C_{\mathrm{D}}^{d} C_{\mathrm{E}}^{e}}{C_{\mathrm{A}}^{a} C_{\mathrm{B}}^{b}} = K_a \frac{\gamma_{\mathrm{A}}^{a} \gamma_{\mathrm{B}}^{b}}{\gamma_{\mathrm{D}}^{d} \gamma_{\mathrm{E}}^{e}} \qquad (t \text{ const.}) \tag{10}$$

Since the activity coefficients for each solute depend on the total solute concentration and not alone on that of the individual solute, it will be evident that the right-hand side of equation (10) will often be nearly constant; we shall frequently be content to assume it constant and write the expression

$$\frac{C_{\mathrm{D}}^{d} C_{\mathrm{E}}^{e}}{C_{\mathrm{A}}^{a} C_{\mathrm{B}}^{b}} = K_c \qquad (t \text{ const.}) \tag{11}$$

as a sufficient approximation for our purposes in a first treatment of equilibrium in aqueous solutions.

In the use of this expression for solutions, calculated concentrations will differ from measured equilibrium concentrations somewhat more than was true in gaseous systems. But such calculations will not often be in error by 10 per cent and may be within 1 or 2 per cent in many instances. The expedient of employing the approximate equation is commonly a necessary one, for the use of the exact equation (9) is excluded by a lack of sufficient data on activity coefficients in all but a few mixtures at a single temperature. We shall see in some instances that more exact calculations may be made by assuming that activity coefficients which have been determined for one solute are applicable to another solute of the same ionic type or to mixtures of two solutes of the same type. We turn now to some calculations that are useful.

Ionization of Weak Acids.—We have seen in Chap. VII that the relatively small change of equivalent conductance with changing concentration of a "largely ionized" solute is probably not due to a changing ion concentration, but to other factors. In solutions of slightly ionized solutes such as acetic acid or lactic acid, on the other hand, the change of equivalent conductance with concentration is largely (though not entirely) due to a change in the fractional ionization. Thus, the ratio Λ/Λ_0 of the equivalent conductance of lactic acid at a concentration C to the limit that it approaches as C approaches zero is nearly a measure of the fractional ionization. The chemical equation for the ionization of lactic acid, which is $CH_3CHOHCOOH$, may be abbreviated

$$\text{HLac} = \text{H}^+ + \text{Lac}^-$$

and if we follow the common custom of denoting the concentration of a solute by its symbol in parenthesis, so that $(\text{H}^+) = C_{\text{H}^+}$, for example, the equilibrium expression is

$$\frac{(\text{H}^+)(\text{Lac}^-)}{(\text{HLac})} = K_c \tag{12}$$

Each of the ion concentrations in the numerator is $C\Lambda/\Lambda_0$, and the concentration of nonionized acid is the difference between C and this quantity. The equivalent conductances at 25° are as follows:[1]

C	0 0634	0 0374	0 0136	0 00741	0.00354
Λ	17.9	23 4	38 0	50 3	70 7
$10^4 K_c$	1.41	1 44	1.44	1 43	1.43

They lead to values of K_c that are substantially constant over a concentration range of twentyfold, and thus the value 1.43×10^{-4} is the ionization constant of lactic acid at 25°.

The equilibrium expression for this ionization in terms of activities is

$$K_a = \frac{a_{\text{H}^+} a_{\text{Lac}^-}}{a_{\text{HLac}}}$$

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[1] MARTIN and TARTAR, *ibid.*, **59**, 2672 (1937). The limiting equivalent conductance Λ_0 is 388 5, derived from extrapolation of the data for sodium lactate as shown on p. 268.

If the concentrations of the ions are measured by the conductance ratio, the activities are obtained by multiplying by the appropriate activity coefficients. In the strongest solution for which conductance is given above, the ion concentration is about 0.003, for which the activity coefficient would be 0 95; in the weaker solutions, it would increase; and, for the weakest solution, it would be about 0 97 Even though this factor appears in the numerator raised to the second power, its effect upon the numerical value of K_c will not be great, and the variation in K_c within this range because of assuming an activity coefficient of unity will be about 4 per cent But in more highly ionized acids, such as sulfurous acid or chloroacetic acid, larger variations in the approximation K_c must be expected, and greater deviations of K_c from K_a must also be expected.

Although the constant K_c was derived from measurements on solutions containing only lactic acid, it applies in solutions containing other ions as well For illustration, (H^+) is about 0.0013 in 0 0136*m*. lactic acid as shown by the data above. Addition of 0.01 mole of HCl to 1 liter of this solution would largely increase (H^+) and require a corresponding reduction in the lactate ion concentration if the relation in equation (12) is to be maintained. Let α be the fraction of HLac ionized in a solution containing 0.0136 mole of HLac and 0 010 mole of HCl per liter. Since HCl is substantially all ionized, $(H^+) = 0.01 + 0\,0136\alpha$; $(Lac^-) = 0.0136\alpha$, and by difference $(HLac) = 0\,0136(1 - \alpha)$ Upon substituting these quantities in equation (12), we find α is reduced from about 0 1 to 0.014, and (Lac^-) becomes about 1.9×10^{-4}. The addition of 0.01 mole of sodium lactate to the acid solution in which $C = 0\,0136$ would change (H^+) in the solution to $1\,9 \times 10^{-4}$; the addition of 0.10 mole of sodium lactate would reduce (H^+) to about 1.9×10^{-5}.

Similar considerations would apply to the ionization of any acid whose ionization was slight, though not to the ionization of HCl in the presence of NaCl They would apply to a weak base whose ionization was shown by $BOH = B^+ + OH^-$ and for which

$$\frac{(B^+)(OH^-)}{(BOH)} = K_c$$

This relation is valid in solutions containing BOH alone, and also for BOH in the presence of an added strong base like NaOH, or a salt of the base, such as BCl

Some ionization constants for use in solving problems are given in Table 63 for 25°. These constants have somewhat different values at other temperatures, as is true of most equilibrium constants, but they may be used at 18° or 20° as well as for 25° for most approximate calculations, since the change in this small range of temperature is no greater than the possible error in the values of the constants

Table 63.—Some Ionization Constants at 25°[1]

Solute	K_c	Solute	K_c
Formic acid	1.7×10^{-4}	Ammonium hydroxide	1.8×10^{-5}
Acetic acid	1.8×10^{-5}	Methylammonium hydroxide	4×10^{-5}
Propionic acid	1.3×10^{-5}	Dimethylammonium hydroxide	5×10^{-5}
Acetoacetic acid	1.5×10^{-4}	Trimethylammonium hydroxide	6.5×10^{-5}
Chloroacetic acid	1.4×10^{-3}	Pyridine hydroxide	2.3×10^{-9}
Phenylacetic acid	5.5×10^{-5}	Aniline hydroxide	4×10^{-10}
Nitrous acid	4.5×10^{-4}	Boric acid	6.6×10^{-10}
Hydrofluoric acid	7×10^{-4}	Hydrocyanic acid	4×10^{-10}
Butyric acid	1.5×10^{-5}	Cinnamic acid	3.5×10^{-5}
Valeric acid	1.5×10^{-5}	Benzoic acid	6.2×10^{-5}
Lactic acid	1.4×10^{-4}		
Hypochlorous acid	5.6×10^{-8}		

Polybasic Acids

	K_1	K_2	K_3
Phosphoric acid	7.5×10^{-3}	6×10^{-8}	2×10^{-12}
Carbonic acid	4.5×10^{-7}	5.6×10^{-11}	
Sulfurous acid	1.7×10^{-2}	6×10^{-8}	
Oxalic acid	5×10^{-2}	5×10^{-5}	
Hydrogen sulfide	1.1×10^{-7}	1×10^{-15}	

Ionization of Polybasic Acids.—Weak acids, such as phosphoric acid, carbonic acid, tartaric acid, and hydrogen sulfide, ionize in steps, and an equilibrium expression may be written for each step. For example, carbonic acid gives in its first-step ionization

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[1] For many more ionization constants, see Latimer and Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Company, New York, 1940.

hydrogen ions and bicarbonate ions, as shown by the chemical equation

$$H_2CO_3 = H^+ + HCO_3^-$$

and its corresponding equilibrium expression[1] is

$$\frac{(H^+)(HCO_3^-)}{(H_2CO_3)} = K_1 \tag{13}$$

The denominator of this expression means ($H_2CO_3 + CO_2$), of course, since in all experiments it is this quantity that is measured; but we follow the usual custom of writing it simply (H_2CO_3) to indicate all the dissolved, nonionized carbon dioxide.

The bicarbonate ion acts as a weaker acid than carbonic acid, from which it came, and ionizes into hydrogen ions and carbonate ions, $HCO_3^- = H^+ + CO_3^{--}$, for which the equilibrium expression is

$$\frac{(H^+)(CO_3^{--})}{(HCO_3^-)} = K_2 \tag{14}$$

It should be noted that K_2 is written for the *ionization of an ion* into other ions. The expression (H^+) in the numerator of K_2 indicates total hydrogen-ion concentration in solution, not merely that part of it which came from the ionization of bicarbonate ions

The first step in the ionization of phosphoric acid is shown by the equation

$$H_3PO_4 = H^+ + H_2PO_4^-$$

for which the ionization expressions are

$$K_c = \frac{(H^+)(H_2PO_4^-)}{(H_3PO_4)} \quad \text{and} \quad K_a = \frac{a_{H^+}a_{H_2PO_4^-}}{a_{H_3PO_4}} = 0.0075 \text{ at } 25°$$

Phosphoric acid is intermediate between "strong" and "weak" electrolytes in its ionization (about 25 per cent ionized into H^+

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[1] For a careful determination of the constant $K_a = \frac{(H^+)(HCO_3^-)}{(H_2CO_3)} \frac{\gamma_{H^+}\gamma_{HCO_3^-}}{\gamma_{H_2CO_3}}$ see MacInnes and Belcher, *J. Am Chem Soc*, **55**, 2630 (1933), who find $K_a = 4.54 \times 10^{-7}$ at 25°. The change of K_a with temperature is given by Shedlovsky and MacInnes [*ibid*, **57**, 1705 (1935)] as follows·

t .	0°	15°	25°	38°
$K_a \times 10^7$	2.61	3.72	4.31	4.82

and $H_2PO_4^-$ at $0.1m.$); the activity coefficients for the ions would differ materially from unity, and thus K_c computed from conductance data would not be a satisfactory constant. The second and third steps in its ionization are shown by the equations

$$H_2PO_4^- = H^+ + HPO_4^{--} \qquad \text{and} \qquad HPO_4^{--} = H^+ + PO_4^{---}$$

and the corresponding equilibrium equations are

$$\frac{(H^+)(HPO_4^{--})}{(H_2PO_4^-)} = K_2 \tag{15}$$

and

$$\frac{(H^+)(PO_4^{---})}{(HPO_4^{--})} = K_3 \tag{16}$$

These expressions are, of course, valid in the presence of phosphates and when acids other than phosphoric are present.

Ionization of Strong Electrolytes.—We have already stated that there is no known measure of the fractional ionization of a salt or strong acid or base in dilute aqueous solution and that the bulk of the evidence points toward substantially complete ionization of these solutes. The figures in Table 64 show that the conductance ratio is a most unsatisfactory measure of the fraction ionized. The "constants" in this table result from taking $C\Lambda/\Lambda_0$ as a measure of the ion concentration and calculating the ionization "constant" from these ion concentrations. Their wide variation from a constant value is no reflection upon the law of chemical equilibrium but only an illustration of the

TABLE 64.—"IONIZATION CONSTANTS" FOR SALTS OF DIFFERENT TYPES[1]

KCl		$Ba(NO_3)_2$		$K_4Fe(CN)_6$	
Concentration	K	Concentration	K	Concentration	K
0.0001	0.0075	0.001	0.000017	0.0005	0.7
0.001	0.035	0.005	0.00018	0.0020	18.0
0.01	0.132	0.01	0.00045	0.012	1,171
0.1	0.495	0.10	0.97	0.1	41,190
1.0	2.22			0.4	842,100

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[1] LEWIS, *Z physik Chem*, **70**, 215 (1909).

fact that the fractional ionization of a salt is not to be measured in this way. We shall assume that salts and strong acids and bases are completely ionized in the calculations that follow.

Equilibriums Involving Ions.—There are many chemical reactions involving ions with one another or ions with non-ionized solutes, which lead to equilibriums that may be calculated from the ionization constants of the weak electrolytes. For example, the reaction of the salt of a weak acid and another weak acid is represented by the chemical equation

$$Na^+Ac^- + HNO_2 = Na^+NO_2^- + HAc$$

in which HAc is used for acetic acid, which is CH_3COOH Since complete ionization of the salts is assumed, we may write this reaction

$$Ac^- + HNO_2 = NO_2^- + HAc$$

and the corresponding equilibrium expression for the displacement of one acid by the other is

$$\frac{(HAc)(NO_2^-)}{(Ac^-)(HNO_2)} = K_c$$

The ratios (HAc)/(Ac⁻) and (NO₂⁻)/(HNO₂) in this equilibrium expression show that the ionization equilibriums of nitrous acid and acetic acid must also be satisfied in the solution Upon multiplying numerator and denominator of this expression by (H^+), we find a convenient means of evaluating K_c for the acid displacement, namely,

$$\frac{(H^+)(HAc)(NO_2^-)}{(H^+)(Ac^-)(HNO_2)} = K_c = \frac{K_{HNO_2}}{K_{HAc}} \qquad (17)$$

This means of evaluating equilibrium constants is one that we shall use again and again. In any equilibrium expression in which the concentration of a weak acid or weak base and the concentration of a product of its ionization appear as a ratio, this expedient should be considered.

In the presence of their salts, these weak acids are very slightly ionized, so that in the expression for electrical neutrality, which is

$$(Na^+) + (H^+) = (NO_2^-) + (Ac^-)$$

the sum $(NO_2^-) + (Ac^-)$ is very nearly equal to (Na^+). We thus neglect (H^+) as an addition to (Na^+), but, of course, we cannot call (H^+) negligible as a multiplying factor in such expressions as

$$\frac{(H^+)(NO_2^-)}{(HNO_2)} = 4.5 \times 10^{-4} \quad \text{and} \quad \frac{(H^+)(Ac^-)}{(HAc)} = 1.8 \times 10^{-5}$$

Since all the molecular and ionic solutes appearing in these equations for the ionization of the acids are present in the solution containing the two salts and the two acids, both these equilibriums must be satisfied. Upon dividing the first of these ionization constants by the second, we obtain as before

$$\frac{(H^+)(NO_2^-)(HAc)}{(H^+)(Ac^-)(HNO_2)} = \frac{4.5 \times 10^{-4}}{1.8 \times 10^{-5}} = 25 \text{ at } 25^\circ$$

for the numerical value of K_c in equation (17). There can be only one (H^+) in the solution, of course; therefore, it may be canceled from the expression.

A numerical example will make the use of the equations clearer. Suppose a liter of solution containing 0.1 mole of NaAc is added to a liter of solution containing 0.2 mole of HNO_2, and let x be the equilibrium concentration of nitrite ion in the resulting solution. The chemical equation shows that x is also the concentration of HAc, since they form in equal quantities. The total (HNO_2) + (NO_2^-) is 0.2 mole in 2 liters, which gives (HNO_2) = $(0.1 - x)$; also, (Ac^-) = $(0.05 - x)$. [We have neglected (H^+) in setting (Ac^-) + (NO_2^-) equal to (Na^+), and we shall find in a moment that this assumption is justified by the very small value of (H^+).] Upon making these substitutions in the equilibrium equation,

$$\frac{x^2}{(0.1 - x)(0.05 - x)} = 25$$

we find $x = 0.0482$ and this is the equilibrium concentration of NO_2^- and of HAc.

If each of the original solutions had been 0.2*m*. the equilibrium expression would have been

$$\frac{x^2}{(0.1 - x)^2} = 25$$

from which $x = 0.0833$. Thus, in this second system NaAc was present in larger quantity at the start, and therefore a larger quantity of it reacted.

Returning now to the first system in which (HAc) = 0.0482, (NO_2^-) = 0.0482, (HNO_2) = 0 0518, and (Ac^-) = 0.0018, we may insert these concentrations in either of the equilibrium relations

$$\frac{(H^+)(Ac^-)}{(HAc)} = 1.8 \times 10^{-5}$$

or

$$\frac{(H^+)(NO_2^-)}{(HNO_2)} = 4.5 \times 10^{-4}$$

and solve for (H^+), which is 4 8 × 10^{-4}. Thus, in taking (HNO_2) as $(0.1 - x)$ in the calculation above, we have neglected 4.8 × 10^{-4} in comparison with 10^{-1}, which is justified in view of other assumptions that introduce a larger error.

The equilibrium in terms of activities for this system is

$$\frac{a_{HAc}a_{NO_2^-}}{a_{Ac^-}a_{HNO_2}} = K_a = \frac{(HAc)\gamma_{HAc}(NO_2^-)\gamma_{NO_2^-}}{(Ac^-)\gamma_{Ac^-}(HNO_2)\gamma_{HNO_2}}$$

In dilute aqueous solutions the activity coefficients of nonionized solutes are substantially unity, and the activity coefficients for ions of the same valence in a mixture are determined largely by the total ion concentration, which is unchanged in this system as the reaction proceeds Hence K_c and K_a are substantially equal *in this system.* But it must be understood that, in the equilibriums shown in equations (12) to (16) and in many others to follow, there will be a real difference between K_c and K_a.

The Ionization of Water.—The slight ionization of water into hydrogen ions and hydroxyl ions is of the greatest importance in some respects and of no consequence whatever in other respects. Since the equilibrium hydrogen-ion concentration in pure water at 25° is 1 mole in 10,000,000 liters of water, only one molecule out of 550,000,000 is ionized at any given moment, and it seems surprising that this could be of any consequence or indeed that the dissociation could be measured. There are several ways in which the ion product (H^+)(OH^-) may be determined, and of these the conductance of pure water has already been mentioned Other ways will appear later, some of them in this chapter, and some in Chap. XIX. Following the standard procedure, we write the chemical equation

$$H_2O = H^+ + OH^-$$

and formulate the equilibrium expression

$$(H^+)(OH^-) = K_w \qquad (t \text{ const.}) \qquad (18)$$

It will be noted that the concentration of water has not been included in the ionization equilibrium. In a dilute aqueous solution the concentration of water is substantially constant when a small fraction of the water ionizes; thus we are justified in including this constant concentration in the value of K_c. There would, of course, be no objection to inserting the concentration of water wherever water is a reacting substance, but one must consistently write the water concentration in the equilibrium expression or consistently include its value in K_c. We follow the more common custom of including the concentration of water in K_c and of writing this special constant as K_w. In the hydrolysis reactions considered in the next section and, in general, whenever water is a reacting substance in dilute solutions, we shall also include the water concentration in K_c.

TABLE 65.—ION PRODUCT FOR WATER[1]

t, °C	$10^{14}K_w$	t, °C	$10^{14}K_w$
0	0.11	60	9.65
10	0.29	80	23
20	0.68	100	52
25	1.00	150	230
30	1.47	200	550
40	2.91	250	700
50	5.48	300	400

Not only does the ion product K_w change with temperature as do other equilibrium constants—it is conspicuous for the rapidity of this change. The value at several temperatures is given in Table 65. Equilibrium between hydrogen and hydroxyl ions prevails in every aqueous solution, whether acid, alkaline, or neutral, and regardless of the presence of other solutes. This is not to say that the ionization of water is important or even of

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[1] The values from 0 to 50° are by Harned and Mannweiler, *J. Am. Chem. Soc.*, **57**, 1873 (1935); they are based upon the electromotive force of an acid-alkali cell that is described in Chap. XIX. See also Harned and Geary, *ibid.*, **59**, 2032 (1937). The values for 60° and above are by Bjerrum in "International Critical Tables," Vol. VI, p. 152.

any consequence in every solution. In aqueous solutions of strong acids, strong bases, and their salts and in solutions of all but the weakest acids and bases in the absence of their salts, water behaves as a nonionized, inert solvent. But the alkaline reaction of sodium carbonate solution or potassium cyanide solution and the acid reaction of ammonium chloride solution are connected with the ionization of water in a way that is explained in the next section Since the product $(H^+)(OH^-)$ is constant at a given temperature, it will be clear that increase of one concentration requires a decrease in the other. If the hydrogen ions in water are removed by union with some other ion, more water ionizes to restore the equilibrium, and (H^+) will no longer be equal to (OH^-). Even so, the product $(H^+)(OH^-)$ will remain constant at equilibrium.

Hydrolysis. *a. Negative Ions*—Since *salts* of weak acids ionize in the same way and to the same extent as the salts of strong acids, an aqueous solution of such a salt contains negative ions of a weak acid from the ionization of the salt and hydrogen ions from the ionization of water. These ions require the presence of nonionized weak acid at a concentration that satisfies the ionization equilibrium for the weak acid. The chemical reaction that supplies this acid is called hydrolysis. As an illustration, the hydrolysis of cyanide ion is shown by the equation

$$CN^- + H_2O = OH^- + HCN$$

and the equilibrium expression for the reaction is

$$\frac{(OH^-)(HCN)}{(CN^-)} = K_c \qquad (t \text{ const.})$$

We combine the water concentration with K_c, as was done for the ionization of water. In this system the equilibriums $(H^+)(OH^-) = K_w$ and $(H^+)(CN^-)/(HCN) = K_{HCN}$ must both be satisfied; and, upon dividing the first of these by the second, we obtain the numerical value of the hydrolysis constant

$$\frac{(H^+)(OH^-)(HCN)}{(H^+)(CN^-)} = \frac{K_w}{K_{HCN}} = K_c \quad (t \text{ const.}) \qquad (19)$$

In the presence of cyanide ions the fractional ionization of HCN is very small; thus its concentration is the salt concentration multiplied by the fraction hydrolyzed. We may express the concentrations of all of the solutes in terms of these quantities, since, if h is the fraction hydrolyzed at the concentration C, $Ch = (OH^-) = (HCN)$, and $C(1 - h) = (CN^-)$. Substituting also the numerical value of the constants in the expression for K_c, we have

$$\frac{Ch^2}{1 - h} = \frac{1 \times 10^{-14}}{4 \times 10^{-10}} = 2.5 \times 10^{-5} \text{ at } 25^\circ \tag{20}$$

The fraction hydrolyzed may be reduced by adding KOH or HCN to the solution; but if this is done, the special relation $Ch^2/(1 - h)$ is no longer a proper one, though equation (19) is still valid. For instance, if to a liter of solution 0.1*m.* in KCN we add 0.01 mole of KOH, (OH^-) becomes $(0.1h + 0.01)$, (CN^-) is $0.1(1 - h)$, and (HCN) is $0.1h$.

It will be understood that as hydrolysis removes H^+ to form HCN, more water ionizes to satisfy the equilibrium expression $(H^+)(OH^-) = K_w$. Since the chemical reaction of the salt with water forms a strong base and a weak acid in chemically equivalent quantities, the solution at equilibrium is alkaline. In 0.1*m.* KCN, h is about 0.016 and $(OH^-) = 0.0016$, and the concentration of H^+ is 6×10^{-12}.

Similar behavior is shown by the negative ions of all weak acids, with smaller fractions hydrolyzed when the ionization constants are larger. Hydrolysis is not confined to ions of unit valence and is indeed more likely for ions of higher valence. For example,

$$S^{--} + H_2O = HS^- + OH^-$$

is a reaction that takes place when any sulfide dissolves in water. Carbonate ions hydrolyze, as shown by the equation

$$CO_3^{--} + H_2O = HCO_3^- + OH^-$$

and form alkaline solutions when carbonates dissolve in water.

b. Positive Ions.—Salts of weak bases yield the positive ions of the base when dissolved in water, and thus equilibrium between these ions and hydroxyl ions from water is established. The hydrolysis of ammonium ion is shown by the equation

$$NH_4^+ + H_2O = NH_4OH + H^+$$

for which the equilibrium expression and its relation to K_w and

K_{NH_4OH} are given by the equation

$$K_c = \frac{(NH_4OH)(H^+)}{(NH_4^+)} = \frac{K_w}{K_{NH_4OH}} \quad (t \text{ const.}) \qquad (21)$$

This hydrolytic reaction forms a weak base and hydrogen ion in chemically equivalent quantities; and since the slight ionization of the weak base is greatly repressed by the relatively high concentration of ammonium ion from the salt, the resulting solution is slightly acid at equilibrium. In the absence of added acid or added NH_4OH, the fraction hydrolyzed at any salt concentration is given at 25° by an equation similar to (20), namely,

$$\frac{Ch^2}{(1 - h)} = \frac{1 \times 10^{-14}}{1\,8 \times 10^{-5}} = 5.5 \times 10^{-10} \text{ at } 25°$$

whence $h = 7.4 \times 10^{-5}$ at 0.1*m*. and $(H^+) = 7.4 \times 10^{-6}$. In mixtures of NH_4OH and NH_4Cl the hydrogen-ion concentration is shown by a rearrangement of equation (21),

$$(H^+) = 5.5 \times 10^{-10} \frac{(NH_4^+)}{(NH_4OH)} \text{ at } 25°$$

The fact that polyvalent positive ions hydrolyze in steps is not as commonly realized as it should be. Ferric chloride solutions are known to be acid, and ferric hydroxide is known to be almost insoluble (about 10^{-9} mole per liter), and yet the common explanation is the formation of hydrogen ions and ferric hydroxide. The hydrolytic reactions are

$$Fe^{+++} + H_2O = FeOH^{++} + H^+$$

and

$$FeOH^{++} + H_2O = Fe(OH)_2^+ + H^+$$

Both the species $FeOH^{++}$ and $Fe(OH)_2^+$ have been shown to exist in ferric solutions,[1] and the equilibrium constant for the first reaction has been shown[2] to be about 5×10^{-3}.

c. Hydrolysis of Both Ions.—When salts derived from weak acids and weak bases dissolve in water, hydrogen ions from water combine with the negative ion of the salt to form the weak acid, hydroxyl ions combine with the positive ion of the salt to form

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[1] LAMB and JACQUES, *J. Am. Chem Soc.*, **60**, 967 (1938)

[2] RABINOWITCH and STOCKMAYER, *ibid*, **64**, 335 (1942).

a weak base, and the extent of hydrolysis is much greater. For an illustration consider ammonium lactate, for which the hydrolytic reaction may be written as follows if Lac^- denotes $CH_3CHOHCOO^-$,

$$NH_4^+Lac^- + H_2O = NH_4OH + HLac$$

and the equilibrium expression is

$$\frac{(NH_4OH)HLac)}{(NH_4^+)(Lac^-)} = K_c \qquad (t \text{ const.}) \qquad (22)$$

In order to evaluate K_c for this hydrolysis, we note that the ionization constants of the acid, the base, and water must all be satisfied in the equilibrium system By multiplying both numerator and denominator of equation (22) by (H^+) (OH^-) we see that $K_c = K_w/K_{HLac}K_{NH_4OH} = 4 \times 10^{-6}$ at 25° in this system and that the fraction hydrolyzed in $0.1m$ NH_4Lac is $h = 0.002$ In this solution (H^+) $(OH^-) = K_w$, as is always true in any aqueous solution; but since the weak acid and weak base are not ionized to the same extent, (H^+) and (OH^-) are not equal. The equilibrium concentrations are $(Lac^-) = 0.0998$ and $(HLac) = 0.0002$, whence, from the ionization constant of the acid, we calculate $(H^+) = 2.8 \times 10^{-7}$. Thus, it is shown that in the above calculation the concentration of Lac^- derived from the ionization of the *acid* is an insignificant quantity compared with that from the *salt*.

Experiment[1] shows that ammonium phenolate is 84 per cent hydrolyzed at 25°. If we abbreviate the equation

$$NH_4^+PH^- + H_2O = NH_4OH + HPh$$

in which Ph stands for C_6H_5O, the hydrolysis equilibrium may be written

$$\frac{(NH_4OH)(HPh)}{(NH_4^+)(Ph^-)} = K_c = \frac{K_w}{K_{NH_4OH}K_{HPh}} \qquad (23)$$

If C is the original concentration and h the fraction hydrolyzed (which we have stated to be 0.84), we see that

$$(NH_4OH) = (HPh) = Ch \qquad (NH_4^+) = (Ph^-) = C(1 - h)$$

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[1] This fraction is given by O'Brien and Kenny for 25° over the concentration range 0 25 to 1 0, in *J. Chem Education*, **1939**, p 140

and upon substituting these equalities in the equilibrium expression, C cancels out, leaving

$$\frac{h^2}{(1-h)^2} = K_c = \frac{K_w}{K_{NH_4OH}K_{HPh}} = 28 \text{ at } 25°$$

For salts of weak bases and weak acids, in the absence of added free base or free acid, the extent of hydrolysis is thus seen to be independent of the salt concentration, to the extent that the variation in the activity coefficients can be ignored. It will be recalled that equation (20) contained the concentration of the salt; thus for the hydrolysis of positive ions alone or negative ions alone the extent of hydrolysis varies with the concentration. The measured fractional hydrolysis and the known values of K_w and K_c for the ionization of NH_4OH enable us to calculate from equation (23) that K_c for the ionization of phenol as an acid is 2×10^{-11}. Other experiments upon phenolates lead to a somewhat larger ionization constant for phenol at 25°, namely, about 1.3×10^{-10}, which would correspond to about $\frac{2}{3}$ for the fractional hydrolysis of ammonium phenolate. In this instance, as in so many in physical chemistry, it is difficult to choose between conflicting determinations of a given physical quantity, and one should remember that the experimental difficulties of measuring a quantity as small as 10^{-10} or 10^{-11} are great.

In general, the numerical values of K_a and K_c will be rather close together for the hydrolysis of a positive ion or a negative ion alone in a given solution, and the difference between K_a and K_c will be much greater when both ions hydrolyze Denoting by γ the activity coefficient that applies to all the ions in a solution and remembering that the activity coefficients for nonionized solutes in dilute solution are very close to unity, we find the equilibrium expressions for the hydrolysis of a single ion and of both ions to be

$$K = \frac{(Ch\gamma)Ch}{C(1-h)\gamma} \quad \text{and} \quad K_a = \frac{Ch \cdot Ch}{C^2\gamma^2(1-h)^2}$$

It will be seen from these expressions that the activity coefficient γ for the ions cancels from the expression for the hydrolysis of a single ion and appears as the square in the denominator of the expression for the hydrolysis of both ions.

Hydrolysis and Ionization of Intermediate Ions.—The ions formed in the first ionization of dibasic acids, such as HS^- from H_2S, HCO_3^- from H_2CO_3, or HSO_3^- from H_2SO_3, may hydrolyze and ionize in such quantity that both reactions must be considered in the same solution. For example, the reactions

$$HS^- + H_2O = OH^- + H_2S$$
$$HS^- = H^+ + S^{--}$$

both occur in a solution of NaHS. The fact that the solution is alkaline shows that the first reaction is more important than the second. In such a solution there are six solutes at equilibrium, Na^+, H^+, HS^-, S^{--}, H_2S, and OH^-. If we consider a solution $0.1m$ in NaHS at 25°, (Na^+) is 0.1 and the five other equilibrium concentrations are fixed by five equations: an equation for electrical neutrality, which always exists in any ionic solution; a sulfur balance; and three ionization constants. The equations are

$$(Na^+) + (H^+) = (HS^-) + 2(S^{--}) + (OH^-) \qquad (a)$$
$$0.1 = (HS^-) + (S^{--}) + (H_2S) \qquad (b)$$
$$\frac{(H^+)(HS^-)}{(H_2S)} = 1.1 \times 10^{-7} \qquad (c)$$
$$\frac{(H^+)(S^{--})}{(HS^-)} = 1 \times 10^{-15} \qquad (d)$$
$$(H^+)(OH^-) = 1.0 \times 10^{-14} \qquad (e)$$

A solution of five simultaneous equations is of course possible, but tedious, and is unnecessary for the present purpose if some suitable approximations are made. If we neglect (H^+) in comparison with (Na^+) and equate the right sides of equations (*a*) and (*b*), we have

$$(S^{--}) + (OH^-) = (H_2S)$$

We may show that (S^{--}) is small in comparison with (OH^-) by dividing (*d*) by (*e*) and noting that (HS^-) is nearly 0.1, which shows that $(S^{--})/(OH^-)$ is approximately 0.01.

Thus we see that hydrolysis of the negative ion is the important reaction in this solution, and that $(OH^-) = (H_2S)$ within 1 per cent. The equilibrium relation for the hydrolysis and the value of its constant are given by an equation like equation (19), namely,

$$\frac{(H_2S)(OH^-)}{(HS^-)} = \frac{K_w}{K_1} = 9 \times 10^{-8} \text{ at } 25°$$

Recalling that (H_2S) and (OH^-) are nearly equal and that (HS^-) is about 0.1, we find $(H_2S) = (OH^-) = 9.5 \times 10^{-5}$. From the value of K_w, $(H^+) = 1 \times 10^{-10}$; and, upon substituting this in (*d*), we find that $(S^{--}) = 10^{-6}$ and (HS^-) is between 0.0999 and 0.1. Thus all the equilibrium concentrations are fixed within a per cent or two, which is as close as the numerical values of the constants will justify.

In a solution of 0.1*m.* in $NaHSO_3$ hydrolysis and the ionization of HSO_3^- are of nearly equal importance. The chemical equations for the processes are

$$HSO_3^- + H_2O = OH^- + H_2SO_3$$
$$HSO_3^- = H^+ + SO_3^{--}$$

As before, we have five solutes in addition to sodium ion, H^+, OH^-, HSO_3^-, SO_3^{--}, and H_2SO_3, requiring five equations. They are again an electrical balance, a sulfur balance, and three equilibrium constants

$$(Na^+) + (H^+) = (HSO_3^-) + 2(SO_3^{--}) + (OH^-) \qquad (a)$$
$$0.1 = (HSO_3^-) + (SO_3^{--}) + (H_2SO_3) \qquad (b)$$
$$\frac{(H^+)(HSO_3^-)}{(H_2SO_3)} = 0\,017 = K_1 \qquad (c)$$
$$\frac{(H^+)(SO_3^{--})}{(HSO_3^-)} = 6 \times 10^{-8} = K_2 \qquad (d)$$
$$(H^+)(OH^-) = 10^{-14} = K_w \qquad (e)$$

For a first approximation we neglect (H^+) and (OH^-) in (*a*) and equate the right sides of (*a*) and (*b*), though because of the smaller ionization constant of H_2SO_3 the neglect of (H^+) may not be justified, and find

$$(SO_3^{--}) = (H_2SO_3) \qquad (f)$$

Upon multiplying (*c*) by (*d*) and noting the equality in (*f*), we find

$$(H^+) = \sqrt{K_1K_2} = 3.2 \times 10^{-5}$$

Now substitute this (H^+) in (*c*), and note that (HSO_3^-) is nearly 0.1, whence

$$(H_2SO_3) = 1.9 \times 10^{-4} = (SO_3^{--})$$

the last concentration following from (*f*). Finally, from (*e*),

$$(\mathrm{OH^-}) = \frac{K_w}{(\mathrm{H^+})} = 3 \times 10^{-10}$$

The results of such a calculation should always be reviewed to check the assumptions made. In this calculation we see that $(\mathrm{H^+})$ is 17 per cent of the calculated $(\mathrm{H_2SO_3})$ and hence not negligible in equation (*a*), but we see also that $(\mathrm{OH^-})$ as an addition quantity is negligible in this equation.

As a second approximation, transpose $(\mathrm{H^+})$ to the right side of (*a*), then equate this to the right side of (*b*), which gives

$$(\mathrm{SO_3^{--}}) = (\mathrm{H_2SO_3}) + (\mathrm{H^+}) \qquad (g)$$

If we take $(\mathrm{HSO_3^-})$ as 0.1 in (*c*), it follows that

$$(\mathrm{H^+}) = 0.17(\mathrm{H_2SO_3})$$

whence, from (*g*), $(\mathrm{SO_3^{--}}) = 1.17(\mathrm{H_2SO_3})$; this relation is now substituted into (*c*) to obtain $(\mathrm{H^+})$, and then the other operations are performed as before to obtain the other concentrations.

$(\mathrm{H_2SO_3}) = 2.1 \times 10^{-4}$, $(\mathrm{SO_3^{--}}) = 2.5 \times 10^{-4}$, and
$(\mathrm{OH^-}) = 3.6 \times 10^{-10}$

From (*b*), $(\mathrm{HSO_3^-}) = 0.0995$ in place of 0.10.

It should be noted that, while hydrolysis is more important than ionization of $\mathrm{HS^-}$ in NaHS and while hydrolysis and ionization are about equal in $\mathrm{NaHSO_3}$, both the effects are small. Whenever hydrolysis involves only a negative ion or only a positive ion, the fraction hydrolyzed will usually be small at moderate or high concentrations. But at extreme dilutions the fraction hydrolyzed may be large, as, for example, in a saturated solution of $\mathrm{CaCO_3}$ in which the molality is about 10^{-4} and more than half the solute is in the form of hydrolysis products.

Buffer Solutions.—In a mixture of a weak acid and one of its salts the acid is very slightly ionized, and the salt is assumed to be completely ionized, so that the very small hydrogen-ion concentration is dependent on the *ratio* of salt concentration to acid concentration at a given temperature. Such a solution will have a hydrogen-ion concentration that is unchanged upon moderate dilution and nearly unchanged by the addition of a relatively small amount of acid or base. Thus in a solution containing 0.1 mole of acetic acid and 0.09 mole of sodium acetate per liter of solution, the hydrogen-ion concentration is

$$(\mathrm{H}^+) = K_c \frac{(\mathrm{HAc})}{(\mathrm{Ac}^-)} = 1.8 \times 10^{-5} \frac{0.1}{0.09} = 2 \times 10^{-5} \text{ at } 25^\circ$$

Dilution with a liter of water would leave the ratio $(\mathrm{HAc})/(\mathrm{Ac}^-)$ unchanged to the extent that K_c is unchanged, and thus (H^+) would also be unchanged within the same limitation. It will be recalled that for the ionization of acetic acid $K_a = K_c\gamma^2$; and since this dilution changes γ from 0.82 to 0.87, K_c and (H^+) will change about 10 per cent. Hydrogen ions to yield 2×10^{-5} mole per liter would come from the ionization of an amount of acetic acid that is negligible in comparison with the total acid present, and thus the solution is "buffered" to maintain a nearly constant (H^+).

The ionization constant for the second hydrogen ion of phosphoric acid is 6×10^{-8} at 25°, whence, by rearranging the expression for its ionization equilibrium, we have

$$(\mathrm{H}^+) = 6 \times 10^{-8} \frac{(\mathrm{H_2PO_4^-})}{(\mathrm{HPO_4^{--}})} \text{ at } 25^\circ$$

In a solution containing 0.10 mole of $\mathrm{NaH_2PO_4}$ and 0.06 mole of $\mathrm{Na_2HPO_4}$ in any reasonable volume of water at 25° the ratio $(\mathrm{H_2PO_4^-})/(\mathrm{HPO_4^{--}})$ is $^{10}/_{6}$, (H^+) is 1.0×10^{-7}, and therefore (OH^-) is also 1.0×10^{-7}. Addition of 0.001 mole of HCl to such a solution would cause the reaction

$$\mathrm{H^+ + HPO_4^{--} = H_2PO_4^-}$$

to take place, reducing the quantity of $\mathrm{HPO_4^{--}}$ from 0.060 to 0.059, increasing the quantity of $\mathrm{H_2PO_4^-}$ to 0.101, and changing the ratio $(\mathrm{H_2PO_4^-})/(\mathrm{HPO_4^{--}})$ by about 2 per cent; accordingly (H^+) would be changed by this amount. Addition of 0.001 mole of HCl to a liter of water would change (H^+) from 10^{-7} to 10^{-3}. This solution is a "buffer" that maintains a nearly constant (H^+), while water has no capacity to maintain a constant (H^+) against small amounts of acid or base. Of course, this phosphate mixture is also a buffer against small amounts of alkali, and against dilution as well.

Since the ionization constants of many weak acids are not accurately known, the usual practice is to make up a series of solutions of different ratios of $(\mathrm{H_2PO_4^-})$ to $(\mathrm{HPO_4^{--}})$, or other salts and acids, and to determine the hydrogen-ion activity in them from the potential of a cell composed of a hydrogen electrode dipping into the solution and a reference electrode. The electromotive force of such a cell is

$$E = 0.0592 \log a_{H^+} + \text{constant}$$

as we shall see in Chap. XIX, and, for the approximation we have been using, this becomes $E = 0.0592 \log (H^+) + \text{constant}$. For illustration, solutions of 9.08 grams of KH_2PO_4 per liter and 11 88 grams of $Na_2HPO_4\,2H_2O$ per liter, respectively, when mixed in the quantities shown below, yield buffers in which (H^+) at 25° has the value given under each mixture, determined from the potential of a cell

Ml Na_2HPO_4	0 5	1 0	2 0	3 0	4 0	5 0	6 0	7 0	8 0	9 0
Ml KH_2PO_4	9 5	9 0	8 0	7 0	6 0	5 0	4 0	3 0	2 0	1 0
$10^7(H^+)$	25	13	5	3	2 5	1 6	1 0	0.6	0 4	0 2
pH	5 6	5 9	6 3	6 5	6 6	6 8	7 0	7 2	7 4	7 7

The hydrogen-ion concentrations of buffer solutions will change with changing temperature, for K_w and the ionization constants of the acids or acid ions change with temperature at unequal rates. For illustration, K_w is 10^{-15} at 0°C , 10^{-14} at 25°C., and 5×10^{-13} at 100°C ; and in this range of temperature the ionization constant for acetic acid would change only a few per cent.

Consider a solution containing 0 1 mole of K_2HPO_4 and 0.1 mole of KH_2PO_4 in 1000 grams of water at 25°. By titrating a portion of this solution with bromophenol blue as indicator it would appear to be about 0.1 *N* base, by testing it with nitrazine yellow it would appear to be "neutral," and by titrating it with phenolphthalein as indicator it would appear to be about 0.1 *N* acid. The terms "acid," "neutral," and "alkaline" are all inappropriate for describing this solution; the correct statement applying to it is found in the sixth column of the table above, namely, $(H^+) = 1.6 \times 10^{-7}$.

The pH Scale.—In the range between "slightly acid" solutions and "slightly alkaline" solutions the change of (H^+) is so large relatively, though (H^+) is very small in all of them, that a logarithmic scale is convenient. This scale was suggested by Sørensen in 1909 and defined as

$$\text{pH} = -\log (H^+) \qquad \text{or} \qquad \text{pH} = \log \frac{1}{(H^+)} \tag{24}$$

The pH values given for the phosphate mixtures above are expressed in this way. For illustration, when $(H^+) = 5 \times 10^{-7}$, $\log (H^+) = -6.3$ and pH = 6.3. This is a reciprocal logarithmic scale of acidities as defined and as commonly used; therefore, the actual acidity of a solution in which pH is 7.3 is one-tenth of that in a solution whose pH is 6.3. (Occasionally the alkalinity of a solution is expressed as pOH, which is the logarithm of the reciprocal of the hydroxide-ion concentration, but the use of pH is more common.)

Such a definition is clear enough for most purposes when the acidity is produced by an acid alone. But we have seen in the preceding pages that pH is difficult to control without the use of buffers when it lies between 4 and 10. The activity coefficient γ in a mixture of an acid and a salt depends on the total ion concentration, its value is 0 8 to 0 9 when the salts added to the weak acid in buffer solutions are 0.1 to 0 01*m.*, and in these mixtures $a_{H^+} = m_{H^+}\gamma_{H^+}$ Two other definitions, among the many proposed for one reason or another, will suffice to show that confusion results unless one states *which* definition of pH is being used, namely, $\text{pH} = -\log a_{H^+}$ and

$$\text{pH} = \frac{E - E^\circ}{2.3RT/F}$$

in which F is Faradays' constant, E° is the potential of a constant "reference electrode," and E is the potential of an electrolytic cell:

Pt, H_2 (1 atm.), [unknown solution], KCl (satd.), ref. elec.

There are valid objections, apparently, to any one definition of pH and an obvious need for a single definition of pH that has not yet been met. The distinctions are best reserved for a second consideration of physical chemistry and omitted from a first consideration,[1] but beginners should realize that the confusion exists. Admitting its existence, we postpone consideration of the definition in terms of cell potentials until Chap. XIX,

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[1] See, for example, MacInnes, Belcher, and Shedlovsky, *J Am. Chem Soc.*, **60,** 1094 (1938), for a discussion of this topic and data on pH to be assigned to acetate and phthalate buffers. Other buffer solutions and the corresponding pH values in the range 2.27 to 11.68 are given by Bates, Hamer, Manov, and Acree, in *J. Research Nat. Bur. Standards*, **29,** 183 (1942).

and consider $pH = -\log (H^+)$ as a sufficient approximation for the purpose of discussing indicators and titration errors.

Experimentally, the pH in a solution is measured either from the potential of a cell[1] or by comparisons of indicator colors in the solution with the colors in solutions of known pH. Each method has certain advantages, and each has certain limitations that are not as commonly appreciated as they should be. These limitations will be given later in this chapter for the indicator method and in Chap. XIX for the potential method, but we may say here that there is no method of determining pH applicable to every kind of solution. "Interfering" materials, especially oxidizing or reducing agents, colloids, protein, and other organic materials, and certain salts, may cause "measured" pH values to be in error by 1 to 5 units, and many values recorded to 0 1 unit are in error by several times this amount.

Indicators.—An indicator is a substance that changes its color with changing hydrogen-ion concentration. Most of the acid-alkali indicators familiar in analytical chemistry change color conspicuously within a pH range of 1.0 or less, and this rapid change is desirable for such work Other indicators change over ranges as wide as 2.0 pH, and they are useful for other purposes. But an indicator is not in general a substance that changes color at the true end point of a titration; it fulfills this desirable condition only when it is properly selected for the titration to be done. The hydrogen-ion concentration at the end point should be that in a solution of the pure salt formed from the acid and base, for only under this condition will the acid (or base) added be equivalent to the base (or acid) being titrated. Since the hydrogen-ion concentration in 0.2*m*. ammonium chloride differs from that in 0.2*m*. sodium acetate by about 4 pH units, it will be evident that an indicator suitable for ammonium hydroxide will not serve for titrating acetic acid.

Most indicators *behave as if* they were weak acids that change color when neutralized, though the color changes result from structural changes that accompany the neutralization, rather than from simple ionization. For our purposes we may consider an indicator as a weak monobasic acid whose color changes upon neutralization, and we define the "indicator constant" as

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[1] For descriptions of the apparatus and procedure see catalogues EN96 and EN96 (1) of Leeds and Northrup Co

$$K_i = (\mathrm{H}^+) \frac{(\mathrm{In}^-)}{(\mathrm{HIn})} \tag{25}$$

in which expression the ratio $(\mathrm{In}^-)/(\mathrm{HIn})$ is the ratio of the concentration of indicator ion to nonionized indicator. If we let x be the fraction of the indicator showing its "alkaline" color and $(1 - x)$ be the fraction having its "acid" color, whether or not these are actually ions and free acids, respectively, this equation may be arranged in the form

$$(\mathrm{H}^+) = K_i \frac{1 - x}{x} \tag{26}$$

and used to determine hydrogen-ion concentration after K_i is known

When the indicator constant is much smaller than the ionization constant of a weak acid being titrated, nearly all the acid is neutralized before the indicator is neutralized, as may be seen from an equation like (17). When the indicator is present in much smaller quantity than the acid, as is commonly true, the residual acid is negligible when the indicator is neutralized, if one of the proper K_i has been chosen.

In the presence of relatively large amounts of neutral salts such as KCl, the value of K_i as defined in equation (25) changes with the salt concentration,[1] and change of color at constant (H^+) is observed upon the addition of KCl. These changes in K_i are not much greater than those which would be observed in the ionization constant K_c for any weak acid in the presence of KCl at these concentrations. They arise from changing activity coefficients and from other causes that are obscure In dilute

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[1] See Chase and Kilpatrick, *J Am Chem. Soc*, **54,** 2284 (1932). The ratio of K_i in 0 1m KCl to its value in other molalities of KCl to give correct (H^+) is as follows for three common indicators:

Molality KCl	Ratio K_i to K_i in 0 1m KCl		
	Bromocresol green	Chlorophenol red	Methyl red
0 5	1 31	1 22	0 89
1 0	1 18	1 48	0 75
2 0	0 95	1 20	0 51
3 0	0 78	0 72	0 28

solutions and when great precision in pH measurement is not required, they may be ignored. But it should not be forgotten that when (H^+) is very small the other ion solutes are not ideal at their much greater concentrations and that the activity coefficient for hydrogen ion depends on the total ion concentration rather than on its concentration alone

Indicators give pH indications of reasonable accuracy when they are used under proper conditions, and they are open to moderate or serious errors when applied under improper conditions. It is therefore important to realize that such conditions exist as a limitation to the use of indicators, and we now turn to some of them. (1) Proper temperature control is essential. Some indicators change "range" by one pH unit or more for a temperature change of 50°; and since ionization constants and K_w are also temperature functions, the use of indicators at other than the standard temperature yields uncertain pH determinations (2) Organic liquids, such as alcohol, may shift pH indications by one unit or more, up or down, and no simple method of estimating the shift is known. (3) Proteins shift pH indications so seriously that indicators may not be used in their presence except for rough measurements. (4) Colloids, soap, soil suspensions, and colored solids in general render pH indications in error by unpredictable amounts (5) Oxidizing or reducing agents may bleach the color of an indicator and render its pH indication wholly false. (6) Insufficient buffering leads to false pH indications; for some of the indicators are acids, and others are made up in dilute sodium hydroxide solution. The most-quoted illustration is the shift of pH from 7 to 5 by the addition of a few drops of methyl red to a test tube of pure water, but many other less extreme examples are known.

While this list of restrictions to the use of color indicators is discouragingly long, it is far better to realize that pH indications are subject to these limitations than to make measurements in ignorance of the conditions and rely on inaccurate results.

Most of the commercial indicators are described in terms of the "pH range" within which color changes are observed, as, for example, bromothymol blue, yellow to blue, 6.0 to 7.6. Permanent color standards for steps of 0.2 pH are available or may be prepared in the laboratory from buffer solutions to which measured volumes of dilute indicator solutions are added. Table 66 shows the range of some common indicators.[1] No satisfactory indicators for solutions more alkaline than pH = 11 are known [2]

TABLE 66.—SOME INDICATOR RANGES

Indicator	pH range	Color change
Metacresol purple	1 2– 2 8	Red-yellow
Bromophenol blue	3 0– 4 6	Yellow-blue
Methyl orange	2 8– 4 0	Orange-yellow
Methyl red	4 2– 6 3	Red-yellow
Bromocresol green	4 0– 6 0	Yellow-green
Bromocresol purple	5 2– 6 8	Yellow-purple
Nitrazine yellow	6 4– 6 8	Yellow-blue
Bromothymol blue	6 0– 7 6	Yellow-blue
Phenol red	6 8– 8 4	Yellow-red
Cresol red	7 2– 8 8	Yellow-red
Phenolphthalein	8 4–10 0	Colorless-pink
Thymol blue	8 0– 9 6	Yellow-blue
Orthocresolphthalein	8 2– 9 8	Colorless-red
Thymolphthalein	10 0–11 0	Colorless-red

Titration Errors.—While a perfect titration of an acid with a base requires that the indicator change color at the (H^+) of the salt solution and not over a range of pH, this condition is neither possible to meet nor necessary for an acceptable titration For example, in the titration of lactic acid with NaOH, we may assume that the sodium lactate concentration at the end point is about 0.1*m.* and calculate the fraction of the lactate ion hydrolyzed and (H^+) from equation (20),

$$\frac{(\mathrm{OH^-})(\mathrm{HLac})}{(\mathrm{Lac^-})} = K_h = \frac{0.1h^2}{1-h} = \frac{10^{-14}}{1.4 \times 10^{-4}} \text{ at } 25^\circ$$

from which $h = 8.5 \times 10^{-6}$, $(\mathrm{OH^-}) = 8.5 \times 10^{-7}$, and

$$(\mathrm{H^+}) = 1.2 \times 10^{-8}$$

in the solution at the true end point But, in a solution in which the end point is 0.1 per cent short, the ratio of free lactic acid to lactate ion is 1:1000; and, upon substituting this ratio into

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[1] For other data see "International Critical Tables," Vol I, p 81 Discussion and procedures will be found in Clark, "Determination of Hydrogen Ions," Britton, "Hydrogen Ions," and "The A B.C of Hydrogen Ion Control," by the LaMotte Chemical Products Company.

[2] See *Ind. Eng Chem.*, Anal. Ed., **1**, 45 (1929).

the ionization expression K_c for lactic acid, $(H^+) = 1.4 \times 10^{-7}$. If the end point is 0 1 per cent overrun, hydrolysis of the lactate ion is negligible in the presence of a slight excess of base. and the titrated solution acts as a diluent for the excess standard base. For each 100 ml. of base required for the titration, 0.1 ml. in excess is diluted to the final volume of the titrated solution, which might be about 200 ml. Thus, if the standard solution were 0.2 N, $(OH^-) = 0.2 \times (0.1/200) = 10^{-4}$ and (H^+) would be 10^{-10}. If an error of less than 0.1 per cent is acceptable, any indicator that changes color between 1.4×10^{-7} and 1×10^{-10} is satisfactory, and all those listed between phenol red and ortho-cresolphthalein in Table 66 (or any others of similar pH range) will serve.

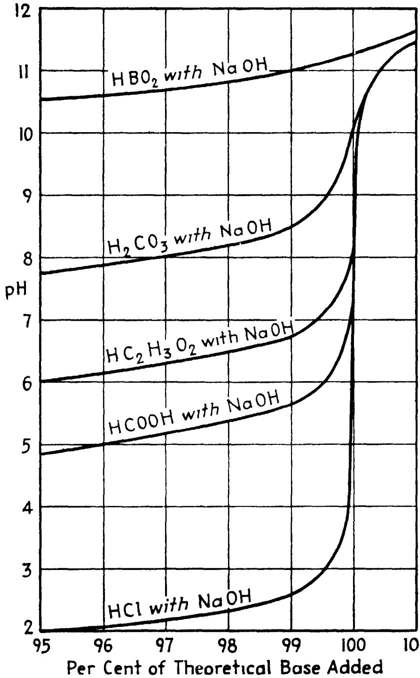

FIG 46 —Titration diagram for acids.

The "titration curves" that are familiar from analytical chemistry are only curves that show the fraction of a base or acid titrated in terms of the pH of the solution. Points on these curves are calculated in the way shown in the previous paragraph. For the titration of a strong acid with a strong base, any indicator that changes color between pH = 4 and pH = 10 will serve; for weak acids or bases the range is narrower; and, for extremely weak acids such as hydrocyanic acid or boric acid, the range of pH for accurate titration is impossibly small. Titration curves for a few acids are shown in Fig. 46. It may be seen from this figure that an indicator which changes color at pH = 7 (true neutrality) would cause an error of 0.5 per cent in titrating acetic acid and an error of more than 10 per cent in titrating carbonic acid. Thymol blue would be excellent for acetic acid but would cause an error of perhaps 1 per cent with carbonic acid.

TABLE 67.—PERCENTAGE DISSOCIATION OF GASES[1] AT 1 ATM. PRESSURE

T_{abs}	CO_2	H_2
1,000	0.00002	
1,200	0.00093	
1,400	0.0146	
1,600	0.110	0.005
1,800	0.546	0.029
1,900	1.04	
2,000	1.84	0.112
2,200	5.0	0.392
2,500	15.6	1.61
3,000	48.5	9.03
3,400		24.5
4,000		62.5

Change of Chemical Equilibrium with Temperature.—Since an increase in the temperature of a chemical system at equilibrium requires the absorption of heat by the system, the qualitative effect on equilibrium is seen to be a change of composition in which the chemical reaction absorbing heat is favored. The dissociations of SO_3, NH_3, NOBr, and N_2O_4 are attended by the absorption of heat, and the data quoted for these substances earlier in the chapter show an increased extent of dissociation at higher temperatures for all of them. Hydrogen and CO_2 also

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[1] These figures are quoted from Langmuir, *J. Am. Chem. Soc.*, **37,** 417 (1915), *Ind. Eng. Chem.*, **19,** 667 (1927), slightly different extents of dissociation are given by Giauque, *J. Am. Chem. Soc.*, **52,** 4816 (1930); by Gordon, *J. Chem. Phys.*, **1,** 308 (1933); and by Kassel, *J. Am. Chem. Soc.*, **56,** 1838 (1934).

dissociate with the absorption of heat, and the data of Table 67 show that they are more highly dissociated at higher temperatures. The dissociation of NO into N_2 and O_2 evolves heat, and the extent of its dissociation therefore decreases with increasing temperature.

Before giving the quantitative relation between ΔH and the equilibrium constant, we review the conventions followed in writing chemical-equilibrium expressions and thermochemical equations: Write a balanced chemical equation for the process involved; append ΔH for the complete reaction as written, with due regard to sign; and formulate K, with the partial pressures or concentrations of the reaction products in the numerator. One may reverse the direction in which the reaction is written, change the sign of ΔH, and invert the expression for K_p or K_c, but one may not perform some of these operations without performing all of them.

The change of equilibrium constant with temperature for a system of ideal gases or ideal solutes is shown by the differential equation

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \tag{27}$$

This equation, which is usually called van't Hoff's equation, may be derived for a system of ideal gases from the second law of thermodynamics through the use of a reversible cycle of operations involving the desired chemical reaction in one direction at T and in the opposite direction at $T - dT$. (Another derivation of the van't Hoff equation will be given in Chap. XVIII)

In such a reversible cycle operating between two temperatures and absorbing q cal. at the higher temperature, the summation of the work done is related to the fraction of the heat converted into work during the cycle by the equation

$$\Sigma w = q \frac{dT}{T}$$

in which dT/T is the fraction of the heat converted into work by the cycle. (The equation is derived on page 39.)

We consider the general chemical reaction

$$a\text{A} + b\text{B} + \cdots = d\text{D} + e\text{E} + \cdots$$

for which ΔH is the heat absorbed in the *complete reaction* and to which the equilibrium relation

$$\frac{p_D{}^d p_E{}^e}{p_A{}^a p_B{}^b} = K_p \qquad (t \text{ const.})$$

applies. The derivation is accomplished through an "equilibrium box" in which this reaction takes place and which serves as the "engine" in the cycle. The equilibrium box is a chamber containing these substances at equilibrium, it is fitted with four cylinders, each containing one of the substances. Each cylinder is closed by a frictionless piston; each connects with the equilibrium mixture through a membrane permeable only to the substance in that cylinder, so that through motion of these pistons the individual substances may be forced into or out of the equilibrium chamber. The pressure of each substance in its cylinder is thus equal to its equilibrium pressure in the mixture.

Each of the four steps in the cycle is conducted "reversibly," or so slowly that equilibrium is maintained at all stages of it.

1. In the first step at T, a moles of A at p_A and b moles of B at p_B are forced isothermally and reversibly into the equilibrium mixture, and during these operations d moles of D at p_D and e moles of E at p_E are withdrawn from the mixture through their respective membranes into their cylinders isothermally and reversibly. The change in state which is the sum of these operations is

$$a\text{A (at } p_A) + b\text{B (at } p_B) = d\text{D (at } p_D) + e\text{E (at } p_E)$$

Since the equilibrium box is unchanged in its contents by this change, the work done is the sum of the $p\ \Delta v$ changes at each of the cylinders. Denoting the volume of a moles of A by v_A, b moles of B by v_B, etc., this summation is

$$w_1 = -p_A v_A - p_B v_B + p_D v_D + p_E v_E$$

and ΔH is the heat absorbed by the change at T.

2. Each piston is clamped in a fixed position, and the whole system is cooled to $T - dT$, by which the equilibrium pressures become $p_A - dp_A$, $p_B - dp_B$, $p_D - dp_D$, and $p_E - dp_E$. The volume remains constant during this change, and thus $w_2 = 0$

3. In the third step d moles of D at $p_D - dp_D$ and e moles of E at $p_E - dp_E$ are forced isothermally and reversibly into the equilibrium chamber, and at the same time a moles of A at $p_A - dp_A$ and b moles of B at $p_B - dp_B$ are withdrawn into their cylinders isothermally and reversibly The change in state that is the sum of these operations is

$$d\text{D (at } p_D - dp_D) + e\text{E (at } p_E - dp_E) = a\text{A (at } p_A - dp_A) + b\text{B (at } p_B - dp_B)$$

The work done in this step is the summation of the $(p - dp)\Delta v$ changes, which is

$$w_3 = v_A(p_A - dp_A) + v_B(p_B - dp_B) - v_D(p_D - dp_D) - v_E(p_E - dp_E)$$

4. Finally, the system is restored to its original state by heating to T at constant volume, for which $w_4 = 0$

The work summation for the entire cycle of operations is

$$\Sigma w = -v_A\,dp_A - v_B\,dp_B + v_D\,dp_D + v_E\,dp_E$$

and since each substance is assumed an ideal gas, $v_A = aRT/p_A$, $v_B = bRT/p_B$, etc Upon making this substitution into the equation above and putting $d \ln p$ for dp/p we have

$$\begin{aligned}\Sigma w &= RT\,(-d \ln p_A{}^a - d \ln p_B{}^b + d \ln p_D{}^d + d \ln p_E{}^e)\\ &= RT\,d \ln K_p\end{aligned}$$

By the second-law equation this summation is dT/T times the heat absorbed at the higher temperature T, which was ΔH for the chemical reaction Equating these quantities,

$$RT\,d \ln K_p = \Delta H\left(\frac{dT}{T}\right)$$

which rearranges to give the van't Hoff equation

$$\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2} \qquad (27)$$

It must be understood that ΔH in the van't Hoff equation is for the complete change in state shown by the chemical reaction on which K_p is based, and not for the incomplete reaction which takes place when the substances on the left side of the equation are mixed in the specified quantities. It is ΔH for the formation of d moles of D and e moles of E. For gaseous reactions at moderate pressure, ΔH calculated from equilibrium constants through the van't Hoff equation will be in substantial agreement with ΔH calculated for the same temperatures from enthalpy tables and heat-capacity data. At high pressures, $(dH/dp)_T$ is not zero for actual gases, and therefore ΔH calculated from equilibrium constants uncorrected for deviation from the ideal gas law may not be the same as ΔH calculated for the reaction at 1 atm. pressure.

If ΔH is sufficiently constant over the temperature interval involved, equation (27) may be integrated between limits and becomes

$$2.303 \log \frac{K_2}{K_1} = \frac{\Delta H}{R}\left(\frac{T_2 - T_1}{T_2 T_1}\right) \tag{28}$$

In using this equation, R is expressed in calories if the heat of reaction is so expressed Since the equilibrium constants appear in this equation as a ratio, any units may be used in formulating them, provided that the same units are employed at both temperatures. Thus, if the partial pressures are in atmospheres in K at one temperature, they must be at the other also.

By putting equation (27) in a form suitable for plotting, namely,

$$d \ln K = \frac{-\Delta H}{R}\, d\left(\frac{1}{T}\right) \tag{29}$$

it may be seen that a plot of ln K against the reciprocal of T is a straight line of slope $-\Delta H/R$ if ΔH is independent of T When the change of ΔH with T is slight, the plot will be almost a straight line, and this condition is true of most of the data given in this chapter. A plot of $\log_{10} K_p$ for the reaction

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 = NH_3$$

at 10 atm. total pressure, as shown by the data of Table 60, against $1000/T$ yields a straight line of slope $-\Delta H/2.3R$, whence $\Delta H = -12.7$ kcal. between 350 and 500°C. Since this chemical system at 10 atm. pressure does not behave as a mixture of ideal gases, which is required for the use of equation (29), one might expect the derived ΔH value to be considerably in error. Yet a precise calculation[1] in which an accurate equation of state is used, together with an adjustment for ΔC_p, yields $\Delta H = -12.66$ kcal. at 500°. Evidently some compensation yields a more precise value in the ΔH calculated from equation (29) than one would expect.

Application of the van't Hoff equation to the equilibrium data on page 341 for the reaction $SO_2(g) + \frac{1}{2}O_2(g) = SO_3(g)$ yields a straight lines of slope $-\Delta H/2.3R$ such that $\Delta H = -22.6$ kcal. when $\log K_p$ is plotted against $1000/T$. Calculations of this ΔH from thermochemical data lie between -21.9 and -23.0, which is satisfactory agreement.

It is somewhat generally true that plots of $\log K$ against $1/T$ are more nearly straight and yield better values of ΔH than would be indicated by the deviation of the systems from ideal gas behavior. But when precise values are required, ΔH should be expressed as a function of temperature, and pressures should be low enough for ideal gas behavior, or an exact equation of state should be employed to calculate the equilibrium partial pressures

The calculation involving ΔH as a function of the temperature may be illustrated by the dissociation of carbon dioxide at atmospheric pressure and high temperatures, which Table 67 shows to be 5 0 per cent at 2200°K. and 1 atm. We write the reaction $2CO_2 = 2CO + O_2$ and calculate $K_p = 67 \times 10^{-6}$ for partial pressure in atmospheres Since ΔH is given as a function of temperature on page 322 for half of the reverse reaction, we obtain ΔH for the dissociation by multiplying the equation there given by -2, which gives

$$\Delta H = 134{,}200 + 4.88T - 0.0044T^2 + 0.68 \times 10^{-6}T^3$$

for the reaction as written above. Upon substituting this ΔH in equation (27) and integrating between $T = 2000$ and $T = 2200$, we find the ratio $K_{2200}/K_{2000} = 20$, and K_{2000} is 3.3×10^{-6}. This corresponds to 1.9 per cent dissociated, and Langmuir gives 1.84 per cent for 1 atm. total pressure. More recently Kassel[2] has calculated from other data that CO_2 is 1.55 per cent dissociated at 2000°K.

Calculations such as the one just outlined are tedious rather than difficult, and for many purposes it is sufficient to assume

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[1] Gillespie and Beattie, *Phys. Rev.*, **36**, 1008 (1930).

[2] *J. Am. Chem. Soc*, **56**, 1838 (1934).

ΔH constant unless the temperature interval is quite large. For most of the data quoted in this chapter on change of K_p with temperature, there are no reliable data on the heat capacities of some of the substances involved, and for many systems the equilibrium data and thermal data are not accurate enough to justify calculations in which ΔH is assumed to vary with the temperature.

Since ΔH may not be expressed by an equation in powers of T over a range in which some substance changes its *state of aggregation*, it is obvious that the van't Hoff equation may not be used over such a temperature range. It is necessary to calculate up to the temperature at which the change in state of aggregation occurs, adjust ΔH for the new conditions, and compute it anew for the heat capacities corresponding to the new states of aggregation.

The van't Hoff equation also applies to reactions in aqueous or other solutions; but when these are attended by a change in the number of ions, ΔH is usually a temperature function for which allowance must be made. Such data as we have show that ΔC_p is not only large but a temperature function as well, though there are comparatively few data at temperatures other than 25°C. For example, the change in the second ionization constant for carbonic acid with temperature requires an equation

$$\Delta H = 13{,}278 - 0.1088T^2$$

for the heat absorbed in the ionization The data[1] and the derived quantities are

T	273		283		293		303		313		323
$10^{11}K_2$	2.36		3.24		4.20		5.13		6.03		6.73
ΔH_i	5158		4565		3927		3278		2608		1915
ΔC_p		−59.3		−63.8		−64.9		−67.0		−69.3	

The numbers in the last line of this table show that ΔH_i is not a function of the first power of temperature. From the equation above, which is valid in a 50° range, one may *calculate* that ΔH_i will be zero at 349°K. and negative above this temperature. To the extent that an extrapolation of data taken over a 50° range is valid outside of that range, K would appear to pass through a maximum at 76°C. and decrease with further rise in temperature. Since the data for other weak acids often show

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[1] HARNED and SCHOLES, *ibid.*, **63**, 1706 (1941).

that K reaches a maximum at a characteristic temperature and then decreases, it is probable that carbonic acid shows this effect, but questionable whether the maximum is at 76°C.

The ionization constant of lactic acid reaches a maximum value at 22.5°C., which requires that ΔH_i be zero at this temperature, positive below it, and negative above it. The data are as follows:[1]

t	0	10°	20°	22.5°	25°	30°	50°
10^4K	1.317	1.356	1.388	1.389	1.387	1.378	1.274
ΔH_i	768	458	98	0	−102	−315	−1313

It has been shown by Harned and Embree[2] that the ionization constant passes through a maximum with increasing temperature for many weak acids. In the neighborhood of the temperature at which the maximum occurs the change of K with temperature is given by a single equation for all the weak acids studied, namely,

$$\ln \frac{K_T}{K_{\max}} = -1.15 \times 10^{-4}(T - T_{\max})^2 \tag{30}$$

Upon differentiating this equation with respect to T, combining with the van't Hoff equation, and solving for ΔH_i, we find a general equation for the heat of ionization of the acids,

$$\Delta H_i = -2.3 \times 10^{-4}(T - T_{\max})RT^2 \tag{31}$$

Applying this general equation to the ionization of lactic acid, for which $T_{\max}$ is 295.6, we find

$$\Delta H_i = 0.1355T^2 - 4.58 \times 10^{-4}T^3 \tag{32}$$

which is the value given on page 324.

Since the temperature at which the maximum in K is observed is different for different acids, the general equation (30) does not require that all acids have the same ΔH_i, even though there is only a single constant in the equation.

Problems

Numerical data should be sought in the tables in the text

1. A constant bromine pressure of 0.107 atm. is maintained at 503°K by the dissociation $2CuBr_2(s) = 2CuBr(s) + Br_2(g)$, and at this temperature the equilibrium constant for the gaseous reaction $2NO + Br_2 = 2NOBr$ is

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[1] Martin and Tartar, *ibid.*, **59,** 2672 (1937).

[2] *Ibid.*, **56,** 1050 (1934).

0.050 for partial pressures in atmospheres. Calculate the final pressure at equilibrium and the composition of the solid residue if 0.2 mole of $CuBr_2(s)$ and 0 2 mole of $CuBr(s)$ are put into a 25-liter vessel containing 0.23 mole of NO and 0 10 mole of Br_2 at 503°K.

2. When 0 090 mole of chlorine is dissolved in a liter of water at 25°C, 36 per cent of the chlorine reacts with water to form un-ionized HClO and completely ionized HCl (*a*) How many moles of HCl must be added to this solution to reduce the fraction of chlorine hydrolyzed to 0 20? (*b*) How many moles of NaCl would be required to produce the same result? (*c*) The partial pressure of chlorine above the original solution containing 0 09 mole of chlorine is 0 96 atm. Calculate the total solubility of chlorine when the chlorine pressure is increased to 2 0 atm

3. When 0 0060 mole of iodine is added to a liter flask containing 0 0140 mole of nitrosyl chloride, the gaseous reaction $2NOCl + I_2 = 2NO + 2ICl$ takes place incompletely, and the equilibrium pressure at 452°K becomes 0 922 atm. (*a*) Calculate K_1 for this reaction at 452°K with partial pressures in atmospheres (*b*) At 452°K the equilibrium constant K_2 for the reaction $2NOCl = 2NO + Cl_2$ is 0 0026 atm Calculate K_3 for the reaction $2ICl = I_2 + Cl_2$ at 452°K (*c*) Show that the partial pressure of chlorine in the equilibrium mixture of part (*a*) is a negligible part of the total pressure.

4. The dissociation $2CuBr_2(s) = 2CuBr(s) + Br_2(g)$ maintains a constant bromine pressure of 0 046 atm at 487°K when both solids are present. Neither solid reacts with iodine, and when 0 10 mole of iodine is introduced into a 10-liter space containing an excess of $CuBr_2(s)$ at 487°K, the reaction $Br_2(g) + I_2(g) = 2IBr(g)$ produces an equilibrium pressure of 0 746 atm (*a*) Calculate the equilibrium constant for this reaction (*b*) The equilibrium constant for this reaction at 387°K is 190 Calculate ΔH for the reaction (The answer should check the answer to Problem 22, page 329.)

5. Calculate the upper and lower limits between which the hydrogen-ion concentration must lie for a titration of 0 02 N benzoic acid with 0 02 N sodium hydroxide to be correct within 0 5 per cent

6. The apparent molecular weight of acetic acid vapor, as defined by the equation $M = dRT/p$, changes with the total pressure at 100°C. as follows:

p, atm	0 122	0 274	0 396
M	83 1	93.1	97.4

(*a*) Calculate the equilibrium constant for the reaction

$$(CH_3COOH)_2 = 2CH_3COOH$$

at 100°C., assuming that this reaction is wholly responsible for the change of M with p. (*b*) The apparent molecular weight of the vapor at 120°C and 0.396 atm. is 85.7, at 158°C. and 0 396 atm it is 70.9 Calculate ΔH for the dissociation of the dimer [Ritter and Simons, *J Am. Chem. Soc.*, **67,** **757** (1945). There is said to be evidence of the formation of some tetramer at temperatures below 140°C.]

7. Calculate K_p for the reaction $2NO_2 = 2NO + O_2$ from the data on page 346 for 600, 700, 800, and 900°K., plot log K against $1000/T$, and determine ΔH for the reaction from the slope of the curve.

8. A small amount of phenolphthalein is added to a solution prepared by mixing 20 ml. of 0.1 N NH_4Cl with 3 ml. of 0.1 N NH_4OH. Calculate the hydrogen-ion concentration in solution and the fraction of the indicator transformed to the pink form if $K_i = 10^{-10}$.

9. A solution 0.1m in phosphoric acid is titrated with NaOH, using methyl orange as indicator, and the end point is taken when pH = 4.3. (*a*) Calculate what fraction of the acid has been converted into NaH_2PO_4. (*b*) What fraction has been converted into Na_2HPO_4? (*c*) What per cent error results from taking the end point at this pH?

10. The 0.1m H_3PO_4 is titrated with NaOH, using phenolphthalein as indicator, and the end point is taken when pH = 8.7. Calculate the ratio $(H_2PO_4^-)/(HPO_4^{--})$ and the ratio $(HPO_4^{--})/(PO_4^{---})$ corresponding to this end point. How much NaOH (0.10 N) would be required for the titration of 100 ml. of 0.1m H_3PO_4 to this end point?

11. The solubility of cinnamic acid ($C_6H_5CH{:}CHCOOH$ = HCin, mol. wt. 148) in water at 25° is 0.0038m. Carbon dioxide is passed into a liter of 0.1m sodium cinnamate at 25° in a 2-liter bottle (containing no air) until 0.010 mole of cinnamic acid is precipitated. (*a*) Calculate the equilibrium constant of the reaction $NaCin + H_2CO_3 = HCin + NaHCO_3$. (*b*) Calculate (H^+) in the solution. (*c*) Calculate the pressure of CO_2 at equilibrium and the quantity of CO_2 required in the process. The solubility of CO_2 is 0.034m at 1 atm. pressure. (Note that the concentration of *un-ionized* cinnamic acid is constant in the presence of the solid acid.)

12. (*a*) Calculate K_p at 773°K. for the gaseous reaction $2NH_3 = N_2 + 3H_2$ at 10, 30, and 50 atm. from the data of Table 59, assuming the ideal gas law to apply. (*b*) Plot these values of K_p against the pressure, and extrapolate the curve to 1 atm. (*c*) Calculate from this K_p the equilibrium quantity of NH_3 at 773°K. and 1 atm. in a system made from 1 mole of N_2 and 1 mole of H_2. (*Ans.* about 0.002 mole of NH_3.)

13. Calculate the total pressure at equilibrium after 0.030 mole of chlorine has been pumped into the mixture described in Problem 13, page 99.

14. Calculate the equilibrium constant of the reaction

$$H_2S + NaHCO_3 = NaHS + H_2CO_3 \text{ at } 25°$$

and the concentration of free H_2S in a mixture of equal volumes of 0.02m. H_2S and 0.02m $NaHCO_3$. No gases escape from solution.

15. (*a*) If a liter of 0.1m ammonium formate is added to a liter of 0.1m. acetic acid, what fraction of the salt will be converted to NH_4Ac? (*b*) What will be the fraction converted to acetate when a liter of 0.1m. ammonium formate is added to 0.5 liter of 0.3m acetic acid.

16. A series of buffer solutions is to be prepared covering the range pH 4.0 to 5.4 in steps of 0.2 by mixing 0.1m. acetic acid with 0.1m. sodium acetate. What volume of sodium acetate solution must be added to 10 ml. of acetic acid for each of these solutions?

17. The equilibrium constant for the reaction $HgBr_2(g) = Hg(g) + Br_2(g)$ is 0.040 at 1100°C for partial pressures in atmospheres. At what total pressure would (partly dissociated) mercuric bromide vapor have a density of 1 gram per liter at 1100°?

18. When 0.20 mole of bromine and 0.30 mole of iodine reach equilibrium in a 10-liter flask at 373°K., the reaction $\frac{1}{2}I_2(g) + \frac{1}{2}Br_2(g) = IBr(g)$ takes place incompletely, part of the iodine remains as a crystalline phase, and the total pressure becomes 1.181 atm. The vapor pressure of iodine at 373°K is 0.0604 atm. (*a*) Calculate the equilibrium constant for the reaction and the quantity of solid iodine remaining. (*b*) The equilibrium constant changes with the Kelvin temperature as follows:

T	298	400	600	800	1000
K_p	20.66	11.42	6.37	4.80	3.99

Determine ΔH for the reaction from a suitable plot.

19. When a mixture of 1 mole of C_2H_4 and 1 mole of H_2 is passed over a suitable catalyst, part of the ethylene is converted into ethane, and the density of the mixture at equilibrium is 0.267 gram per liter at 973°K and 1 atm. (*a*) Calculate K_p for the reaction $C_2H_4(g) + H_2(g) = C_2H_6(g)$. (*b*) For this reaction $\Delta H = -32.6$ kcal., and $\Delta C_p = 0$. Calculate K_p for the reaction at 1173°K.

20. Calculate the concentration of each important solute molecule or ion in each of the following aqueous solutions at equilibrium at 25°. (*a*) 0.034*m* H_2CO_3, (*b*) 0.034*m* $NaHCO_3$, (*c*) 0.034*m* Na_2CO_3. Note that of the solutes H_2CO_3, HCO_3^-, CO_3^{--}, H^+, OH^-, and Na^+, some concentrations are negligible in comparison with others in these solutions.

21. (*a*) Calculate the hydrogen-ion concentration at the correct end point for 0.2 *N* NH_4OH titrated with 0.2*N* HCl. (*b*) Calculate also the hydrogen-ion concentration when the end point is 0.1 per cent short of the true one and when it is 0.1 per cent overstepped.

22. At 100°C ammonium acetate in 0.01*m* solution is 4.5 per cent hydrolyzed, and at 100° the ionization constant for ammonium hydroxide is 1.3×10^{-5}. Calculate the ionization constant for acetic acid at 100°.

23. (*a*) Calculate the hydrogen-ion concentration in solutions formed when 100 ml. of 0.2 *N* acetic acid is titrated with 99, 99.8, 100, and 100.2 ml. of 0.2 *N* sodium hydroxide. (*b*) What indicator would be suitable for this determination?

24. The solubility of H_2S in water at 25° is 0.10*m*. when the pressure of H_2S is 1.0 atm. H_2S is passed into a liter of 0.1*m*. $NaBO_2$ in a 25.5-liter vessel (containing no air) until $(H^+) = 10^{-8}$ in the solution. (*a*) What fraction of the $NaBO_2$ is changed to NaHS? (*b*) How many moles of H_2S are required?

25. (*a*) Calculate the concentration of hydroxide ion in 0.1*m*. Na_2CO_3 solution at 100°C., assuming that hydrolysis of carbonate ion is the only important chemical reaction, and given the following data: for the ionization $HCO_3^- = H^+ + CO_3^{--}$, $\Delta H_{298} = 3600$ cal., and $\Delta C_p = -60$ cal.; for the ionization $H_2O = H^+ + OH^-$, $\Delta H_{298} = 13{,}360$ cal., and $\Delta C_p = -50$ cal. (*b*) Calculate (H^+) in the solution at 100°C.

26. *Problem basis* 27.1 grams of PCl_5 vapor at 523°K. and 1 atm. pressure in a 10-liter vessel. (*a*) Calculate the dissociation constant of PCl_5 for partial pressures in atmospheres. (*b*) Chlorine is added to this 10-liter vessel at 523°K. until the total pressure at equilibrium becomes 2 atm. What fraction of the PCl_5 is dissociated? What quantity of chlorine was required? (*c*) The original 10 liters of vapor is expanded to 20 liters at 523°K. What fraction of the PCl_5 is dissociated? (*d*) Chlorine is added to this 20-liter vessel until the total pressure becomes 1 atm. What fraction of the PCl_5 is dissociated at equilibrium? What quantity of chlorine was added? [Note that the quantity is not the same as in (*b*).]

27. When 46 grams of iodine and 1 gram of hydrogen are heated to equilibrium at 723°K., the reaction mixture matches in color a similar vessel containing 1.9 grams of iodine alone. (*a*) Calculate the fraction of the hydrogen converted to HI and the equilibrium constant of the reaction $H_2 + I_2 = 2HI$. (*b*) Calculate the fractional dissociation of $HI(g)$ at 723°K.

28. *Problem basis* 0.30 mole C_4H_8 and 0.30 mole HI in 10 liters at 425°K. (*a*) The total pressure at equilibrium is 1.16 atm., and the only important chemical reaction is $C_4H_8 + HI = C_4H_9I$. Calculate K_p for partial pressures in atmospheres. (*b*) If C_4H_8 is added to the mixture until the total pressure becomes 1.50 atm., how many moles will be required? (*c*) If nitrogen is added to the original mixture until the total pressure becomes 1.5 atm., how many moles will be required? [(*d*) Students with sufficient curiosity may calculate the partial pressures of H_2 and I_2 in the equilibrium mixture of part (*a*) from the data in Problem 27 above and on page 296 or from that in Problem 35 below.]

29. Calculate ΔH for the reaction $CO_2(g) + H_2(g) = CO(g) + H_2O(g)$ at 1100°K. from the equilibrium constants on page 347, and compare with the result obtained in Problem 21, page 328.

30. From the data on page 185 calculate the equilibrium "constant" for the reaction $(C_6H_5OH)_2 = 2C_6H_5OH$ in benzene, assuming the whole deviation from Raoult's law is due to this reaction.

31. When a mixture of 2 moles of $CH_4(g)$ and 1 mole of $H_2S(g)$ is heated at 973°K. and 1 atm. total pressure, the reaction

$$CH_4(g) + 2H_2S(g) = CS_2(g) + 4H_2(g)$$

takes place incompletely, and the partial pressure of hydrogen becomes 0.16 atm. at equilibrium. (*a*) Calculate the equilibrium constant for the reaction. (*b*) Calculate the density of the equilibrium mixture in grams per liter.

32. Hydrogen sulfide is passed into a 20-liter vessel at 25° containing 1.0 mole of $NaHCO_3$ in 10,000 grams of water (and no air), until the total pressure is 5.03 atm., of which water vapor is 0.03 atm. The solubility of H_2S at 1 atm. partial pressure is 0.102 mole per liter, and that of CO_2 is 0.034*m*. (*a*) Calculate the equilibrium constant of the reaction

$$NaHCO_3 + H_2S = NaHS + H_2CO_3$$

(*b*) What are the partial pressures of H_2S and CO_2 above the solution at equilibrium? (*c*) How many moles of H_2S were required?

33. At 1600°K the equilibrium constant of the reaction $SO_2 + \frac{1}{2}O_2 = SO_3$ is 0.026 for partial pressures in atmospheres, and at 1 atm and this same temperature CO_2 is 0.11 per cent dissociated into carbon monoxide and oxygen. Calculate the equilibrium constant at 1600°K. for the reaction

$$SO_3 + CO = SO_2 + CO_2$$

34. For certain reactions the enthalpy change in calories at 298°K, the increase in heat capacity, and the equilibrium constant at 298°K are as follows:

Reaction	ΔH_{298}	ΔC_p	K_c
$H_2O = H^+.Aq + OH^-.Aq$	13,360	−50	1.0×10^{-14}
$NH_4OH.Aq = NH_4^+.Aq + OH^-.Aq$	865	−30	1.8×10^{-5}
$HBO_2.Aq = H^+.Aq + BO_2^-.Aq$	3,360	−43	6.6×10^{-10}

(*a*) From the above data express ΔH for the hydrolysis of ammonium borate as a function of temperature. (*b*) Calculate the fractional hydrolysis of 0.1*m* ammonium borate at 75°C (= 348°K). (*c*) Calculate the fraction hydrolyzed in a solution 0.1*m* in NH_4BO_2 and 0.2*m* in NH_4OH at 348°K.

35. The equilibrium constant for the reaction $2HI(g) = H_2(g) + I_2(g)$ is 1.84 at 700°K, $\Delta H = 3070$ cal, and ΔC_p is negligible. Calculate the fractional dissociation of $HI(g)$ at 800°K.

36. The equilibrium constants K_1 for the reaction

$$2NO(g) + 2ICl(g) = 2NOCl(g) + I_2(g)$$

and K_2 for the reaction $2NOCl(g) = 2NO(g) + Cl_2(g)$ change with the temperature as follows.

T, °K	409	422	437	452
K_1	0.255	0.159	0.090	0.055
10^4K_2	3.09	6.08	13.1	25.7

(*a*) Calculate K_3 for the reaction $2ICl = I_2 + Cl_2$ for each of these temperatures. (*b*) Calculate ΔH for the dissociation of 2 moles of ICl [McMorris and Yost, *J. Am. Chem. Soc.*, **54**, 2247 (1932).]

37. Calculate the pH of the second, sixth, and tenth mixtures of Na_2HPO_4 and KH_2PO_4 described on page 371 from the ionization constants in Table 63, assuming the salt-concentration ratio is equal to the ion-activity ratio.

38. (*a*) What volumes of 0.1*m*. NH_4Cl should be added to 10.0-ml portions of 0.1*m*. NH_4OH to produce buffer solutions of pH 8.0 to 9.4 in steps of 0.2 pH? (*b*) If 1.0 ml of 0.1*m*. HCl were added to the buffer solution of pH = 9, what would be the resulting pH?

39. Calculate the ionization constant of monoethanolammonium hydroxide from the data in Problem 18, page 291.

40. Calculate the equilibrium constant for the reaction

$$(HCOOH)_2(g) = 2HCOOH(g)$$

at 20°, 40°, and 60° from the data on page 72, and determine ΔH for the dissociation.

41. The equilibrium constants for the reaction $SO_2(g) + \frac{1}{2}O_2(g) = SO_3(g)$ at several temperatures are given on page 341. (*a*) Plot log K against $1000/T$, allowing a sufficient range for extrapolating to 1600°K, and show that the constant given in Problem 33 on page 390 is in reasonable conformity with these data. (*b*) Determine ΔH for the dissociation of 1 mole of SO_3 from the slope of the plot.

42. In the following table p_0 is the theoretical pressure of $I_2(g)$ calculated on the assumption of no dissociation, p is the observed pressure after the reaction $I_2(g) = 2I(g)$ has reached equilibrium, and T is the temperature of the experiment:

T	1273°	1173°	1073°	973°
p_0, atm	0 0736	0 0684	0 0631	0 0576
p, atm	0 1122	0 0918	0 0750	0 0624

(*a*) Calculate the equilibrium constant for the reaction at each temperature, assuming all the pressure difference to be due to the dissociation. (*b*) Calculate ΔH for the dissociation of a mole of iodine. [Perlman and Rollefson, *J. Chem. Phys.*, **9**, 362 (1941)]

CHAPTER X

HETEROGENEOUS EQUILIBRIUM

In many important chemical systems the equilibrium composition of a given phase is closely related to that of another phase. The concentration or pressure of one substance in a mixture may be fixed by the presence of its solid phase in excess, and this in turn establishes the concentrations or pressures of other substances through the equilibrium constant and a material balance. We have already seen that the partial pressure of a volatile solute controls its mole fraction in a solution (Henry's law), that the partial pressure of solvent controls its mole fraction in solution (Raoult's law), that equilibrium between a solid solvent and a solution is described by the freezing-point law, and that the partial pressure of a single gaseous dissociation product is kept constant by the presence of solid phases with which it is in equilibrium In this chapter we shall consider other aspects of chemical equilibrium in the gaseous phase or in a solution at a constant temperature in the presence of solid phases It will be true of these systems, as it was of homogeneous systems, that the equilibrium constants apply only to the particular temperature at which the measurements were made but to systems of all compositions at this temperature so long as all the solids involved are present at equilibrium.

The value of the equilibrium constant K for a given temperature changes with changing temperature in these systems as required by the van't Hoff equation; and in this equation ΔH is for the complete change in state as used in formulating the equilibrium constant. If the equilibrium involved is a change of solubility with changing temperature, ΔH derived from the van't Hoff equation is for dissolving the solid into the saturated solution, a "partial molal" heat of solution. The relation between this partial quantity and the total heat of solution has been given on page 317.

It should not be assumed without proof that a system is at equilibrium just because the phases have been in contact for some time; they must be in contact for *enough time* for the attainment of true equilibrium. For example, in measuring the equilibrium pressure for the reaction $Mg(OH)_2(s) = MgO(s) + H_2O(g)$ at 485°K., the pressure of water vapor in a system reacting toward the formation of water vapor was 53 0 mm. after 2 days and the pressure in a system reacting in the opposite direction was 55 2 mm. After 6 days the pressures still differed by 1 mm.; after 11 days they became identical at 54.4 mm and of course remained identical after equilibrium was reached.[1]

In the study of heterogeneous equilibrium, as was true of homogeneous equilibrium, it is first necessary to determine the chemical changes involved. This includes correct identification of the solid phases present as well as the composition of the gas or solution in equilibrium with them. For illustrations, the pressure of $CO_2(g)$ in equilibrium with $PbO(s)$ and $PbCO_3(s)$ is not the same as that for the solid phases $PbO.PbCO_3$ and $PbCO_3$; the pressure of water vapor in equilibrium with $Na_2HPO_4\ 7H_2O$ and its saturated solution is not the same as that between $Na_2HPO_4\ 12H_2O$ and its saturated solution; the crystals in equilibrium with a liquid mixture of bismuth and cadmium are the pure crystals of the elements, but there is no liquid mixture of bismuth and magnesium that is in equilibrium with crystals of the two pure elements

We are first to consider systems in which only one important chemical reaction takes place and then some systems in which two or more reactions must be considered at the same time. Whether there is one reaction or several, the necessary chemical equations are written and balanced; a definite material basis is completely defined (giving the quantities of all solids, liquids, gases, and solutions); the equilibrium expression is formulated in the way described in the next section; and the equilibrium composition of the system is described in terms of the minimum number of unknowns, before any calculations are begun.

Activities of Solid Phases.—The activity or equilibrium effect of a *pure solid phase* at a given temperature remains constant without regard to the quantity of solid present, since its partial pressure or concentration is constant, and it is convenient to define its activity as unity. Thus, for the equilibrium change

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[1] GIAUQUE and ARCHBOLD, *J. Am. Chem. Soc.*, **59**, 561 (1937).

in state at 800°C.,

$$\mathrm{CaCO_3}(s) = \mathrm{CaO}(s) + \mathrm{CO_2}(g,\ 0.220\ \mathrm{atm.})$$

the equilibrium expression might be written

$$\frac{a_{\mathrm{CaO}} f_{\mathrm{CO_2}}}{a_{\mathrm{CaCO_3}}} = K_a \qquad (t\ \text{const.})$$

but if the activities of the solids are unity and the fugacity of the gas is equal to its pressure (as will be substantially true for moderate pressures) this may be written more simply.

$$p_{\mathrm{CO_2}} = K_p \qquad (t\ \text{const.})$$

The expression in this form is in agreement with the experimental fact that the pressure of CO_2 in equilibrium with $CaO(s)$ and $CaCO_3(s)$ is constant at a given temperature, regardless of the relative quantities of the three substances present. There would, of course, be no objection to writing K_p for this equilibrium in the form

$$\frac{p_{\mathrm{CaO}} p_{\mathrm{CO_2}}}{p_{\mathrm{CaCO_3}}} = K' \qquad (t\ \text{const.})$$

but we have no information on the vapor pressures of the solids, only the belief that they are constant at a given temperature. If this expression is rewritten with these two constant (though inappreciable) pressures combined with K'

$$K' \frac{p_{\mathrm{CaCO_3}}}{p_{\mathrm{CaO}}} = p_{\mathrm{CO_2}} = K_p \qquad (t\ \text{const.})$$

the same result is obtained as by defining the solid activities as unity. For equilibriums in which the solid or liquid phases have determinable vapor pressures either procedure may be followed, but it is important to indicate clearly which one has been followed, since this special definition that the activity of a solid phase is unity at every temperature makes neither its vapor pressure unity nor its solubility unity on a molality scale. One may, of course, insert the partial pressure or the concentration of any substance involved in a chemical reaction into the equilibrium expression that governs it. The point is that, if the pressure is not constant, it *must* be included in the equilibrium expression; if it is constant, it may be put in the equilibrium expression or put in the value of the constant.

Dissociation Pressures.—We have considered above the dissociation

$$CaCO_3(s) = CaO(s) + CO_2(g)$$

for which the equilibrium was represented by

$$K_p = p_{CO_2} \qquad . \quad (t \text{ const.})$$

This dissociation pressure (in atmospheres) changes with the centigrade temperature as follows.[1]

t	775°	800°	855°	894 4°	1000°	1100°
p_{CO_2}	0 144	0 220	0 556	1 000	3 87	11 50

It should be clearly understood that the expression $K_p = p_{CO_2}$ is not applicable if only one of the solid phases is present; this constant pressure for a given temperature requires that both solid phases be present. In the absence of CaO the pressure of CO_2 at 894 4°C. may be any pressure greater than 1 atm., and in the absence of $CaCO_3$ the pressure of CO_2 may be any pressure less than 1 atm. The implications attending $K_p = p_{CO_2}$ might be written $p_{CO_2} =$ const. (t const., CaO and $CaCO_3$ present); and, whether written or not, these conditions are essential for true equilibrium in this system.

For any given temperature the equilibrium pressure is independent of the direction of approach, whether by mixing CaO and CO_2 or by the direct dissociation of $CaCO_3$, and it is likewise independent of the relative quantities of the solid phases present. The same considerations apply in the dissociation of $MnCO_3$, $FeCO_3$, $ZnCO_3$, $PbCO_3$, etc

In any of these systems the pressure is a function of temperature alone, which is the characteristic of a univariant system. The Clapeyron equation describes the change of equilibrium pressure with temperature in such a system. For the dissociation $CaCO_3 = CaO + CO_2$, Δv is due to the formation of a mole of gas and a mole of solid from a mole of another solid and is thus substantially equal to the volume of the gas, since the solids have very small volumes by comparison. Upon substituting RT/p for Δv in the Clapeyron equation, we have

$$\frac{dp}{dT} = \frac{p\,\Delta H}{RT^2}$$

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[1] SMYTH and ADAMS, *ibid.*, **45**, 1167 (1923); SOUTHARD and ROYSTER, *J. Phys Chem.*, **40**, 435 (1936)

which rearranges to give the van't Hoff equation

$$\frac{d \ln p}{dT} = \frac{\Delta H}{RT^2}$$

since p is equal to K_p for this system, by the equation above.

The system at equilibrium which is represented by the chemical equation

$$BaCl_2.8NH_3(s) = BaCl_2(s) + 8NH_3(g)$$

is also a monovariant system in which the change of equilibrium pressure with changing temperature is shown by the Clapeyron equation. But it must be recalled that this equation is

$$\frac{dp}{dT} = \frac{\Delta H}{T\,\Delta v}$$

and hence, if ΔH is the heat absorbed by the chemical reaction as written above, $\Delta v = 8RT/p$ and not RT/p, since the dissociation of a mole of $BaCl_2.8NH_3(s)$ yields 8 moles of gas.

As another illustration, the pressure of oxygen in equilibrium with silver and silver oxide changes with the centigrade temperature as follows:[1]

t	150°	173°	178°	183 1°	188 2°	190 0°	191 2°	200°
p_{O_2}, mm	182	422	509	605	717	760	790	1050

If the equation for this dissociation is written

$$Ag_2O(s) = 2Ag + \tfrac{1}{2}O_2(g)$$

the equilibrium expression must be written

$$K_p = p_{O_2}^{\,1/2} \qquad (t \text{ const })$$

and ΔH taken for the dissociation of 1 mole of Ag_2O. Of course, the chemical reaction may be written for $2Ag_2O$, when $K_p = p_{O_2}$ and ΔH is for the dissociation of 2 moles of silver oxide.

The equilibrium expression for the dissociation of HgO into oxygen and liquid mercury, $2HgO(s) = 2Hg(l) + O_2(g)$, may be written

$$K_p = p_{O_2} \qquad (t \text{ const.})$$

but, since the vapor pressure of liquid mercury is not negligible in the temperature range in which this dissociation has been studied, p_{O_2} is not equal to the total pressure. When the reaction is

$$2HgO(s) = 2Hg(g) + O_2(g)$$

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[1] BENTON and DRAKE, *J. Am. Chem. Soc.*, **54**, 2186 (1932)

in the absence of *liquid* mercury, the equilibrium constant must be written

$$K_p = p_{\mathrm{Hg}}{}^2 p_{\mathrm{O_2}} \qquad (t \text{ const.})$$

If mercuric oxide dissociates into an evacuated space, p_{Hg} is two-thirds of the dissociation pressure (*i.e.*, of the total pressure developed by the dissociating oxide) and

$$K_p = (\tfrac{2}{3}p)^2(\tfrac{1}{3}p) = 0.148p^3$$

The value of K_p so determined will also apply when HgO dissociates into a space containing excess oxygen or excess mercury vapor, but $(\tfrac{2}{3}p)^2(\tfrac{1}{3}p)$ will not be applicable, since the mercury vapor pressure is not twice the oxygen pressure under these conditions. For example, the dissociation pressure is 90 mm. at 360°C and $K_p = (60)^2(30) = 1.08 \times 10^5$ for partial pressures in millimeters. If p is the total pressure at equilibrium when HgO dissociates into a closed space containing oxygen at an initial pressure of 25 mm., the equilibrium pressures in this system are $p_{\mathrm{Hg}} = \tfrac{2}{3}(p - 25)$ and $p_{\mathrm{O_2}} = [\tfrac{1}{3}(p - 25) + 25]$, and by substituting these quantities into the equilibrium expression one may solve it for the equilibrium pressure.

The total pressure, in millimeters, developed by the dissociation of solid HgO into oxygen and mercury vapor changes with the centigrade temperature as follows:[1]

t	360°	380°	400°	420°	440°	460°	480°
p, mm	90	141	231	387	642	1017	1581

Further illustration of the equilibrium between solids and gases is afforded by the evaporation and complete dissociation of solid NH_4HS. The equilibrium constant is $K_p = p_{\mathrm{H_2S}}p_{\mathrm{NH_3}}$, and each partial pressure is half the total pressure when this substance evaporates into empty space. For its evaporation into a space already containing ammonia at a pressure p_0, the partial pressure of H_2S would be $\tfrac{1}{2}(p_t - p_0)$, or half the difference between p_0 and the equilibrium total pressure p_t, and the pressure of NH_3 would be $p_0 + \tfrac{1}{2}(p_t - p_0)$.

The evaporation of ammonium carbamate is attended by complete dissociation, with the formation of three moles of gas

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[1] TAYLOR and HULETT, *J. Phys Chem* , **17,** 565 (1913).

for one of solid, as shown by the reaction

$$NH_4CO_2NH_2(s) = 2NH_3(g) + CO_2(g)$$

for which the equilibrium is written

$$K_p = p_{NH_3}{}^2 p_{CO_2}$$

Other illustrations are the dissociation of salt hydrates into water vapor and lower hydrates or anhydrous salts and the dissociation of $CuBr_2$ into CuBr and bromine vapor. The dissociation of $NaHCO_3$ yields another solid and two moles of gas, as shown by the reaction

$$2NaHCO_3(s) = Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

for which the equilibrium constant is

$$K_p = p_{H_2O} p_{CO_2}$$

The value of this constant for a given temperature is obtained from the total pressure developed when $NaHCO_3$ dissociates into an evacuated space, for which the data are[1]

t	30°	50°	70°	90°	100°	110°
p, atm	0.00816	0.0395	0.158	0.545	0.962	1.645

In the absence of any other vapor each of the partial pressures would be half the total pressure, and the numerical value of the equilibrium constant would be $p^2/4$ This constant also applies when $NaHCO_3$ dissociates into a space containing excess CO_2 or excess water vapor; but it is the product $p_{CO_2} p_{H_2O}$ which must be used under these circumstances, and not $p^2/4$, which applies only when all the vapor comes from dissociation of the $NaHCO_3$. It may be worth saying again that the equilibrium which is represented by the product of the two pressures applies only when both solid phases are present. It places no restriction on a product that lies below the equilibrium value if $NaHCO_3$ is absent or above the equilibrium product if Na_2CO_3 is absent. In the drying of moist $NaHCO_3$, for instance, it is desired to *prevent* the formation of Na_2CO_3, and therefore the product $p_{H_2O} p_{CO_2}$ must be kept above the equilibrium value. So long as the product of these partial pressures exceeds the equilibrium value, no $NaHCO_3$ will decompose; and so long as the partial pressure of water vapor in the equilibrium mixture is less than

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[1] CAVEN and SAND, *J. Chem. Soc. (London)*, **99**, 1359 (1911); **105**, 2752 (1914).

that of water from the saturated $NaHCO_3$ solution which is to be dried, water may enter the vapor space. But if the total pressure is constant, that of CO_2 decreases as water evaporates; and when the product of the two partial pressures falls below the equilibrium value, dissociation becomes a possibility.

Reactions between Solids and Gases.—Equilibrium as shown by the chemical equation $Ag_2S(s) + H_2(g) = 2Ag(s) + H_2S(g)$ has been investigated over a range of temperature. The equilibrium may be formulated

$$K_a = \frac{a_{Ag}^2 f_{H_2S}}{a_{Ag_2S} f_{H_2}} \qquad (t \text{ const.})$$

as was done for the dissociation of $CaCO_3$ Since in the temperature range of these experiments the fugacities are substantially equal to partial pressures and the activities of the solid phases are defined as unity, we may use the simpler expression

$$K_p = \frac{p_{H_2S}}{p_{H_2}} \qquad (t \text{ const.})$$

This ratio changes with the centigrade temperature as follows:[1]

t	476°	518°	617°	700°
p_{H_2S}/p_{H_2}	0.359	0.325	0.278	0.242

Although the equilibrium ratio in the gaseous phase is independent of the quantities of the solid phases present, the composition and quantity of the gas phase provide data for calculating the quantities of the solids through a material balance that takes into account the quantities at the start (the "working basis"). If at 476° a mole of silver sulfide were put into contact with 10 moles of hydrogen, 1 mole of hydrogen sulfide would be formed and 9 of hydrogen would remain, but no silver sulfide would be present. This condition is one of true chemical equilibrium between H_2, H_2S, and Ag, but it is not the equilibrium to which the constant ratio of hydrogen sulfide to hydrogen applies, for this requires the presence of solid Ag_2S as well as solid Ag.

The least quantity of hydrogen that would reduce 1 mole of silver sulfide at 476° is 1 mole for the actual chemical process plus $(1/0.359 = 2.79)$ moles to maintain the equilibrium ratio, or a total of 3.79 moles. If a smaller quantity of hydrogen reacts upon a mole of silver sulfide, equilibrium is established in

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[1] KEYES and FELSING, *J. Am. Chem Soc.*, **42**, 246 (1920).

the gaseous phase before all the sulfide is reduced; if a larger quantity of hydrogen is employed, complete reaction takes place without forming enough hydrogen sulfide to produce the equilibrium ratio of partial pressures.

These figures illustrate the importance of equilibrium considerations, for one who took no account of them and supposed the substances involved to react completely as shown by the chemical equation would calculate the efficiency of this reaction at 476° to be 1/3.79, or about 26 per cent, whereas this yield is all that could possibly be attained.

Reactions of similar type occur between metallic oxides and carbon monoxide. The most common one in chemical industry is

$$FeO(s) + CO(g) = Fe(s) + CO_2(g)$$

for which data at various temperatures will be found in Problem 1 at the end of this chapter. As in the previous illustration, the equilibrium constant is written for the gaseous substances only, namely, $K_p = p_{CO_2}/p_{CO}$. Such an equilibrium constant is also obtained when oxides of nickel or cobalt are the solid phases reduced, but it should not be inferred that every metallic oxide will reach equilibrium in the sense $MO + CO = M + CO_2$. For example, aluminum oxide is not reduced at all by carbon monoxide, and molybdenum dioxide is reduced to molybdenum carbide by carbon monoxide. In these systems, as in all chemical systems, the first requisite in studying chemical equilibrium is a correct knowledge of the reactions taking place.

Another reaction of the same type is

$$FeO(s) + H_2(g) = Fe(s) + H_2O(g)$$

for which equilibrium data at various temperatures are also given in Problem 1 at the end of this chapter. Equilibrium between hydrogen and water vapor in this sense is also observed for other metallic oxides, and experimental studies have been published for the oxides of nickel, cobalt, and tin which show a constant ratio of p_{H_2O}/p_{H_2} at a constant temperature, regardless of the relative quantities of the solid phases, but provided both solid phases are present at equilibrium.

The fact that a chemical equation showing the reaction involved should always attend the formulation of an equilibrium constant is of such importance as to justify its repetition and further illustration. For the reaction

$$FeO(s) + H_2(g) = Fe(s) + H_2O(g)$$

$K_p = p_{H_2O}/p_{H_2}$; and the numerical value of this equilibrium ratio is 0.332 at 600°C. in the presence of FeO and Fe. For the reaction

$$CoO(s) + H_2(g) = Co(s) + H_2O(g)$$

K_p is again p_{H_2O}/p_{H_2}; but the equilibrium ratio at 600°C. is 46 when the solid phases are CoO and Co.

Supplementary Equilibriums in Vapor-solid Systems.—In the illustrations of equilibrium between metals, metallic oxides, hydrogen, and water vapor (or CO and CO_2), we have not mentioned the presence of oxygen in the vapor phase, and there is no *experimental* evidence of its presence in these systems at these temperatures. But it is well known that water vapor and CO_2 dissociate at high temperatures and that the extent of dissociation changes with the temperature as required by van't Hoff's equation. Hence there must be in these systems enough oxygen to satisfy the dissociation equilibriums of H_2O or CO_2 and to maintain the dissociation pressures of the oxides, such as that of NiO into Ni and oxygen. Moreover, if H_2 and H_2O in a certain ratio are in equilibrium with Ni and NiO, they must be in equilibrium also with a mixture of CO and CO_2 that is in equilibrium with Ni and NiO. The relations among the various constants are as follows:

$$NiO(s) = Ni(s) + \tfrac{1}{2}O_2(g) \quad (1)$$

$$K_1 = p_{O_2}^{\frac{1}{2}}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(g) \quad (2)$$

$$K_2 = \frac{p_{H_2O}}{p_{H_2}p_{O_2}^{\frac{1}{2}}}$$

Adding (1) and (2),

$$NiO(s) + H_2(g) = Ni(s) + H_2O(g) \quad (4)$$

$$K_4 = \frac{p_{H_2O}}{p_{H_2}} = K_1K_2$$

$$NiO(s) = Ni(s) + \tfrac{1}{2}O_2(g) \quad (1)$$

$$K_1 = p_{O_2}^{\frac{1}{2}}$$

$$CO(g) + \tfrac{1}{2}O_2(g) = CO_2(g) \quad (3)$$

$$K_3 = \frac{p_{CO_2}}{p_{CO}p_{O_2}^{\frac{1}{2}}}$$

Adding (1) and (3),

$$NiO(s) + CO(g) = Ni(s) + CO_2(g) \quad (5)$$

$$K_5 = \frac{p_{CO_2}}{p_{CO}} = K_1K_3$$

Subtracting equation (5) from equation (4), we have

$$H_2(g) + CO_2(g) = H_2O(g) + CO(g) \qquad (6)$$

for which the equilibrium constant is

$$K_6 = \frac{p_{H_2O}p_{CO}}{p_{H_2}p_{CO_2}} = \frac{K_4}{K_5} = \frac{K_2}{K_3}$$

The data on page 347 for the water-gas reaction were obtained from the equilibrium ratios corresponding to K_4 and K_5, when the solid phases are Fe and FeO, in the way indicated above.

It will be difficult for beginners to avoid making a simple equilibrium system appear too complex or a complex system appear too simple; for which purpose experience and a sense of proportion are required. However, in most chemical systems some possible equilibriums are not important, and in general only one or two important reactions need be considered. In the illustration above, p_{O_2} was a negligible part of the total pressure, and the sum of the pressures of H_2 and H_2O (or of CO and CO_2) in the systems shown by the chemical equations (2), (3), (4), and (5) is equal to the total pressure. But p_{O_2} as a multiplying factor in the equilibrium expressions for equations (2) and (3) would obviously not be neglected when it is small. The following routine procedure in solving problems should prove helpful:

(1) Write and balance the chemical equation for the important chemical reaction involved. (2) Formulate the equilibrium expression in the standard way. Substances present as pure solid or liquid phase may have their partial pressures or concentrations included in the value of K, or they may appear in the equilibrium expression as desired; but it is important to indicate which procedure has been followed. "Mixed" constants, which contain the pressures of some substances and the concentrations of others, may be used to advantage in some problems. (3) State the "working basis" for the problem, the initial state of the system that reacts to equilibrium. (4) List all the molecular species present, gases, liquids, solids, solutes, and solute ions. (5) Cross out all the pressures or concentrations that are negligible in condition equations; for example,

$$p_{CO} + p_{CO_2} + \cancel{p_{O_2}} = p_{\text{total}}$$

(6) Set up a "mole table" for the necessary pressures or concentrations in terms of a single unknown. (7) Consider all possible equilibriums supplementary to the main equilibrium, and dis-

card those which are not important. (8) Solve the problem, and check the equilibrium pressures through a material balance from the working basis.

Distribution between Two Liquid Phases.—The distribution of a solute between two mutually insoluble solvents in which it has the same molecular weight was considered on page 189. When passage of the solute from one solvent to the other is attended by partial ionization or dissociation or polymerization, the distribution ratio C_1/C_2 is no longer a constant, if C_1 and C_2 denote total concentrations, for it will be remembered that the distribution ratio is constant only with respect to a *single molecular species.* Some slightly ionized organic acids exist almost wholly as single molecules in water and almost wholly as double molecules in some organic solvents. An illustration of this is the distribution of benzoic acid, which is written HBz for C_6H_5COOH, between water and benzene. The only relation given by the distribution law is between the concentration of single molecules of benzoic acid in water and the concentration of single molecules of benzoic acid in benzene. We see from the equilibrium constant for the reaction $\frac{1}{2}(\mathrm{HBz})_2 = \mathrm{HBz}$ in benzene, which we call K_1, that $(\mathrm{HBz})_1 = K_1\sqrt{(\mathrm{HBz})_2}$; and since nearly all the acid in benzene is in the form of the dimer, $(\mathrm{HBz})_1$ in benzene is nearly $K_1C_B^{1/2}$, in which C_B is the total concentration in benzene. Combining all the constants into a single one, we show, in the fourth column of Table 68, $C_w/C_B^{1/2}$, which is substantially con-

TABLE 68.—DISTRIBUTION OF BENZOIC ACID BETWEEN WATER AND BENZENE[1] AT 6°

C_w	C_B	C_w/C_B	$C_w/C_B^{1/2}$	$C_w(1-\alpha)/[C_B(1-\beta)]^{1/2}$
0 00329	0 0156	0 210	0 0263	0 0245
0 00435	0 0275	0 158	0 0264	0 0246
0 00493	0 0355	0 139	0 0262	0 0245
0 00579	0 0495	0 117	0 0261	0 0244
0 00644	0 0616	0 105	0 0260	0 0244
0 00749	0 0835	0 089	0 0259	0 0244
0 00874	0 1144	0 076	0 0258	0 0243
0 00993	0 148	0 067	0 0258	0 0243
0 0114	0 195	0 058	0 0258	0 0244

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[1] CREIGHTON, *J Franklin Inst.*, **180**, 63 (1915).

stant. The ratio C_w/C_B, which takes no account of the different molecular condition of the solute in the two layers, is not even roughly constant, as may be seen in the third column. By applying a correction for the small fraction of the acid ionized in water and for the small part in the benzene that is not in the form of dimer and by again grouping all the constants into a single one, we obtain the figures in the last column of Table 68[1]

A similar variation in the distribution ratio is shown by other organic acids, though the explanation may not be the formation of a dimer in the organic solvent. For example, the concentrations of picric "acid" distributed between water and benzene at 18° are as follows:

C_w	0.0334	0.0199	0.0101	0.00327	0.00208
C_B	0.1772	0.070	0.0199	0.00225	0.00093

From these data the simple distribution ratio C_w/C_B varies from 0.188 to 2.24, and the ratio $C_w/\sqrt{C_B}$ is more nearly constant but varies from 0.079 to 0.068. If complete ionization in water is assumed, with no polymer in benzene, the equilibrium relation is C_w^2/C_B, which is the square of the constant written for the assumption of polymerization in benzene. Distribution data alone do not allow us to chose between these possibilities or to exclude the possibility of both effects to differing extents.

Freezing-point depressions for picric acid in water give $\Delta t_F/m$ ratios that vary from 3.7 to 3.2, which is typical of the behavior of strongly ionized solutes like HCl. If we suppose the important equilibrium to be

$$\text{HP (in benzene)} = \text{H}^+ + \text{P}^- \text{ (in water)}$$

upon writing HP for $HOC_6H_2(NO_2)_3$, the equilibrium expression becomes

$$\frac{(C_w\gamma)^2}{C_B} = K_2$$

No activity coefficients are available for picric acid, but if we

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[1] WALL, *J. Am. Chem. Soc.*, **64,** 472 (1942). Equilibrium constants $K = (RCOOH)^2/([RCOOH]_2)$ for some other organic acids in benzene are given by Wall and Banes, *ibid.*, **67,** 898 (1945): for example, this constant for benzoic acid is 0.0023 at 32.5°C. and 0.00633 at 56.5°.

use the ones for HCl, which are typical of uni-univalent electrolytes in general, the calculated K_2 is nearly constant, as follows:

C_w	0 0334	0 0199	0 0101	0 00327	0 00208
Act coeff	0 84	0 88	0 90	0 94	0 95
10^3K_2 .	4 4	4 3	4 2	4 2	4 2

Thus assumptions of complete ionization in water, no polymerization in benzene, and correction for activity coefficients yield a satisfactory constant. It should be noted that without supplementary data, such as freezing-point depressions in one solvent or the other, polymerization in one layer and ionization in the other are equally probable interpretations of the distribution data alone.

There are other variations of the distribution ratio with changing concentration of the distributed solute for which neither ionization in one phase nor polymerization in the other appears a probable or acceptable explanation. Under such circumstances, a plot of the distribution ratio against the concentration in one layer or the other will be useful, even though the explanation of the deviation is not known.

Solids and Dissolved Substances.—The simplest equilibrium between a solid and a dissolved substance is that of a saturated solution of a substance which does not ionize upon solution, the concentration of this solution depending on the temperature alone.[1] For a given temperature the equilibrium expression is

$$K_c = C \qquad (t \text{ const.})$$

When the nature of the crystalline phase is unchanged over a

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[1] Strictly speaking, it depends upon the pressure as well, but the small changes in atmospheric pressure produce only a negligible effect that need not be taken into consideration A suitably large increase in pressure will cause considerable change in the solubility of a substance; for example, the solubility of thallous sulfate in water at 25° changes with the pressure as shown in the following table [Cohen and van den Bosch, *Z. physik. Chem* , **114,** 453 (1925)]:

Pressure	1	500	1000	1500 atm
Solubility	0 123	0 160	0 198	0 232*m*.

Increase of pressure usually increases the solubility in water for sulfates, carbonates, sulfides, fluorides, and hydroxides of alkali, alkaline earth, and heavy metals The solubilities of most other salts decrease with increase of pressure. [GIBSON, *Am. J. Sci.*, **35A,** 49 (1938).]

temperature range, a plot of C against the temperature is a smooth curve, and usually (but not always) it shows an increase in solubility at higher temperatures.

An illustration of this simple equilibrium is the variation of solubility of melamine in water with temperature.[1] The solubility, in moles per 1000 grams of water, is

T	293	308	323	337	348	368	372
m	0.0257	0.0468	0.083	0.135	0.190	0.365	0.402

A plot of log m against $1/T$, based on these solubilities, is a straight line, of which the slope is $-\Delta H/2.3R$ and from which $\Delta H = 8200$ cal. per mole for the heat of solution.

When a saturated aqueous solution of a slightly ionized solute, such as benzoic acid, and its crystalline phase are in contact, the equilibriums may be represented as follows:

$$\overbrace{\mathrm{HBz}(s) \underset{K_1}{\rightleftharpoons} \mathrm{HBz(dissolved)} \underset{K_2}{\rightleftharpoons} \mathrm{H^+} + \mathrm{Bz^-}}^{K_3}$$

These expressions represent (1) a constant equilibrium concentration of un-ionized benzoic acid in all saturated aqueous solutions containing other solutes or solute ions at low concentrations, such as $0.01m$. or less, (2) ionization equilibrium between the dissolved acid molecules and its ions, whether derived from benzoic acid or from small additions of other acids or of benzoates, and (3) a constant solubility product for the H^+ and Bz^- ions in the presence of the crystalline phase, all for a constant temperature. According to this third equilibrium, addition of a little hydrochloric acid or nitric acid to a saturated aqueous solution of benzoic acid should decrease the Bz^- concentration materially. In the absence of an added acid, benzoic acid in its saturated solution ($0.026m$. at 25°) is about 4 per cent ionized; (H^+) is about 0.001, and K_3 is about 10^{-6}; hence, addition of 0.01 mole of nitric acid to a liter of saturated benzoic acid solution would reduce (Bz^-) to 10^{-4} and cause the precipitation of about 0.0009 mole of benzoic acid, but nitric acid in such a small concentration would leave the concentration of un-ionized benzoic acid substantially unchanged at $0.025m$.

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[1] CHAPMAN, AVERILL, and HARRIS, *Ind. Eng. Chem*., **35**, 137 (1943).

When salts such as KCl or KBr or $BaCl_2$ are dissolved in saturated aqueous solutions of benzoic acid in considerable quantities, they materially reduce the solubility of the acid by changing the activity coefficients for all the solutes present. If S_0 is the solubility of benzoic acid in pure water and S the solubility in an electrolyte of molality m (both S_0 and S being corrected for ionization of benzoic acid), the decreased solubility is shown by the relation $\log S/S_0 = km$, where k is a different constant for each electrolyte. To illustrate the magnitude of this change in solubility of benzoic acid in water by the addition of salts not yielding benzoate ions, we may note that for 1*m*. solutions of the added salts[1] at 35° the ratio S/S_0 is 0.8 for KBr, 0.7 for LiCl, and 0.5 for $BaCl_2$. Salts cause similar changes in the solubilities of other un-ionized solutes, but it would not be true that S/S_0 would be 0.8 for 1*m*. KBr with some other solute.

The recorded data on the change in solubility of benzoic acid in water with changing temperature may be used to show the necessity for a critical consideration of data and the use and the limitations of calculations based on the van't Hoff equation. The data are

m	0 0139	0 0172	0 0238	0 0282	0 0336	0 0458	0 0948	0 222	0.482
t ...	0°	10°	20°	25°	30°	40°	60°	80°	100°

If we calculate ΔH of solution from the solubilities at 0° and 10° we find 3240 cal., and from the solubilities at 30° and 40° we calculate 5860. It is possible, but not probable, that the heat of solution would change so much in this temperature range. A plot of $\log m$ against $1/T$ from these figures will show that all of them except $\log m$ for 0° fall on a smooth curve, but not on a straight line; and that from 10° to 40° the slope is substantially constant, corresponding to $\Delta H = 5700$ cal. The calculation of the solubility at 0° from this ΔH shows that 0.012 is more reasonable than 0.0139. The curve also shows that 5700 cal. is not the proper heat of solution to use above 40°; for example, it leads to a calculated solubility of 0.078 at 60° in place of 0.0948.

There is another fact which is not indicated by the data but which is of the greatest importance, namely, that above 90° the

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[1] GOELLER and OSOL, *J. Am. Chem. Soc.*, **59**, 2132 (1937). In these experiments it is found that $\log S$ is a linear function of m for these salts and for KI and KCl up to 2*m*.

equilibrium is between an aqueous solution and a *liquid* phase containing mostly benzoic acid and some water and not between an aqueous solution and crystalline benzoic acid. It is another type of system. While the melting point of benzoic acid is 122°, water lowers the "freezing point" to about 90° when added in sufficient quantity. Thus at 90° there may be three phases present at equilibrium in a system of benzoic acid and water—a liquid of 5.6 per cent acid, a liquid of about 80 per cent acid, and crystalline benzoic acid. This is not the type of system that we started out to discuss. We shall return to it in the chapter on phase diagrams, but we must note here that the equilibrium described on page 406 is not applicable above 90° in this system.

Solubility Product for Ionized Solutes.—The current theory of solutions assumes no appreciable concentration of nonionized molecules in dilute solutions of "highly ionized" solutes; thus equilibrium between a slightly soluble salt such as silver acetate and its saturated solution is represented by an equation such as

$$\mathrm{AgAc}(s) = \mathrm{Ag}^+ + \mathrm{Ac}^-$$

for which the equilibrium expression is

$$K_a = \frac{a_{\mathrm{Ag}^+}a_{\mathrm{Ac}^-}}{a_{\mathrm{AgAc}}} = \frac{m_{\mathrm{Ag}^+}\gamma_{\mathrm{Ag}^+}m_{\mathrm{Ac}^-}\gamma_{\mathrm{Ac}^-}}{a_{\mathrm{AgAc}} = 1} \qquad (t \text{ const.})$$

If the solutions involved are "sufficiently" dilute, the change in activity coefficient with slight additions of $AgNO_3$ or KAc may be ignored, and an approximation written

$$\frac{K_a}{\gamma_{\mathrm{Ag}^+}\gamma_{\mathrm{Ac}^-}} = K_c \doteq m_{\mathrm{Ag}^+}m_{\mathrm{Ac}^-} = \text{solubility product}$$

The data in Table 69 show that K_c is nearly constant in "dilute" solutions of silver acetate to which potassium acetate has been added but that in solutions over 0.1*m.* in potassium acetate K_c increases. On the assumption that the activity coefficients for silver nitrate at equivalent total molality apply to mixtures of silver acetate and potassium acetate, the activity product K_a remains practically constant, as is shown in the last column of Table 69.

The use of a similar procedure for additions of silver nitrate to silver acetate leads to a less satisfactory constant K_a and indicates that some further explanation is needed. The activity coefficients for salts of the same ionic type at the same molality are not quite the same, and this may be the explanation. It has also been suggested that "complexes" are responsible for the variation in K_a. But it will generally be true that the use of activity coefficients for one salt in solutions of another salt is not wholly justified, and variations in a quantity supposedly constant will result to about the extent shown in solutions of silver nitrate and silver acetate.

TABLE 69.—SOLUBILITY OF SILVER ACETATE IN POTASSIUM ACETATE[1]

KAc	AgAc	Total Ac	$(Ag^+)(Ac^-)$	Activity coefficient	Activity product
0	0.06674	0.06674	44.5×10^{-4}	0.76	25.4×10^{-4}
0.01144	0.06135	0.07279	44.6×10^{-4}	0.75	25.0×10^{-4}
0.04956	0.04867	0.09821	47.7×10^{-4}	0.72	25.0×10^{-4}
0.1028	0.03763	0.1404	52.8×10^{-4}	0.68	24.4×10^{-4}
0.1965	0.02796	0.2245	63.8×10^{-4}	0.63	25.4×10^{-4}
0.4828	0.01925	0.5021	96.7×10^{-4}	0.51	25.0×10^{-4}
0.6751	0.01722	0.6923	119.0×10^{-4}	0.45	24.8×10^{-4}
1.001	0.01575	1.0168	161×10^{-4}	0.40	25.8×10^{-4}

SOLUBILITY OF SILVER ACETATE IN SILVER NITRATE[2]

$AgNO_3$	AgAc	Total Ag	$(Ag^+)(Ac^-)$	Activity coefficient	Activity product
0.04920	0.05008	0.09928	49.7×10^{-4}	0.72	26×10^{-4}
0.07063	0.04555	0.11618	52.8×10^{-4}	0.70	26×10^{-4}
0.09491	0.04107	0.13598	55.9×10^{-4}	0.69	26×10^{-4}
0.10590	0.03999	0.14589	58.4×10^{-4}	0.68	27×10^{-4}
0.19900	0.03145	0.23045	72.6×10^{-4}	0.62	28×10^{-4}
0.2009	0.03135	0.2322	72.6×10^{-4}	0.62	28×10^{-4}
0.3104	0.02745	0.33785	92.7×10^{-4}	0.56	29×10^{-4}

It should be understood that the variation of the activity product in the last column of Table 69 arises from using estimated activity coefficients, for the product $a_{Ag^+}a_{Ac^-}$ is a constant whenever equilibrium exists between solid silver acetate and its saturated solution.

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[1] MACDOUGALL and ALLEN, *J. Phys. Chem.*, **46**, 730 (1942).

[2] MACDOUGALL, *ibid.*, **46**, 738 (1942).

Application of the van't Hoff equation to changing solubility with changing temperature is rendered difficult by lack of data on the heat effects attending the process of solution and by lack of data on heat capacities of ions at temperatures other than 25°. The change in ΔH with temperature is somewhat compensated by changing activity coefficients as the solubility changes; thus approximate agreement between experiment and solubilities calculated from K_c, uncorrected for activity coefficients, is sometimes found. For example, the solubility of $KClO_4$ changes with the temperature as follows:

t, °C	0	20	40	80	100
S	0 052	0 121	0 268	1 04	1 56

Taking $K_c = S^2$, without correction for activity coefficients, one calculates from the solubilities at 0° and 20° that ΔH is 13,700 cal., from which S is calculated to be 0.256 at 40°, compared with 0.268 by experiment; and S at 100° is calculated to be 1.51, compared with 1.56 by experiment. Such close agreement, which is somewhat due to compensations in the incorrect assumptions, will not always be found, and in general the agreement will be better for smaller solubilities.

Solubility products apply as well in systems containing ions of valence other than unity, but the form of the expression is different when some of the ions have unit valence and others have not. For example, the solubility product for lead iodate, for which the chemical equation is

$$Pb(IO_3)_2(s) = Pb^{++} + 2IO_3^-$$

is the product of the lead-ion activity and the square of the iodate-ion activity. In the absence of added iodate the molality of the iodate ion is twice that of the lead ion, and thus the equilibrium expression is

$$K_a = m_{Pb^{++}}\gamma_{Pb^{++}}(m_{IO_3^-}\gamma_{IO_3^-})^2 = 4S_0^3\gamma^3$$

in which S_0 denotes the solubility in pure water, 3.6×10^{-5} *m.* at 25°. The solubility of lead iodate in, say, 0.01*m.* KIO_3 would then be shown by the equation

$$K_a = S\gamma[(2S + 0.01)\gamma]^2$$

An equation of similar form would apply to the solubility product for PbI_2, $Mg(OH)_2$, or Ag_2SO_4. The exact application of solubility products such as these to calculations of solubility in the presence of added salts with an ion in common is usually complicated by a lack of accurate activity coefficients to use in them. "Estimates" of activity coefficients from those of other salts of the same ionic type are not very satisfactory. For example, the activity coefficient for 0.01*m*. $PbCl_2$ is 0.61, and that for 0.01*m*. $Mg(NO_3)_2$ is 0.71; and since these coefficients are raised to the third power in the equilibrium expressions, the error is too large for satisfaction.

Formation of "Complex" Ions.—Some slightly soluble salts react with solutes to form "complexes" that result in an increased solubility. For example, silver iodate ($AgIO_3$) is soluble in water only to the extent of 1.75×10^{-4} mole per liter at 25°. It reacts with ammonia to form the familiar complex $Ag(NH_3)_2^+$, thus removing one of the ions of silver iodate and increasing the solubility. The chemical reaction and its equilibrium constant K_c are

$$AgIO_3(s) + 2NH_3 = Ag(NH_3)_2^+ + IO_3^-$$

$$K_c = \frac{[Ag(NH_3)_2^+](IO_3^-)}{(NH_3)^2} = \frac{S^2}{(m - 2S)^2} \quad (t \text{ const.})$$

where m is the total ammonia. It will be noted that the activity coefficient for the ions would appear in the numerator of this expression as γ^2 and that the activity coefficient for nonionized ammonia is substantially unity. In dilute ammonia another correction is required for the formation of NH_4^+ and OH^- ions, since these ions are not concerned in the reaction with $AgIO_3$. Thus the complete expression for the equilibrium constant in terms of activities is

$$K_a = \frac{(S\gamma)^2}{[(m - 2S)(1 - \alpha)]^2}$$

in which α is the fractional ionization of the ammonia. The data in Table 70 show that K_c is not constant and that K_a is constant. Activity coefficients for the ions of $Ag(NH_3)_2IO_3$ are not available, and those for $AgNO_3$ at the same molality have been used in the table.

The existence of another type of "complex" ion, which is strictly an intermediate ion, is shown by the increased solubility of $Pb(IO_3)_2$ in the presence of acetates. The increase is due to the formation of $PbAc^+$. Activity coefficients for mixtures such as $Pb(IO_3)_2$ and NH_4Ac are not available; but since the activity coefficient is nearly constant in a mixture of constant ionic concentration, a simple expedient is available, namely, the solubility of $Pb(IO_3)_2$ is determined in a mixture of NH_4ClO_4 and NH_4Ac at a constant total molality that is high compared with the molality of lead ion, with increasing proportions of acetate and decreasing proportions of perchlorate. The perchlorate takes no part in the formation of a complex, and there is no evidence of the presence of ions such as $PbClO_4^+$ or $PbIO_3^+$. In Table 71 the third column gives the solubility (in moles per 1000 grams of water) of $Pb(IO_3)_2$ at 25° in the mixtures of NH_4Ac and NH_4ClO_4 shown in the first two columns; the fourth column gives the molality of lead ion calculated on the assumption that the solubility product K_c of lead iodate is constant in this mixture; the fifth column gives by difference the molality of $PbAc^+$; and the last column gives K_c for the reaction $PbAc^+ = Pb^{++} + Ac^-$. The fact that this K_c is substantially constant is evidence for the formation of the ion $PbAc^+$.

TABLE 70.—SOLUBILITY OF SILVER IODATE IN AMMONIA AT 25°[1]

$(NH_3) = m$	$(IO_3^-) = S$	$K_c = \frac{S^2}{(m - 2S)^2}$	γ = act. coeff.	α = frac ionized	$K_a = \frac{S^2\gamma^2}{[(m - 2S)(1 - \alpha)]^2}$
0.01241	0.003665	0.520	0.93	0.060	0.51
0.02481	0.007430	0.558	0.91	0.042	0.51
0.03085	0.009358	0.595	0.89	0.038	0.51
0.06180	0.01901	0.639	0.87	0.027	0.51
0.1028	0.03223	0.708	0.83	0.022	0.51
0.1847	0.05937	0.810	0.78	0.017	0.51
0.2487	0.08125	0.888	0.75	0.014	0.51

It should be noted that the solubility of lead iodate given in the first line of Table 71 is not the solubility in pure water but a much higher value because of the smaller activity coefficient in a mixture of salts. The assumption is that since the total ionic concentration is substantially constant in these mixtures the activity coefficient will be *constant*, not that it will be nearly unity, and thus that K_c will be constant throughout the series of experiments.

[1] DERR, STOCKDALE, and VOSBURGH, *J. Am. Chem. Soc.*, **63**, 2670 (1941).

TABLE 71.—SOLUBILITY OF LEAD IODATE IN AMMONIUM ACETATE[1]

NH_4Ac	NH_4ClO_4	$Pb(IO_3)_2 \times 10^4$	$(Pb^{++}) \times 10^4$	$(PbAc^+) \times 10^4$	$\frac{(Pb^{++})(Ac^-)}{(PbAc^+)}$
0	1 0	1 950	1 950		
0 05	0 95	3 557	0 586	2 97	$9\ 86 \times 10^{-3}$
0 10	0 90	4 370	0 388	3 98	$9\ 75 \times 10^{-3}$
0 20	0 80	5 584	0 238	5 35	$8\ 89 \times 10^{-3}$
0 50	0 50	7 265	0 141	7 12	$9\ 85 \times 10^{-3}$
1 00	0 0	9 11	0 089	9 02	$9\ 92 \times 10^{-3}$

Other lead salts would also react with acetate ions to form the $PbAc^+$ ion, as, for instance, in the procedure of qualitative analysis in which lead sulfate is dissolved in ammonium acetate solution.

The solubility of mercuric bromide ($HgBr_2$) in potassium bromide solutions is quantitatively explained by the formation of a complex ion $HgBr_3^-$. Since mercuric halides are substantially un-ionized in aqueous solutions, it is the concentration of $HgBr_2$, and not the solubility product $(Hg^{++})(Br^-)^2$, that remains constant in solutions in equilibrium with solid $HgBr_2$. The solubility of $HgBr_2$ in KBr at 25° is as follows:[2]

KBr molality	. 0	0 010	0 030	0 080	0 100	0 300
Total Hg dissolved..	0 0170	0 0235	0 0365	0 0692	0 0825	0 213

Corresponding solubility data for HgI_2 in KI are not so simply interpreted and probably indicate two complexes HgI_3^- and HgI_4^{--}. The ratio of chloride ion to dissolved mercury in solutions of KCl saturated with $HgCl_2$ varied fortyfold when the KCl molality increased from 0.1 to 5.0.

There are numerous instances of increased solubility of salts produced by adding comparatively large quantities of another salt with one ion in common. Thus, silver chloride is much more soluble in strong sodium chloride solution than in pure water, and dilution causes the precipitation of silver chloride. Similar behavior is shown by AgSCN dissolving in aqueous solutions of KSCN as follows:[3]

KSCN, moles per liter	0 312	0 564	0 870	1 124
AgSCN, moles per liter . .	0 00202	0 0121	0 0458	0 0985

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[1] EDMONDS and BIRNBAUM, *ibid*, **62**, 2367 (1940)

[2] GARRETT, *ibid.*, **61**, 2745 (1939).

[3] RANDALL and HALFORD, *ibid.*, **52**, 189 (1930).

The formation of "complex" salts such as $NaAgCl_2$ or $KAg(SCN)_2$ seems a logical assumption but does not account for the facts, and no adequate *quantitative* explanation of either solubility increase is known. But numerous increases in solubility are quantitatively explained by the formation of similar compounds.

Solubility of Hydrolyzed Salts.—Salts of weak acids, such as carbonates and sulfides, are hydrolyzed in aqueous solution to an extent that increases as the concentration decreases. Hence in the saturated solutions of such salts allowance must be made for the hydrolytic reaction as well as for the equilibrium demanded by the solubility product. In a saturated solution of $CaCO_3$, for example, the equilibrium

$$K_{sp} = (\mathrm{Ca}^{++})(\mathrm{CO_3}^{--})$$

must of course be maintained, but the ion concentrations are not equal because of the reaction

$$\mathrm{CO_3}^{--} + \mathrm{H_2O} = \mathrm{HCO_3}^{-} + \mathrm{OH}^{-}$$

for which

$$K_c = \frac{(\mathrm{HCO_3}^{-})(\mathrm{OH}^{-})}{(\mathrm{CO_3}^{--})} = \frac{K_w}{K_2}$$

If S is the total calcium ion concentration, $(\mathrm{CO_3}^{--}) = S(1 - h)$, and $(\mathrm{HCO_3}^{-}) = (\mathrm{OH}^{-}) = Sh$. Upon substituting these quantities and the numerical values of the appropriate constants for 25° into the above equilibrium equations, we have

$$5 \times 10^{-9} = S^2(1 - h) \qquad \text{and} \qquad \frac{Sh^2}{1 - h} = 1.8 \times 10^{-4}$$

These two equations contain only two unknowns, whence we find $h = 0.68$ and $S = 1.2 \times 10^{-4}$. (The equations may, if preferred, be solved by successive approximations, on the basis of a value of S greater than the square root of the solubility product, h being solved in the hydrolytic equilibrium, and the process repeated until a suitable value of S is found.) Thus we see that the solubility, which is of course total calcium, is nearly double the square root of the solubility product in this system.

A similar calculation could be made for any slightly soluble carbonate, but one should not merely repeat these operations as routine. For example, a similar calculation for the solution in equilibrium with $MgCO_3.3H_2O(s)$ at 25°C. yields $h = 0.2$ and $S = 3.7 \times 10^{-3}$, but the concentrations of Mg^{++} and OH^- corresponding to these figures lead to a product $(Mg^{++})(OH^-)^2$ that exceeds the recorded solubility product by a hundredfold. Thus a new solid phase appears, which renders the calculation that assumes no precipitation of $Mg(OH)_2$ valueless. While a *calculation* of the concentrations of all the ions in a solution in equilibrium with both hydroxide and carbonate as solid phases could readily be carried out, one must first establish that these substances are the solid phases present at equilibrium and that "basic carbonates" are absent.

The recorded solubility product of PbS is 10^{-29}, which is of course $(Pb^{++})(S^{--})$, but the square root of this solubility product would have little relation to the solubility of lead sulfide in water. A saturated solution of PbS in water would certainly contain HS^- and OH^- and probably H_2S and $PbOH^+$; therefore, the equilibrium is a far more complex matter than merely the equilibrium between a solid phase and the ions of which it consists.

Solubility of Carbonates in Carbonic Acid.—In the presence of dissolved carbon dioxide at moderate concentration hydrolysis of the carbonate ion is negligible, and the reaction that governs the equilibrium is the formation of bicarbonate. Since most bicarbonates are more soluble than the corresponding carbonates, solubility increases are the result. For example, the equilibrium corresponding to the reaction

$$FeCO_3(s) + H_2CO_3 = Fe^{++} + 2HCO_3^-$$

has been studied over a wide range of concentration,[1] and the equilibrium expression is

$$\frac{(Fe^{++})(HCO_3^-)^2}{(H_2CO_3)} = K_c \qquad (t \text{ const.})$$

Let S denote the solubility of ferrous salt in the carbonic acid solutions, *i.e.*, its molal concentration in carbonic acid solution in equilibrium with solid ferrous carbonate. If the notation previously employed is followed, the ferrous-ion concentration is S; the bicarbonate-ion concentration is $2S$, since the solubility of $FeCO_3$ as such is negligibly small. The ionization of carbonic

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[1] Smith, H. J., *ibid.*, **40,** 879 (1918)

acid is slight and in the presence of dissolved ferrous bicarbonate, which is highly ionized, may be neglected entirely in the calculation. Table 72 shows the results of experiments at 30°, where the equilibrium constant is

$$K_c = \frac{S(2S)^2}{(H_2CO_3)} \qquad (t \text{ const.})$$

TABLE 72.—SOLUBILITY OF FERROUS CARBONATE IN CARBONIC ACID

Total concentrations at 30°		Equilibrium constant K_c
H_2CO_3	$Fe(HCO_3)_2$	
0 196	0 00256	$34\ 2 \times 10^{-8}$
0 230	0 00274	$35\ 6 \times 10^{-8}$
0 309	0 00304	$36\ 5 \times 10^{-8}$
0 326	0 00311	$37\ 0 \times 10^{-8}$
0 401	0 00332	$36\ 5 \times 10^{-8}$
0 655	0 00402	$39\ 8 \times 10^{-8}$
0 755	0 00434	$43\ 3 \times 10^{-8}$

This constant K_c is seen to be almost constant as long as the molalities are low enough, which is to say that the activity coefficients are almost constant (though not almost unity). At higher molalities K_c increases, as is often true of such equilibrium constants.

In this system we may equate K_c to $K_{sp}K_1/K_2$ as we have done before and calculate the solubility product for ferrous carbonate. This solubility product is 4.5×10^{-11}, but the square root of K_{sp} would have little relation to the solubility of ferrous carbonate in water because of hydrolysis and the probable precipitation of ferrous hydroxide.

Dissolved carbon dioxide also produces increased solubility for other carbonates. Experimental studies for $CaCO_3$, $MgCO_3 \cdot 3H_2O$, and $ZnCO_3$ are given in the data for problems at the end of the chapter, and other systems have also been studied.

Conversion of One Solid into Another.—A familiar example of this type of reaction is the conversion of barium sulfate into barium carbonate by boiling it with sodium carbonate solution in excess. The chemical equation is

$$BaSO_4(s) + 2Na^+ + CO_3^{--} = BaCO_3(s) + 2Na^+ + SO_4^{--}$$

and the equilibrium expression in terms of activities is

$$K_a = \frac{a_{BaCO_3}a_{SO_4^{--}}}{a_{BaSO_4}a_{CO_3^{--}}} \qquad (t \text{ const.})$$

Assuming that the ratio of the ion activities is equal to the ratio of ion molalities and defining the activities of the solid phases as unity, as we have done so often before, this reduces to

$$K_c = \frac{(SO_4^{--})}{(CO_3^{--})} \qquad (t \text{ const.})$$

In the presence of the solid barium compounds there must be a very small concentration of barium ion of such amount that the solubility products $K_1 = (Ba^{++})(SO_4^{--})$ for saturated barium sulfate and $K_2 = (Ba^{++})(CO_3^{--})$ for saturated barium carbonate are both satisfied. These values are, respectively, 1×10^{-10} and 25×10^{-10} at 25°, and dividing K_1 by K_2 we obtain a value of K_c.

$$K_c = \frac{(SO_4^{--})}{(CO_3^{--})} = \frac{K_1}{K_2} = 0.04 \text{ at } 25°$$

In any solution in equilibrium with both barium sulfate and barium carbonate, the carbonate-ion concentration must be 25 times the sulfate ion concentration. Therefore, for the complete conversion of a mole of barium sulfate to barium carbonate a mole of sodium carbonate will be required for the chemical reaction, and 25 moles of sodium carbonate will be required to maintain the equilibrium ratio, or 26 moles in all. This calculation has been made for 25°, but no smaller quantity of sodium carbonate could be used in a boiling solution safely, since the solution is cooled while filtering.

Suppose 2.33 grams (0.01 mole) of barium sulfate is shaken a long time with 100 ml. of 1.0*m*. sodium carbonate solution, which contains 0.1 mole of sodium carbonate. Let x be the moles of sodium carbonate remaining in solution at equilibrium; then $(0.1 - x)$ moles of sodium sulfate are in solution, and

$$\frac{(0.1 - x)}{x} = 0.04$$

whence $x = 0.0962$ mole of sodium carbonate remaining. Then 0.0038 mole of sodium carbonate has reacted, forming 0.0038 mole of barium carbonate, and leaving 0.0062 mole, or about two-thirds of the original barium sulfate unchanged. It is clear that too little carbonate solution has been used. As stated above, the minimum quantity required is 26 times the moles of barium sulfate to be converted to carbonate, or 260 ml. of molal sodium carbonate solution. Any quantity of this solution greater than 260 ml. will convert the sulfate completely to carbonate. Experiments of this kind may be used to determine the solubility product of one salt when that of another is known, since the equilibrium constant is the ratio of the two solubility products.

Equilibrium between Metals and Ions.—Silver reacts with ferric salts, forming ferrous salts and silver salts. The reaction is

$$\mathrm{Ag}(s) + \mathrm{Fe}^{+++} + 3\mathrm{NO_3}^- = \mathrm{Ag}^+ + \mathrm{NO_3}^- + \mathrm{Fe}^{++} + 2\mathrm{NO_3}^-$$

and the equilibrium expression is[1]

$$\frac{(\mathrm{Ag}^+)(\mathrm{Fe}^{++})}{(\mathrm{Fe}^{+++})} = K_c = 0.128 \text{ at } 25°$$

From this value of K_c it may be seen that unless the silver-ion concentration is very small, complete reduction of ferric nitrate to ferrous nitrate will not take place. For example, suppose $0.2m.$ ferric nitrate to be shaken with an excess of silver until equilibrium is reached. If x is the ferrous-ion concentration, $(0.2 - x)$ is the ferric-ion concentration, and x is the silver-ion concentration, since the chemical equation shows that a silver ion is formed for each ferrous ion. Substituting in the above expression, we have $x^2/(0.2 - x) = 0.128$, whence x is 0.108, the concentration of ferrous salt, and the ferric-salt concentration is 0.092. This shows that about half the ferric salt has been reduced by silver. If some salt is added that precipitates silver ions as soon as formed and that does not react with the iron salts, then in the presence of solid silver the ferric-salt concentration must be very small compared with the ferrous-salt concentration. Addition of a thiocyanate serves this purpose,[2] and by this means ferric iron may be reduced for titration; the

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[1] NOYES and BRANN, *ibid.*, **34,** 1016 (1912).

[2] EDGAR and KEMP, *ibid.*, **40,** 777 (1918).

thiocyanate furnishes at the same time an indicator for complete reduction. The excess thiocyanate is removed by adding silver nitrate solution just before the titration.

TABLE 73 —EQUILIBRIUM BETWEEN TIN AND LEAD PERCHLORATE AT 25°C.

Molal concentration of solution at start of experiment		Equilibrium concentrations, moles per liter		$K = \frac{(\text{Sn}^{++})}{(\text{Pb}^{++})}$
Tin perchlorate	Lead perchlorate	Sn^{++}	Pb^{++}	
0 094		0 0704	0 0233	3 02
0 050		0 0393	0 0123	3 19
0 050		0 0413	0 0132	3 14
	0 096	0 0716	0 0237	3 04
	0 060	0 0457	0 0148	3 08
	0 050	0 0369	0 0119	3 11
0 038	0 019	0 0428	0 0145	2 96
0 051	0 037	0 0697	0 0239	2 92
0 066	0 027	0 0692	0 0235	2 95
0 086	0 024	0 0821	0 0275	2 98

Another reaction of this type is that between lead perchlorate and metallic tin,[1] according to the equation

$$\text{Sn}(s) + \text{Pb}^{++} + 2\text{ClO}_4^- = \text{Pb}(s) + \text{Sn}^{++} + 2\text{ClO}_4^-$$

for which $K_c = (\text{Sn}^{++})/(\text{Pb}^{++})$. The experimental results for 25° are shown in Table 73. In some of the experiments the original solution contained lead perchlorate alone or tin perchlorate alone; in other experiments both perchlorates were present in solution; excess of both solid metals was always used, and the solutions were shaken at 25° until they had reached equilibrium. As shown by the value of K_c in the last column of the table, the ratio of tin salt to lead salt in solution at equilibrium is about 3.0, whether the reaction proceeded in one direction or the other and regardless of the relative quantities of tin perchlorate and lead perchlorate in solution at the start.

The constancy of K_c in this system shows, not that the activity coefficients are nearly unity, but only that they are nearly constant. In a mixture of salts of the same ionic type, such as we have in this system, the same activity coefficient would apply

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[1] NOYES and TOABE, *ibid*, **39**, 1537 (1917).

to stannous ions and lead ions, whether or not their molalities were the same. The exact equilibrium relation is

$$K_a = \frac{(\mathrm{Sn}^{++})\gamma_{\mathrm{Sn}^{++}}}{(\mathrm{Pb}^{++})\gamma_{\mathrm{Pb}^{++}}} \qquad (t \text{ const.})$$

and the activity coefficients cancel to make K_a equal to K_c in this particular system. For the solutions described in Table 73 the activity coefficients would be about 0.5.

This equilibrium ratio would also apply in the presence of negative ions other than perchlorate, for instance, in dilute lead chloride and stannous chloride. If 0.2*m*. $SnCl_2$ and excess lead react to equilibrium, the ratio $(\mathrm{Sn}^{++})/(\mathrm{Pb}^{++}) = 3.0$ would prevail; but under these conditions solid $PbCl_2$ would form, and thus the solubility relations of $PbCl_2$ in the presence of excess chloride ions would also prevail.

The need for considering activity coefficients is better illustrated by the reaction[1]

$$2\mathrm{Fe}^{+++} + 6\mathrm{ClO}_4^- + 2\mathrm{Hg}(l) = 2\mathrm{Fe}^{++} + \mathrm{Hg}_2^{++} + 6\mathrm{ClO}_4^-$$

for which the equilibrium constant K_c is

$$K_c = \frac{(\mathrm{Fe}^{++})^2(\mathrm{Hg}_2^{++})}{(\mathrm{Fe}^{+++})^2}$$

If this constant is calculated in the usual way, it varies with the total iron as follows, in the presence of 0.01*m*. perchloric acid at 35°:

Total Fe	0 004	0.002	0 001
K_c . .	0 0820	0.0862	0.0975

In these mixtures the activity coefficients are neither near unity nor nearly constant. The correct equilibrium relation is

$$K_a = \frac{(\mathrm{Fe}^{++})^2\gamma_{\mathrm{Fe}^{++}}{}^2(\mathrm{Hg}_2^{++})\gamma_{\mathrm{Hg}_2^{++}}}{(\mathrm{Fe}^{+++})^2\gamma_{\mathrm{Fe}^{+++}}{}^2}$$

This equation shows how the equilibrium should be handled; but it does not provide the data for carrying out the calculation, since in a mixture of salts of three different ionic types the exact calculation of activity coefficients is not within the powers of the theory.

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[1] FLEHARTY, *ibid.*, **55**, 2647 (1933).

It should be said again that, unless the solid phases concerned in an equilibrium are correctly identified and are all present, the equilibrium relations are not correctly given. As one more illustration, consider the reaction

$$CaSO_4(s) + 2Na^+ + CO_3^{--} = CaCO_3(s) + 2Na^+ + SO_4^{--}$$

If the sodium carbonate solution is dilute, we may evaluate K_c from the ratio of the solubility products, as was done for the reaction of $BaSO_4$ with Na_2CO_3, as follows:

$$K_c = \frac{(SO_4^{--})}{(CO_3^{--})} = \frac{(sp)_1}{(sp)_2} = \frac{2.3 \times 10^{-4}}{5 \times 10^{-9}} = 4.6 \times 10^4$$

Thus in dilute solution the conversion is complete with a very small excess of sodium carbonate. But in strong solutions a new solid phase, $CaCO_3.Na_2CO_3.5H_2O$, appears, and the ratio of sulfate to carbonate at equilibrium is reduced from 46,000 to 19[1] in the presence of new solid phases.

Problems

1. For the reaction $FeO(s) + H_2(g) = Fe(s) + H_2O(g)$, the equilibrium constants are [EMMETT and SHULTZ, *J. Am. Chem. Soc.*, **52**, 4268 (1930)]

$K_1 = p_{H_2O}/p_{H_2}$	0.422	0.499	0.594	0.669	0.78
T, °K	973	1073	1173	1273	1400

and for the reaction $FeO(s) + CO(g) = Fe(s) + CO_2(g)$ the equilibrium constants are [EASTMAN, *J. Am. Chem. Soc*, **44**, 975 (1922)]

$K_2 = p_{CO_2}/p_{CO}$	0.678	0.552	0.466	0.403	0.35
T, °K	973	1073	1173	1273	1400

(*a*) Calculate the equilibrium constant K_3 for the reaction

$$CO_2(g) + H_2(g) = CO(g) + H_2O(g)$$

at these temperatures from the above data. (*b*) Plot log K_3 against $1/T$ for these constants, add those given on page 347, draw a "best straight line" through the points, and determine ΔH for the reaction. (The result should check that of Problem 21, page 328.) (*c*) How many moles of CO would be required to reduce 1FeO at 1273°K.? (*d*) From the data above and those in Table 67, calculate the partial pressure of oxygen in equilibrium with Fe(*s*) and FeO(*s*) at 1400°K. [For data on these systems at higher temperatures, see Darken and Gurry, *J. Am. Chem. Soc.*, **67**, 1398 (1945).]

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[1] HERTZ, *Z. anorg. Chem.*, **71**, 206 (1911).

2. (*a*) Calculate the equilibrium constant for the reaction $HgBr_2(s) + Br^- = HgBr_3^-$ from the solubility data on page 413. (*b*) Calculate the solubility of $HgBr_2$ in 0.2*m* KBr.

3. Ten grams of Ag_2S remains in contact with a liter of hydrogen at 873°K. and 1 atm. until equilibrium is established. (*a*) Calculate the equilibrium constant for the reaction $Ag_2S + H_2(g) = 2Ag + H_2S(g)$ at 873°K., from the data on page 399. (*b*) Calculate the quantities of all four substances present at equilibrium. (*c*) What is the least quantity of hydrogen required for reduction of all of the Ag_2S at 873°K.?

4. Calculate ΔH for the dissociation of $CaCO_3$ into CaO and CO_2 from the data on page 395. (The result should check that of Problem 3, page 326.)

5. Hydrogen may be prepared by passing steam over hot iron and condensing out the unchanged water. (*a*) From the data in Problem 1 above, calculate the moles of steam passing over iron per mole of hydrogen produced, if the reaction occurs at 1273°K. Calculate the composition of the gas phase and the quantities of Fe(*s*) and FeO(*s*) present at equilibrium in systems at 1273°K. containing initially 1 mole of $H_2O(g)$ with (*b*) 0.3 atomic weight of iron, (*c*) 0.5 atomic weight of iron, and (*d*) 0.8 atomic weight of iron.

6. Experiments on the solubility of zinc carbonate in water containing carbon dioxide in excess gave the following results at 298°K., in moles per liter of solution:

Total CO_2	0.184	0.454	0.768
Total Zn	0.0021	0.0029	0.0034

(*a*) Calculate the equilibrium constant K_c for the reaction

$$ZnCO_3(s) + H_2CO_3 = Zn^{++} + 2HCO_3^-$$

at 298°K. (*b*) Calculate the solubility product for $ZnCO_3$. (*c*) Calculate the solubility of $ZnCO_3$ in 0.25*m*. H_2CO_3 at 298°K.

7. Ammonium carbamate dissociates completely in the vapor phase as shown by the equation $NH_4CO_2NH_2(s) = 2NH_3(g) + CO_2(g)$, and at 25° the dissociation pressure at equilibrium is 0.117 atm. The dissociation pressure at 25° for the equilibrium $LiCl.3NH_3(s) = LiCl.NH_3(s) + 2NH_3(g)$ is 0.168 atm. (*a*) Neglecting the volume of the solid phases in comparison with the volume of the vapor phase, calculate the final *total pressure* when equilibrium is reached in a 24.4-liter vessel at 25° containing initially 0.050 $CO_2(g)$ and 0.20 $LiCl.3NH_3(s)$. The solid phases at equilibrium are $NH_4CO_2NH_2(s)$, $LiCl.NH_3(s)$, and $LiCl.3NH_3(s)$. (*b*) Calculate the moles of each solid phase present at equilibrium. (*c*) Calculate the equilibrium total pressure at 25° in a 24.4-liter vessel containing initially 0.050 $CO_2(g)$ and 0.10 $LiCl.3NH_3(s)$.

8. The equilibrium constant for the reaction

$$ZnO(s) + CO(g) = Zn(g) + CO_2(g)$$

with partial pressures in atmospheres changes with the Kelvin temperature as follows:

T	1073	1173	1273	1373
K_p	1.24×10^{-3}	7.38×10^{-3}	3.29×10^{-2}	1.17×10^{-1}

(*a*) Determine ΔH for the reaction. (*b*) Calculate the ratio of CO_2 to CO at equilibrium with ZnO(*s*), Zn(*l*), and Zn(*g*) at 1173°K. The boiling point of zinc is 1180°K, and its latent heat of evaporation is 29,170 cal. per atomic weight near the boiling point. [TRUESDALE and WARING, *J. Am. Chem. Soc.*, **63,** 1610 (1941).]

9. The equilibrium constant K_c for the reaction

$$Ag(s) + Fe^{+++} = Ag^{+} + Fe^{++}$$

is 0.128 at 25°C. (*a*) What fraction (x) of the ferric ion will be reduced when 0.1*m* ferric nitrate is shaken with excess silver until equilibrium is established? (*b*) What fraction of 0.1*m* ferric *chloride* will be reduced by excess silver? (The solubility of AgCl in water at 25° is 1.3×10^{-5} mole per liter.)

10. The solubility product for $CaCO_3$ at 25°C is given in chemical literature as 5×10^{-9}, and its solubility increases in the presence of dissolved CO_2 because of the chemical reaction

$$CaCO_3(s) + H_2CO_3 = Ca^{++} + 2HCO_3^{-}$$

(*a*) Write the equilibrium expression for this reaction, and evaluate K_a at 25°, assuming the solubility product is an activity product and using the ionization constants of carbonic acid. (*b*) The measured solubility of $CaCO_3$ is 0.0039*m* when the equilibrium pressure of CO_2 above the solution at 25° is 0.1 atm., and the solubility of CO_2 in water at 25° is 0.034*m* when the pressure of CO_2 is 1.0 atm. Calculate the equilibrium constant K_c from these facts. (*c*) Calculate the value of the activity coefficient that would be required to obtain the same value of K_a from these measurements as from part (*a*).

11. Calculate the equilibrium constant for the reaction

$$Pb(IO_3)_2(s) + Ac^{-} = PbAc^{+} + 2IO_3^{-}$$

from the solubility data in Table 71.

12. The pressure in a 500-ml. bulb containing 1.0 gram of NH_4Cl changes with temperature as follows:

p, atm	0.050	0.112	0.217	0.408	0.730	1.22
T, °K	520	540	560	580	600	620

The pressure in a 500-ml. bulb containing 0.091 gram of NH_4Cl changes with temperature as follows:

p, atm . .	0.079	0.158	0.303	0.335	0.346	0.357
T, °K . .	530	550	570	590	610	630

(*a*) Plot both sets of data on the same paper, and draw lines that fit a reasonable interpretation of the observed pressures. (*b*) The density of *saturated* NH_4Cl vapor changes with the temperature as follows:

T, °K	555	585	593	608
p, atm	0.192	0.471	0.621	0.922
grams per liter	0.114	0.269	0.347	0.500

Determine the extent of dissociation of the vapor from these densities. (*c*) Calculate the equilibrium constant for the reaction

$$NH_4Cl(s) = NH_3(g) + HCl(g)$$

at several temperatures, plot log K against $1/T$, and determine ΔH for the reaction. (*d*) The dissociation pressure is 1.0 atm at 613°K. How much solid NH_4Cl forms at equilibrium when 0.10 mole of $NH_3(g)$ and 0.15 mole of $HCl(g)$ are introduced into a 5-liter vessel at 613°K ?

[Data from Smits and deLange, *J. Chem. Soc.* (*London*), **1928,** 2945.]

13. The equilibrium pressure for the reaction $2NaH(s) = 2Na(l) + H_2(g)$ changes with the temperature as follows:

t, °C	300	320	340	360	380
p, mm	8.02	18.6	41.7	89.1	182

The boiling point of sodium is 878°C., and its latent heat of evaporation is 25,300 cal. per atomic weight. (*a*) Determine whether the vapor pressure of sodium is a negligible part of the dissociation pressures given above. (*b*) Calculate ΔH for the reaction from a suitable plot. (*c*) Calculate the dissociation pressure at 400°C. [*Ans.* (*b*) 28,100 cal., (*c*) 355 mm.]

14. The density (in grams per liter) of the vapor in equilibrium with $NH_4Br(s)$ and the total pressure (dissociation pressure) change with temperature as follows:

T	631	645	653.7	668
d	0.346	0.474	0.590	0.820
p, atm	0.366	0.539	0.662	0.953

Problem basis: 3.46 grams of saturated vapor at 631°K. and 0.366 atm. (*a*) Show whether the vapor consists of NH_3 and HBr only or whether $NH_4Br(g)$ is present in significant quantity. (*b*) Calculate the equilibrium constant from the dissociation pressure. (*c*) Calculate the total pressure at equilibrium and the moles of $NH_4Br(s)$ present after 0.040 mole of $HBr(g)$ has been forced into the space. [Smits and Purcell, *J. Chem. Soc.* (*London*), **1928,** 2936.]

15. For the reaction $NiBr_2 \cdot NH_3(s) = NiBr_2(s) + NH_3(g)$, $\Delta C_p = 0$, $\Delta H = 20{,}600$ cal., and the equilibrium pressure of $NH_3(g)$ is 0.50 atm. at 609°K. (*a*) Calculate the equilibrium pressure at 617°K. (*b*) At 617°K. the dissociation pressure for the reaction $NH_4Br(s) = NH_3(g) + HBr(g)$ is 0.243 atm., and the vapor is completely dissociated. Calculate the total pressure at equilibrium and the moles of each solid phase present at 617°K. in a space of 50.4 liters containing originally $1NiBr_2(s)$, $1NH_3(g)$, and $0.25HBr(g)$. The only chemical reactions in the system are those given above, and all three solids, $NiBr_2.NH_3$, $NiBr_2$, and NH_4Br, are present.

16. The solubility product for $MgCO_3 \cdot 3H_2O$ in water at 25° is 1.1×10^{-5}, and the solubility of CO_2 in water at 25° and 1 atm. is 0.034*m*. When equilibrium is established between $MgCO_3 \cdot 3H_2O(s)$ and water over which a partial pressure of CO_2 of 0.05 atm. is *maintained*, the molality of $Mg(HCO_3)_2$ is 0.049. (*a*) Calculate the equilibrium constant K_c from the solubility data without allowance for activity coefficients. (*b*) Calculate the solubility when the equilibrium pressure of CO_2 is 0.01 atm. (The measured solubility at this pressure is 0.027.) (*c*) Calculate the equilibrium constant K_a in terms of activities, using the solubility product above as an activity product and using K_1 and K_2 from Table 63. (*d*) What activity coefficient is required to calculate the correct solubility from K_a when the equilibrium pressure of CO_2 is 0.05 atm.? (*e*) The measured solubility is 0.217*m* when the equilibrium pressure of CO_2 is 1 atm. Calculate this solubility from K_c without allowance for activity coefficients. Calculate the solubility again from K_a, taking 0.42 as the activity coefficient. [No measured activity coefficients for $Mg(HCO_3)_2$ are available; 0.46 is the activity coefficient for 0.2*m*. $Mg(NO_3)_2$ and 0.42 for 0.2*m*. $Ca(NO_3)_2$.]

17. (*a*) Calculate ΔH for the dissociation of $2NaHCO_3(s)$ from the dissociation pressures given on page 398, and compare the result with that of Problem 4, page 327. (*b*) Calculate the minimum quantity of $CO_2(g)$ that must be added to a 10-liter space at 100°C. containing 0.10 mole of $Na_2CO_3(s)$ and 0.20 mole of $H_2O(g)$ to convert the solid completely into $NaHCO_3(s)$. (*c*) A cylinder with a movable piston is charged with 0.10 mole $Na_2CO_3(s)$, 0.20 mole of $CO_2(g)$, and 0.20 mole of $H_2O(g)$ at 100°C. Calculate the total pressure and the quantities of $Na_2CO_3(s)$ and $NaHCO_3(s)$ present when the volume is 15, 10, and 5 liters. (It is not assured that both solids are present for every volume.) (*d*) In order to dry moist $NaHCO_3$ at 100°C. and 1 atm. total pressure, a mixture of $CO_2(g)$ and $H_2O(g)$ containing the minimum of water vapor necessary to prevent decomposition is passed over the moist $NaHCO_3$. How many moles of water vapor can be evaporated into each mole of this mixture without decomposing any $NaHCO_3$, the total pressure being kept at 1 atm.?

18. Plot the dissociation pressures of $Ag_2O(s)$, given on page 396 against the absolute temperature, and determine ΔH at 463°K. for the dissociation of $2Ag_2O$. (Reserve the plot for use in Problem 7, page 460.)

19. Determine the total pressure developed at equilibrium by the dissociation of HgO into a space containing oxygen at 0.10 atm. and 400°C. from the data on page 397.

20. When *dilute* HCl is saturated with solid CuCl at 25°C. the following data are obtained [Noyes and Chow, *J. Am. Chem. Soc.*, **40,** 739 (1918)]:

Total Cu	0.00596	0.0134	0.0198	atomic weights per liter
Total Cl	0.1038	0.2290	0.3364	atomic weights per liter

(*a*) Show that the formation of a complex, $CuCl_2^-$, explains this solubility of CuCl in HCl, and calculate the equilibrium constant $(CuCl_2^-)/(Cl^-)$ for 25°. (*b*) This equilibrium ratio is 0.0453 at 15°. Calculate ΔH for the equilibrium reaction, and state explicitly the change in state to which this

ΔH applies. (*c*) At higher HCl concentrations the data for 25°C are as follows:

Total Cu .	0.047	0.15	0.29	atomic weights per liter
Total Cl . . .	0.944	1.90	3.15	atomic weights per liter

These solutions precipitate cuprous chloride upon dilution with water Would the reaction assumed in part (*a*) account for the precipitation? Consider the possibility of a complex bivalent ion such as $CuCl_3^{--}$, and state any conclusion to be drawn

21. When 0.2*m* $SnCl_2$ is shaken to equilibrium at 25° with excess solid lead, lead chloride precipitates and the concentration of stannous ion becomes 0.0465 mole per liter (*a*) Calculate the composition of the equilibrium solution from the data of Table 73 (*b*) Calculate the solubility product K_c for lead chloride, and calculate from this the solubility of lead chloride in water. (*Ans.:* About 0.04*m*) (*c*) Calculate the composition of the equilibrium solution when 0.02*m*. $SnCl_2$ is shaken to equilibrium with excess solid lead.

22. For the reaction $NH_4HS(s) = NH_3(g) + H_2S(g)$, $\Delta H = 22{,}400$ cal. and $\Delta C_p = 0$. At 298°K the dissociation pressure of NH_4HS is 0.592 atm , and the vapor contains only $NH_3(g)$ and $H_2S(g)$ Calculate the equilibrium total pressure at 308°K. and the moles of solid NH_4HS formed when 0.60 mole of $H_2S(g)$ and 0.70 mole of $NH_3(g)$ are added to a vessel of 25.25 liters volume

23. The solubility product of PbI_2 is 9.5×10^{-9} at 25°, and the solubility product of $PbSO_4$ is 16×10^{-9} at 25° (*a*) What volume of 0.1*m*. K_2SO_4 is required for the complete conversion of 0.010 mole of $PbI_2(s)$ to $PbSO_4(s)$? (*b*) What volume of 0.1*m*. KI is required for the complete conversion of 0.010 mole of $PbSO_4(s)$ to $PbI_2(s)$?

24. The solubility of $AgIO_3$ in water at 25° is 0.000175, and its solubility in ammonia solutions is given in Table 70. Calculate K_c for the reaction $Ag(NH_3)_2^+ = Ag^+ + 2NH_3$

25. The equilibrium constant K_p (in atmospheres) for the reaction $C(s) + CO_2(g) = 2CO(g)$ changes with the Kelvin temperature as follows:

T	1123	1173	1223	1273	1323
K_p.	14.1	43.1	73.8	167	268

(*a*) Calculate ΔH for this reaction from a plot of log K against $1/T$ (*b*) In the calculation of Problem 15, page 328, the partial pressure of CO_2 was neglected Estimate this pressure, assuming equilibrium was attained in the reactor (*c*) Estimate the very small partial pressure of oxygen in the mixture in this problem from the data in Table 67. [Data from "International Critical Tables," Vol. VII, p. 243.]

CHAPTER XI

PHASE DIAGRAMS

In this chapter we are to consider another aspect of heterogeneous equilibrium, the change in the number and composition of phases at equilibrium with changing temperature or pressure or gross composition. The experimental facts are commonly shown by "phase diagrams" that cover variations in composition from 0 to 100 per cent of a given component. As a guiding principle we have Gibbs's "phase rule," which limits the number of phases in terms of allowable variations of pressure or temperature. Before discussing these topics, it will be convenient to define two or three new terms and to repeat the definitions of some other terms previously used.

A *system* is any combination of matter on which we choose to focus attention. For our own convenience we consider a restricted system and study the effect of varying one or another of the external conditions that govern its behavior; the container and any other objects in contact with the system are considered as "surroundings."

The *phases* of a system are its homogeneous parts, separated from one another by definite physical boundaries. A gas or a gaseous mixture is a single phase, as is a liquid solution or solid solution, but two mutually saturated liquid layers, such as ether and water, constitute two phases. Each pure crystalline substance is a separate phase, and a mixture of rhombic and monoclinic sulfur, for example, is two phases.

The *components* of a system are the chemical substances required to make each of its phases in whatever quantity they may be present. Thus one substance, water, is capable of forming all the phases of the water system; but if the system under consideration is a solution, water and the solute are its components. The number of components is defined as the smallest number of chemical substances required to form all the parts of the system in whatever proportion they may exist. For example, one system composed of calcium oxide, calcium carbonate, and carbon dioxide may be made from a single substance, calcium carbonate. But it is possible for these three phases to exist together when the amount of calcium oxide is not chemically equivalent to the carbon dioxide present. Since all three substances may be formed in any desired quantity from calcium oxide and carbon dioxide, these two substances may be called the components of the system. It would serve equally well to designate the components as calcium oxide and calcium carbonate, for by adding or removing these two substances any desired quantity of each phase could be brought into a system. The three-phase system $CaO(s)$, $CaCO_3(s)$, $CO_2(g)$ is thus a two-component system.

The *variance* of a system, also called the degree of freedom, is the number of intensive properties that can be altered independently and arbitrarily (within certain limits) without causing the disappearance of a phase or the appearance of a new phase. For example, in a one-component liquid system both temperature and pressure may be varied within limits without causing the appearance of solid or vapor, and hence the variance is 2. Since both these properties must be specified to define completely the state of the system the variance is also the number of intensive properties that must be specified to define the state of the system and to fix all its properties. In a two-phase one-component system, such as a pure liquid in equilibrium with its vapor, there is only one pressure for each temperature at which the two phases exist in equilibrium or one temperature for a specified pressure and thus the variance of the system is 1. The Clapeyron equation has been used to describe such systems many times in the preceding text. If three phases exist in a one-component system, neither temperature nor pressure may be varied without causing the disappearance of a phase, and the variance of the system is zero. If there are two components and only one phase, pressure, temperature, and composition may be varied, and the variance of the system is 3.

It will be true of every statement in this chapter, as it was of every statement in the two preceding chapters, that equilibrium is a necessary condition. In spite of the repeated use of the word equilibrium on almost every page, students sometimes fail to realize that systems are not necessarily at equilibrium when no reaction or change is evident and that equilibrium considerations do not apply to systems not yet at equilibrium. None of the common metals is in equilibrium with air, and yet they exist in contact with air for years without any evident change; the calculated dissociation pressure of potassium chlorate exceeds any attainable pressure of oxygen, and yet it does not dissociate at an observable rate; sodium bicarbonate is not in equilibrium with dry air, but it does not decompose under ordinary storage for long periods of time. None of these systems is at equilibrium, and accordingly none of the statements in this chapter would apply until true equilibrium is established.

Gibbs's Phase Rule.[1]—If the number of phases in a system is denoted by P, the number of components by C, and the variance by V, Gibbs's phase rule is expressed by the equation

$$P + V = C + 2$$

This is a law limiting the number of phases that may exist together at equilibrium in a system. It tells nothing as to *what* phases exist, but only the maximum *number* that may exist under specified conditions. Moreover, it is not concerned with the relative proportions of the phases; it relates only to intensive properties of the phases. The three-phase two-component system consisting of $CaO(s)$, $CO_2(g)$, and $CaCO_3(s)$ would have one degree of freedom, *i.e.*, one may specify the pressure (say, 1 atm.) but not the temperature at which these three phases exist under this pressure. If we specify 1 atm. pressure and 800°C., the phase rule says that two phases may exist, but it does not say which phases. The data on page 395 show that these phases may not be $CaO(s)$ and $CO_2(g)$, but the phase rule is not capable of furnishing this information; it shows only that *some* two phases may exist. Actually $CaCO_3(s)$ and $CO_2(g)$ or $CaCO_3(s)$ and $CaO(s)$ may exist together at 800° and 1 atm., but all three phases exist at 800° only when the pressure of CO_2 is 0.220 atm. It should be further noted that the phase rule gives only the maximum number of phases permitted but does not forbid a smaller number. For example, under 1 atm. pressure at 800° the system might be $CaCO_3(s)$ alone. If all three

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[1] For a full discussion of this equation see Alexander Findlay, "The Phase Rule and Its Applications," 1927; Marsh, "Principles of Phase Diagrams," McGraw-Hill Book Company, Inc., New York, 1935.

phases exist at equilibrium at 800° and 0.220 atm., the addition of further quantities of solid CaO would change the composition of the system as a whole but would not change the composition or any intensive property of any phase; hence, this is still the same system to the phase rule.

Phase Diagrams.—The quantitative relations in heterogeneous systems at equilibrium are frequently shown in the form of phase diagrams in which (for plane diagrams) some two variables which are of interest are plotted while the others are kept constant. For systems of one component the common forms are *p-v* isotherms (Fig. 10) and *p-t* diagrams (Figs 47, 48); for two-component systems the usual variables are temperature-composition at constant pressure (Figs. 31 and 34, and most of those in this chapter) or pressure-composition at constant temperature (Fig. 28)

Solid models are, of course, required to show *p-v-T* relations in a one-component system, and they are also used to describe temperature-composition equilibrium in systems of three components. Perspective drawings of such models are difficult to draw and to study except for the simplest systems. In this brief treatment we shall not have space in which to consider either the models or drawings of them, notwithstanding their great practical importance. We turn first to pressure-temperature diagrams for one-component systems and then to temperature-composition diagrams for two-component systems at atmospheric pressure.

SYSTEMS OF ONE COMPONENT

Pressure-temperature Diagrams.—Many pure substances have two or more crystalline phases of different form (crystal habit), solubility, and other physical properties. When these solids have transition temperatures at which phase changes occur reversibly among them or to liquid or vapor, the equilibrium conditions may be shown on diagrams. Substances (such as phosphorus) that do not have reversible transitions but do form different solid phases are called monotropic; those in which transitions are reversible (tin and sulfur, for example) are called enantiotropic. For substances of the latter class we may draw diagrams showing the temperature and pressure corresponding to the stable existence of single phases, pairs of phases, and triple points.

Any single phase in a system composed of only one chemical substance may exist throughout a certain temperature range and under a variety of pressures; two phases coexist at a certain definite pressure for each temperature and cannot exist at any other pressure at this temperature; when three phases are present at equilibrium in a system of one chemical substance, neither the temperature nor the pressure can be varied. For example, liquid water may exist under any pressure greater than its vapor pressure and at any temperature above the freezing point and below the boiling point corresponding to the pressure imposed, but liquid water and water vapor exist together at any chosen temperature only under the vapor pressure. If at 100° the external pressure is maintained at less than 1 atm., no liquid water condenses; if the pressure is made greater than 1 atm., all the vapor condenses. Only when the pressure is exactly 1 atm. can both liquid water and water vapor exist at 100°. Under these conditions, however, the two phases can exist at equilibrium in any relative quantities whatever—a drop of liquid in contact with a large volume of vapor, or a single bubble of vapor in equilibrium with a large quantity of liquid.

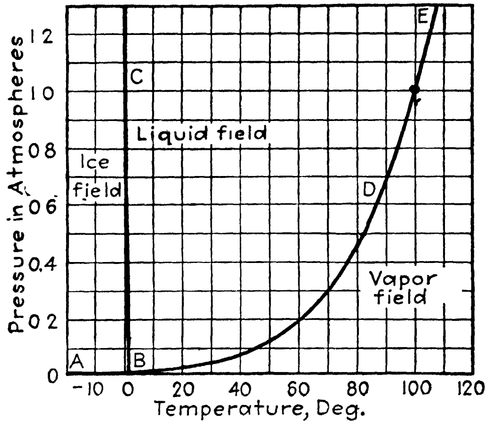

FIG 47 —Phase diagram for water.

Only at the triple point and under the vapor pressure of ice can all three phases exist. Thus the presence of three phases in a system of one component fixes both the temperature and the pressure, and this is an *invariant* system. A two-phase system of one component may exist at one particular pressure for each temperature or at one particular temperature for each chosen pressure. Since one condition (pressure or temperature) of such a system may be arbitrarily varied, it is a *univariant* system.

A simple diagram describing the phases of water is shown in Fig. 47. The line *BDE* is a vapor-pressure line, *i.e.*, a line showing the pressure at which liquid and vapor exist at equilibrium for each temperature. It is a line on which a monovariant system prevails, a line whose slope is shown by the equation

$$\frac{dp}{dT} = \frac{\Delta H}{T\,\Delta v}$$

which applies to any monovariant system. The diagram shows that the vapor pressure of water at 60° is 0.196 atm.; accordingly if water at 60° is acted upon by a greater pressure, all of it remains as liquid; if the pressure is reduced below 0.196 atm , liquid vaporizes until the equilibrium pressure is reached or until all the liquid is evaporated. At a lower pressure than 0.196 atm. the system composed of water at 60° consists of vapor only. Hence the line *BDE* is a two-phase line, defining the pressure at which two phases coexist for each temperature on the diagram.

The temperature at which ice and water saturated with air exist in equilibrium under a pressure of 1 atm. is defined as 0° on the centigrade scale; but since the vapor pressure of ice at 0° is only 0.006 atm., this is not the temperature at which all three phases exist. As calculated on page 148, the melting point of ice is lowered 0.0075° for each atmosphere increase of pressure; hence, at 0.006 atm. the equilibrium temperature is raised +0.0075°, and after allowing for a further temperature rise of 0.0023° due to the removal of air as a solute +0.0098° is the three-phase temperature or triple-point temperature. The pressure at the triple point is 0.006 atm., which is the vapor pressure of both ice and water at 0.0098°, since they are in equilibrium with each other at this temperature. The slight effect of pressure upon the melting point of ice is shown by the slope of the line *BC* of Fig. 47 to the left. This effect becomes large for very high pressures as may be seen from the data in Problem 23, page 462.

A consideration of the phases of urethane ($CO.NH_2OC_2H_5$) will further illustrate phase diagrams for a system of one component.[1] It forms a vapor, a liquid, and three different solid phases, which we may designate by I, II, and III. As urethane boils at 180°, the vapor field would occupy only a very small area at the bottom of the diagram, corresponding to vapor pressures of less than 1 atm. for the temperature range shown. The position of this vapor field is indicated in Fig. 48, showing the pressures and temperatures at which each of the other phases exists.

Between 52° and 70° equilibrium between liquid and solid I is shown by the line *ab*. It will be noted that this line slopes in the opposite direction to the liquid-solid line for water, indicating that an increase of pressure raises the melting point. As increase of pressure at constant temperature always results in the formation of a more dense substance, solid I is more dense than liquid and will sink in it. At 70° and 2200 atm. (*b*) there is a change in the character of the solid phase, and during transition from I to II there are three phases present. This is an invariant point, and neither temperature nor pressure can change until some

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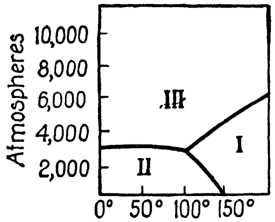
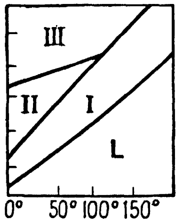
[1] Bridgman, *Proc. Am. Acad. Arts Sci.*, **52,** 57 (1916); *Proc Nat. Acad. Sci.*, **1,** 513 (1915) The following diagrams show the phases for three other systems of one component Recent work in this field is summarized in *ibid.*, **23,** 202 (1937) About 150 substances have been examined, of which nearly half have shown unmistakable evidence of polymorphism at high pressures. The distribution given by Dr. Bridgman is as follows:

Number of solid phases	1	2	3	4	5	6	7	8
Number of examples	80	45	13	7	0	3	1	0

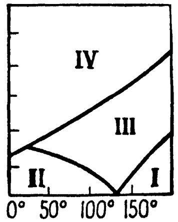
Experimental technique for pressures of 50,000 atm. is described in *Phys. Rev.*, **48,** 893 (1935). Data for 35 new polymorphic solids and negative results on about 60 others are given in *Proc. Am. Acad. Arts Sci.*, **72,** 45 (1937). Means of attaining pressures of 425,000 atm. are described by Bridgman in *J Applied Phys.*, **12,** 461 (1941).



· Silver Iodide



Carbon Tetrachloride



Potassium Nitrate

phase disappears. Which one will be exhausted first depends on the conditions of experiment. If heat is added to the system, and such a pressure is maintained that liquid is always present, phase I disappears, and the equilibrium between II and liquid is shown by the line *bc*. The point *c* corresponds to another triple point involving the liquid phase; point *d* is the triple point of all three solids.

Suppose a quantity of urethane to be kept at 60° while (through the steady motion of a piston in a cylinder) its volume is slowly decreased. As the melting point is 52°, the system consists of a liquid at the start—a one-phase, one-component system that may exist under various temperatures and pressures, but we have fixed arbitrarily upon a temperature of 60°. The system remains liquid as the volume decreases until a pressure of about 900 atm. is reached at a point on the line *ab*. Here phase I appears; and until all the liquid is changed to I, we have a two-phase system at a fixed temperature. Hence the pressure will remain constant while the volume decreases to that of the solid alone. As heat is evolved during the solidification, it must be removed from the system in order to keep it at 60°. Finally, all the liquid changes to solid I, and a further movement by the piston causes an increase of pressure in the system. When a pressure of 2500 atm. is reached (line *bd*), I changes to II at a constant temperature and pressure, with a further decrease in volume. Then II is compressed until the pressure reaches about 3800 atm. (line *dc*), where it changes to III. Further

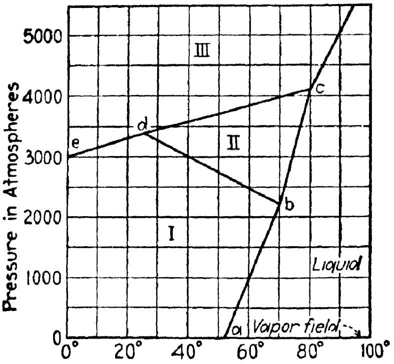


FIG. 48.—Phase diagram for urethane.

decrease in volume does not cause the appearance of any new phases.

Multiple solid phases at high pressures, as well as at 1 atm. pressure, are formed by many substances. Problems 20, 23, and 24 at the end of this chapter are illustrations, and many others are known.

Heat Effects of Phase Changes.—The Clapeyron equation may be used to calculate the heat absorbed during any of these phase changes, since all of them are in monovariant systems, when Δv and the change of transition pressure with temperature are known. If Δv is the increase in volume attending transition of a gram of substance from one phase to another at the temperature T and if dp/dT is the change in transition pressure in atmospheres per degree, ΔH will be in milliliter-atmospheres absorbed per gram. Calories may be converted to these units by multiplying by 41.3.

SYSTEMS OF TWO COMPONENTS[1]

Temperature-composition Diagrams.—Equilibrium in systems of two components is most commonly shown on diagrams in which the temperature is plotted against the composition of the whole system (gross composition) while the pressure is kept constant (usually at 1 atm.). Although these are sometimes inaptly called "phase-rule diagrams," they furnish quantitative information as to how the compositions and quantities of the phases in a system at equilibrium change with the temperature and composition of the system as a whole. The phase rule cannot furnish such information. In the diagrams that we now consider, the abscissas show the composition of the *whole system* and the ordinates show temperature changes at a constant pressure of 1 atm. A vertical line in such a diagram shows the composition of a phase that is unchanging as the temperature changes. Horizontal lines show a constant equilibrium temperature with changing gross composition, and since for the main-

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[1] Phase diagrams for metallic systems of two components are given by M Hansen in "Aufbau der Zweistofflegierungen," 1936, in which some hundreds of systems are described See also "International Critical Tables," Vol. II, pp. 400–455. Silicate systems are described by Hall and Insley in *J. Am. Ceram. Soc.*, **16**, 463 (1933), **21**, 113–156 (1938); other inorganic systems are given in "International Critical Tables," Vol. IV, pp. 77*ff*.

tenance of a constant temperature in a two-component system at a fixed pressure the phase rule allows only three phases, these lines show three-phase equilibriums. The compositions of two of these phases are shown by the ends of the horizontal line, and that of the third phase by an intermediate point where some other line joins the horizontal line.

System: Cadmium and Bismuth.—The simplest systems of two components are illustrated by two substances that mix in all proportions in the liquid state and that do not form compounds or crystals other than those of the two pure components. Mixtures of cadmium and bismuth satisfy these conditions and will be considered first. Cadmium melts at 323°, and a solution containing increasing quantities of bismuth begins to deposit solid cadmium at lower and lower temperatures, as shown in Fig. 49, in which equilibrium temperature is plotted against the gross composition of the system. The left-hand portion of this figure shows the depression of the freezing point of the metallic solution, or the temperature at which solutions of increasing bismuth content are in equilibrium with crystalline cadmium. Bismuth melts at 273°, and equilibrium between solid bismuth and a liquid mixture of bismuth and cadmium comes at lower temperatures as the percentage of cadmium increases. Obviously any liquid mixture of these metals in any proportion becomes solid at a sufficiently low temperature. The two "freezing-point curves" intersect at this minimum temperature, shown at c on the diagram. A liquid mixture containing 60 per cent of bismuth deposits neither solid until 140°, but at this temperature it deposits both solids at once. The field above

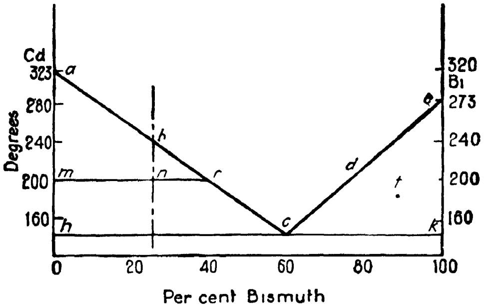

FIG 49.—Phase diagram for bismuth and cadmium.

abcde is the "liquid field"; systems of any composition consist of one liquid phase at all points above this line and below the boiling points of the solutions for a pressure of 1 atm.

Let us study the behavior of a solution containing 25 per cent of bismuth when it is cooled from 400° to 100° The path of this process is indicated by the dot-and-dash line on Fig. 49. The system under a pressure of 1 atm consists of liquid until about 240° (point *b* on the figure); at this temperature solid cadmium begins to separate from the melt. The composition *of the system* remains constant, but a new phase appears whose composition is shown by the left-hand margin (*i.e.*, pure cadmium); and owing to the separation of cadmium from the melt the percentage of bismuth in the liquid increases. At 200° considerable cadmium will have separated out, and the liquid is about 40 per cent bismuth.

If heat has been withdrawn from the system at a uniform rate of so many calories per minute, the fall of temperature will take place more slowly after reaching *b*, owing to the "latent" heat evolved when cadmium solidifies. As the cooling proceeds, more solid cadmium separates, and the composition of the liquid is shown for each temperature by the line *bc*, until at 140° the liquid is saturated with both metals Upon further cooling, both metals solidify from the liquid, and the temperature remains constant during the cooling until all the liquid phase disappears. It should be noted that a system may evolve heat at a constant temperature if a source of heat exists within it; for cooling consists in taking away heat, and this may not cause a change in temperature in all systems.

Let us return to a consideration of the system at 200°, which is at the point *n* in the field *ahc*. The system contains 25 per cent of bismuth, and 75 per cent of cadmium; but one phase of the system is pure cadmium; hence the other phase must be poorer than the system as a whole in this component. There is another fact to be derived from the dimensions of the diagram, namely, that the relative quantities of solid cadmium and of solution at 200° are to each other as the lengths *nr* and *nm*.

The proof of this relation is as follows: Let *w* be the weight of the system that at 200° consists of solid cadmium and *s* grams of a solution of composition *r*. Note that *hk* corresponds to 100 per cent and that *mn*/*hk* is the fraction of bismuth in the whole system. The weight of the bismuth in the system is $w(mn/hk)$ Since only solid cadmium has separated, all the bismuth is still in the liquid, and s grams of the liquid contains $s(mr/hk)$ grams of bismuth. On equating these two expressions for the weight of bismuth, we get

$$w\frac{mn}{hk} = s\frac{mr}{hk} \qquad \text{whence} \qquad w:s = mr:mn \qquad \text{or} \qquad s = \frac{mn}{mr}w$$

The weight of solid cadmium that has separated from solution must be $w - s$, and this is equivalent to $w(nr/mr)$.

At b in Fig. 49 the length corresponding to nr is zero, which means that no solid cadmium has yet separated; at 150° the length nr is longer in proportion to that of nm, corresponding to a further separation of solid cadmium at the lower temperature For all temperatures and gross compositions shown by the field ahc of Fig. 49, the phases at equilibrium are solid cadmium and liquid solution. Horizontal lines drawn across a two-phase field are called "tie lines," and the ends of a tie line show the compositions of the phases in equilibrium at the temperature for which it is drawn and for all gross compositions on the tie line. For illustration, a tie line through the point t in Fig. 49 shows that at 180° solid bismuth is in equilibrium with a liquid containing 70 per cent bismuth. Since the qualitative significance of all the tie lines in any one two-phase field is the same, we may mark each field to show what phases are at equilibrium in it. In Fig. 49 the area above $abcde$ is the liquid field, ahc shows equilibrium between cadmium and liquid, cke shows equilibrium between bismuth and liquid, and the area below hck that between the two solid phases.

On the line hck three phases exist in equilibrium, solid cadmium, solid bismuth, and a liquid of composition c. When heat is withdrawn from such a system, the temperature, the composition of the system, and the composition of any phase do not change; hence, neither a phase diagram nor the phase rule can show the relative quantities of the three phases present at equilibrium. It should be noted that this line hck is not a tie line in a two-phase field but a three-phase line. The compositions of two of these three phases are shown by the ends of the line, and that of the liquid is shown by the point c; but the relative quantities of the phases present in systems of gross compositions shown on the line are not given by the lengths of any lines on the diagram.

This diagram is typical of two-component systems if the substances mix in all proportions in the liquid state, and provided that they do not form any crystalline phases other than the two pure components; it is the simplest type of such diagrams. Other examples of mixtures with the same type of phase diagrams are shown in Fig. 50.

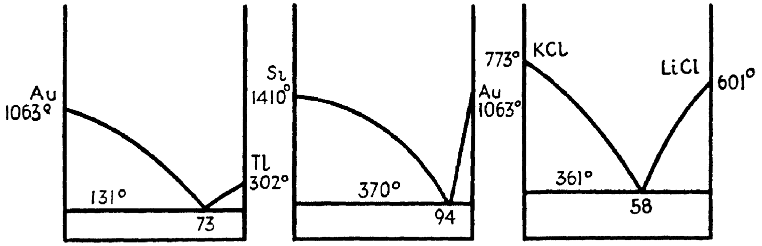

FIG. 50.—Phase diagrams of simple two-component systems

The Eutectic Mixture.—A mixture of two solids such as that which separates from the bismuth-cadmium system at 140° is usually referred to as "the eutectic," but it should be clearly understood that it is a mixture of two separate phases. There is no such thing as the "eutectic phase." When a liquid is cooled, the component that first separates usually appears in larger crystals than those forming at the eutectic temperature. Both solid phases separate at this temperature in an intimate mixture that is of finer grains (smaller crystals) than the crystals of the single component already separated, but this mixture may be seen under a microscope to consist of separate crystals of each substance. The phases of the eutectic are those indicated by the two intersecting curves. The eutectic mixture is that intimate mixture of two solid phases separating at the constant temperature which marks the lower limit for the existence of liquid.

Cooling Curves.—If the temperature of a system that is evolving heat at a uniform rate is measured at suitable intervals and a diagram is drawn showing these temperatures against time as abscissas, abrupt changes in slope will indicate the processes occurring during cooling. A group of such curves for a series of mixtures of cadmium and bismuth is shown in Fig. 51.

In cooling a mixture containing 15 per cent of bismuth from 400° to 270°, there is no process occurring in the system that evolves heat except loss of heat from the liquid phase. At 270° solid cadmium begins to separate, giving rise to more heat, and hence the rate at which the temperature falls is slower, though heat is being withdrawn from the system at a constant rate. There will, therefore, be a break in the slope of the curve at this point (1 in Fig. 51). At 140°, where both solids are separating, since this is a three-phase condition in a two-component system under a specified pressure, the temperature remains constant (2, 3), even though heat is being taken from the system. The fourth curve of Fig. 51 is a cooling curve for a solution of 60 per cent bismuth, which deposits both solids at 140°; the next one is a cooling curve for a solution containing 75 per cent of bismuth. At the point 12 (190°) solid bismuth begins to separate, and the composition of the melt changes along the line *edc* of Fig. 49 as the temperature falls; at point 10 (140°) both solids separate, as in cooling the other solutions. For pure bismuth all the solid deposits at the melting point, 273°.

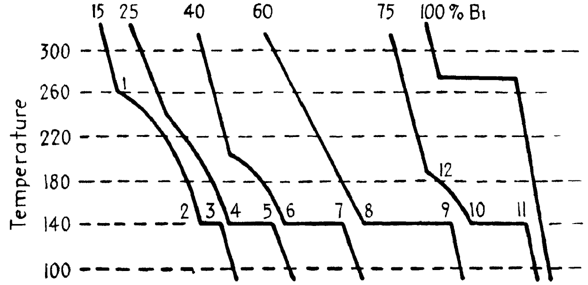

Fig. 51.—Cooling curves for mixtures of cadmium and bismuth.

Thermal Analysis.—In a piece of apparatus in which a constant rate of heat loss can be maintained, the time interval during which eutectic mixture is separating is proportional to the weight of the solids formed. In other words, the quantities of eutectic mixtures are proportional to the lengths of the horizontal portions of curves like those in Fig. 51. If these portions of curves for the rate of cooling of a fixed quantity of the various mixtures—such as (2, 3), (4, 5), and (6, 7) of the curves of Fig. 51—are plotted vertically against the composition of the system as a whole, a triangle is obtained, as shown in Fig. 52, in which 8, 9 of

Fig. 51 is the altitude. From this plot it is possible to make a rough analysis of an unknown mixture of the two components by determining the length of time required to solidify all its eutectic in the standard apparatus. Knowing the weight of system taken, we may estimate from the weight of eutectic the percentage of each component. It is necessary to determine in some other way whether the given sample lies on the right-hand or left-hand side of the eutectic, but this is usually known. The chief uses of such diagrams are in locating the liquid composition at the eutectic temperature and in showing the compositions of the solid phases separating when they are not the pure crystalline components.

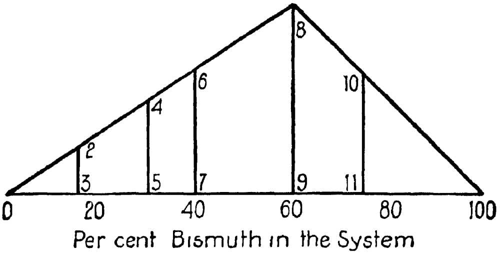

Fig. 52.—Eutectic pauses in cooling curves

Quenching Method.—The cooling-curve method has been successfully applied to metal systems and to mixtures of crystalline salts It has not proved to be a useful means of studying silicate systems, such as ceramic materials and other refractories, partly because of the high viscosity of the liquids, with a resultant undercooling and delayed crystallization, and partly because the energy changes attending the chemical reactions involved are not large in comparison with radiation losses from these systems at high temperatures. Such systems are usually studied by a "quenching method." This method consists in heating a finely ground charge or mixture of the appropriate solids until equilibrium is reached at the desired temperature, after which it is dropped from the furnace into cold mercury. In this manner the system is "frozen" in the condition at which it was in equilibrium in the furnace, and a microscopic examination of the quenched material shows what phases were present at this temperature. If it is found that the system contains more than one crystalline phase, new charges of identical composition are heated to higher temperatures, quenched, and examined until one is found that contains only one crystalline phase, this being the primary solid phase characteristic of that part of the system. The process is continued until a temperature is found at which the primary solid phase disappears from the quenched mixture and leaves only liquid (glass at room temperature). This temperature and the composition locate a point on the liquid-solid curve of the system.

The quenching method is also applicable to metal systems provided that quenching is carried out so rapidly as to "freeze" the equilibrium. It involves the preparation of many charges in order to determine the equilibrium points for one composition, and is more laborious than the cooling-curve method, but it furnishes much information not to be had from cooling curves.

Two-component Systems in Which a Compound Forms.—If the two components of a system mix in all proportions in the liquid state but form a solid compound, a diagram of somewhat different character shows the phase equilibrium. Each component dissolves in the compound to lower its freezing point, and the compound dissolves in each pure component to lower its freezing point. The phase diagram for such a system may be constructed from breaks in the cooling curves, of the kind described in Table 74. Magnesium melts at 651° and calcium at 810°. It will be seen that a compound is formed which contains 55 per cent calcium by weight, or 55/40 = 1.38 atomic weights of calcium to 45/24.3 = 1.85 of magnesium, that is, Ca_3Mg_4, and that it melts at 721°. Further, the eutectic formed of pure magnesium and compound solidifies at 514°, and that composed of compound and calcium solidifies at 466°. The new diagram will consist of two portions, each similar to Fig. 49. The composition of the second eutectic is shown by the 79 per

TABLE 74 —SYSTEM MAGNESIUM AND CALCIUM

Weight percentage of calcium in system	10	20	30	45	55	65	79	90
First break in cooling curve	600°	525°	620°	700°	721°	650°	466°	720°
Horizontal portion of cooling curve.........	514°	514°	514°	514°	721°	466°	466°	466°

cent solution solidifying all at one temperature; that of the other eutectic is not given but may be obtained as shown below. Inserting the known points on a diagram and connecting with lines, we obtain the diagram of Fig. 53; and, by extending the freezing curves smoothly, the first eutectic is seen to contain about 19 per cent of calcium. The left-hand 55 per cent of this diagram corresponds to the two-component system magnesium + Ca_3Mg_4; the right-hand 45 per cent, to a system Ca_3Mg_4 + calcium; but it is convenient to cover the whole range of composition on a single sketch. Each portion of this diagram may be treated exactly as was Fig. 49. The relative weights of compound and liquid melt, in a system consisting of 50 per cent by weight of calcium at 600°, are to each other as the lengths *nr* and *mn* on this diagram. When the cooling of a system containing 70 per cent of calcium is carried out as indicated on Fig. 53 by the dot-and-dash line, compound separates from the melt at 590° and the melt changes composition during cooling as shown by the line *cd* until 466° is reached, where both compound and pure calcium separate at a constant temperature until all the liquid phase is exhausted.

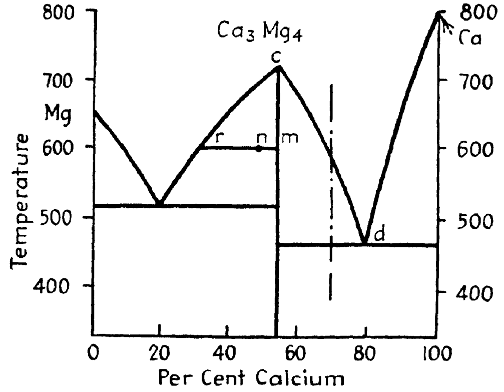

FIG. 53 —Phase diagram for calcium and magnesium.

Systems which form a compound have, in general, this type of diagram when the solid phases are those indicated, but before applying these considerations to a given system it is first necessary to ascertain that the solid phases are the pure components or are compounds formed from them. As in the case of chemical reactions involving solutions and solids, the equilibrium conditions cannot be represented quantitatively on a diagram unless the chemical composition of each phase is known.

Two other metallic systems in which stable compounds form are shown in Fig. 54. Other systems in which this occurs are Te + Bi, Al_2O_3 + TiO_2, and TlCl + $BaCl_2$; H_2O + SO_3 form five compounds, as do CCl_4 and Cl_2. It should be noted with respect to Fig. 54 that because of the scale of the drawing no triangular area for equilibrium between bismuth and liquid or between sodium and liquid appears. Nevertheless, such areas must exist. Note that the melting point of sodium is 97°, that the eutectic temperature is given as 95°, and that the first horizontal line on the Bi-Mg diagram is 2° below the melting point of pure bismuth.

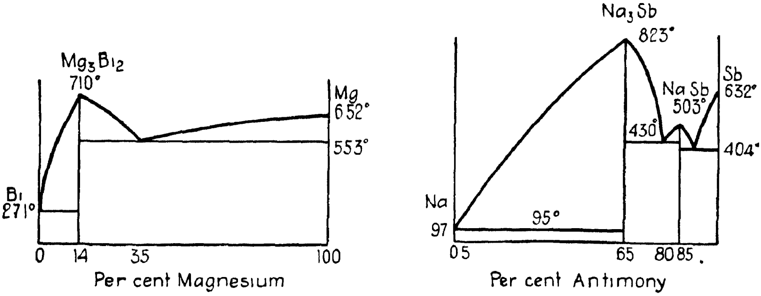

FIG 54 —Compound formation in metallic systems

Peritectics ("Concealed Maxima").—Numerous examples are known in which a compound does not melt upon being heated but decomposes reversibly into a new solid phase and a liquid phase saturated with respect to both solids. So far as phase equilibrium is concerned, this condition is the same as that at a eutectic point, but the term eutectic is restricted to the equilibrium temperature below which no liquid phase exists; and we shall see presently that liquid does exist below the decomposition temperature in certain ranges of gross composition.

For example, the compound Na_2K, which contains 46 per cent potassium, decomposes reversibly at 7° into solid sodium and a liquid containing 56 per cent potassium. While this decomposition is going on there are three phases at equilibrium in a system of two components at a specified pressure of 1 atm., which requires a constant temperature. Hence continued heating causes all the compound to decompose at 7°, after which the temperature rises and equilibrium prevails between solid sodium and a solution of varying composition, as shown by the line *ab* of Fig 55 The various areas below *abcd* correspond to equilibrium between different pairs of phases that may be identified by drawing horizontal tie lines and by considering the gross compositions, as in the diagram for cadmium and bismuth.

If the lines *bc* and *ef* of Fig. 55 are projected until they intersect, an imaginary melting point for Na_2K is indicated, and thus what might have been a melting point is "concealed" by the phase field *ajb* in which equilibrium prevails between solid sodium and a liquid. For this reason such a decomposition is sometimes called a "concealed maximum." No *equilibrium* relation is really concealed, and this "melting point" is not observed when equilibrium prevails in the system. The term peritectic is more suitable for this equilibrium; 7° is called the "peritectic temperature," and the process observed when Na_2K is heated at 7° is called peritectic decomposition. The line *jeb* indicates that at 7° and for gross compositions up to 56 per cent potassium, three phases may be at equilibrium. As usual, the compositions of two of the phases are shown by the ends of the line and that of the third phase by the point at which *ef* meets this line.

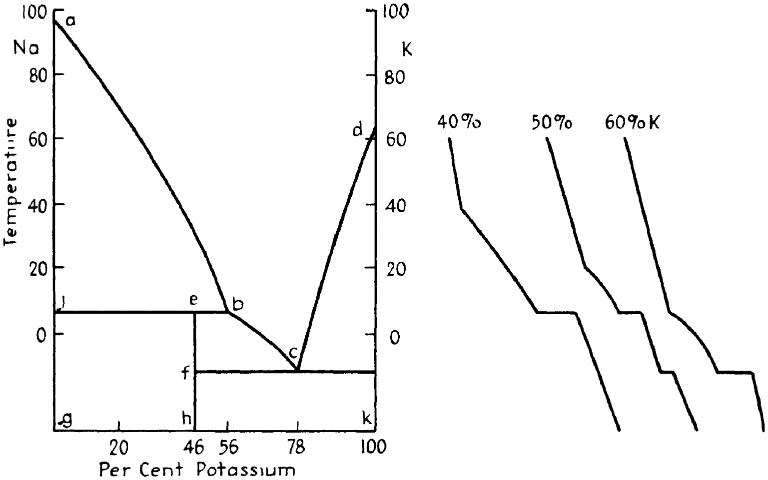

Fig 55—Phase diagram and cooling curves for sodium and potassium.

Careful attention should be given the cooling curves at the right of this figure. A system containing 40 per cent potassium deposits pure sodium between 40° and 7°, and at 7° a liquid of composition *b* reacts with solid sodium, producing the compound Na_2K until all the liquid is exhausted. Since this compound contains 46 per cent of potassium and the system as a whole has 40 per cent of this element, it is clear that excess solid sodium remains. This describes the significance of the phase area *gjeh*, in which solid sodium and solid compound Na_2K exist When any system of gross composition between 46 and 56 per cent potassium is cooled, it deposits solid sodium until 7° is reached, and at this peritectic temperature solid sodium reacts

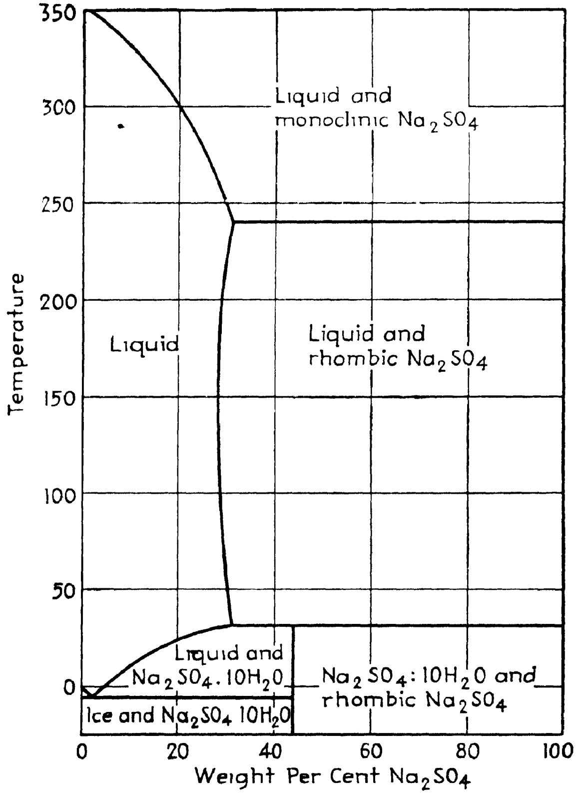

FIG. 56—Phase diagram for sodium sulfate and water.

with liquid to form solid Na_2K until the solid sodium is exhausted. Since the system contains more potassium than does the compound Na_2K, some liquid remains, and this two-phase system upon cooling deposits more Na_2K, while the liquid composition changes along the line *bc* until −12° is reached. At this eutectic temperature the liquid deposits solid potassium and Na_2K until the liquid is exhausted. The cooling curve marked 50 per cent in Fig. 55 applies to such a process.

Peritectics occur in many other systems, ferrous and nonferrous alloys, inorganic salts, silicate systems, organic mixtures, and salt hydrates. The phase diagram for Na_2SO_4 and water is shown in Fig. 56, in which the lines on the right-hand side of the liquid field are the solubility curves for the various solid forms.[1] The decahydrate $Na_2SO_4.10H_2O$ decomposes peritectically at 32.383° into rhombic anhydrous Na_2SO_4 and a liquid containing about 32 per cent Na_2SO_4. The solubility of this anhydrous form decreases slightly with increasing temperature and goes through a minimum of solubility at 120°, after which the solubility increases slightly with temperature up to 241°C. At this temperature Na_2SO_4 undergoes another phase transition to monoclinic crystals of the same composition, and the slope of the solubility curve changes abruptly. The solubility at this temperature is 32 per cent by weight, and it decreases to 2.4 per cent at 350°C. It will be understood, of course, that at these temperatures the pressure is not 1 atm., but a sufficient pressure to prevent boiling of the solution, namely, about 100 atm. at 310° and over 150 atm. at 350°. While solubilities change slightly with pressure, no correction for these changes has been applied to the data we are using.

The decomposition at 32.383° absorbs about 20,000 cal.; of course, this quantity of heat is evolved by the reverse change. Since this temperature has been well established,[2] lies within ordinary temperature range, occurs in a chemical system that is readily available in a high state of purity, and is independent of

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[1] Solubilities below 150°C. are from *ibid.*, Vol IV, p. 236, those above 150°C. are from Schroeder, Berk, and Partridge, *J. Am Chem Soc.*, **59,** 1790 (1937).

[2] Richards and Wells, *Proc. Am Acad Arts Sci.*, **38,** 431 (1903). For the peritectic temperatures of other salt hydrate transitions see Richards and Yngve, *J. Am. Chem. Soc.*, **40,** 89 (1918).

changes in atmospheric pressure, it is an accepted secondary standard on the thermometric scale.

Many other salt hydrates show similar behavior. Those of disodium hydrogen phosphate are $Na_2HPO_4.12H_2O$ (stable from $-2°$ to $+36°$), $Na_2HPO_4.7H_2O$ (stable from 36° to 48°), and $Na_2HPO_4.2H_2O$ (stable from 48° to 95°). A plot of solubility against temperature shows abrupt changes in slope at 36°, 48°, and 95°, as would be true of any substance when there was a change in the character or composition of the solid phase in equilibrium with the solution. This system has three peritectic transitions, and other systems also contain more than one. For example, in the Au-Pb, Al-Co, and Ce-Fe systems two peritectic transitions occur, as well as in many others. Two more illustrations are given in Problems 25 and 26 at the end of this chapter.

Solid Solutions.—By analogy to liquid solutions, in which one substance (a solute) is molecularly dispersed in another (a solvent) to form a homogeneous liquid phase (a solution) of variable composition, a crystalline phase of variable composition in which molecules or atoms of one component are molecularly dispersed in the other is called a solid solution or a crystalline solution. Such a crystal is not a chemical compound, since a substance is considered to be a compound only when it has a constant composition. Solid solutions are not heterogeneous mixtures of the crystals of two substances, and the term "mixed crystals" that is sometimes used for solid solutions is an unfortunate one in that it implies such a mixture. A solid solution is a *single crystalline phase* in which the composition may vary over a certain range when the substances have limited solubilities or over the whole range from one pure substance to the other when the solubilities are not limited. Intermetallic solid solutions are somewhat better known than those involving inorganic compounds or organic compounds, though the latter types of solid solution are not uncommon.

For illustration, when a liquid mixture of 30 per cent copper and 70 per cent nickel is cooled so slowly that equilibrium is established, the composition of *every crystal* in the crystalline phase is 30 per cent copper. If another liquid containing 29 per cent copper is cooled slowly, *every crystal* in the solid phase contains 29 per cent copper. In the system Ni + Cu the atoms of nickel in the crystal space-lattice are replaceable by copper to any extent, and a complete "series" of solutions ranging from pure copper to pure nickel is formed.

In the formation of metallic solid solutions over any considerable range of composition the governing quantities appear to be (1) the relative radii of the atoms, (2) the amount of distortion that the crystal lattice can tolerate, and (3) the electronic structure of the atoms. Solid solubilities are usually very small unless the radii of the atoms are within 14 or 15 per cent of one another. Although this requirement seems to be of the greatest importance, it must not be inferred that meeting it is alone sufficient to produce unlimited solubility of one metal in the crystals of another metal. For example, silver and copper both have face-centered lattices, and their "atomic radii" are 1.44×10^{-8} and $1\ 28 \times 10^{-8}$ cm , respectively, which differ by 12 5 per cent of the smaller radius. They do not form a continuous series of solid solutions, as may be seen from Fig. 58. Bismuth (1.82) and antimony (1.61) have atomic radii that differ by 12 per cent of the smaller quantity, and they form a complete series of solid solutions as shown in Fig 57.

Some metals are able to enter to a limited extent the crystal structure of others having a different structure. For example, cobalt has a face-centered structure, which means a coordination number of 12, with an atomic radius of $1\ 26 \times 10^{-8}$; molybdenum has a body-centered structure, which means a coordination number of 8, with an atomic radius of 1.40×10^{-8}; but these metals form solid solutions of 0 to 29 per cent molybdenum. In these crystals of varying composition molybdenum has 12 neighbors when it replaces cobalt; it thus accepts a different coordination number in these solutions from the one in its own pure crystals up to the limit of 29 per cent molybdenum. Beyond this composition the system has other characteristics, to which we shall return a little later, and the series is "interrupted" at this point.

We have considered here only "primary" solid solutions, those in which substitution of one atom for another in the space-lattice takes place. The more restricted interstitial solid solutions are formed when the solute element is so small that it fits into the spaces between those of the solvent. Only hydrogen, boron, carbon, and nitrogen form important interstitial solid solutions in metallic solvents, and we shall not have space to discuss them.[1]

Primary solid solutions do not form or at least are not likely to form when there is a marked tendency to form stable compounds. Thus elements which are strongly electropositive tend to form compounds with those which are strongly electronegative, even when the size factor is favorable for solid solutions. Elements in columns of the periodic table that are far apart usually tend to form compounds rather than solid solutions, but there are exceptions; and, of course, metallic elements in the same column of the periodic table may form compounds rather than solid solutions. This is true of sodium and potassium, in which the size factor is unfavorable even though both elements have body-centered lattices, and of calcium (face-centered) and magnesium (body-centered). An illustration of near neighbors forming a complete series of solid solutions is antimony and bismuth, which do so over the whole range of composition.[2]

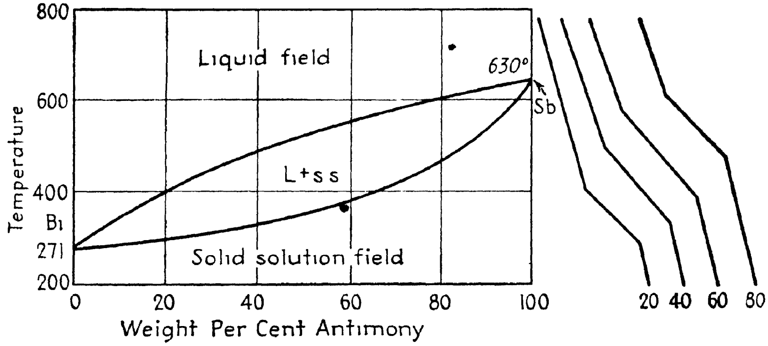

FIG. 57—Phase diagram and cooling curves for bismuth and antimony.

The equilibrium in bismuth-antimony systems is shown in Fig. 57, of which the upper field shows liquid composition as

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[1] See William Hume-Rothery, "The Structure of Metals and Alloys," Part IV, which is No. 1 of the Institute of Metals Monograph and Report Series; 1936. He discusses the factors that determine solid solubilities of both kinds.

[2] Other substances forming complete series of solid solutions are Au + Pt, Al_2O_3 + Cr_2O_3, ThO_2 + ZrO_2, MgO + NiO, C_6H_6 + C_4H_4S, $SnBr_4$ + SnI_4, Cu + Mn, and Cu + Au. In the last two systems a minimum occurs similar to the minimum boiling system of Fig 34.

usual and the lower field shows crystalline solutions of varying composition from pure bismuth to pure antimony. This is a one-phase area in which the gross composition is the composition of every crystal. Within the area bounded by the two curved lines, two solutions exist at equilibrium, one of which is crystalline. A system of 60 per cent antimony at 500° consists of a liquid phase containing 43 per cent antimony and a crystalline solution of 86 per cent antimony. When this system is cooled to 400°, the phases at equilibrium contain 20 and 70 per cent antimony, and the crystals deposited at higher temperature (and therefore richer in antimony when deposited) have now changed to crystals of 70 per cent antimony. This change in composition probably takes place by diffusion in the crystalline phase, rather than the re-solution into the liquid, and adequate time for this adjustment must be allowed if equilibrium is to be attained. When cooling is too rapid, the solid is not homogeneous and the condition of equilibrium is not reached.

Liquids of other compositions show the same behavior. Some typical cooling curves are shown in Fig. 57. It should be noted that these curves have no horizontal portions, for this would require three phases to maintain a constant temperature, and the solid solution is a single phase. No more than two phases exist at equilibrium in this system at any temperature or gross composition.

Figures 31 and 34 in Chap. VI are also phase diagrams for constant pressure, with two-phase equilibrium shown in the area bounded by the liquid-composition and the vapor-composition lines and one phase in all other portions of the diagram. Cooling curves for these systems would be similar to those in Fig. 57. Minimum melting solid solutions with phase diagrams similar in appearance to Fig. 34 are known; for example, chromium and cobalt, nickel and manganese, arsenic and antimony, copper and gold form systems in which a liquid phase exists below the melting point of the lower melting component and in which complete series of solid solutions form. Solid solutions over the whole range of composition are also formed by metallic oxides, by silicates, by other inorganic components, and by organic compounds, sometimes with minimum melting, and occasionally with maximum melting systems. The phase equilibrium has the same general character in all of these systems.

Solid Solutions of Incomplete Solubility.—Copper and silver form solid solutions in one another to a limited extent only, yielding the phase diagram of Fig. 58. At the eutectic temperature in this system the crystalline phases contain 9 and 92 per cent copper by weight; and when a system of gross composition between these limits is cooled, these mutually saturated solid solutions separate from a liquid containing 28.5 per cent copper at 779°. The areas at the right and left of the diagram, marked with the Greek letters α and β, are one-phase areas in which systems of varying composition consist of a single solid solution; the area below the horizontal line is marked $\alpha + \beta$ to indicate two saturated solid solutions. Crystalline silver does not exist in equilibrium with any liquid phase other than pure liquid silver, and at 960°. A liquid containing 5 per cent copper has a cooling curve of the same type as those in Fig. 57, with no horizontal portion; and this system in equilibrium at 700° consists of a single solid phase, with 5 per cent of copper and 95 per cent of silver in every crystal.

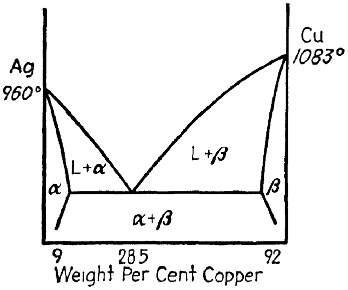

FIG. 58 —Phase diagram for copper and silver

The slanting lines separating the α field and the β field from the $\alpha + \beta$ field indicate decreasing solid solubilities as the temperature falls. In most phase diagrams where such lines are vertical, the inference to be drawn is that the solubilities have not been determined below the eutectic temperature, rather than that they are constant. This is true of the vertical lines bounding the solid-solution areas in Fig. 59, which indicate only that two phases exist in the area below the horizontal line at the eutectic. Their omission from the diagram would indicate falsely a single phase in this area at lower temperatures, whereas there are two phases at all points within it.

The cooling curves for systems containing between 9 and 92 per cent copper would be similar to those shown in Fig. 51. Application of the method illustrated in Fig. 52, in which the length of eutectic pause is plotted against the gross composition of the system, yields a triangle whose base shows the compositions of the saturated solid solutions at the eutectic temperature.

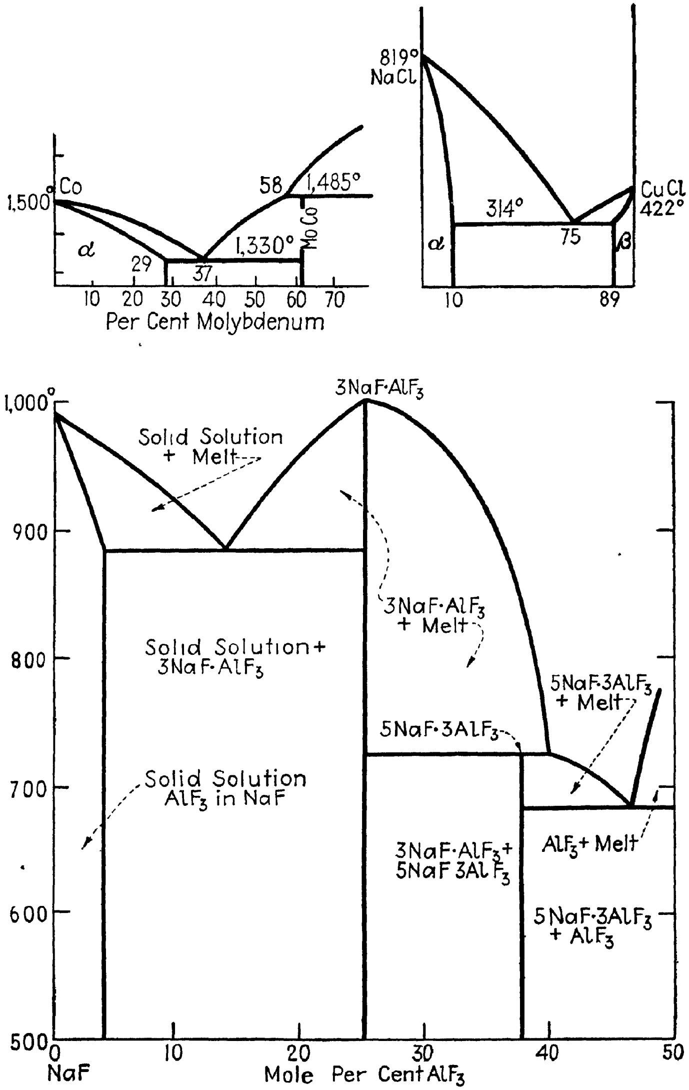

FIG. 59.—Phase diagrams showing solid solutions of limited solubility.

Solid solutions of limited solubility also form between compounds as components, sometimes only on one side of the diagram, sometimes on both sides. A few illustrations are shown in Fig. 59, a few more are described in the problems at the end of the chapter, and hundreds of others are known.

Partially Soluble Liquids.—Many pairs of liquids, such as ether and water, aniline and hexane, aluminum and chromium, lead and zinc, SO_2 and $TiBr_4$, have mutual solubilities that are limited at certain temperatures and that increase as the temperature rises. These systems form two liquid layers when the components are mixed in proportions lying between the mutual solubilities. In these systems complete solubility is usually attainable at sufficiently high temperatures, though this may not occur below the boiling point for 1 atm. pressure. For example, phenol and water at 25° form two layers containing 8 and 72 per cent phenol by weight, respectively, when mixed in proportions lying between these figures; as the temperature rises, each solubility increases; thus at 50° the layers contain 11 and 62 per cent phenol, and solubility in all proportions prevails above 66.8°. The layers in a mixture of aniline and water at 0° contain 3.3 and 95.6 per cent of aniline, respectively, at equilibrium; at 100° these solubilities are 7.2 and 89 7 per cent, and complete solubility is attained at 167° with the application of sufficient pressure to prevent the formation of vapor.

Bismuth and zinc are completely soluble in one another above 825° and have limited solubilities below 825° as shown in Fig. 60, in which tie lines drawn in the dome-shaped area show these solubilities. The horizontal line at 416° shows three phases at equilibrium, solid zinc and two liquid layers containing 15 and 98 per cent zinc, respectively. The behavior of a system containing 25 per cent zinc when cooled from 900° to 200° will serve to describe the phase diagram. Such a system consists of a single layer at temperatures above 600°; at this temperature a second layer forms, containing at first 90 per cent zinc, and as the temperature falls the equilibrium compositions of the two liquid layers change along the right and left portions of the line defining the two-liquid zone. At 416° crystalline zinc deposits; and since the system then contains three phases at a fixed pressure, the temperature remains constant while heat is withdrawn from the system until the zinc-rich liquid is exhausted. As zinc deposits, the bismuth in this liquid passes to the other liquid with enough zinc to keep its composition 15 per cent zinc. When one liquid phase is exhausted, further removal of heat causes the temperature to fall and zinc to deposit while the liquid composition changes from 15 toward 2.7 per cent zinc. At 254°, which is the eutectic temperature, bismuth and zinc crystallize from the liquid until it is exhausted, and cooling causes the formation of no new phases. A liquid containing less than 15 per cent zinc does not separate into two liquids at any temperature; upon cooling, it deposits zinc first if its composition is between 2.7 and 15 per cent, and it deposits bismuth first if it contains less than 2 7 per cent zinc; finally, it deposits both metals at 254°. The phase equilibrium diagrams for any of the other systems described in the preceding paragraph are of the same character.

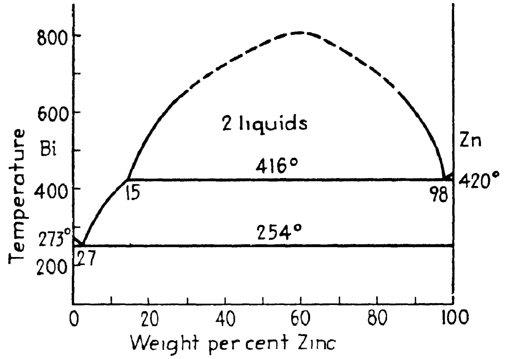

FIG. 60.—Phase diagram for bismuth and zinc.

SYSTEMS OF THREE COMPONENTS

Three substances may form three systems of two components each; and if, for the simplest illustration, we choose three substances of complete solubility in one another, which form no compounds and no solid solutions, the three two-component systems may be represented by three diagrams similar to Fig. 49. These are shown[1] side by side at the top of Fig. 61 for biphenyl (abbreviated BP), bibenzyl (BB), and naphthalene (N) and are called edge sections.

(A much clearer understanding of the discussion that follows may be obtained by making a copy of the upper part of Fig. 61

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[1] LEE and WARNER, *J Am Chem. Soc.*, **57**, 318 (1935).

on stiff paper 7½ in. across, so that each of the two-component diagrams is 2½ in. at the base, cutting it out along the upper lines which show the liquid-solid equilibrium, folding it into a triangular prism, and standing this up on the lower part of Fig. 61.)

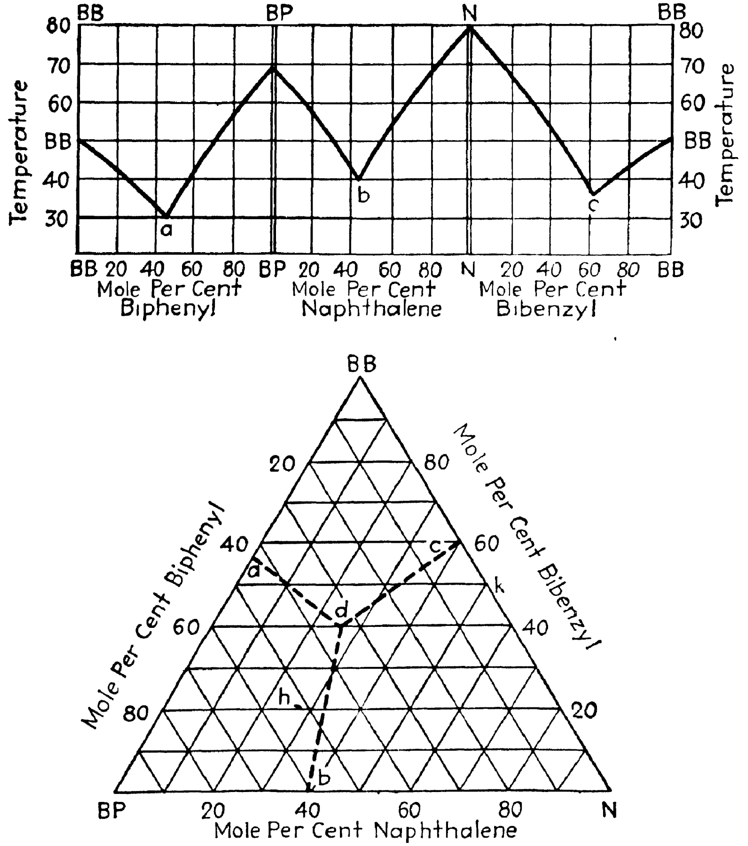

FIG. 61.—Edge sections and composition triangle for the three-component system. biphenyl-naphthalene-bibenzyl

When all three substances are present in a single system, the compositions of mixtures are shown in a triangular plot such as that at the bottom of Fig. 61 and temperature is plotted vertically. A solid figure results, of which the base is the composition plot and the three side elevations, or edge sections, are shown at the top. The eutectic for BP and BB is marked *a*, that for

BP and N is *b*, and that for N and BB is *c*. A system of three components under 1 atm. pressure is univariant when a liquid and two solid phases are present Thus a line *ad* begins at point *a* (29.6°, 44 3 mole per cent BP), showing the changing composition of liquid in equilibrium with two solids, BP and BB, as their mole fractions are decreased by the addition of N. It will be seen that, while *a* is the eutectic point in a two-component system, equilibrium along the *ad* line has not the properties of the eutectic The addition of N introduces a new component, and another degree of freedom. As the addition of N continues, point *d* is approached. This point is the common intersection of three 3-phase lines *ad*, *bd*, and *cd*, and it is the ternary eutectic At *d* (17 4°, 33 8 mole per cent BP, 39 2 mole per cent BB, and 27 mole per cent N) three pure solid substances are in equilibrium with a liquid under a fixed pressure, and the phase rule shows that this is an invariant point As heat is withdrawn, all three components solidify as pure crystalline phases at a constant temperature.

In the triangular figure, all compositions within the area BP*bda* will deposit BP as the first solid when cooled; those in the area N*cdb* will deposit N first; and those in the area BB*cda* will deposit BB first. Which solid will deposit next will depend on the composition For example, a mixture of 20 mole per cent N, 20 mole per cent BB, and 60 mole per cent BP (point *h* in Fig. 61) will first deposit solid BP at about 57°; but as BP deposits, the ratio of BB to N remains unity, and the liquid composition will change along a straight line drawn from *h* toward *k*. Such a line will intersect the *bd* line at about 40 mole per cent BP, 30 mole per cent N; and, on further cooling, *both* these components will separate as solid phases while the liquid composition changes along *bd* to *d*, the ternary eutectic.

The student should draw a cooling curve for the process just described, as a study exercise to clarify the phase equilibriums involved.

In the system described, the components are chemically similar, and the laws of ideal solutions apply closely. For example, the calculated eutectic temperature *a* for BB and BP is 29.3°, and the experimental temperature is 29.6°.

Similar phase diagrams describe the three-component mixtures of metals lead, cadmium, and tin and mixtures of the salts

$LiNO_3$, $NaNO_3$, and KNO_3. But such ideal simplicity is rare. Most mixtures of three components exhibit one or several of the features for two components described earlier in this chapter. They may form binary or ternary compounds; these compounds may melt without decomposition or decompose at peritectic temperatures; they may form two liquid phases of variable solubility; the components or their compounds may form solid solutions of partial solubility; they may do all these things in a single system.

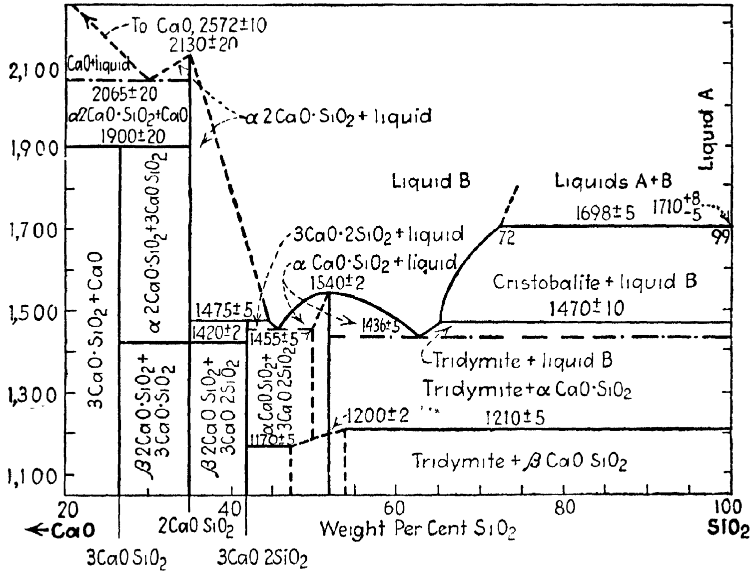

FIG 62—Phase diagram for calcium oxide and silica

Thus the investigation of three-component systems may well be a very complex problem. From the CaO-SiO_2 edge section of the three-component system CaO-SiO_2-Al_2O_3 shown in Fig. 62 it will be evident this system is a complex one.[1] Yet a full understanding of this system is essential for much work in ceramics, for example, the manufacture of portland cement, and it has been completely worked out experimentally through

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[1] See "International Critical Tables," Vol. IV, p. 93, for this and similar diagrams. Three-component metallic systems are given in Vol II, diagrams for ceramic materials are collected in *J. Am. Ceram. Soc*, **16,** 463 (1933).

thousands of quenching experiments. Many of the three-component metallic systems have also been studied experimentally, but their consideration is beyond the scope of this text.[1]

Diagrams Involving Several Phases.—The various phenomena that apply to phase equilibriums have now been described and illustrated with data for systems involving each feature separately. More complex systems involving several of these features at the same time are frequently met in the study of metallography or of ceramic materials, but the interpretation of these more complicated diagrams does not involve any new principles. Thus, mixtures of calcium oxide and silica are described by the phase diagram of Fig. 62, with one peritectic, two compounds that melt without decomposition, and two liquid phases. As a study exercise the student should draw carefully to scale a set of idealized cooling curves that will describe the whole system shown in Fig. 62, with intervals of 5 per cent or less between curves. Note that any phase which separates on cooling evolves heat as it separates and that the longest interval of constant temperature for any three-phase equilibrium corresponds to the largest quantities of new phases being formed at that temperature. (Refer if necessary to the preceding pages describing the separate occurrences.)

Problems

For the systems described in Problems 1 to 18 draw phase diagrams reasonably to scale, letter all the phase fields to show what phases are at equilibrium within them, and draw a sufficient number of typical cooling curves on the same temperature scale to correspond with all the important characteristics of each system Choose reasonable points when data are lacking, but do not include any features not required by the data. The centigrade melting points of the elements involved in these problems are:

Aluminum	658°	Copper	1083°	Palladium	1555°
Antimony	630°	Iron	1535°	Silver	960°
Bismuth	273°	Lead	327°	Sodium	98°
Calcium	810°	Manganese	1260°	Thallium	303°
Cerium	775°	Magnesium	651°	Tin	232°
Cesium	26°	Mercury	−39°	Zinc	420°
Chromium	1615°	Molybdenum	2535°		
Cobalt	1480°	Nickel	1452°		

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[1] See MARSH, *op. cit.*

1. Mercury and lead dissolve in all proportions in the liquid state, and they form no compounds. A liquid phase is in equilibrium at −40° with two crystalline phases, containing 35 and 100 per cent Hg, respectively

2. Iron and Fe_3Sb_2 (m.p 1015°) form solid solutions in one another to a limited extent, and $FeSb_2$ decomposes at 728° into a liquid and the other compound. The eutectics are at 1000° and 628°

3. Na_3Bi melts at 775°, and NaBi decomposes at 446° into Na_3Bi and a liquid. The eutectic temperatures are 97° and 218°

4. Al_2O_3 (m p 2050°) and SiO_2 (m p 1710°) form a compound $3Al_2O_3$-$2SiO_2$ known as mullite, which decomposes at 1810° into Al_2O_3 and a liquid phase containing about 40 per cent SiO_2 The eutectic is at 1545° and 93 per cent SiO_2

5. Lead and palladium form four compounds, $PdPb_2$ (m p 454°), PdPb (decomposes at 495° into a liquid and Pd_2Pb), Pd_2Pb (decomposes at 830° into a liquid and Pd_3Pb), and Pd_3Pb (m p 1240°) Solid solutions from 77 to 100 per cent Pd are formed, but there is only one liquid solution. The eutectic temperatures are 260°, 450°, and 1185°

6. CoSb melts at 1190°, $CoSb_2$ decomposes at 900° into CoSb and a liquid containing 91 per cent Sb. There are eutectics at 1090° and 40 per cent Sb and at 620° and 99 per cent Sb, and a solid-solution area exists up to 12 per cent Sb

7. Silver oxide has the dissociation pressures given on page 396.

8. Aluminum and cobalt form three compounds, of which AlCo melts at 1630°, Al_5CO_2 decomposes at 1170°, and Al_4Co decomposes at 945°. AlCo and Co form an incomplete series of solid solutions, with α of 84 per cent Co, liquid of 89 per cent Co, and β of 92 per cent Co in equilibrium at 1375°.

9. Magnesium and nickel form a compound $MgNi_2$ that melts at 1145° and a compound Mg_2Ni that decomposes at 770° into a liquid containing 50 per cent Ni and the other compound The eutectics are at 23 per cent Ni and 510° and at 89 per cent Ni and 1080°

10. Bismuth and lead form no compounds, solid solutions containing 1 and 63 per cent lead are in equilibrium with a liquid containing 43 per cent lead at 125°

11. Calcium and sodium mix in all proportions in the liquid state above 1150°, the mutual solubilities are 33 per cent Na and 82 per cent Na at 1000°, liquids of 14 and 93 per cent Na are in equilibrium with solid calcium at 710°, the eutectic temperature is 97.5°, and no compounds or solid solutions form.

12. Al_3Ca decomposes at 700° into Al_2Ca and a liquid containing 14 per cent Ca; Al_2Ca melts at 1079°. The eutectics are at 616° and 7 per cent Ca and at 545° and 73 per cent Ca.

13. Liquid and solid phases of the composition Hg_5Tl_2 are in equilibrium at 14°; the phases at 0° are a liquid of 40 per cent Tl and solid solutions of 32 and 84 per cent Tl; the phases at −59° are Hg, a liquid of 8 per cent Tl, and a solution of 22 per cent Tl.

14. Cerium and iron form two compounds, of which $CeFe_2$ decomposes at 773° into Ce_2Fe_5 and a liquid containing 91 per cent Ce and Ce_2Fe_5

decomposes at 1094° into a liquid containing 65 per cent Ce and a solid solution containing 15 per cent Ce

15. SbCr melts at 1110°, a compound Sb_2Cr decomposes at 675° into a liquid and the other compound The eutectic temperatures are 620° and 1100°, and at the latter temperature the crystalline phases are solid solutions containing 32 and 88 per cent Cr.

16. Nickel and molybdenum form one compound, MoNi, which decomposes at 1345° into molybdenum and a liquid containing 53 per cent Mo. The phases at the only eutectic (1300°) are MoNi, a liquid of 49 per cent Mo, and a solid solution of 32 per cent Mo.

17. Copper and cerium form four compounds, $CeCu_5$ (m p 940°), $CeCu_4$ (which decomposes at 780° into $CeCu_5$ and a liquid containing 42 per cent Ce), $CeCu_2$ (m p 820°) and CeCu (which decomposes at 515° into $CeCu_2$ and a liquid containing 79 per cent Ce). The eutectic points are at 16 per cent Ce and 880°, 45 per cent Ce and 760°, and 85 per cent Ce and 415°. There is but one liquid solution, and no solid solution.

18. $MgZn_2$ melts at 590°, and there are four temperatures in the Mg-Zn system at which three phases exist, with percentages of zinc as follows:

340°	α (8 per cent) + liquid (53 per cent) + MgZn
354°	liquid (55 per cent) + MgZn + $MgZn_2$
380°	liquid (96 per cent) + $MgZn_2$ + $MgZn_5$
364°	liquid (97 per cent) + $MgZn_5$ + Zn

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19. (*a*) Describe in detail, by reference to Fig 48, what would happen if urethane at 35° and 5000 atm were allowed to expand slowly while the temperature remained constant (*b*) Do the same for a temperature of 100°C. (*c*) Draw diagrams showing the change of volume with change of pressure for the compression of urethane at 20°, 30°, 60°, and 70°.

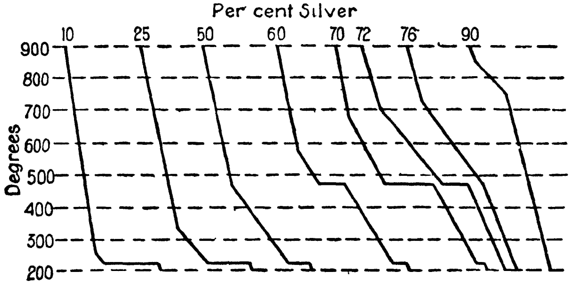
20. Potassium acid sulfate ($KHSO_4$) forms four solid phases, and the triple points are as follows·

I–II–IV	199°	1830 atm
II–III–IV	118°	2900 atm

Phase III is stable at room temperatures and pressures, and it changes to IV at about 48° and 6000 atm. The transition points under 1 atm are 164° and 180°, and phases I and IV are in equilibrium at 220° and 2500 atm. (*a*) On a diagram covering the range 40° to 350° and 0 to 6000 atm , draw lines representing the equilibrium between the solid phases, and letter each field to show what phase is stable within it. (*b*) The melting point is 210°, and the solid sinks in the liquid. Draw a short line (0 to 200 atm , say) showing the equilibrium between liquid and solid, and show by the slope of this line whether the melting point is raised or lowered with increase of pressure. (*c*) Tell in detail all that would happen if $KHSO_4$ were heated very slowly from 40° to 260° under a pressure of 2500 atm., but do not draw any conclusions that are not justified by the data given in the problem.

21. Phenol (m p 42°) and water dissolve in one another in all proportions at temperatures above 67° but are only partly soluble below this temperature. At 50° the liquid phases contain 11 and 62 weight per cent phenol, at 5° they contain 7 and 75 weight per cent, and at 1.3° there are two liquid phases containing 6.8 and 76 per cent phenol in equilibrium with solid phenol. Ice and solid phenol are in equilibrium with a solution containing 5.8 per cent phenol at −1.3°. (*a*) Draw a temperature-composition diagram for this system. (*b*) What would happen at 50° if successive small portions of phenol were added to water until the system was 99 per cent phenol? (*c*) Draw cooling curves for systems containing 6, 10, 60, and 80 per cent phenol, covering 70° to −10°. [CAMPBELL and CAMPBELL, *J. Am. Chem. Soc.*, **59**, 2481 (1937).]

22. The cooling curves below are for mixtures of silver and tin containing the indicated percentages of silver. Construct the phase diagram, and letter each field to show what phases exist within it.



23. The phase equilibrium for water involves a liquid and six solid phases for pressures up to 45,000 atm. Denoting the liquid by L and the solids by I, II, III, V, VI, and VII (no phase designated IV has been obtained), the triple points in the system are at the following temperatures and pressures:

I–III–L	−22°	2,045 atm.
I–II–III	−34.7°	2,100 atm.
III–V–L	−17°	3,420 atm.
II–III–V	−24.3°	3,400 atm.
V–VI–L	+0.16°	6,175 atm.
VI–VII–L	+81.6°	22,400 atm.

The pressures and temperatures of some two-phase equilibriums in this system are as follows:

I–II	−75°	1,800 atm.
II–V	−32°	4,000 atm.
V–VI	−20°	6,360 atm.
VI–VII	−80°	20,000 atm.
VII–L	+149°	32,000 atm.

(*a*) Draw a phase diagram for this system in the range −80° to +160° and 1 to 45,000 atm., and letter the phase fields. (*b*) Which of the crystalline forms will float in the liquid? [Data from Bridgman, *Proc. Am. Acad.*, **47**, 440 (1912), and *J. Chem. Phys.*, **5**, 964 (1937); the diagram for deuterium oxide ("heavy water") is given in *ibid*, **3**, 597 (1935).]

24. Carbon tetrabromide forms three solid phases. II changes to I at 50° and 1 atm.; I melts at 92° with an increase in volume; the liquid boils at 190°. The triple point for I, II, and III is at 115° and 1000 atm, and there are two phases at 2000 atm and 135° and at 2000 atm. and 200°. (*a*) Draw the phase diagram, and letter its phase fields. (*b*) Draw a curve showing how pressure changes with volume at 120° for a pressure increase from 1 atm. to 2000 atm.

25. Zinc nitrate forms hydrated crystals containing 9, 6, 4, 2, and $1H_2O$. The solubility, in grams of $Zn(NO_3)_2$ per 100 grams of solution, and the composition of the solid phase change with the temperature as follows:

% $Zn(NO_3)_2$	Temp.	Solid phase	% $Zn(NO_3)_2$	Temp.	Solid phase	% $Zn(NO_3)_2$	Temp.	Solid phase
30.0	−16.0	Ice	66.2	34.6	VI-IV	81.6	50.6	II
39.6	−29.5	Ice-IX	67.9	40.0	IV	84.0	55.4	II
40.1	−25.0	IX	70.0	43.2	IV	86.3	52.1	II-I
42.0	−20.0	IX	72.5	44.7	IV	87.6	59.2	I
44.6	−18.0	VI	77.2	39.7	IV	90.0	70.7	I
48.6	0	VI	78.0	37.2	IV-II			
63.4	36.1	VI	79.7	43.6	II			

Draw a phase diagram for this system, and indicate the phases at equilibrium in each phase area. [The data are from Wiss. *Abh. Phys.-Tech. Reichsanstalt*, **3**, 348 (1900), and *J. Am. Chem. Soc.*, **55**, 4827 (1933).]

26. Two substances, *M* (= $MnSO_4$, mol wt 151) and *W* (= H_2O), form one liquid phase and three stable compounds MW_7, MW_5, and MW. The equilibrium between liquid and solid phases is as follows:

Temperature	Per cent *M* by weight in liquid	Solid phase or phases
−10.5°	32.2	$MW_7 + W$
0°	34.8	MW_7
9°	37.0	$MW_7 + MW_5$
20°	38.5	MW_5
27°	39.5	$MW_5 + MW$
40°	38.3	MW
70°	33.3	MW
100°	26.5	MW

Draw a phase diagram for this system, covering −20° to 100°, letter all the phase fields, and draw cooling curves for systems containing 35, 38, 50, 60, and 70 per cent *M*.

27. Draw diagrams similar to Fig. 52, which apply to the eutectic pauses in the systems shown in Figs. 53, 56, and 58.

CHAPTER XII

KINETICS OF HOMOGENEOUS REACTIONS

This chapter presents the experimentally determined rates at which some chemical reactions in gases or in solutions proceed isothermally toward equilibrium, the effect of temperature upon these rates, and some simple equations that are in approximate agreement with the experiments. Although the rates of hundreds of reactions have been studied, interpretation of the data is often complicated by side reactions, by reactions proceeding in steps of different velocities, by mechanisms other than those indicated from the chemical equation expressing the initial and final states, by the influence of the walls of the container upon reactions involving only dilute gases as initial and final substances, and by many other factors that are not understood. Reactions among gases or in solutions sometimes proceed very slowly, sometimes at measurable rates, sometimes so rapidly as to make their measurement difficult or impossible. Reactions involving only ions are usually too fast to be measured. Most reactions increase in speed with increasing temperature, though there are a few exceptional reactions that proceed more slowly at higher temperatures.

The fact that the theory of reaction rates is still incomplete is no indication of neglect of the field; it is an unavoidable consequence of the complexity of the rate processes. Reacting molecules must not only "collide"; they must collide with sufficient energy or be sufficiently "activated"; they must be properly "oriented"; they must satisfy other conditions. The resources of statistical mechanics, quantum mechanics, the kinetic theory, and careful experimental research have been employed by many capable investigators in an effort to develop an adequate theory. Much progress has already been made, but much remains to be done.[1] In this brief chapter we must be content with some

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[1] See GLASSTONE, LAIDLER, and EYRING, "The Theory of Rate Processes," McGraw-Hill Book Company, Inc., New York, 1941. The preface and introduction of this excellent text present the nature of the problem, discuss its difficulties, and outline current progress.

simple equations showing approximately the rates of reactions involving one, two, or three molecules when these proceed isothermally in one phase or when surface effects are relatively unimportant.

Although the rate of disappearance of reactants or the rate of formation of products may usually be formulated in terms of the concentrations or pressures of the reacting substances, as we shall do below, there are many puzzling facts about these rates. For example, the two chemical reactions

$$2NO + O_2 = 2NO_2$$
$$2CO + O_2 = 2CO_2$$

in the gaseous state each involve 2 moles of a lower oxide and 1 mole of oxygen, but it is not to be inferred from the similarity in the equations expressing the over-all effects of the reactions that the oxidations take place by molecular mechanisms which are the same for both or at comparable rates. If molecular collisions were the chief requirement for these reactions to proceed, they should have comparable rates at the same temperature. The experimental facts are that the oxidation of NO at ordinary temperature is very rapid and the oxidation of CO is immeasurably slow. Equilibrium requires substantially complete oxidation in both systems. Although both reactions probably require collisions among the molecules and in systems of comparable compositions at the same temperature the number of collisions would be approximately the same for both, the rates evidently depend to a governing extent upon other factors. Moreover, the rate of the faster reaction is extremely slow compared with that calculated for a gaseous system in which every collision causes a reaction. Thus, the number of collisions that are *effective* is very much smaller than, and must be clearly differentiated from, the *total* collisions. Later in the chapter we shall attempt an approximate estimate of this fraction in some simple systems

In the experiments discussed in this chapter it has been possible to determine the change of concentration with time for a reacting substance or a product of the reaction and then through stoichiometry to express the concentrations of all the reacting substances as functions of time. Interpretation of these concentrations in terms of the chemical reaction expressing the "over-all" change in state sometimes shows that the time reaction is not the same as the reaction showing the change in state but that some "intermediate" product forms slowly and decomposes rapidly or forms rapidly and decomposes slowly. We shall presume a mechanism for the time reaction that is in harmony with the observed rate, but it must not be forgotten that such a presumption may be wrong, even though probable in the light of *present* knowledge. Additional experiments upon a given system may require a revision of the interpretation placed upon the data now available.

The "Order" of a Reaction.—Aside from complicating *initial* conditions that are sometimes important and sometimes negligible, all reactions proceed at rates that decrease with time if the temperature is kept constant, and equations of different algebraic form apply to different types of reactions. The experiments determine concentrations or pressures at suitable time intervals. If the rate of a reaction is proportional to the first power of the concentration of some reacting substance, the reaction is said to be of the first order with respect to that substance. When the rate depends upon the first power of the concentration of two substances or upon the square of the concentration of one substance it is called a reaction of the second order. A reaction whose rate depended upon C_A and C_B^2 would be a third-order reaction with respect to both substances but could be considered a first-order reaction with respect to A alone or a second-order reaction with respect to B alone For example, if the initial concentration of B were very large compared with that of A, the concentration of B would remain almost constant, even though a large fraction of A had reacted, and the reaction rate would be proportional to the momentary concentration of A

As has been said before, the "order" of a reaction as measured by rate experiments may not be that expected from the chemical reaction describing the over-all change in state. There are also numerous observed reaction rates that do not conform to any simple order, possibly because reactions of different order or of different rates are proceeding consecutively, or for other reasons. It has been possible to isolate consecutive reactions in enough instances to show that this is one of the explanations. Other reasons include influence of the walls of the reaction container, self-catalysis by a reaction product, reverse reactions, simultaneous reactions, and factors not yet discovered.

Although it is not possible at present to predict the order of a reaction from the over-all change in state, it is conversely true that an experimental determination of the rate of a reaction often furnishes an important clue as to the mechanism by which the change in state occurs. Some examples will be given presently, and many more are known.[1]

Reactions involving more than one phase, such as those between gases or solutes reacting upon a solid surface and hence catalyzed by the surface, are more complicated than the rates of homogeneous reactions, and they require special methods of treatment[2] Many such reactions can be interpreted upon the assumption that one particular step in the process is so slow compared with the others that it governs the observed rate. This step might be (1) the rate of adsorption of the reactants or (2) the rate of desorption of a reaction product that covers the surface or (3) the rate of reaction upon the surface by molecules that adsorb and desorb rapidly. If (1) were the governing process, the reaction might well appear to be homogeneous; if (2) governed, the rate would be nearly independent of the concentrations or pressures of the reacting substances; if all three processes had comparable rates, no simple equation could express it. For example, the rate of reaction between CO and O_2 on a silver catalyst is independent of the pressure of CO_2, which indicates that the desorption rate is rapid by comparison with the rate-governing process; but the fact that the rate is independent of the oxygen pressure also when the ratio of CO to O_2 is high is more difficult to interpret simply.[3] Since glass may function as a catalyzer, it is sometimes necessary to vary the ratio of volume to surface exposed (for example, by "packing" the reaction vessel with broken glass of the same composition) in a series of experiments in order to demonstrate that the reaction is or is not homogeneous.

In the discussion that follows we shall write the *initial* concentration of a reacting substance as C_0, meaning the concentration for zero time, or its initial pressure as p_0. When equal volumes

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[1] See especially HAMMETT, "Physical Organic Chemistry," Chap. IV, McGraw-Hill Book Company, Inc., New York, 1940.

[2] See HINSHELWOOD, "Kinetics of Chemical Change," Chap. VIII, Oxford University Press, New York, 1940.

[3] BENTON and BELL, *J. Am. Chem. Soc*, **56**, 501 (1934).

of 0.10*m*. solutions of two reacting substances are mixed, C_0 will thus be 0.050 for both. The concentration at a time t will be written C, from which it will be evident that in any given experiment C_0 is a constant while C and t are variables. The *fraction reacted* at a given time is $(C_0 - C)/C_0$, which will be denoted by x. We define the *specific reaction rate* as the rate at an instant when the concentrations of all reacting substances are unity, and we denote it by k. For a constant temperature k will be constant; when the temperature changes, k will change, but this change may *not* be calculated from the thermochemical ΔH for the reaction.

Experimental Methods.—When there is a change in the number of molecules attending a homogeneous gaseous reaction, the change of pressure with time at constant volume and constant temperature may be used to follow the extent of a reaction. Similarly, if the color, conductance, optical rotation, acidity, or any quickly measurable property of the system changes as the reaction proceeds, this property may be used to follow the reaction. But it is not the pressure (or other property) that measures the extent of the reaction—it is the *change* of pressure (or other property) that does so. A few illustrations will make this clearer. Suppose the reaction to be a gaseous one in which one molecule yields three, A = 3B. If p_0 is the initial pressure of A, the final total pressure will be $3p_0$, and the total increase in pressure will be $2p_0$. At some time t the pressure is observed to be p, and the increase in pressure for this time is $\Delta p = p - p_0$, whence the fraction reacted is $x = \Delta p/2p_0$. The partial pressure of A is p_0 times the fraction *not* reacted, $p_0(1 - x)$, which is $p_0(2p_0 - \Delta p)/2p_0$, or $p_0 - \frac{1}{2}\Delta p$, and the partial pressure of B is $\frac{3}{2}\Delta p$.

Let α_0, α_t, and α_{end} represent the optical rotation of a reacting system at the start, after the time t, and at the end of the reaction. No one of these quantities measures the extent of the reaction, but $(\alpha_0 - \alpha_{\text{end}})$ measures the change in rotation for the completed reaction, and $(\alpha_0 - \alpha_t)$ measures the change in the time t, whence $x = (\alpha_0 - \alpha_t)/(\alpha_0 - \alpha_{\text{end}})$ gives the fraction changed at the time t.

If m is *any* measure of the concentration of a *reacting substance*, this quantity will be m_0 at the start, m_t at a later interval, and m_{end} when the reaction is completed, so that the fraction reacted is $(m_0 - m_t)/(m_0 - m_{\text{end}})$. Whenever the progress of a reaction is measured by the quantity of a *reaction product* formed, this measure will be zero at the start of the reaction, and m_t/m_{end} will give x, the fraction reacted.

Applying these relations to the decomposition A = 3B that was our first illustration, the partial pressure of A is its measure, namely, p_0 at the start, $(p_0 - \frac{1}{2}\,\Delta p)$ at t, and zero at the end. Then

$$\frac{p_0 - (p_0 - \frac{1}{2}\,\Delta p)}{p_0 - 0} = \frac{\Delta p}{2p_0} = x$$

In terms of the reaction product B, zero is its measure at the start, $\frac{3}{2}\,\Delta p$ is its measure at t, and $3p_0$ its measure at the end, whence $x = \frac{3}{2}\,\Delta p/3p_0 = \Delta p/2p_0$ as before.

The choice of a suitable measure is not always easy, however; for while the partial pressure of a gas above a solution measures its concentration in solution *at equilibrium*, equilibrium is not certainly attained quickly in a system in which a gas is increasing its concentration with time. The measured pressure on a gaseous system in which the pressure is changing must be measured by a device in which there is no time lag if it is to be an instantaneous pressure and therefore a definite quantity at a fixed time. When the concentration of a substance is determined by titration, the time consumed in the titration must not be long enough for the reaction to proceed appreciably while titration is in progress.

First-order Reactions.—A reaction whose rate is proportional to the first power of the concentration of one substance is a first-order reaction. A monomolecular reaction would be first order, but there are reactions that conform to the first-order equation in their rates and yet are not monomolecular. As the reaction proceeds, the concentration of the reacting substance decreases and the reaction proceeds more slowly, so that equilibrium is approached at a decreasing rate. For such reactions the rate at a constant temperature is given by the equation

$$-\frac{dC}{dt} = kC \tag{1}$$

Upon integrating this equation between concentration limits C_0 and C and time limits 0 and t we have

$$\ln \frac{C_0}{C} = kt \tag{2}$$

Since $(C_0 - C)/C_0$ is the *fraction* reacted, the equation in terms of this fraction is

$$\ln \frac{1}{1 - x} = kt \qquad \text{or} \qquad 2.3 \log \frac{1}{1 - x} = kt \tag{3}$$

It will be noted that equation (3) for the fraction reacting in a time interval does not contain C_0, which shows that in *first-order reactions* the time required for a given fraction of the substance to react is independent of the initial concentration. This is not to say that the rate in moles per liter per minute is independent of C_0, for this is not true. Dilution with an equal volume of solvent for a reaction in solution or reducing p_0 to half its value in a gaseous system reduces to half the rate in moles per liter per minute and doubles the volume of the system, so that the quantity per total system per minute is unchanged.

A common procedure for determining whether a reaction is or is not of the first order is to determine the "half time," the time in which $x = 0.50$, for different initial pressures or concentrations. If the half time is independent of C_0 or p_0, the reaction is shown to be of the first order. (We shall see later that for reactions of the second order the half time is inversely proportional to C_0 or p_0.)

All the transformations of radioactive substances (to be discussed later in Chap. XV) follow the first-order equation. It is usual to describe their reaction rates in terms of "half life," or the time required for one-half the substance to be transformed into its decomposition products, whether or not these products undergo further decompositions at new characteristic rates. By substituting $x = 0.5$ into equation (3) it will be seen that the relation between t for half decomposition and k is $t_{0.5} = 0.693/k$.

Obviously these equations imply that the reaction velocity at a given temperature depends only upon the concentration of a single reacting substance. Otherwise, all the other factors that influence the rate are collected into k; and since it sometimes happens that not all these conditions are known and kept constant, the "constant" derived from experimental data proves to be a variable instead. For example, some reactions involving only dilute gases as initial and final substances take place upon (or at least under the influence of) the wall of the reacting vessel, and thus their rates depend upon the ratio of surface to volume of container. These reactions are not homogeneous reactions and are not to be described by equation (1) without allowance for the "wall effect." Other reactions are accelerated by solutes whose concentrations do not change as the time reaction proceeds. Such solutes are called catalyzers and will be discussed presently; we note here only that equation (1) would apply to experimental data in a catalyzed homogeneous first-order reaction only when the catalyzer concentration is kept constant, and hence its effect is included in k.

The significance of k, the reaction-rate constant, is that, when $C = 1$, the reaction rate is equal to k. It is thus a *specific reaction rate*, which will have the dimensions of t^{-1}; it will be (min.)$^{-1}$ when time is expressed in minutes, or (sec.)$^{-1}$ when time is expressed in seconds. This rate will not be *maintained* when a solution of unit concentration reacts, for C decreases with time, and the rate $-dC/dt = kC$ is no longer equal to k when C falls below unity.

As has been said before, k includes the influence of every factor other than the concentration of a reacting substance, whether these factors are known or unknown. When variable values of k are derived from a set of experimental data, this shows some influence that has not been controlled in the experiments and indicates the need of further experimentation.

Decomposition of Nitrogen Pentoxide.—This reaction has been extensively studied,[1] both in the gas phase and in solution. The chemical reaction that describes the change is

$$2N_2O_5(g) = \underset{\displaystyle 4NO_2(g)}{\underset{\downarrow\!\uparrow}{2N_2O_4(g)}} + O_2(g)$$

but experiment shows that the rate is given by the first-order equations

$$\frac{-dp_{N_2O_5}}{dt} = kp_{N_2O_5} \qquad \text{or} \qquad \frac{-dC_{N_2O_5}}{dt} = kC_{N_2O_5}$$

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[1] DANIELS and JOHNSTON, *ibid.*, **43**, 53 (1921); RAMSPERGER and TOLMAN, *Proc. Nat. Acad. Sci.*, **16**, 6 (1930); EYRING and DANIELS, *J. Am. Chem. Soc.*, **52**, 1486 (1930).

One would expect from the chemical equation that a second-order reaction is taking place, which is contrary to the experimental evidence. If it is assumed that a first-order reaction is a monomolecular one, the reaction governing the rate *might be*

$$N_2O_5 = NO_2 + NO_3 \qquad \text{or} \qquad N_2O_5 = N_2O_3 + O_2$$

or

$$N_2O_5 = \text{any compounds of N and O}$$

followed by secondary reactions of much higher velocities whose final products are N_2O_4 and O_2. The available experimental facts do not indicate which reaction is more probable than the others.

Some of the experimental data for 35°C. are given in Table 75. It should be noted that in order to follow this reaction rate from the pressure increase it was first necessary to show that the equilibrium between N_2O_4 and NO_2 is established instantly and to determine the equilibrium constant for this reaction.[1] The values of k in the last column are obtained through equation (3) in terms of the fractions decomposed at the designated times. If the equation in terms of the partial pressure of N_2O_5 given above is integrated between time limits t_1 and t_2, it is

$$\ln \frac{p_1}{p_2} = k(t_2 - t_1)$$

and constants obtained from this equation by substituting corresponding times and pressures are said to be calculated by

TABLE 75[2]—DECOMPOSITION OF NITROGEN PENTOXIDE AT 35°

Time, min.	Total pressure, mm.	Partial press. N_2O_5, mm.	Fraction decomposed	k
(0)	308.2	(308.2)		
20	368.1	254.4	0.175	0.0096
30	385.3	235.5	0.236	0.0089
40	400.2	218.2	0.292	0.0086
50	414.0	202.2	0.345	0.0084
60	426.5	186.8	0.394	0.0083
100	465.2	137.2	0.554	0.0080
140	492.3	101.4	0.672	0.0080
200	519.4	63.6	0.792	0.0078

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[1] The equilibrium constant $p_{NO_2}^2/p_{N_2O_4} = 0.32$ atm. or 243 mm. at 35°.

[2] DANIELS and JOHNSTON, *ibid.*, **43**, 53 (1921).

the "interval" method. They may magnify the errors of any single experiment, but they are usually a more sensitive test for "drift" in the constant. In the absence of experimental errors this procedure obviously yields the same k as integration from zero time.

Thermal Decomposition of Paraldehyde.[1]—This reaction, for which the chemistry may be abbreviated P = 3A, is also a reaction of the first order which may be followed by observing the total pressure. For constant volume and constant temperature the rate may be expressed, in terms of the partial pressure of paraldehyde,

$$\frac{-dp_{\text{par}}}{dt} = kp_{\text{par}} \qquad (t \text{ const.})$$

but since the observed physical quantity is the *total* pressure p, this equation may be expressed in terms of experimental data by noting that at any moment the pressure of acetaldehyde is three times the loss in pressure of paraldehyde. If p_0 is the original pressure of paraldehyde and p_t its pressure at a time t, the acetaldehyde pressure is $3(p_0 - p_t)$, whence $3(p_0 - p_t) + p_t$ is equal to p, the total pressure, or $p_t = \frac{1}{2}(3p_0 - p)$ The fraction decomposed is $x = 1 - (p_t/p_0)$, and this quantity may be substituted into equation (3) in order to calculate k. If preferred, the expression for p_t may be substituted directly into the rate expression in terms of this quantity to attain the same result. This equation then becomes

$$\frac{-d(3p_0 - p)}{(3p_0 - p)} = k\,dt \quad .$$

Upon integration between the pressure limits p_0 and p for total pressure, and the time limits 0 and t, we have

$$2.3 \log \frac{2p_0}{3p_0 - p} = kt \quad .$$

The value of k in this equation for time expressed in seconds changes with the temperature as follows:

Absolute temp . . .	501.9°	512.2°	519.3°	526.8°	534.9°	542.8°
$k \times 10^4$.	0.634	1.61	3.05	5.44	10.2	19.3

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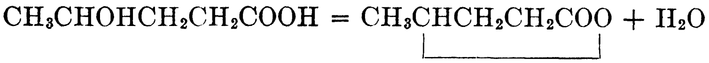
[1] COFFIN, *Can J. Research*, **7**, 75 (1932).

First-order Reactions in Solutions.—When one molecule of a dissolved substance changes into one or more new substances, the rate of its reaction may also be expressed by equation (3) The conversion of hydroxyvaleric acid into valerolactone is an illustration of such a reaction, and it may readily be followed by titrating samples with standard base from time to time. The chemical change is shown by the equation



$$CH_3CHOHCH_2CH_2COOH = CH_3CHCH_2CH_2COO + H_2O$$

[The rate of decomposition of hydroxyvaleric acid, which is a weak acid, is accelerated by the presence of hydrochloric acid almost in direct proportion to the concentration of hydrogen ion. In the presence of HCl the ionization of hydroxyvaleric acid is negligible, and therefore the rate at which the concentration of the hydroxyvaleric acid changes with time is shown by the equation

$$\frac{-dC}{dt} = k(H^+)C \tag{4}$$

Substances that accelerate a reaction without changing their concentrations as the reaction proceeds, as is true of HCl in these experiments, are called catalyzers and will be discussed in the next section.]

As the reaction proceeds, hydroxyvaleric acid undergoes the change shown in the chemical equation, and a sample of the reacting mixture requires less standard base for its titration. Complete reaction corresponds to titrating the hydrochloric acid "catalyzer" only; hence the fraction of hydroxyvaleric acid

TABLE 76.—RATE OF CONVERSION OF HYDROXYVALERIC ACID TO VALEROLACTONE AT 25° (CATALYZED BY 0.025 N HYDROCHLORIC ACID)

Time, min.	Fraction changed	k	Time, min.	Fraction changed	k
48	0 173	0 158	46	0 166	0 157
76	0 257	0 156	125	0 388	0 157
124	0 389	0 158	174	0 498	0 158
204	0 556	0.159	221	0 583	0 158
238	0 613	0.159	262	0 643	0 157
289	0 681	0 158	307	0 703	0 158

decomposed at a time *t* is obtained by subtracting the volume of base used by a sample at that time from the volume employed in the initial titration of a portion of the same volume and by dividing this difference by the difference between the first titration and that corresponding to complete reaction. Two series of experiments are shown in Table 76. It will be seen from the figures in the third and sixth columns of this table that a sufficiently constant value for k is obtained by substitution in equation (4).

Catalysis.—Substances that accelerate chemical reactions without being exhausted as the reaction proceeds are called catalyzers. Gaseous substances that increase the speed of gaseous reactions or solutes that accelerate reactions in solution are called "homogeneous" catalyzers, and in these systems the catalyzer concentration remains constant as the reaction proceeds. A catalyzer does not alter the nature of the reaction products or the equilibrium relations of the final chemical system; it must lead to the formation of the same, and only the same, end products as the slower reaction in its absence. There are also numerous "heterogeneous" catalyzed reactions, in which a solid serves as the accelerator for reactions in the gas phase or in solution. The mechanism whereby these effects are produced is unknown in most systems; more or less plausible explanations are available for a few systems.[1]

Nitrous oxide probably decomposes into its elements by a primary process which is shown by the equation

$$N_2O = N_2 + O$$

which occurs as an aftermath of a collision in which the necessary energy is given to the molecule and which is followed by the reunion of oxygen atoms to form molecules through some suitable mechanism. Since the energy requirement for this dissociation is much higher than that of an average collision, only a small fraction of the collisions is effective. Effective collisions may occur,

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[1] Attention should be called to the statement of Dr. C. N. Hinshelwood in *J. Chem. Soc.* (*London*), **1939**, 1203: "There is no theory of catalysis. The only question is whether we understand catalytic phenomena well enough to arrange them into a picture of which we like the pattern." A survey of the field, with references to the literature, is given in the National Research Council's "Twelfth Report of the Committee on Catalysis," 1940.

not only among N_2O molecules themselves, but between them and CO_2 or N_2 or A; and the different substances are specific in their action. The efficiency of such collisions must be connected with their capacity for communicating energy directly to the reacting molecules, but a full knowledge of the laws governing these energy exchanges is lacking. The efficiency of halogens in accelerating the decomposition of N_2O is of a different order of magnitude and probably through a different mechanism. The activation energy of the reaction $N_2O = N_2 + O$ is about 60,000 cal., and that of the reaction with a halogen atom X as shown by the equation

$$N_2O + X = N_2 + XO$$

would be less by the energy of formation of XO. One may assume a minute dissociation of halogen gas molecules into atoms, $X_2 = 2X$, and that these free halogen atoms could seize the oxygen of N_2O, giving halogen oxides which are more stable than the free elementary *atoms*. Since these oxides are unstable with respect to the *molecules* of halogen and oxygen, a supplementary reaction such as $2XO = O_2 + 2X$, or $2XO = X_2 + O_2$, takes place, and the series of reactions is then repeated.

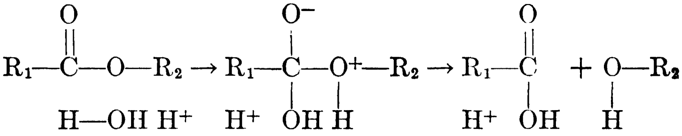
Series of reactions whereby unstable compounds are formed and then decomposed to regenerate the catalyzer are plausible explanations of many reactions. Another illustration is the oxidation of SO_2 by oxygen, which is accelerated by oxides of nitrogen. A large amount of experimental work has been done upon this important reaction, but a full explanation is still lacking. The fact that a compound of the composition $(NO_2)HOSO_2$ (nitrosyl sulfuric acid) may be prepared from SO_2, N_2O_3, O_2, and H_2O and decomposed by water into H_2SO_4 and N_2O_3 is often advanced as an explanation of this catalysis, and it is a plausible one. It should be remembered in this connection that in the actual operation of a sulfuric acid "chamber," it is desirable to *prevent* the formation of this compound. Other reactions of equal plausibility may be written for the formation of sulfuric acid which involve other mechanisms and the final results of which are in conformity with the chemistry of the total change in state.

In connection with the mechanism of any catalytic process it should be borne in mind that the "intermediate" compounds are not necessarily those which are stable with respect to the other molecules in the system. In such a series as

$$\begin{aligned} N_2O + Cl &= N_2 + ClO \\ 2ClO &= Cl_2 + O_2 \\ Cl_2 &= 2Cl \end{aligned}$$

the progress of the primary reaction is accelerated if the tendency of the first reaction to occur is greater than that of the reaction $N_2O = N_2 + O$, however unstable ClO may be with respect to Cl_2 and O_2. If the second and third of these reactions are fast enough to keep the concentration of Cl constant, the reaction will appear to be accelerated by Cl_2.

The numerous reactions in which water or the elements of water enter into the change in state are often accelerated by H^+ or OH^- almost in proportion to the strong acid or strong base from which they come. The effect of the former is sometimes ascribed to hydrated hydrogen ion, or hydronium ion H_3O^+, though it is often difficult to see how the assumption is helpful in understanding the mechanism of water addition. As an illustration of such a catalysis, the following scheme has been used to explain the acid catalysis of ester hydrolysis:[1]



$$R_1-\overset{\displaystyle O}{\overset{\|}{C}}-O-R_2 \rightarrow R_1-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle O^-}{\overset{|}{C}}}}-\underset{\displaystyle H}{\underset{|}{O^+}}-R_2 \rightarrow R_1-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle O}{\overset{\|}{C}}}} + \underset{\displaystyle H}{\underset{|}{O}}-R_2$$

$$H-OH\ H^+ \qquad H^+ \qquad H^+$$

In this scheme water yields only the OH^- to the hydrolysis, the H^+ comes from the catalyst, and a new H^+, which is the remainder of the water molecule, appears and is ready to catalyze again. On the other hand, it is a permissible point of view that the H^+ which appears in the first stage is present in the second and third and may thus be only a "bystander."

The rate of conversion of hydrolyvaleric acid to valerolactone, which is accelerated by hydrogen ions, was shown by the equations

$$-\frac{dC}{dt} = k(H^+)C \qquad \text{or} \qquad -\frac{dC}{dt} = k'C$$

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[1] HINSHELWOOD, *J. Chem. Soc.* (*London*), **1939**, 1203.

In order to show that the rate is proportional to the hydrogen-ion concentration, we quote the data of Table 77.

TABLE 77.—CATALYZER CONCENTRATION AND VELOCITY CONSTANT k'

Concentration of catalyst	$10^4k'$	$k'/(H^+) = k$
0 10 N	156	0 156
0 05	78 8	0 157
0 025	39 3	0 157
0 010	15 7	0 157

In this chapter we denote the specific reaction rate by k; and whenever some other constant quantity such as a catalyzer concentration, or the logarithmic conversion factor, or an initial concentration is combined with this k, we write it k'.

All the illustrations thus far mentioned are "homogeneous" catalyzers, gases that accelerate gaseous reactions or solutes that accelerate reactions in solution. Many other examples are known, but "heterogeneous" catalyzers are much more common. They are solids that accelerate reactions in gases or solutions, and thousands of reactions catalyzed by solids are known.[1] The reactions include hydrogenation of double bonds, reduction of benzene to cyclohexane, aromatics to aliphatics, and of unsaturated acid to saturated acid or to unsaturated alcohol, reduction of nitrobenzene to aniline, of acids to aldehyde, of aldehyde to alcohol or acid to alcohol in one step, of heptane to toluene, of methanol from CO and hydrogen, and of benzaldehyde from C_6H_6 and CO, and countless organic syntheses, decompositions, oxidations, and reductions. The catalyzers are metals, alloys, metal oxides, charcoal, clay, silica gel, inorganic salts, and other substances. Careful control of experimental conditions is essential. For example, hydrogen on a nickel catalyst may change an unsaturated acid to a saturated acid or to an unsaturated alcohol, depending on the temperature and hydrogen pressure.

For many of these reactions no explanation is known, though plausible assumptions are sometimes offered, such as preferential adsorption on the surface where reaction is favored, followed by

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[1] See, for example, Berkman, Morrell, and Egloff, "Catalysis," Reinhold Publishing Corporation, New York, 1940, for references.

desorption of the reaction product and adsorption of new quantities of reacting substances. Such an explanation is offered for the decomposition of nitrous oxide by platinum. An estimate of the activation energy for the reaction

$$N_2O = N_2 + O \text{ (on Pt)}$$

is 30,000 cal., so that collisions with the solid surface capable of supplying this smaller quantity of energy would be more numerous than those from which the 60,000 cal for the direct decomposition are available Oxygen atoms on platinum being unstable with respect to oxygen molecules, the latter form and clear the platinum surface for fresh acceleration of the decomposition.

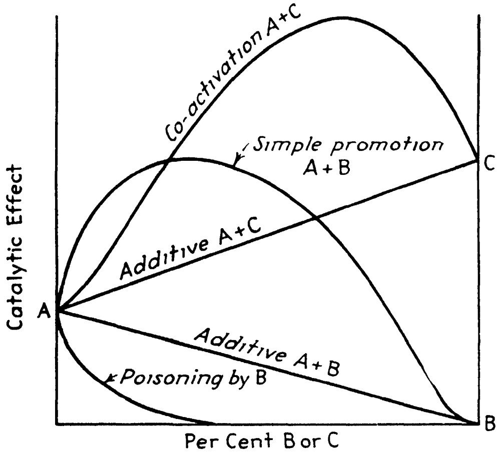

FIG. 63.—Catalytic effect of mixtures.

For many heterogeneous catalyzers, the effectiveness is proportional to the exposed surface rather than to the weight of catalyst. Some of them are "promoted" by the presence of small quantities of substances that are not themselves catalyzers; some catalysts are "poisoned" by the presence of small amounts of other substances and regenerated when these "poisons" are removed; some mixtures follow a simple mixture law. The general effects are shown in Fig. 63, in which *A* is a moderately effective catalyzer, *C* is a better one, and pure *B* has no effect.

Sugar Hydrolysis.—The hydrolysis of dilute solutions of sucrose into dextrose and levulose as shown by the equation

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$

proceeds at a rate proportional to the sucrose concentration The concentration (or activity) of the water is substantially constant for this reaction, as it is in all reactions involving water in dilute aqueous solutions, and thus its effect is commonly included in k. This reaction is accelerated by hydrogen ions, almost in proportion to the acid concentration for strong acids. Thus, the rate at which the concentration of sucrose decreases is

$$-\frac{dC}{dt} = kC_{\text{water}}C_{\text{H}^+}C_{\text{sucrose}} \tag{5}$$

Upon integration of this equation between time limits 0 and t and substitution of x for $(C_0 - C)/C_0$, the fraction decomposed in the time t, we have

$$\log \frac{1}{1-x} = \frac{kC_{\text{water}}C_{\text{H}^+}}{2.3}\,t = k't \tag{6}$$

TABLE 78—SUGAR HYDROLYSIS AT 30° IN 2.5m FORMIC ACID[1]

Initial sugar concentration 0.44m.			Initial sugar concentration 0.167m		
Elapsed time, hr.	Rotation of plane of light	$k' = \frac{1}{t}\log\frac{\alpha_0 - \alpha_f}{\alpha_t - \alpha_f}$	Elapsed time, hr	Rotation of plane of light	$k' = \frac{1}{t}\log\frac{\alpha_0 - \alpha_f}{\alpha_t - \alpha_f}$
0	(57.90)		0	(22.10)	
2	53.15	0.0146	2	20.30	0.0146
4	48.50	0.0149	5	17.85	0.0145
6	44.40	0.0147	10	14.15	0.0148
8	40.50	0.0147	15	11.10	0.0147
11	35.20	0.0146	20	8.65	0.0145
15	28.90	0.0146	26	6.00	0.0146
21	20.70	0.0146	30	4.50	0.0147
27	13.50	0.0149	39	1.90	0.0146
35	6.75	0.0148	45	0.35	0.0149
40	3.40	0.0147	59	−1.80	0.0146
46	− 0.40	0.0149	73	−3.20	0.0148
52	− 2.95	0.0148	94	−4.30	0.0147
66	− 7.45	0.0146	133	−5.10	0.0147
85	−11.25	0.0146	Complete	−5.50	
112	−13.80	0.0147			
Complete	−15.45				

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[1] ROSANOFF, CLARK, and SIBLEY, *J. Am. Chem. Soc.*, **33**, 1911 (1911).

It should be noted that in this equation the catalyzer concentration, the water "concentration," and the logarithmic conversion factor 2.3 are grouped with the specific reaction constant k and denoted by the single constant k'.

The velocity of this reaction is generally followed by observing the change in optical rotary power of the solution. Let α_0 and α_f represent the initial rotation and final rotation, and let α_t represent the rotation at any time t. Then x, the fraction of sugar decomposed at t, is given by the equation

$$x = \frac{\alpha_0 - \alpha_t}{\alpha_0 - \alpha_f}$$

Values of x so derived may be substituted in equation (3), or the expression may be rearranged to contain the observed rotations. It then becomes

$$k' = \frac{1}{t} \log_{10} \frac{\alpha_0 - \alpha_f}{\alpha_t - \alpha_f}$$

Table 78 shows the results of experiments at 30° on sugar solutions in which the catalyzer is 2.50m. formic acid. It will be observed that the values of k' are constant and independent of the sugar concentration or the extent to which the reaction has progressed.

Second-order Reactions.—We have already defined a reaction as of the second order when its rate is proportional to the first power of the concentrations of two reacting substances. For the general reaction

$$\mathrm{A} + \mathrm{B} = \text{products}$$

the expression for its rate in terms of the momentary concentrations of A and B is

$$-\frac{dC_\mathrm{A}}{dt} = kC_\mathrm{A}C_\mathrm{B} \tag{7}$$

If $C_{0\mathrm{A}}$ and $C_{0\mathrm{B}}$ are the initial concentrations of A and B, the integral of this equation between limits is

$$\frac{2.3}{C_{0\mathrm{A}} - C_{0\mathrm{B}}} \log \frac{C_{0\mathrm{B}}C_\mathrm{A}}{C_{0\mathrm{A}}C_\mathrm{B}} = kt \tag{8}$$

In experimental work it is important that the initial concentrations be made distinctly different or exactly equal. For the special condition of equal initial concentrations of A and B the rate equation is

$$-\frac{dC}{dt} = kC^2$$

and its integral between time limits 0 and t is

$$\frac{C_0 - C}{C_0 C} = kt \tag{9}$$

This equation is readily transformed into one in terms of the fraction reacted at a given time interval, whereas equation (8) cannot be so treated since equal quantities of A and B are unequal fractions of unequal initial concentrations. We note that $x = (C_0 - C)/C_0$, and equation (9) becomes

$$\frac{x}{1 - x} = kC_0 t \tag{10}$$

In treating any given set of data C_0 may be combined with k into a single constant k' if desired, but this has the disadvantage of implying by the appearance of the equation that the fraction decomposed in a given time interval is independent of C_0, which is not true.

Saponification of Esters.—Reactions between hydroxyl ions and esters in aqueous solutions, such as

$$OH^- + CH_3COOC_2H_5 = CH_3COO^- + C_2H_5OH$$

TABLE 79.—SAPONIFICATION OF ESTERS AT 25°

Ethyl acetate			Methyl acetate		
Time, min.	Fraction saponified	$kC_0 = \frac{1}{t}\frac{x}{1-x}$	Time, min.	Fraction saponified	$kC_0 = \frac{1}{t}\cdot\frac{x}{1-x}$
5	0.245	0.0649	3	0.260	0.117
7	0.313	0.0651	5	0.366	0.115
9	0.367	0.0645	7	0.450	0.117
15	0.496	0.0650	10	0.536	0.115
20	0.566	0.0652	15	0.637	0.117
25	0.615	0.0642	21	0.712	0.118
33	0.680	0.0644	25	0.746	0.118

are second-order reactions. If the ester and base are mixed in equivalent quantities, equation (10) is applicable; if unequal, we use equation (8). For either condition the fraction of base reacted may be determined from the conductance of the solution, since esters and alcohols are not ionized. As the reaction proceeds, hydroxyl ion is replaced by acetate ion that has a much slower mobility, and the conductance decreases as the reaction proceeds. If L_0, L_t, and L_f denote the initial, temporary, and final conductances of the solution, the fraction x of the NaOH that has reacted is

$$x = \frac{L_0 - L_t}{L_0 - L_f}$$

Table 79 shows some data[1] for methyl acetate and ethyl acetate at 25°. The evident fact that the derived constants are substantially constant shows that these reactions are second order.

Formation of Carbonyl Chloride.—As an example of a second-order reaction in the gas phase, we consider the formation of carbonyl chloride (phosgene), as shown by the equation

$$CO + Cl_2 = COCl_2$$

The rate of this reaction is shown by the equation

$$-\frac{dC_{CO}}{dt} = kC_{CO}C_{Cl_2}$$

Since there is a decrease in the number of moles when $COCl_2$ is formed, the progress of the reaction may be followed by

TABLE 80.—FORMATION OF PHOSGENE

Time, minutes	Concentrations		$k = \frac{1}{tC_0}\frac{x}{1-x}$
	CO or Cl_2	$COCl_2$	
0	0.500		
6	0.488	0.0115	0.00780
12	0.479	0 0205	0.00712
18	0.471	0.0286	0.00676
24	0.463	0.0371	0.00676
30	0.455	0.0452	0.00664
36	0.447	0.0528	0.00654
42	0.439	0.0606	0.00660

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[1] WALKER, *Proc. Roy Soc.* (*London*), (*A*)**78**, 157 (1906).

measuring the decrease in pressure with time at constant volume and constant temperature Table 80 shows some data[1] for this system, from which it is seen that k is not constant. We have assumed that the mechanism is direct union of 1 mole of CO with 1 of chlorine and that the reaction takes place in the gas phase uninfluenced by the walls of the vessel. The drift in the supposed constant k indicates that one of these assumptions is not correct; or, at least, it shows that some important factor is not controlled, though there is no indication from these data alone as to what this factor may be.

Third-order Reactions.—A reaction whose *mechanism* is shown by an equation such as A + B + C = products is of the third order. Its rate is given by the equation

$$-\frac{dC_{\text{A}}}{dt} = kC_{\text{A}}C_{\text{B}}C_{\text{C}} \tag{11}$$

For the special condition of equal initial concentrations of all three substances, the fraction x changed at t is given by the equation

$$\frac{x(2-x)}{(1-x)^2} = 2ktC_0{}^2 = k't \tag{12}$$

As an illustration of a reaction that is third order, the change $NO + NO + O_2 = 2NO_2$, or, as usually written,

$$2NO + O_2 = 2NO_2$$

is a reaction whose rate is proportional to the oxygen concentration and the square of the NO concentration. Its rate is

$$-\frac{dC_{O_2}}{dt} = -\frac{1}{2}\frac{dC_{\text{NO}}}{dt} = kC_{O_2}C_{\text{NO}}{}^2 \tag{13}$$

If we start with an initial concentration C_0 for oxygen and $2C_0$ for NO, the fraction x decomposed at time t is given by equation (12) above.

Application of this equation to the oxidation of NO by oxygen[2] in an extended series of tests showed that the rate was correctly

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[1] ALYEA and LIND, *J. Am. Chem. Soc.*, **52,** 1853 (1930). The experiments are at 27° and an initial pressure of 709 mm., under which conditions a molal volume is 26.7 liters. In Table 80, C_0 is in moles per 26.7 liters.

[2] WOURTZEL, *Compt. rend.*, **170,** 229 (1930).

described by it and hence indicated the reaction to be a true third-order reaction.

On the other hand, a reaction whose *stoichiometry* indicates it to be of the third order is not always found to be third order when studied. Collisions involving three molecules properly oriented and of sufficient energy to react are very rare. More commonly these systems are found to react in steps of which one is so much slower than the others that it determines the rate of the whole series. Under these conditions the order of the reaction is that corresponding to the mechanism of the slow reaction.

Reactions of Higher Order.—The equation for a general change in state which we have used before is

$$aA + bB + \cdots = dD + eE + \cdots$$

In considering the kinetics of such a reaction, we must establish that the mechanism of the process is that shown by the equation, or use an equation that fits an actual mechanism other than this. It would be a very rare collision among a molecules of A and b molecules of B that would bring so many molecules together properly oriented and of sufficient energy to react, and thus an expression such as

$$-\frac{dC_A}{dt} = kC_A{}^aC_B{}^b \cdots \tag{14}$$

would have no practical value and might be definitely misleading. As was stated in the previous section, many reactions for which the over-all change in state involves several molecules are found to take place in steps of varying velocities. When the rates of more than two steps are nearly equal, the experimental difficulties involved are too great for reasonable solution. Most of the available data are for systems in which one slow reaction occurs, and the supplementary or preliminary ones are comparatively rapid. We consider now some examples.

Consecutive Reactions (Series Reactions).—If a chemical reaction takes place in steps of widely different speeds, the measured velocity will be that of the slowest step. For example, hydrogen peroxide is decomposed catalytically by iodides, and the velocity is proportional to the first power of the H_2O_2 concentration. It is proportional to the iodide concentration as well, but this remains constant during a reaction. It has been suggested[1] that the slow reaction is

$$H_2O_2 + I^- = H_2O + IO^-$$

and that this is followed by the practically instantaneous reaction

$$IO^- + H_2O_2 = H_2O + I^- + O_2$$

which regenerates the iodide ions. This suggestion is supported by the experimental data. The rate of the slow reaction is

$$-\frac{dC}{dt} = kC_{I^-}C_{H_2O_2}$$

and since C_{I^-} is constant, the integral in terms of the fraction decomposed is

$$\log\frac{1}{1-x} = \frac{kC_{I^-}}{2.3}t = k't$$

It will be seen from Table 81 that the value of k', which includes 0.02*m*. KI, is constant and thus that the suggested mechanism of the reaction is a probable one for this system.

The rate of decomposition of hydrogen peroxide is catalyzed by HBr in proportion to the *square* of its concentration. A reasonable interpretation is that the slow reaction is

$$H_2O_2 + H^+ + Br^- = H_2O + HBrO$$

TABLE 81.—DECOMPOSITION OF HYDROGEN PEROXIDE[2]

Time	Fraction decomposed	$k' = \frac{1}{t}\log\frac{1}{1-x}$
5	0 130	0.0124
10	0.242	0.0122
15	0.339	0.0116
25	0.497	0.0119
35	0.620	0.0120
45	0.712	0.0120
55	0.782	0.0121
65	0.835	0.0120
75	0.885	0.0125

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[1] BREDIG and WALTON, *Z. physik. Chem.*, **47,** 185 (1904).

[2] HARNED, *J. Am. Chem. Soc.*, **40,** 1467 (1918).

followed by the very rapid reaction

$$H_2O_2 + HBrO = H_2O + O_2 + H^+ + Br^-$$

which regenerates the catalyzing ions, and it is well known that hypobromites rapidly decompose hydrogen peroxide. The rate, in the presence of a constant concentration of HBr, may be shown by any of the equations

$$-\frac{dC}{dt} = kC_{H_2O_2}C_{HBr}{}^2 \qquad \text{or} \qquad -\frac{dC}{dt} = kC_{H_2O_2}C_{H^+}C_{Br^-} \qquad \text{or}$$

$$-\frac{dC}{dt} = k'C_{H_2O_2}$$

of which the second form is preferable for clearness.

Another illustration is the reaction whereby chromic ion is oxidized to dichromate by persulfate ion in the presence of silver ion.[1] The *chemical change* is shown by an equation not involving the silver ion,

$$3S_2O_8{}^{--} + 2Cr^{+++} + 7H_2O = 6SO_4{}^{--} + Cr_2O_7{}^{--} + 14H^+$$

but the *rate* of the reaction is independent of the chromic ion concentration and is shown by the equation

$$-\frac{d(S_2O_8{}^{--})}{dt} = k(S_2O_8{}^{--})(Ag^+)$$

The interpretation of the experiments is that the rate-governing reaction is

$$S_2O_8{}^{--} + Ag^+ = 2SO_4{}^{--} + Ag^{+++}$$

which is then followed by a rapid supplementary reaction that oxidizes the chromic ion and regenerates the monovalent silver ion, namely,

$$3Ag^{+++} + 2Cr^{+++} + 7H_2O = Cr_2O_7{}^{--} + 3Ag^+ + 14H^+$$

A similar rate equation applies to the oxidation of manganous ion to permanganate by persulfate and to some other oxidations. While trivalent silver ion will appear new and perhaps improbable to students, there is ample evidence of its formation.

Of the many other instances of series reactions, we shall have space for only two more, though many are known. The rate

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[1] Yost, *ibid.*, **48**, 152 (1926).

of halogenation of acetone in alkaline solution, as shown by the chemical equation

$$CH_3COCH_3 + Br_2 + OH^- = CH_3COCH_2Br + Br^- + H_2O$$

is independent of the halogen concentration and the same for bromine and iodine. The probable steps in the reaction are

$$\begin{aligned} CH_3COCH_3 + OH^- &= CH_3COCH_2^- + H_2O \quad \text{(slow)} \\ CH_3COCH_2^- + Br_2 &= CH_3COCH_2Br + Br^- \quad \text{(fast)} \end{aligned}$$

as indicated by the experimental fact that the observed rate is proportional to the first power of the concentration of acetone and the first power of the OH^- concentration.

The oxidation of arsenious acid by iodine, for which the over-all chemical change is

$$H_3AsO_3 + I_2 + H_2O = H_3AsO_4 + 2H^+ + 2I^-$$

has an observed rate that is shown by the equation

$$-\frac{d(H_3AsO_3)}{dt} = k' \frac{(H_3AsO_3)(I_2)}{(H^+)(I^-)}$$

The suggested explanation is a rapid approach to equilibrium in the reaction

$$I_2 + H_2O = HIO + H^+ + I^-$$

for which the equilibrium constant is

$$K = \frac{(HIO)(H^+)(I^-)}{(I_2)}$$

followed by a slow reaction for which the chemistry and rate equations are

$$HIO + H_3AsO_3 = H_3AsO_4 + H^+ + I^-$$

$$-\frac{d(H_3AsO_3)}{dt} = k_2(H_3AsO_3)(HIO)$$

By solving the equilibrium equation for the concentration of HIO and inserting this in the last equation for the rate, we obtain the first equation, with $k' = k_2K$.

This explanation requires that the rate of the reverse reaction be

$$-\frac{d(H_3AsO_4)}{dt} = k_3(H_3AsO_4)(H^+)(I^-)$$

in order to agree with the equilibrium relation, and experiment shows that this is the rate of the reverse reaction. Additional confirmation of the correctness of the accepted explanation is that the ratio k'/k_3, the observed rates in opposite directions, is 0.15 and that the equilibrium constant K, which is k'/k_3, is 0.16.

Other reactions are known in which more puzzling phenomena may be observed. For example, the oxidation of acetylene by oxygen in the gaseous phase occurs in stages that involve glyoxal, formaldehyde, and formic acid.[1] The rate of the reaction is proportional to the square of the acetylene concentration and independent of the oxygen concentration. This behavior is incomprehensible in the light of the rate equations given above.

Reversible Reactions.—It has already been stated that a chemical system at equilibrium is not one in which there is no reaction proceeding, but one in which equal rates in opposite directions produce a system of constant composition. Thus when equilibrium in the system

$$A + B = D + E$$

is approached by mixing A and B, these substances react; when it is approached by mixing D and E, these react. The rate from left to right is

$$-\frac{dC_A}{dt} = k_1C_AC_B \tag{15}$$

and the rate from right to left is

$$+\frac{dC_A}{dt} = k_2C_DC_E \tag{16}$$

At equilibrium the opposing rates are equal, and hence

$$\frac{C_DC_E}{C_AC_B} = \frac{k_1}{k_2} = \text{const.} \tag{17}$$

which is the expression we have used in preceding chapters for chemical equilibrium. •

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[1] Kistiakowsky and Lenher, *J. Am. Chem. Soc.*, **52**, 3785 (1930).

By the use of radioactive indicators,[1] the rate of oxidation of arsenious acid by iodine *at equilibrium* and the reverse reaction rate *at equilibrium* have been measured. These rates are in agreement with those observed for the oxidation of arsenious acid by iodine in systems far from equilibrium and for the reverse reaction far from equilibrium, by the usual kinetic methods.

Since experiments upon reaction rates are confined to systems in which the mechanism of approach to equilibrium is known, while equilibrium when reached is independent of mechanism, the constants of equilibrium are seldom determined from the rates of the opposing reactions involved. But it is important to realize that at equilibrium the rates are not zero. It is still more important to realize in connection with experimental work that equilibrium is approached at a decreasing rate and that adequate time must be allowed for its complete attainment.

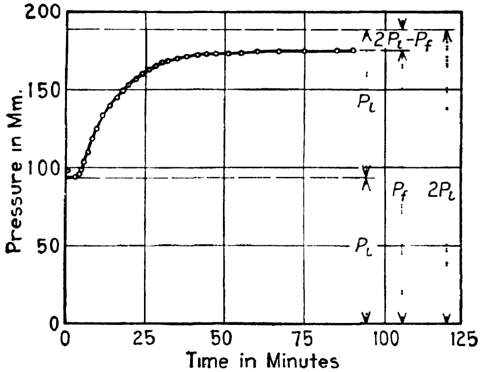

FIG. 64.—Pressure-time curve for the decomposition of ethyl bromide.

Decomposition of Ethyl Bromide.—As an example of reaction rate in a system that reaches equilibrium before decomposition is complete, we may consider the thermal decomposition of ethyl bromide, which has been studied[2] near 400° by observing the change in total pressure with time at constant volume and constant temperature. The data for a typical experiment are shown in Fig. 64, in which p_i is the initial pressure and p_f the

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[1] WILSON and DICKINSON, *ibid.*, **59**, 1358 (1937).

[2] VERNON and DANIELS, *ibid.*, **55**, 927 (1933); FUGASSI and DANIELS, *ibid.*, **60**, 771 (1938).

final pressure at equilibrium. From the reaction equation

$$C_2H_5Br = C_2H_4 + HBr$$

we see that for complete decomposition p_f should be $2p_i$, but the observed final pressure is less than $2p_i$, which shows incomplete decomposition. If the equation written for the process is correct, the *equilibrium* relations follow from Fig. 64, in which $p_{C_2H_5Br} = 2p_i - p_f$ and $p_{HBr} = p_{C_2H_4}$ is half of the difference between p_f and $p_{C_2H_5Br}$, whence $p_{HBr} = p_f - p_i$. Then the *equilibrium constant*, which is the ratio of the rates of decomposition (k_1) and reunion (k_2), is

$$K = \frac{(p_f - p_i)^2}{2p_i - p_f} = \frac{k_1}{k_2}$$

The rate of decomposition of ethyl bromide is given by the usual expression

$$-\frac{dC}{dt} = kC$$

At any time t when the total pressure is p_t, the pressure of ethyl bromide is $2p_i - p_t$, and the pressure of C_2H_4 or HBr is $p_t - p_i$. These pressures and the volume of the system serve to calculate the concentrations of each substance in moles per liter from the ideal gas law. Let C_0 be the *initial* concentration of ethyl bromide, proportional to p_i and therefore constant, and let z be the concentration of HBr or C_2H_4, which is a variable. The rate of increase of z, which is the rate of decomposition of C_2H_5Br, is

$$+\frac{dz}{dt} = k_1(C_0 - z)$$

The reverse reaction, whereby ethylene and HBr form C_2H_5Br, is bimolecular, or of the second order. It proceeds at the rate

$$-\frac{dz}{dt} = k_2z^2$$

and the net rate is the sum of these two rates, or

$$\frac{dz}{dt} = k_1(C_0 - z) - k_2z^2 = k_1(C_0 - z) - \frac{k_1}{K}z^2$$

The rather complex integral of this equation proved to be very sensitive to slight errors in C_0 and thus not satisfactory as a means of determining k_1 from K and measured changes in total pressure with time. Other methods[1] were devised for treating the data from which it was found that k_1 is 5.8×10^{-4} (sec.$^{-1}$).

Effect of the Solvent.—Reaction rates for very few chemical systems have been studied in a variety of solvents. It would appear that a first-order reaction in which the solvent takes no chemical part should proceed at a rate independent of the nature of the solvent, but the data for N_2O_5 do not confirm this supposition. Experiments upon the rate of decomposition of N_2O_5 in several solvents at several temperatures have been used to calculate 10^4k (sec.$^{-1}$), and these values are shown in Table 82 The specific reaction rates are 30 to 100 per cent greater in solution than in the gas phase for this reaction.

TABLE 82 —SPECIFIC DECOMPOSITION RATE OF NITROGEN PENTOXIDE IN DIFFERENT SOLVENTS[2]

Solvent	Values of $k \times 10^4$					
	15°	20°	25°	35°	40°	45°
Nitrogen tetroxide	0.159	0.344	....		.	....
Ethylidene chloride		0.322	....	2.54	(4.22)	(7.26)
Chloroform	.	0.274	0.554	...	(3.78)	(7.05)
Ethylene chloride	.	0.238	0.479	...	(3.70)	(6.21)
Carbon tetrachloride		0.235	0.469	..	(3.62)	(6.29)
Pentachloroethane	...	0.220	0.430	..	(3.26)	(6.02)
Bromine	0.114	0.215	....	.	..	.....
Gas phase	0.079	0.165	.....	...	2.52	4.73
Nitromethane	0.0747	.....	.....	....	(2.14)	4.33

Effect of Temperature upon Reaction Rate.—The usual effect of temperature increase is an increase in rate of reaction, but a few reactions decrease in rate as the temperature is increased. In general, the rate near room temperature increases 10 to 20 per cent for each degree rise in temperature; and for a few reactions the increase is even greater. Since an increase of 1° at ordinary temperatures increases the frequency of collision

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[1] See the original paper, *ibid.*, **55**, 922 (1933) for these methods

[2] EYRING and DANIELS, *ibid.*, **52**, 1472 (1930).

among the molecules only about 0.2 per cent, the increase in reaction rate evidently arises from some cause other than increased collision frequency. An empirical equation, first suggested by Arrhenius,[1] expresses the increase in the specific reaction rate k with increasing temperature,

$$\frac{d \ln k}{dT} = \frac{A}{T^2} \tag{18}$$

In order to test the applicability of this equation, it may be put in the form $d \ln k = -A\ d(1/T)$, when it will be seen that a plot of the common logarithm of k against $1/T$ will give a straight line of slope $-A/2.3$ if the equation is valid. This expectation of a linear plot is realized for most reactions whose velocities have been studied over ranges of temperature. We shall return to a discussion of the meaning of the equation a little later; but since the plotting procedure above was also applied to van't Hoff's equation in Chaps. IX and X we may say now that the quantity A is *not* the heat of the chemical reaction or any quantity which may be calculated from thermal data.

After the quantity A has been shown independent of the temperature, the Arrhenius equation may be integrated between limits, and it then becomes

$$2.3 \log \frac{k_2}{k_1} = A\left(\frac{T_2 - T_1}{T_2 T_1}\right) \tag{19}$$

Activated Molecules.—It is probable from the observed rates of first-order reactions that the molecules which react are in some exceptional state, perhaps one of high energy compared with that of an average molecule. The collisions that cause reactions between two or more molecules are exceptional ones; they may be collisions between molecules of high energy. Molecules that react are called "activated molecules," and a collision

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[1] *Z. physik. Chem.*, **4**, 226 (1899). Equation (18) above is in the form given by Arrhenius as his equation (1). Later in the paper he introduces the form $d \ln k = (E/RT^2)dT$, in which E is clearly stated not to be ΔH for the reaction, and thus the equation is not derived from van't Hoff's equation. If k_1 is the specific rate for a reaction A + B = C + D and k_2 the specific rate for C + D = A + B, then $d \ln k_1/dT = E_1/RT^2$, $d \ln k_2/dT = E_2/RT^2$, whence $d \ln (k_1/k_2) = (E_1 - E_2)/RT^2$. Since k_1/k_2 is the equilibrium constant, $E_1 - E_2$ is ΔH. But it will be evident that one may not calculate either E_1 or E_2 from ΔH unless the other is known.

that causes reaction is called an energy-rich collision or an "activated complex." The fraction of the collisions which produce reaction is approximately

$$\frac{\text{Effective collisions}}{\text{Total collisions}} = e^{-E/RT} = \frac{k}{k_0} \tag{20}$$

in which $e^{-E/RT}$ is the fraction of the molecules having activation energy E above the average, k is the specific reaction rate, and k_0 is the rate that would result if every collision were effective. Taking logarithms, this equation becomes

$$\ln k - \ln k_0 = -\frac{E}{RT} \tag{21}$$

The temperature coefficient of k_0 would be the rate of increase of collisions with increasing temperature, which we have stated to be about 0.2 per cent per degree near room temperature, whereas the temperature coefficient of k at ordinary temperature is of the order of 10 to 20 per cent or more per degree. As a first approximation we neglect the change of k_0 with T, and upon differentiating (21) we obtain

$$d \ln k = \frac{E}{RT^2}\, dT \tag{22}$$

which is the equation found empirically by Arrhenius if we substitute E/R for A in equation (18). The fact that plots of ln k against the reciprocal of T for actual data are straight lines shows that the temperature coefficient of k_0 is negligible, as we have assumed it to be.

For reactions in which equation (20) is assumed to hold, it has not been possible to calculate k theoretically, because, while k_0 could be computed from the kinetic theory, there was no way to calculate E. Even the *principle* of excess energy content as a requirement for reaction is not valid for all reactions, for some few of them proceed at decreasing rates with increasing temperature. The oxidation of NO to NO_2 by oxygen is an example, for which k for the third-order reaction $2NO + O_2 = 2NO_2$ is 36 at 0° and 18 at 50°. Applying these constants to the integral of equation (22), one obtains $E = -2400$, from which k at 25° is calculated to be 25; this agrees with experiments at 25°. But substituting this value of E into equation (20) leads to the absurdity of a collision efficiency greater than 1, which shows that the *interpretation* of the equation is unjustified or incomplete in this instance, even though equation (22) correctly describes the changing rate with changing temperature.

An assumed but unproved explanation for this particular reaction is a rapid polymerization to equilibrium with the evolution of heat, as shown by the equation $2NO = N_2O_2$, followed by a slow reaction $N_2O_2 + O_2 = 2NO_2$. Since the extent of polymerization would be less at higher temperature, the rate of oxidation, which depends upon the concentration of the hypothetical N_2O_2, would also be less at higher temperatures.

This is, of course, merely a suggested explanation. Some other mechanism, such as rapid approach to equilibrium by an exothermic reaction $NO + O_2 = NO_3$, followed by a slow reaction such as $NO + NO_3 = 2NO_2$, is equally plausible; and there are other possibilities.

A common modification of equation (20) designed to allow for circumstances such as negative temperature coefficients is

$$k = pk_0e^{-E/RT} \tag{23}$$

in which p is interpreted as a steric, or orientation, factor.[1]

More generally, p may be regarded as a term that includes all the requirements that the activated complex must satisfy in order to decompose into product molecules, other than the possession of the minimum excess energy E necessary for its formation. The explanation of the negative temperature coefficient in terms of this equation is simply that the chance that the three molecules shall collide with the correct orientation decreases with rising temperature more rapidly than the factor $e^{-E/RT}$ increases. The term $e^{-E/RT}$ is not increasing very rapidly with temperature because E is very small, possibly zero.[2]

The fact that a straight line usually is obtained when log k is plotted against $1/T$ suggests that pk_0 and E are comparatively insensitive to temperature, or that both may be temperature functions in such a way that their product is constant, or that E may vary with T in such a way as to hide the temperature dependence on pk_0.

In order to show what an exceptional molecule an activated one is, note that the A of equation (18) is 22,000 for paraldehyde

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[1] Quoted from Sherman, *Pub. Am. Assoc. Adv. Sci.*, No. 7, 126 (1939).

[2] GERSHINOWITZ and EYRING, *J. Am. Chem. Soc.*, **57**, 985 (1935).

decomposition, or E is 44,000, and $e^{-E/RT}$ at 520°K. is 4×10^{-19}. If we accept equation (20), only this fraction of the total molecules is in a condition for reacting.

There is evidence that some of the activated molecules deactivate without reacting, which is to say that, before a molecule which has acquired sufficient energy to be in a reactive condition has time to react, it may dissipate enough of its energy to bring it into a lower energy state again. We do not imply that an activated molecule is merely one of exceptionally high velocity; for its extra energy may be in the form of vibrational energy, and its reaction may depend upon the accumulation of this energy at the chemical bond to be severed in the reaction.

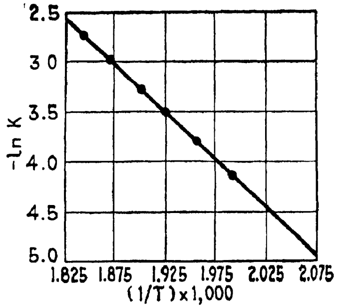

FIG. 65

A plot of $-\ln k$ against $1/T$ for the decomposition of paraldehyde is given in Fig. 65, from which it may be shown that

$$\ln k = 34.83 - \frac{44,160}{RT}$$

whence E is 44,160 cal. per mole, independent of T within this range. For other reactions there is evidence of a variation of E with temperature.[1]

If the energy of activation is taken as 24,700 cal. for the decomposition of nitrogen pentoxide,[2] the reaction constants calculated at other temperatures from the value for 25° agree closely with the measured constants, as may be seen from Table 83.

The fraction of the molecules "activated" to this additional energy content above the average for 25° is exceedingly small; it may be calculated to be $e^{-(890+24,700)/594}$, or 1.6×10^{-19}. Thus, the activated molecule is very exceptional indeed, and questions arise as to its condition. How and in what form does it "contain" so much energy? What can be the source of it? These

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[1] LAMER, *J. Chem. Phys.*, **1,** 289 (1933); HÜCKEL, *Ber.*, **67,** (*A*) 129 (1934); LAMER and MILLER, *J. Am. Chem. Soc.*, **57,** 2674 (1935).

[2] DANIELS and JOHNSTON, *ibid.*, **43,** 53 (1921).

TABLE 83.—CHANGE OF VELOCITY OF REACTION WITH TEMPERATURE

Temperature	10^3k	
	Observed	Calculated
0°	0 047	0.0444
25	2 03	
35	8 08	7 9
45	29 9	28 3
55	90 0	93 2
65	292	286

questions cannot be completely answered, though it seems probable that some of the excess energy must come from collisions. As shown in the distribution curve for velocities (Fig. 6 on page 75), there are a few molecules with very high velocities, and the rare collision between two of them would certainly form at least one that is highly energized. It has been suggested[1] that, even after a molecule has accumulated this most exceptional amount of energy, it may be "deactivated" before it has time to react. Atoms bound into a molecule by a valence bond cannot fly apart in less time than the natural period of vibration of this molecule, and before the energy of activation can be localized in a given bond it may be dissipated to surrounding molecules. Such statements sufficiently illustrate the lack of definiteness associated with the idea of activated molecules. The subject is being investigated intensively by many workers at present; one may expect further light upon it within a reasonable time.

References

BERKMAN, MORRELL, and EGLOFF, "Catalysis," 1940; HINSHELWOOD, "Kinetics of Chemical Change," 1940, KASSEL, "Kinetics of Homogeneous Gas Reactions", HAMMETT, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., 1940. A symposium on kinetics in homogeneous systems will be found in *Chem. Rev.*, **10,** February, 1932, and another in *ibid.*, **17,** August, 1935.

Problems

1. A solution 0.167*m.* in sugar and 2.5*m.* in formic acid has at 30° a rotation of 22.10 deg. Owing to the presence of acid in the solution, inversion takes place at such a rate that the angle of rotation of polarized light is

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[1] EYRING and DANIELS, *ibid.*, **52,** 1472 (1930).

11.10 deg. after 15 hr. and 0.35 deg after 45 hr. (*a*) Calculate the angle of rotation corresponding to complete inversion of the sugar, using the value of k' from Table 78. (*b*) Calculate the time necessary for half the sugar to be inverted. (*c*) The solution was 2.50*m*. in formic acid, whose ionization constant is 1.7×10^{-4}. Calculate the hydrogen-ion concentration in this solution, and estimate the time required for inverting half the sugar when the catalyzing acid is 0.01*m*. hydrochloric acid

2. In a solution containing 0.1 mole of ethyl acetate and 0.1 mole of sodium hydroxide per liter, 10 per cent of the ester is decomposed in 15 min. at 10° and 20 per cent at 25°. What fraction would be decomposed in 5 min at 55°?

3. The decomposition of paraldehyde vapor into acetaldehyde vapor, for which the chemistry may be written $P = 3A$, is a first-order reaction At 262°C. the reaction-rate constant is 0.00102, when time is expressed in seconds. What will be the total pressure 1000 sec after paraldehyde is introduced into a closed space at 262° and an *initial* pressure of 0.10 atm ?

4. How long would it take to convert 40 per cent of hydroxyvaleric acid into valerolactone at 25° in the presence of 0.075 *N* hydrochloric acid?

5. The oxidation of formaldehyde to formic acid by hydrogen peroxide is a second-order reaction. When equal volumes of molal HCHO and molal H_2O_2 are mixed at 60°, the concentration of formic acid is 0.215 after 2 hr. (*a*) In what time would this reaction be 99.44 per cent completed? (*b*) If equal volumes of 0.1*m*. solutions are mixed at 60°, what time would be required for the reaction to be 43 per cent complete? (*c*) In about what time would the reaction be 43 per cent complete at 100°C if equal volumes of molal solutions were mixed?

6. The decomposition of ethylidene diacetate into acetaldehyde and acetic anhydride is a first-order reaction occurring in the gas phase, in which one molecule decomposes into two Equilibrium corresponds to complete decomposition, and the progress of the reaction may be followed by observing the total pressure At 536°K the constant of reaction is 7.24×10^{-4} for time in seconds, and this constant changes with the temperature as shown by the equation $d \ln k/dT = 16{,}450/T^2$. (*a*) Derive an expression for x, the fraction decomposed at a time t, in terms of the initial pressure p_0 and the total pressure p. (*b*) What time would be required for 75 per cent decomposition at 536°K if p_0 were 0.10 atm.? (*c*) What time would be required for 75 per cent decomposition at 573°K.?

7. A liter of a solution of N_2O_5 in CCl_4 at 40° decomposes with the evolution of oxygen at the following rate:

t, min . . .	20	40	60	80	100	Complete
O_2, ml . . .	11.4	18.9	23.9	27.2	29.5	34.75

Show whether the reaction is of the first or second order from a set of reaction constants.

8. Nitrogen pentoxide decomposes slowly at 20°C. according to the equation (1) $N_2O_5 = \frac{1}{2}O_2 + N_2O_4$, and the reaction (2) $N_2O_4 = 2NO_2$ reaches equilibrium instantly. The equilibrium constant, $K_p = 45$, for the second reaction is for pressures in millimeters. The rate at which the pressure of N_2O_5 decreases is given by the equation $-d \ln p/dt = 0.001$ for time in minutes. If the initial pressure is 100 mm. and the reaction is carried out at constant volume at 20°, calculate the partial pressure of the gases N_2O_5, N_2O_4, and NO_2 at the end of 350 min.

9. In a liter of solution at 65° containing 22.9 grams of ammonium cyanate, urea is formed as follows.

t, min	0	20	50	65	150
Urea formed, grams	0	7	12.1	13.8	17.7

The equation for the reaction is $NH_4CNO = (NH_2)_2CO$. (*a*) Determine the order of the reaction by calculating a set of values of the specific reaction constant. (*b*) Estimate the time that would be required to transform half the ammonium cyanate to urea at 65° and at 25°.

10. The conversion of acetochloranilide into parachloroacetanilide in the presence of HCl (which is a catalyst only) proceeds at such a rate that the fraction converted varies with time as follows:

t, min	7.7	15.8	32.2
x	0.159	0.295	0.510

Determine whether the reaction is of the first or second order.

11. The velocity constant for the (first-order) decomposition of NaOCl in aqueous solution changes with the temperature as follows:

t	25°	30°	35°	40°	45°	50°
k	0.0093	0.0144	0.0222	0.0342	0.0530	0.0806

Show that this change takes place in accordance with the Arrhenius equation. [Howell, *Proc. Roy. Soc.* (*London*), (*A*)**104,** 134 (1923).]

12. The second-order reaction between thiosulfate ion and bromoacetate ion may be followed by titrating samples with iodine solution. When equal volumes of 0.1*m* solutions are mixed at 25°, samples of the mixture required the following quantities of iodine solution:

t, min	0	20	35	End
Iodine, ml	27.90	16.16	12.27	0.0

(*a*) Calculate the specific reaction constant for this reaction at 25°. (*b*) The energy of activation is 15,900 cal. for this reaction. What fraction of the thiosulfate ion in the above system will have reacted in 20 min. at 40°?

13. A solution of benzenediazonium chloride in isoamyl alcohol decomposes at 20° with the evolution of nitrogen gas at the following rate:

Time, min	0	100	200	300	410	End
Vol. N_2, ml	0	15.76	28.17	37.76	45.88	69.84

(*a*) Determine whether the reaction is first order or second order. (*b*) The rate at 40°C. is 18.2 times the rate at 20°C. Determine the energy of activation for the reaction. [Waring and Abrams, *J. Am. Chem. Soc.*, **63,** 2757 (1941).]

14. The specific reaction rate of ethyl acetate with NaOH is 6.5 moles per liter per min. at 25°. Calculate the specific conductance of the mixture 1 hr. after a liter of 0.03 N ethyl acetate is added to 500 ml of 0 06 N sodium hydroxide. Ethyl acetate and alcohol do not ionize and do not appreciably change the conductance. The limiting equivalent conductances at 25° are $Na^+ = 50$, $OH^- = 197$, and $Ac^- = 41$.

15. The decomposition of NO_2 into NO and O_2 has been found to be a homogeneous reaction. When 0 105 gram of NO_2 is introduced into a liter bulb at 330°C., the *initial rate* of decomposition is 0 0196 mole per liter per hr , and when the concentration of NO_2 has become 0 00162 mole per liter, the rate of decomposition has fallen to half the initial rate. (*a*) Show whether the reaction is first order or second order. (*b*) Calculate the fraction of the original NO_2 decomposed at the end of 30 min. (*c*) If 70 per cent of this sample of NO_2 is decomposed at the end of 10 min at 354°C., calculate the temperature at which the same percentage decomposition would be obtained in 15 min.

16. The reaction $CH_3CONH_2 + H^+Cl^- + H_2O = CH_3COOH + NH_4^+Cl^-$ may be followed by observing the specific conductance of the mixtures, which changes as follows when equal volumes of 2 N solution are mixed at 63°:

t, min	0	13	34	48
Specific conductance	0 409	0 374	0 333	0 313

$\Lambda_0 = 515$ for H^+, 133 for Cl^-, and 137 for NH_4^+ at 63°. (*a*) Determine the order of the reaction. (*b*) How long would be required for 15 per cent to react if equal volumes of 0 5 N solutions were mixed at 63°? (*c*) About how long would be required to hydrolyze 0.005 mole of acetamide if 0.010 mole were dissolved in a liter of normal HCl?

17. The hydrolysis of methyl bromide is a first-order reaction whose progress may be followed by titrating samples of the reaction mixture with $AgNO_3$ The volumes required for 10-ml samples at 330°K in a typical experiment are

t, min	0	88	300	412	End
$AgNO_3$, ml	0	5 9	17 3	22 1	49 5

Calculate a set of reaction-rate constants for this reaction

18. The decomposition of gaseous silicon tetramethyl may be followed by the increase of pressure at constant volume and constant temperature In an experiment at 679°C. the pressure was 330 mm. at the start, 620 mm. in 10 min., and 990 mm. at the end. (*a*) Calculate k for this first-order reaction at 679°C. (*b*) Calculate the time required for 50 per cent decomposition at 700°C., taking 79,000 cal. as the energy of activation.

19. When COS is dissolved in water, the reaction $COS + H_2O = CO_2 + H_2S$ occurs. If at 30° no gases are allowed to escape from this solution, the concentration of H_2S changes with time as follows:

t, min	0	80	280	525	End
Concentration H_2S, moles per liter	0	0 119	0 342	0 496	0 696

(*a*) To what order does the reaction rate conform? (*b*) For an initial concentration of 1 mole of COS per liter the *initial rate* of formation of H_2S is 18×10^{-3} mole per liter per min at 47° and 1.2×10^{-3} mole per liter per min at 25°. Calculate from these data a value for the specific reaction constant for 30°, and show that this value is in reasonable conformity with that obtained in part (*a*).

20. The same reaction, $COS + H_2O = CO_2 + H_2S$, occurs when dilute solutions of water in alcohol and of COS in alcohol are mixed, and this reaction in alcoholic solution is second order. When equal volumes of 0.20*m*. alcoholic solutions of COS and of water are mixed at 75°, the *initial rate* of formation of H_2S is 4×10^{-5} mole per liter per min. (*a*) Calculate the specific reaction rate at 75°. (*b*) What time would be required for the H_2S concentration to reach 0.020*m*. at 75°?

21. Tertiary butyl chloride decomposes thermally into HCl and isobutylene as shown by the equation $(CH_3)_3CCl = (CH_3)_2CCH_2 + HCl$. The following data were obtained in a liter flask at 295°C.:

t, min	30	50	60	80
$p(CH_3)_3CCl$, mm	28.20	18.10	14.20	9.13

(*a*) Show to what order the reaction rate conforms. (*b*) Calculate the initial pressure of *t*-butyl chloride in the flask. [Brearley, Kistiakowsky, and Stauffer, *J. Am. Chem. Soc.*, **58**, 42 (1936).]

CHAPTER XIII

RADIATION AND CHEMICAL CHANGE

In addition to chemical reactions that take place whenever the reacting substances are brought together, proceeding at a rate governed by the concentration and approaching equilibrium spontaneously, there are other reactions that depend upon the absorption of light for their initiation and progress. When the reactants are mixed as gases or in solution and no light is supplied, no reaction takes place, even upon long standing. But when the system is illuminated with light of the proper wave length or "color," reaction occurs; and the extent of the chemical reaction is governed by the quantity of radiant energy absorbed into the reacting system, or the absorbed light may increase the rate enormously from that of the "dark reaction," as in the formation of phosgene.

In general, the chemical reactions produced by the absorption of light are of the same nature as reactions produced in other ways. They include synthesis and decomposition, oxidation, reduction, polymerization, rearrangement, and condensation. Photochemical processes are sometimes more complex than one would suppose from the chemical equation, and the kinetics of the reaction are often not obvious from the nature of the reacting substances. However, photochemical research may assist in the study of the mechanism of "dark reactions" as was found in the formation of HBr. It will be necessary to distinguish clearly between experimental fact and plausible explanation in this topic as well as in others previously discussed, or perhaps to a greater extent than usual in this particular case—for the study of photochemical reactions is newly developed, and the experimental work requires considerable skill. Some of the research reported in the current literature of physical chemistry has been done with inadequate apparatus, occasionally with insufficient skill as well, and frequent discrepancies may be found in the reports of different observers apparently studying the same reacting system. This is not to question the integrity of any of them, but to emphasize the difficulty of some of the measurements, the insufficient control over the experimental conditions, and the uncertainties inherent in the exploration of a new field of research before *adequate* methods of experimentation have been perfected. Moreover, the theoretical interpretations have frequently changed in the past few years, and there are indications that further revision may be required.

The light energy absorbed by a molecule may be temporarily stored as potential energy, which may redistribute itself in the molecule, rupturing the molecule at its weakest link. Instead of dissociation taking place, the absorbed energy may raise some of the external electrons to a level such that the molecule is temporarily more reactive.

It will be seen later that absorption of light by a system undergoing photochemical reaction is attended by a change in the concentration of some reacting substance. Thus the kinetics of a photochemical change are the same as for any other chemically reacting system; the absorption of more light produces more active material and causes a more rapid reaction. The quantity of reactive material is proportional to the quantity of light (of the proper wave length) absorbed

The initial velocity of reaction between hydrogen and bromine at 200° is proportional to the concentration of hydrogen and to the square root of the bromine concentration. Since the dissociation equilibrium $\frac{1}{2}Br_2 = Br_1$ is shown by the relation $(Br_1) = K(Br_2)^{\frac{1}{2}}$, it is probable that the reaction whose velocity controls the formation of HBr is between H_2 and Br_1 and that subsequent reactions (of much higher velocity) are necessary to complete the over-all reaction. Bromine is dissociated into atoms by the absorption of light, which thus changes the concentration of a reacting substance.

The discussion in this chapter will be limited to the simplest aspects of a few chemical changes that are dependent upon the absorption of light for their progress.[1] It will be seen that photochemical reactions are usually more sensitive to certain frequencies or ranges of frequency of the absorbed light, and an

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[1] See Rollefson and Burton, "Photochemistry and the Mechanism of Chemical Reactions" (Prentice-Hall, New York, 1939), for an excellent treatment of the theory and experimental data on many reactions.

explanation of this fact must be sought in the experimental data. In making the experiments themselves, it is necessary to work with monochromatic light or at least to limit the light supplied to a rather narrow range of wave lengths, in order to observe the changing photochemical effect that sometimes accompanies change of color of the light.

The Grotthuss-Draper law states that only radiant energy that is *absorbed* by a system can be used in producing chemical changes in it; transmitted light can have no effect. This simple fact makes it necessary to measure quite accurately the intensity of the transmitted light as well as that of the entering light, in order to determine the actual amount of energy absorbed by a reacting system. In cloudy media, scattered light must not be considered as absorbed One should not consider that light is acting as a catalyst in photochemical reactions; for by definition a catalyst accelerates a reaction without being exhausted as the reaction proceeds, and it is required for a photochemical change that light must be absorbed by the reacting system It may be stated here and explained later that the *absorption of light* by a system is a necessary but not a sufficient condition for photochemical change.

In connection with the absorption of light, Lambert's law should be borne in mind. This states that equal fractions of the incident light are absorbed by successive layers of a homogeneous material of equal thickness. Since the light transmitted by the first layer is that incident upon the second layer, it will be seen that, if half the entering light is absorbed by a first layer of material, half the remainder will be absorbed by a second layer of the same thickness, and so on. Thus, the intensity of light transmitted through a medium is

$$I = I_0 e^{-kl} \tag{1}$$

where l is the length of path in which the intensity of the light is reduced from I_0 to I and k is the extinction coefficient. The decrease of intensity for a given medium varies greatly with the wave length of light considered. Values of k for various wave lengths may be found in tables.[1]

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[1] See "International Critical Tables," Vol V, p. 268. There is difference of usage in expressing absorption. For example, one may use 10 in place of e and thus employ Briggs's logarithms, writing the absorption equation in

Light absorption by a gas or by a dissolved substance usually depends only upon the number of molecules in the absorbing layer and is independent of the pressure or concentration of the absorbing substance (Beer's law).

Energy Quanta.—The fundamental assumption of Planck's quantum theory is that light consists, not of a continuous "wave front," but of quanta or "particles" of energy.[1] The energy content of these quanta depends upon the frequency ν. Since the velocity of light (usually denoted by c) is 3×10^{10} cm. per second, regardless of wave length (λ), the frequency of any radiation may be calculated from the relation $\nu = c/\lambda$. The frequency of visible light includes only the fairly narrow range of about 4×10^{14} per second (red) to 8×10^{14} per second (violet), corresponding to wave lengths of 7000 to 4000Å, respectively (or 700 mμ to 400 mμ),[2] but a very much wider range of frequency must be considered in photochemistry. Ultraviolet light, which is light shorter in wave length than 4000Å, is frequently employed in producing photochemical changes, for a reason that will be evident from the calculations shortly to be presented.

In order to calculate the energy of a quantum, the frequency is multiplied by a universal constant, Planck's constant h, whose

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the form $I = I_0 10^{-Kl}$, in which K is called the extinction coefficient and l is the length of path in centimeters, in which the intensity is reduced from I_0 to I. For dissolved absorbers a molal extinction coefficient ϵ is also recorded, and the intensity relation is $I = I_0 10^{-\epsilon c l}$ In this equation c is the molal concentration of the absorber and l the length of path as before. The variation of ϵ with wave length is strikingly shown by some of the data for chlorine gas In this case (and in general when the molal extinction coefficient is stated for a gas) c is in moles per liter of gas reduced to 0° and 1 atm.

λ, Å	2540	3030	3340	3360	4050	4080	5090	5790
ϵ	0 239	35 2	65 5	27 17	3 99	0 234	0 0452	0 003

[1] In the present state of development of physics, one may not say what light consists of, but only that light has certain properties which resemble those of a wave and certain properties of a particle or corpusle. The corpuscular properties of light are clearly presented in a form not too difficult for beginners in Richtmyer, "Introduction to Modern Physics," 2d ed., p 173; see also A. H. Compton, *Phys. Rev. Suppl.*, **1,** 74 (1929).

[2] The symbol Å denotes 1 angstrom unit, or 10^{-8} cm., but wave lengths are sometimes expressed as millimicrons, for which the symbol is mμ; since a micron is 10^{-4} cm., a millimicron is 10^{-7} cm.

value is 6.542×10^{-27} erg-sec. A single quantum of frequency 4×10^{14} would thus be $4 \times 10^{14} \times 6.542 \times 10^{-27}$ erg, or 2.62×10^{-12} erg. The results of photochemical experiments are expressed as moles of substance decomposed per calorie of absorbed radiation or more frequently as molecules decomposed per quantum of absorbed radiation. Since $h\nu$ is the energy of one quantum, $Nh\nu$ ergs, or $Nh\nu/(4.18 \times 10^7)$ cal., of radiant energy is required to supply one quantum to each molecule in a mole, where N is Avogadro's number, 6×10^{23}. Many reactions take place upon the absorption of light over a range of wave lengths. For example, light of all wave lengths between 3300 and 2070Å decomposes hydrogen iodide, and the yield is 2.0 molecules per quantum of energy absorbed. But since $\nu = c/\lambda$, the energy content of a quantum $h\nu$ is greater for light of shorter wave lengths. Hence *more* energy is absorbed, *more* calories per gram molecule of hydrogen iodide decomposed, in the short wave-length ultraviolet than in the longer ultraviolet region.

When a quantum is absorbed by a molecule or atom, the energy of the system increases, as expressed by the relation

$$\Delta E = h\nu$$

For a system of one gram molecule or one gram atom, the corresponding expression is

$$\Delta E = Nh\nu \tag{2}$$

Einstein Photochemical Equivalence Law.—When a photochemical reaction is produced by the absorption of radiant energy, the yield is proportional to the number of quanta absorbed by the system. Einstein postulated that the system absorbs a quantum for each molecule that reacts, or $Nh\nu$ for each gram molecule. There is thus a definite relation between the energy required in a photochemical change, such as the dissociation of a molecule into atoms, and the frequency of radiation that will be able to produce it.

Avogadro's number of quanta, $Nh\nu$, is sometimes called 1 "einstein," but it should be noted that this is not a constant energy quantity. Since N and h are constants, the energy represented by $Nh\nu$ increases as ν increases, which is to say that it increases as the wave length of the radiation decreases. The energy in calories corresponding to N quanta changes with the wave length as shown in the following table:

Wave Length, Å	$Nh\nu$, cal.
7000 (red)	40,500
6000 (orange)	47,500
5000 (green)	57,000
4000 (violet)	71,000
3000 (ultraviolet)	95,000
2500 (ultraviolet)	113,500
2000 (ultraviolet)	142,000

It does not follow simply from these figures that a given photochemical reaction will be brought about if its thermochemical requirements (translated into radiant energy) are met. For example, the dissociation of iodine vapor into normal atoms absorbs about 34,500 cal., and any wave length in the whole visible range of light should be of sufficient energy to decompose it. Radiation of 4300 to 7000Å is absorbed by iodine vapor, but orange light does not cause it to dissociate, even though the quanta would seem to have sufficient energy. The union of hydrogen with chlorine *evolves* energy and might be supposed to proceed spontaneously, but radiant energy is required for the initiation and progress of the reaction.

The table above shows that red light corresponds to quanta of the lowest energy in the visible region, but infrared radiation would correspond to quanta of still lower energy, of course. Many substances absorb in the red region, but as yet no photochemical reaction has been found to occur under the influence of light of wave length greater than 7000Å. This illustrates the statement above that the absorption of light by a system is not a sufficient condition for photochemical reaction.

Instances in which the final result of photochemical process is the decomposition (photolysis) of a single molecule for each quantum absorbed are rare.[1] The apparent deviations of experiment from this expected yield are often so large that one might well question whether the law has any value whatever. Some data

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[1] The Einstein photochemical equivalence law has been found to apply to the photolysis of malachite green leucocyanide. The yield is one molecule decomposed per quantum within the limit of accuracy of the measurements, which was about 2.4 per cent. Harris and Kaminsky, *J. Am. Chem. Soc.*, **57**, 1154 (1935).

are given in Table 84. Actual yields in various processes experimentally studied vary from less than 0.001 to 1,000,000 molecules reacting per quantum, and the yields in a single process may change greatly with experimental conditions. But constant yields have been obtained in a considerable number of reactions, and plausible explanations of the deviations are available in others. It is still the only theory available, and it is probably a correct explanation of the photochemical "primary process."

TABLE 84.—QUANTUM YIELDS IN PHOTOCHEMICAL REACTIONS

Reaction	Wave length, Å	Absorber	Quantum yield
$H_2 + Br_2 = 2HBr$		Bromine	10^{-3}
$H_2 + Cl_2 = 2HCl$.	4360	Chlorine	Over 6×10^5
$2HI = H_2 + I_2$....	3320–2000	HI	2.0
$2HBr = H_2 + Br_2$	2530	HBr	2 0
$2NOCl = 2NO + Cl_2$.	6300–3650	NOCl	2 0
Oxidation of benzaldehyde	3660	. . ...	10,000
Oxidation of Na_2SO_3	3660	.	50,000
$CO + Cl_2 = COCl_2$	4360	. .	1,000
Chlorination of benzene.		.... .	10^6
$3O_2 = 2O_3$...............	2070	O_2	2 3–3.1
Photolysis of uranyl oxalate	2540	$UO_2C_2O_4$	0 60
	3660	$UO_2C_2O_4$	0 49
Maleic-fumaric transformation	....	Maleic	0 04–0 13
$2Fe^{++} + I_2 = 2Fe^{+++} + 2I^-$	....	I_3^-	1 0
$2O_3 \rightarrow 3O_2$.............	4200	Cl_2	2 0
$2O_3 \rightarrow 3O_2$...............	4200	Br_2	31 0
$2NO_2 = 2NO + O_2$	. .	NO_2	2 0
$2NH_3 = N_2 + 3H_2$	2000	NH_3	2 5

Primary Processes.—The initial encounter between a quantum of energy and an atom or molecule is usually called the primary photochemical process, since through it energy is absorbed by the reacting system. If the primary process is succeeded by others that advance the chemical change under consideration without absorbing more radiant energy, the equivalence of quanta absorbed to molecules reacting would not apply to the complete process initiated by the quantum. It is probable that something of this kind is responsible for quantum yields greater than unity. Low quantum yields may be due to deactivation of the reacting substances before they have time to react or to side reactions.

The actual yield in photochemical reactions often depends on the thermal processes initiated by the absorption of the quantum. Small quantum yields have been obtained in a sufficient number of reactions to indicate that *some* process involving one molecule per quantum takes place in all photochemical processes This "primary" process may be the dissociation of a molecule into atoms or free radicals; it may be the formation of "excited" molecules or atoms, sometimes called "activated" molecules or atoms or molecules "in a higher quantum state." No distinction is yet implied by the use of three terms to describe the unusual condition of a molecule that has "absorbed" a quantum of energy

If the absorbed energy corresponding to an excited state is not dissipated by collision of the excited molecule with other molecules or if it is not reemitted before reaction can occur, the molecule may decompose and thus give a quantum yield of 1. However, the products of the primary decomposition may be so reactive that they immediately take part in secondary reactions and thus mask the applicability of the photochemical equivalence law. For example, the decomposition of hydrogen iodide illustrates a quantum yield of exactly 2.0, and it probably involves the decomposition of *one* molecule per quantum in the primary process. A similar *yield* by a different mechanism is found for the decomposition of NOCl.

It seems well established that a continuous absorption spectrum, without bands, indicates that the primary photochemical process is the dissociation of a molecule and that a banded absorption spectrum indicates the formation of an excited molecule. When dissociation of a molecule into atoms occurs by the absorption of a quantum of greater energy than the minimum calculated from thermochemical data, an "ordinary" atom and an "excited" atom are probably formed. The evidence for this rests almost entirely on the interpretation of spectroscopic data and cannot be discussed here,[1] but the fact itself will be considered in connection with some photochemical decompositions.

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[1] See Franck, *Trans. Faraday Soc.*, **21**, 536 (1926).

Decomposition of Hydrogen Iodide.—The experiments of many investigators have shown that the extent of this decomposition is proportional to the amount of light absorbed and that decomposition is complete for all wave lengths absorbed down to 2000Å, over a considerable range of temperature and for moderate variations in the intensity of illumination and in the partial pressure of hydrogen iodide. The quantum yield is 2.0 over the entire spectral range investigated. Tingey and Gerke[1] have shown that the absorption is continuous, that it begins at about 3320Å and extends down to 2000Å, the limit set by their apparatus.

It may be calculated thermochemically that the dissociation $HI = H + I$ absorbs about 68,000 cal., which would require a value of $Nh\nu$ equivalent to a wave length of about 4000Å. This lies in the violet end of the visible spectrum, but light of this wave length is not absorbed by hydrogen iodide, which is colorless. The continuous absorption does not begin until 3320Å, corresponding to 86,000 cal., which shows that more energy is absorbed in the *primary process* than is required for simple decomposition into atoms. It seems likely that the products of decomposition are an iodine atom and a hydrogen atom. Subsequent steps, not requiring more radiant energy, have been suggested by Warburg[2] as shown by the equations

$$\begin{aligned} HI + Nh\nu &= H + I \\ H + HI &= H_2 + I \\ I + I &= I_2 \end{aligned}$$

The summation of these equations shows two molecules decomposed per quantum of energy absorbed, which is in agreement with experiment. The energy evolved in the second and third steps is probably dissipated as heat, which is to say that it may be distributed among the molecules to increase their velocities.

Without introducing the quantum concept, the data may be expressed as moles of HI decomposed per calorie of absorbed energy of certain wave lengths as follows:

Wave length, Å	2070	2530	2820
Moles HI × 10^5 per cal	1 44	1 85	2 09

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[1] *J. Am. Chem. Soc.*, **46,** 1838 (1926).

[2] *Sitzber. kgl. preuss. Akad. Wiss.*, **1916,** 300.

These figures show a smaller calorie efficiency in the shorter wave regions, as was mentioned before, but they offer no clue whatever as to the reason for this surprising fact, or for the mechanism by which decomposition occurs. When translated into quantum yields, however, the reason for the lower calorie yield becomes evident, and the photochemical mechanism suggested above appears reasonable.

The experimental *fact* should be emphasized that two molecules of HI are decomposed for each quantum absorbed, of whatever wave length. An *interpretation* has been given above that seems the most probable, in view of our present information, but that may require revision at a later time, when more facts are available. It is improbable that the quantum yield will be found to differ much from 2.0.

Hydrogen bromide shows a similar continuous absorption of all wave lengths below 2640Å, and the mechanism of its photochemical decomposition is probably similar to that suggested by Warburg above for hydrogen iodide.

The molecular mechanism by which nitrosyl chloride dissociates is said to be different[1] from that suggested for hydrogen iodide above. A quantum yield of 2 has been obtained for wave lengths from 6300 to 3650Å. Since the absorption spectrum of NOCl is banded throughout the visible part of the spectrum, this is an indication that activated molecules are formed in the primary process. The process may be represented by the equations

$$\mathrm{NOCl} + Nh\nu = \mathrm{NOCl}^*$$
$$\mathrm{NOCl}^* + \mathrm{NOCl} = 2\mathrm{NO} + \mathrm{Cl}_2$$

where the activated molecule is denoted by NOCl*.

Ammonia, acetaldehyde, nitrogen dioxide, ozone, sulfur dioxide, and other substances may be decomposed by light. The quantum yield in these reactions, as in others where it is not unity, depends on the thermal reactions that are subsequent to the primary process.

Dissociation of Iodine Vapor.—The formation of normal atoms from molecules of iodine vapor is attended by the absorption of 34,500 cal., as has been said above, and the $Nh\nu$ value

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[1] KISTIAKOWSKY, *J. Am. Chem. Soc.*, **52**, 102 (1930).

calculated from this corresponds to a wave length in the red just beyond visibility. Iodine vapor absorbs throughout the visible range, but the longest wave length capable of decomposing iodine vapor is about 5000Å, corresponding to $Nh\nu = 57,000$ cal. The suggested explanation is that the products of the dissociation are a normal iodine atom and an "excited" atom of greater energy content. If this excited atom is marked I*, the primary process is

$$I_2 + Nh\nu = I + I^*$$

This "explanation" would not be very satisfactory if other evidence were not available (from spectroscopic data) with which to confirm it. The energy required for excitation of the atom has been calculated[1] at 21,600 cal., which is not far from the difference between the two energy effects just given. Energy equations for the separate effects will make this clearer.

$$\begin{array}{ll} I_2 = I + I^* & Nh\nu = 56,800 \text{ cal absorbed} \\ I^* = I & Nh\nu = 21,600 \text{ cal. emitted} \\ \hline I_2 = I + I & \Delta H = 35,200 \text{ cal. absorbed} \end{array}$$

The difference between this and 34,500 cal. is small enough to indicate that the suggestion of excited atoms is near the truth, for there is some uncertainty regarding the accuracy of the thermal data.

"Chain" Reactions.—This term was first applied by Bodenstein[2] to interpret the fact that in many photochemical processes the number of reacting molecules is much larger than the number of absorbed quanta It is presumed that the quantum initiates a series of reactions which follow one another in such a way that a very reactive intermediate substance is regenerated by a succeeding step. This reactive substance may be a free atom, a free radical, or a highly energized molecule that is regenerated again and again as the series of reactions proceeds. Consequently, it is possible that the occurrence of one elementary reaction will initiate a whole series of such reactions, proceeding until the reactants are exhausted or until something breaks up the chain of activations. This "something" may be the absorption

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[1] Kuhn, *Naturwissenschaften*, **14**, 600 (1926).

[2] *Z. physik. Chem.*, **85**, 329 (1913). For a review of the whole topic of chain reactions, see Bodenstein, *Chem. Rev.*, **7**, 215 (1930).

of the activating energy by inhibitors, collisions with inert molecules present or with the walls of the vessel, which dissipate the energy among several molecules, or other causes. The combination of hydrogen with chlorine is a well-known illustration. Since energy is evolved in the synthesis, it is difficult to see why the reaction series, once it has been started by a quantum, should stop before the reactants are exhausted. But there is the experimental fact that about a million molecules react per quantum,[1] which indicates that the "chain" is broken after a certain length.

Two types of "chains" are described,[2] which differ in the mechanism of the series reactions. A "matter chain" consists in the formation, again and again, of highly reactive intermediate products, such as free hydrogen atoms or free chlorine atoms, which perpetuate the reaction. For example, in the series

$$\begin{aligned} Cl_2 + Nh\nu &= 2Cl \\ Cl + H_2 &= HCl + H \\ H + Cl_2 &= HCl + Cl \end{aligned}$$

the second and third reactions may be repeated one after the other until some disturbing factor "breaks the chain."

Or the series may result from the formation, reaction, and regeneration of an *excited* intermediate product, which would be called an "energy chain" as shown by the equations

$$\begin{aligned} Cl_2 + Nh\nu &= Cl_2^* \\ Cl_2^* + H_2 &= 2HCl^* \qquad \text{or} \qquad HCl^* + HCl \\ HCl^* + Cl_2 &= HCl + Cl_2^* \end{aligned}$$

and the activated Cl_2^* molecule then repeats the cycle. Other series of somewhat the same character have been suggested by different investigators; but the mechanism has not yet been definitely determined, and no very clear explanation is available of how the chain is ended after a definite period. But there are the experimental facts that the hydrogen chloride formed is proportional to the amount of radiant energy absorbed by the reacting system and that the reaction ceases while hydrogen and chlorine remain uncombined unless energy is supplied to the system.

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[1] HARRIS, *Proc. Nat. Acad. Sci.*, **14**, 110 (1928); BODENSTEIN, *Trans. Faraday Soc.*, **27**, 413 (1931).

[2] BODENSTEIN, *Chem. Rev.*, **7**, 215 (1930).

This chain theory has been applied by Bäckström to explain the oxidation of 10,000 molecules of benzaldehyde per quantum when its reaction with oxygen is produced by light of 3660Å. Similarly, 50,000 molecules of sodium sulfite are oxidized per quantum in the absence of inhibitors. In this latter reaction, the effective inhibiting action of isopropyl and benzyl alcohols has been shown[1] to consist in breaking up the chain, with the simultaneous oxidation of the inhibitor to acetaldehyde or benzaldehyde, which are incapable of carrying on the chain.

Other photochemical reactions are open to the same interpretation. Over 1000 molecules of phosgene are formed per quantum absorbed by a mixture of carbon monoxide and chlorine, 1,000,000 molecules of benzene are chlorinated per quantum, and high but less extreme yields result in other halogenations and in the oxidation of oxalates by halogens.

This theory of chain reactions, originally developed for photochemical processes, has also been applied to explosions and other processes not dependent on the absorption of radiant energy. The oxidation of acetylene[2] involves the intermediate products glyoxal, formaldehyde, and formic acid, and, in the presence of reacting acetylene, formaldehyde reacts with oxygen many times faster than when alone.

Sensitized Reactions.—It was stated earlier in the chapter that a photochemical change did not necessarily take place whenever radiant energy of a sufficiently high frequency was supplied. The dissociation of hydrogen molecules requires about 100,000 cal. per mole (as calculated from the data in Table 67 and the van't Hoff equation), and the $Nh\nu$ equivalent of this large heat absorption corresponds to a wave length of about 2600Å. But hydrogen does not absorb until the extremely short wave length 1200Å. Thus the absorption of radiant energy, which is the primary requisite for this photochemical process, does not take place in hydrogen alone between 2600 and 1200Å. An absorber capable of accepting the radiant energy and delivering it to hydrogen molecules is required, and a reaction produced by means of an absorber that is not consumed is called a sensitized reaction.

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[1] Alyea and Bäckström, *J. Am. Chem. Soc.*, **51**, 90 (1929).

[2] Spence and Kistiakowsky. *ibid.*. **52**. 4837 (1930).

Mercury vapor absorbs radiation of 2536Å, and *Nhν* equivalent to this wave length is about 112,000 cal. When a vessel containing both hydrogen and mercury vapor is illuminated with light of 2536Å, chemical effects are observed that indicate the formation of atomic hydrogen, and in similar experiments without the presence of mercury vapor no such chemical effects occur. Thus, in the presence of tungstic oxide, this substance is reduced, water is formed, and hydrogen disappears.

Hydrogen and oxygen form water and hydrogen peroxide when illuminated with light of 2536Å in the presence of mercury vapor and do not form them in its absence. Similarly, ethane forms photochemically from ethylene and hydrogen, when "sensitized" by mercury vapor. Other reactions are sensitized by mercury vapor, and other instances of photosensitization are known. For example, chlorine may act as a sensitizer in the decomposition of ozone or of chlorine monoxide and in other reactions; the photochemical decomposition of colorless N_2O_5 is sensitized[1] by the brown NO_2, etc.

The two most important photochemical reactions known occur in heterogeneous media and are too complicated for a first discussion; they are the change of silver halide on a photographic plate and the reaction of water with carbon dioxide in plants. Authorities by no means agree on the mechanism or quantum yield involved in the reactions on a photographic plate, and a study of the published work demonstrates the extreme difficulty of interpreting the results of seemingly simple experiments. Even the nature of the reaction products is still somewhat in doubt. Of the complex processes that take place in living plants, whereby sugars, cellulose, and the most varied substances are built up from water and carbon dioxide with the absorption of sunlight, even less can be said. Until much more is known of the simpler reactions, it is hardly to be expected that a fair understanding of plant photochemistry will be developed.

The examples of photochemical change already mentioned form only a very small portion of the total already known, and the investigation of light-sensitive chemical reactions has just begun. These reactions, as has been said before, are not illustrations of the catalytic effect of light; rather, they show the energizing of molecules by radiation. As our knowledge increases

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[1] BAXTER and DICKINSON, *J. Am. Chem. Soc.*, **51**, 109 (1929).

and as experimental skill develops through experience, it may be expected that reactions so produced or controlled will be of greater and greater importance.

References

The literature of photochemistry up to 1939 is summarized so completely in "Photochemistry and the Mechanism of Chemical Reactions" by Rollefson and Burton that no other source is needed. This excellent book is suggested for further reading on the topic.

CHAPTER XIV

PERIODIC LAW OF THE ELEMENTS

Mendelejeff's periodic law states that there is a periodic recurrence in properties of the elements when they are arranged in the order of increasing atomic weights. In the few instances in which recurrence came in the seventh element in place of the eighth, Mendelejeff rightly concluded that there was a missing element yet to be discovered, and he predicted with reasonable accuracy the properties that some of these elements were to possess when discovered. By writing the elements in eight columns, in the order of increasing atomic weight, and by leaving blanks where the existence of a new element was indicated, he obtained the periodic table, of which a common version is given in Table 85. Two other versions are given in Tables 86 and 87.

The fact that the atomic weights of many of the elements are "almost" whole multiples of that of hydrogen suggested to Prout in 1815 that elements had structures and that all of them might be built from hydrogen; but the fact that the atomic weights of magnesium (24.32), chlorine (35.46), and some others were definitely not "almost" whole multiples of hydrogen seemed to discredit the assumption, and it was abandoned. The periodic table also suggested that atoms were "built up" in some way; the radioactive changes described in the next chapter furnished another clue to the structure of atoms and a vast bulk of evidence was soon to follow. After brief consideration of these two topics, we shall return to the topic of atomic structure.

The "zero-group" elements were all unknown at the time the periodic table appeared, and the column for these elements has since been added to the table given on page 518.

In this arrangement, as in any form of the periodic table, three "irregularities" appear in the atomic-weight order; argon has a higher atomic weight than potassium, cobalt a higher one than nickel, and tellurium a higher one than iodine; errors in the atomic weights large enough to bring these elements into a weight

TABLE 85.—PERIODIC SYSTEM OF THE ELEMENTS

Period	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII	Group 0
I	1 H 1.0078								2 He 4 002
II	3 Li 6 940	4 Be 9 02	5 B 10 82	6 C 12 000	7 N 14 008	8 O 16 000	9 F 19 00		10 Ne 20 183
III	11 Na 22.997	12 Mg 24.32	13 Al 26.97	14 Si 28 06	15 P 31.02	16 S 32 06	17 Cl 35 457		18 A 39 94
IV	19 K 39.10	20 Ca 40.07	21 Sc 45.10	22 Ti 47 90	23 V 50.96	24 Cr 52.01	25 Mn 54.93	26 Fe 27 Co 28 Ni 55 84 58 94 58 69	
	29 Cu 63.57	30 Zn 65.38	31 Ga 69 72	32 Ge 72 60	33 As 74 93	34 Se 79.2	35 Br 79.916		36 Kr 82 9
V	37 Rb 85.44	38 Sr 87.63	39 Y 88.92	40 Zr 91 22	41 Cb 93.1	42 Mo 96.0	43 Ma .	44 Ru 45 Rh 46 Pd 101.7 102.91 106 7	
	47 Ag 107.880	48 Cd 112.41	49 In 114 8	50 Sn 118 70	51 Sb 121 77	52 Te 127 5	53 I 126.932		54 Xe 130 2
VI	55 Cs 132.81	56 Ba 137.36	57 to 71 Rare earths*	72 Hf 178 6	73 Ta 181.5	74 W 184.0	75 Re 188.7	76 Os 77 Ir 78 Pt 190.8 193.1 195 23	
	79 Au 197.2	80 Hg 200.61	81 Tl† 204.39	82 Pb† 207.22	83 Bi† 209.00	84 Po† 210	85 .		86 Rn† 222
VII	87	88 Ra† 225.97	89 Ac†	90 Th† 232.12	91 Pa .	92 U 238 14†			

* Rare earths:	57 La	58 Ce	59 Pr	60 Nd	61 Il	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
	138.90	140.13	140.82	144 27		150 43	152.0	157 26	159 2	162 46	163 5	167 64	169 4	173 6	175.0

† Certain radioactive isotopes also occupy these positions.

order are quite out of the question. These "irregularities" disappear when the elements are arranged in the order of increasing net charge on the nucleus, which is the atomic number order, as we shall see later in this chapter; but there is still no explanation of why the weight order is valid in all but three instances or why those "out of order" should all be out by only one place.

In spite of certain peculiarities, due to our incomplete knowledge of the fundamental law that the present arrangement partly expresses, the periodic law is the most important generalization in inorganic chemistry. Much study has been given the elements in order to discover the full significance of this periodicity, and some variations of the periodic table will be given later in the chapter. In all these arrangements the periods contain, respectively, 2, 8, 8, 18, 18, and 32 elements, with a final incomplete period of which only 5 elements are known.

The first period contains hydrogen and helium only, and there is abundant evidence (some of which will be given presently and more in Chap. XVI) which makes it very unlikely indeed that there are missing elements between them. Two "short periods" of eight elements follow helium—lithium to neon and sodium to argon—with quite definite recurrence of physical and chemical properties in each group or column.

The next two periods, beginning with potassium and rubidium, contain 18 elements each and are usually called "long periods." They include the groups Fe, Co, Ni and Ru, Rh, Pd, which are placed together in a single column, the significance of which is not well understood.

A certain artificiality appears in this pressing of 18 elements into groups of 8 which is not wholly satisfactory, but other arrangements are available in which this is avoided. Bohr's table uses 2, 8, 8, 18, 18, 32, and 5 elements per "period," and von Antropoff subdivides the periods into two portions. Other expedients, among which it is difficult to choose, have also been tried.

Two more "long periods," the second definitely incomplete, include the remaining elements. The sixth period, beginning with cesium, is broken by the intrusion of the rare earths, and it contains no halogen heavier than iodine. A seventh period contains only 5 elements in place of the expected 32 to match the preceding period, but there is yet no evidence that 27 other natural elements remain to be discovered.

Table 85 contains the rare gases, several rare earths, the radioactive isotopes, and the elements rhenium, masurium, gallium, scandium, and germanium, which were unknown to the discoverer of the periodic law, though he correctly predicted the general properties that some of these elements would have when discovered.

In the arrangement in Table 85, 14 rare earths occupy the place between barium and hafnium. These elements are not isotopes; they are elements of slightly but distinctly different properties and different atomic weights. They are as much entitled to separate positions as chlorine and bromine, and in some of the more complicated periodic arrangements they have separate places. The same difficulty is encountered in von Antropoff's arrangement, and in Bohr's arrangement a "period" of 32 elements results from giving them separate places. There is good evidence from spectroscopy that this is not merely an expedient for finding them places; it has to do with the energy levels of electrons in the atom.

Atomic Numbers.—The order number in which elements appear in the periodic table is called the atomic number; it is also the net positive charge on the atomic nucleus. The experiments of Moseley,[1] in which elements or their compounds were bombarded with electrons of sufficiently high velocity, showed definitely that the atomic number is a fundamental quantity. Under this bombardment the elements emit X rays of characteristic wave length in addition to general X radiation. These X-ray spectrum lines are as characteristic of the elements as are the flame colors that identify some of them, such as yellow for sodium; and the X-ray spectra are simpler than the visible spectra. Like these colors, the X rays consist of more than one "series" of lines. When the square root of the frequency in a given

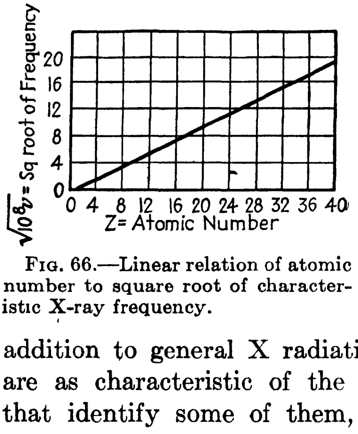

FIG. 66.—Linear relation of atomic number to square root of characteristic X-ray frequency.

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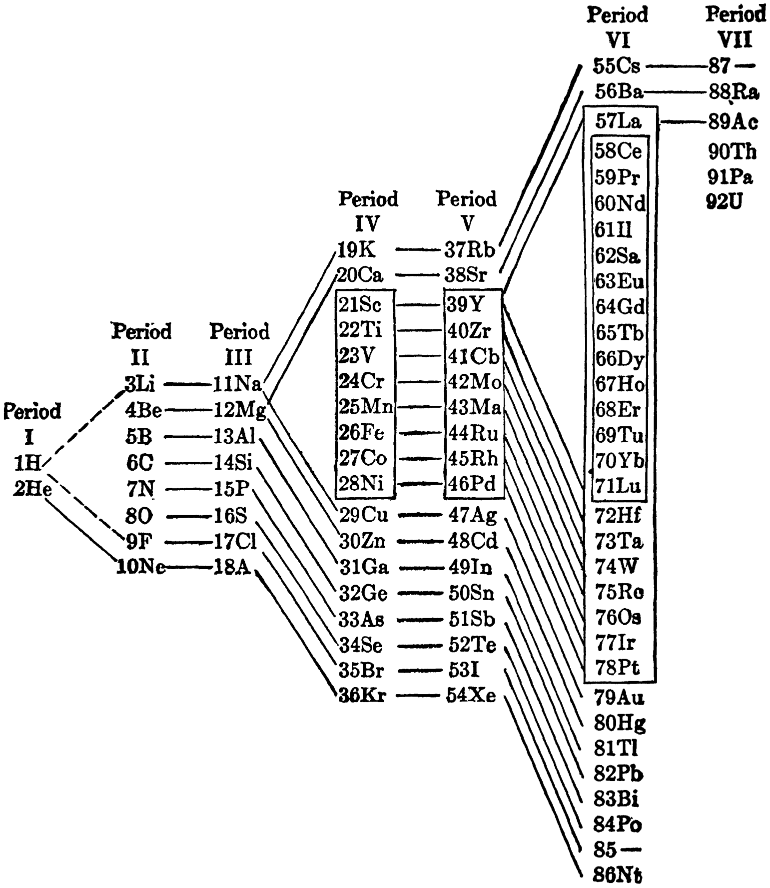
[1] MOSELEY, *Phil. Mag.*, **26**, 1024 (1913), **27**, 703 (1914).

series is plotted against the atomic number, a straight line is obtained, as shown in Fig. 66. Such a plot brings potassium, cobalt, and iodine in the order in which they should appear in the periodic table, as the weight order does not.

TABLE 86 —BOHR'S PERIODIC TABLE OF THE ELEMENTS



When the characteristic frequencies of the L series are used in place of those of the K series, another straight line of different slope is obtained, but the order number of the elements is the same. There is other evidence that the atomic number is the correct order to use in arranging the elements.

The relation of frequency to atomic number, which is known as Moseley's law, is

$$\nu = a(Z - b)^2$$

in which a and b are constants for a given series of lines and Z is the atomic number. For the K_α series, for example,

$$\nu = 0.248 \times 10^{16}(Z - 1)^2$$

Bohr's Arrangement of the Elements.—In this scheme the emphasis on eight columns is abandoned, and the periods contain 2, 8, 8, 18, 18, 32, and 5 elements, as shown in Table 86. Hydrogen and helium constitute the "first period," and the other periods begin and end with the same elements as in Table 85. A systematic increase would lead one to expect 32 elements in the seventh period, but there is as yet no evidence that so many unknown elements exist. The reasons for this arrangement will be better understood after reading the chapter on atomic structure, but its general relation to other periodic tabulations will be evident from an examination of the table. It does not explain the tellurium-iodine and similar irregularities in mass; it groups the rare earths together, as does Table 85, but it does show better than the other arrangements the relation of atomic number to the arrangement of electrons in the atoms.

von Antropoff's Periodic Table.—Another interesting arrangement of the periodic table has been devised by von Antropoff,[1] in which the left-hand and right-hand portions of each group are listed separately after the third period. This arrangement is shown in Table 87. The transitions, which are indicated by arrows for the first and fifth groups only, will be obvious in the other cases from a study of the table. In common with the other arrangements, it has nothing satisfactory with which to replace the crowding of rare earths into a single position, but it does eliminate the appearance of gaps when no elements are missing. The periods contain 2, 8, 8, 18, 18, 32, and 5 elements as before, and, of course, they begin and end with the same elements.

Many other attempts to prepare periodic tables have been made, by the use of plane diagrams, solid figures such as spirals,

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[1] *Z. angew. Chem.*, **39**, 722 (1926).

Although it seems impossible at first thought that any knowledge of the structure of a particle of this size could exist, yet the technique of modern physics and its attending theory have led to assumed structures which are in accord with practically all the experimental data.

It was stated in an earlier chapter that light has certain properties, such as interference, which are best explained by assuming it to possess wavelike characteristics and has other properties which seem to indicate that it is corpuscular. It is even more difficult to understand how such "particles" as atoms can show interference and have wavelike properties, as well as kinetic energies; yet this appears to be true from experiments on the interference of "rays" consisting of atomic "particles" impinging on a grating.

We shall see below that an atom probably consists of a positive nucleus which is not over 10^{-12} cm. in diameter, surrounded by an "atmosphere" of electrons within a radius of 10^{-8} cm. of the nucleus. Evidence on nuclear structure has been derived from radioactivity or from experiments in which the nucleus is shattered with explosive violence, and the disintegration products are inferred from their penetration of air or other matter. Such experiments cannot show how the constituents were arranged or bound together before the shattering took place, any more than the distribution and range of debris from the explosion of a larger object could show its original structure. But this work does show the units of which the nucleus was composed, insofar as these survive the atomic explosion. One must be constantly on guard not to mistake interpretation for experimentation; for interpretation involves a hazardous completion of our understanding that may change decidedly as experimentation proceeds slowly but positively to establish unchanging facts.

Early Speculations.—The fact that so many of the atomic weights are nearly whole numbers led Prout to suggest over a hundred years ago that elements were made up from hydrogen as a "fundamental" particle. As the atomic weights became more precisely known, it was found that half of them were not whole-number multiples of the atomic weight of hydrogen within 0.1 unit, and the hypothesis was abandoned. The periodic table showed that with progressively increasing mass the chemical properties of the elements were partly reproduced every eighth element and that with each increase in mass a change in valence took place. These facts also indicated that elements were composed of some fundamental unit. When radioactivity was shown to be an atomic disintegration and when the products were shown to be electrons (beta rays) and charged helium atoms (alpha particles), there could be no doubt that these radioactive atoms had structures and that electrons and positively charged masses were involved in them.

Since the atomic weights of many abundant elements are not multiples of 4, the atomic weight of helium, some of the mass must come from a lighter particle, and it was again suggested[1] that the masses of light elements, such as nitrogen, are made up of helium and hydrogen, Prout's hypothesis being thus revived in a modified form. But atomic weights that were not multiples of the atomic weights of hydrogen and helium were an insurmountable difficulty for the general application of such a theory unless one were prepared to discard the conservation of mass or to accept the possibility that elements consisted of atoms which were not of the same mass though identical in chemical properties. The periodic table showed that increase in mass was attended by a change in chemical properties, and loss of mass was so improbable in the light of all evidence as to be unacceptable. Here matters rested, awaiting new and fundamental discoveries, one of which was shortly to be made and to the results of which we now turn.[2]

Isotopes.—In the radioactive changes given in a previous chapter, it was shown that the loss of one alpha particle and 2 electrons by successive reactions formed a new element of the same atomic number and same chemical properties, occupying the same place in the periodic table, but four units lighter than the parent element. These elements were called isotopes of the parent element, and their existence suggested the possibility that other elements might consist of isotopes; but since all

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[1] RUTHERFORD, "Radioactive Substances and Their Transformations," p. 621, 1913. In 1919 Rutherford obtained traces of hydrogen by bombarding nitrogen (atomic weight 14) with alpha particles, and in similar experiments upon elements whose atomic weights were multiples of 4 no hydrogen was obtained. This is an early instance, probably the very first instance, of atomic transmutation in a laboratory.

[2] For this timely discovery F. W. Aston was awarded the Nobel Prize in Chemistry in 1922.

attempts to resolve elements into different portions had failed, it was evident that a method based upon some new principle was urgently needed.[1] In 1919, the Aston "mass spectrograph" supplied such a method; it showed that some of the elements were mixtures of atoms of different masses and the approximate (later the exact) proportions in which these were present in the natural elements. But the isolation of weighable quantities of these isotopes was not accomplished by any method until 1934, and not by the use of this method until 1936[2] The operation of the mass spectrograph is shown diagrammatically in Fig. 67. Positive rays from a discharge tube (not shown in the figure) containing the vapor to be investigated are sorted into a thin ribbon on passing through the parallel slits S_1 and S_2 and are then spread into an electric "spectrum" by means of the charged plates P_1 and P_2, of which the latter is negative. A portion of this spectrum deflected through a given angle is selected by the diaphragm D and passes between the circular poles of a powerful electromagnet O, the field of which is such as to bend the rays back again through a greater angle than that of the first deflection. The result of this is that rays having a constant mass (or more properly a constant ratio m/e of mass to charge) will converge to a focus at F and indicate their position on a photographic plate placed as shown, giving a "spectrum" dependent on mass alone. The instrument is called a positive-ray spectrometer, and the spectrum produced is known as a mass spectrum.

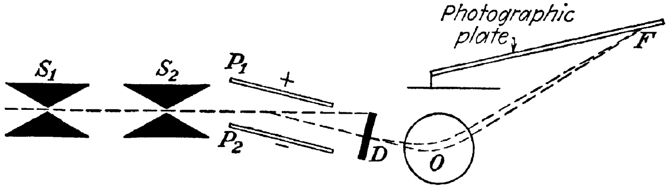

FIG 67.—Diagram of Aston's positive-ray spectrograph.

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[1] Aston's first mass spectrograph is described in *Phil Mag.*, **39,** 454 (1920); see also F. W. Aston, "Isotopes," Edward Arnold & Co., London, 1922. A new instrument of high precision is described in Aston, "Mass Spectra and Isotopes," 2d ed., 1942, which gives also the distribution of the isotopes of various masses in all of the elements

[2] Lithium was separated by Rumbaugh and Hafstead, *Phys. Rev*, **50,** 681 (1936); potassium by Smythe and Hemmendinger, *ibid.*, **51,** 178 (1937); rubidium by Hemmendinger and Smythe, *ibid.*, **51,** 1052 (1937).

Only relative masses are obtained by this method, but the scale may be calibrated by introducing a small amount of some substance of known mass. Oxygen is obviously the most suitable reference substance since it forms the basis of the atomic-weight scale.

A sketch of the mass spectrum for chlorine is shown in Fig. 68. The spots at 28, 32, and 44 correspond to carbon monoxide, oxygen, and carbon dioxide. It will be seen that the chlorine mass spectrum consists of four strong lines at 35.0, 36.0, 37.0, and 38.0; there is no line at 35 46, the accepted atomic weight of chlorine. The lines at 35.0 and 37.0 are due to chlorine atoms; the other lines one unit higher are their corresponding HCl compounds. This is strong evidence that chlorine consists of two isotopes whose atomic weights are whole numbers on the oxygen scale. Of course, these two chlorines are chemically identical in every way and inseparable by chemical means, so that the practical chemistry of chlorine is not disturbed in any way. Since these atoms have different atomic weights, there may be three kinds of chlorine molecules of molecular weight 70, 72, and 74. In the current notation, these molecules would be written Cl_2^{35}, $Cl^{35}Cl^{37}$, and Cl_2^{37}.

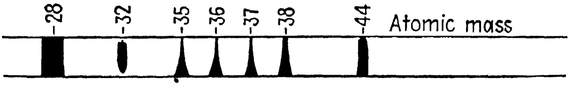


FIG. 68 —Sketch of the mass spectrum of chlorine.

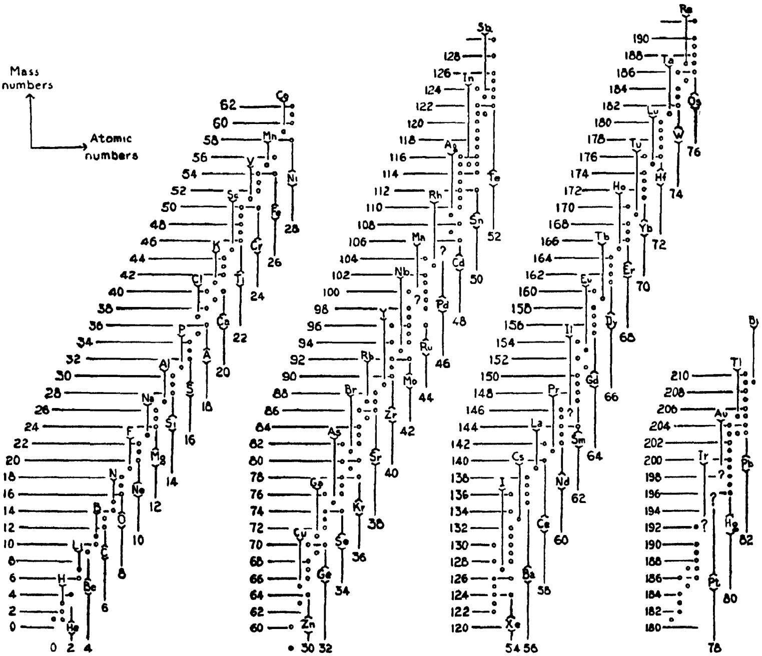
In the discharge tube at such low pressures there will be particles unknown to ordinary chemistry, such as Cl^+, HCl^+, Cl_2^+, Ne^+, and the charged products of dissociation of compounds.

Almost all the elements have now been examined in the mass spectrograph, and a total of about 280 kinds of *atoms* comprise the 92 *elements.* Thus mercury has 9 isotopes, lead 4, and tin 11. Table 92 shows the mass numbers of the atomic nuclei occurring in nature in a stable state, but it omits radioactive isotopes and the unstable synthetic nuclei that show induced radioactivity. Brief mention of these synthetic isotopes will be made later in the chapter.

The most surprising result of work with the high-precision spectographs later developed is that the atomic masses are not *exactly* whole numbers and do not differ by *exactly* whole numbers, when referred to O^{16}, as might have been expected. Thus the isotopes of chlorine have masses of 34.9803 and 36.9779 on this scale. Some other isotopic masses are shown in Table 93.

Studies with the mass spectrograph have shown that radiogenic lead consists of isotopes mixed in varying proportion, thus accounting for the variable atomic weights given in Table 91. The isotopic constitution of ordinary lead and of specimens of radiogenic lead (atomic weight 207.85) from thorite and from pitchblende (atomic weight 206.08) is as follows:

TABLE 92 —MASS NUMBERS AND ATOMIC NUMBERS OF THE ISOTOPES[1]



Mass number	204	206	207	208
Per cent in common lead[2]	1.3	27.3	20.0	51.4
Per cent in 207.85 "lead"	0	4.6	1.3	94.1
Per cent in 206.08 "lead"	0	89.9	7.9	2.3

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[1] *Rev. Sci. Instruments*, **6**, 61 (1935).

[2] This analysis is by Nier, *J. Am. Chem. Soc.*, **60**, 1571 (1938) A search for isotopes of mass numbers 203, 205, 209, and 210 in lead showed that they are very rare, if they exist at all. Others give slightly different proportions of the isotopes; for example, Mattauch, *Naturwissenschaften*, **25**, 763 (1937),

Such figures as these leave us completely in the dark as to the way ordinary lead from all over the earth came to have the same atomic weight. It could scarcely be by coincidence, and it seems improbable now that radioactive end products could have been so exactly mixed. Several radiogenic leads appear to contain *only* isotopes of masses 206, 207, and 208, which is not true of common lead.

TABLE 93.—MASS NUMBER AND RELATIVE ABUNDANCE OF SOME ISOTOPES[1]

Element	Mass	Relative abundance	Element	Mass	Relative abundance
0 *n* 1	1.00893		12 Mg 26	25.9898	11.1
1 H 1	1.00813	99.98	13 Al 27	26.9899	100
1 H 2	2.01473	0.02	14 Si 28	27.9866	98.6
2 He 4	4.00389	100	14 Si 29	28.9866	6.2
3 Li 6	6.01682	7.5	14 Si 30	29.9832	4.2
3 Li 7	7.01814	92.1	15 P 31	30.9823	
4 Be 9	9.01486	99.95	16 S 32	31.9823	97.0
5 B 10	10.01613	20	16 S 33	....	0.8
5 B 11	11.01292	80	16 S 34	33.978	2.2
6 C 12	12.00398	99.3	17 Cl 34	33.981	
6 C 13	13.00761	0.7	17 Cl 35	34.9803	76
7 N 14	14.00750	99.62	17 Cl 37	36.9779	24
7 N 15	15.00489	0.38	17 Cl 38	37.981	
8 O 16	**16.00000**	99.76	19 K 39	. . . .	93.2
8 O 17	17.00450	0.04	19 K 41		6.8
8 O 18	18.00369	0.20	24 Cr 52	51.948	83.8
9 F 19	19.00452	100	28 Ni 58	57.942	68
10 Ne 20	19.99881	90.00	30 Zn 64	63.937	50.9
10 Ne 21	20.99968	0.27	33 As 75	74.934	100
10 Ne 22	21.99864	9.73	35 Br 79	78.929	50.7
11 Na 23	22.9961	100	35 Br 81	80.930	49.3
12 Mg 24	23.9924	77.4	53 I 127	126.993	100
12 Mg 25	24.9938	11.5	55 Cs 133	132.934	100

Other elements have been similarly analyzed. Thus the per cent of the isotopes of various mass numbers in molybdenum is[2]

Mass number	92	94	95	96	97	98	100
Per cent	15.5	7.7	16.3	16.8	8.7	25.4	8.6

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gives 1.5, 24.55, 21.35, and 52.95 per cent in place of the above figures for common lead.

[1] A full table is given by the Committee on Atoms of the International Union of Chemistry in *J. Chem. Soc. (London)*, **1940**, 1416.

[2] MATTAUCH, *Z. physik. Chem.*, **42B**, 288 (1939).

Similar resolutions and "analyses" are available for most of the elements, but it must be clearly understood that separation of the element into its isotopes is not accomplished in this resolution. The percentages are estimated from the intensities of lines on photographic plates in the mass spectrum.

Some of the elements appear to contain no isotopes; for example, F, Na, Al, P, Mn, As, I, Cs, and Au have not yet been shown to have stable atoms of different masses, though experiments directed to their discovery have been made. Perhaps all that can be said safely is that the experimental means which have shown the existence of isotopes for other elements have failed to show them for these elements.

When the weight order was not followed in arranging the elements in the periodic table, it was stated that a reason would be given for believing the atomic number to be more important. This reason is evident from Table 92, in which elements of different properties have isotopes of the same mass. Single elements may have isotopes of several masses, but all of them have identical chemical properties and the same atomic number. Different elements may have atoms of the *same mass* and different chemical properties. These nuclei are called *isobars*, meaning elements of the same mass and different atomic numbers. If we follow the usual custom of indicating the atomic number by a subscript preceding the symbol and the mass number by a superscript following it, some examples of isobars are ${}_{18}A^{40}$, ${}_{19}K^{40}$, ${}_{20}Ca^{40}$; ${}_{26}Fe^{57}$, ${}_{27}Co^{57}$; ${}_{51}Sb^{123}$, ${}_{52}Te^{123}$; and some 60 other pairs besides additional trios. Since all the isotopes of an element have the same atomic number, this number is a more suitable quantity to use in arranging them for chemical properties.

Atomic Weights from the Mass Spectrograph.—Results of mass-spectrograph experiments of the kind shown in Table 93 should not be compared directly with atomic weights from chemical analyses such as the entries in Table 4, for the mixture known as "oxygen," which occurs in nature, is not wholly composed of O^{16} but contains small quantities of the isotopes O^{17} and O^{18}. The ratio of the atomic weight of O^{16} to ordinary oxygen is 1:1.00027, and this correction should be applied before making comparisons.

Atomic weights measured in the mass spectrograph may reveal slight errors in the accepted weights based on chemical methods as, for example, in the atomic weight of cesium, which was given as 132.81 in the 1933 International Table of Atomic Weights. Aston[1] found no isotope of cesium and, after correcting his work to the chemical scale by the factor 1.00027, as has been explained above, suggested that the atomic weight of cesium should be 132.91 in place of 132.81. New experiments[2] upon carefully purified materials gave the ratio CsCl : Ag = 1 : 1.5607, corresponding to an atomic weight of 132.91 for cesium, in confirmation of the value obtained in the mass spectrograph.

Isotopes from Band Spectra.—It will be clear that the moment of inertia of a molecule composed of HCl^{35} would not be the same as that of a molecule of HCl^{37} Since band spectra are associated with vibrations within the molecules and rotations of molecules, the existence of isotopes may be shown from spectroscopic data, and some indication of their relative abundance may also be found in this way.[3] Isotopes O^{18}, O^{17}, and N^{15} have been identified from band spectra. The fact is of interest as confirmation of the existence of isotopes and as a means of finding new ones. It will be noted that several kinds of nitric oxide may result from these isotopes, of which $N^{14}O^{16}$, $N^{15}O^{16}$, $N^{14}O^{18}$, and $N^{14}O^{17}$ have been indicated.

Separation of Isotopes.[4]—From the first discovery of isotopes, research has been directed toward means of separating an element into its constituents of different mass, and fractionation into portions of *slightly* different combining weight were early reported for chlorine, mercury, and a few other elements The first completely successful preparation of a pure isotope was that of H^2 or deuterium,[5] for which the symbol D is now in common use.

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[1] *Proc. Roy Soc (London)*, (*A*) **143,** 573 (1932).

[2] BAXTER and THOMAS, *J. Am. Chem. Soc.*, **56,** 1108 (1934).

[3] See JEVONS, "Report on Band Spectra of Diatomic Molecules."

[4] See Aston, *op. cit.*, for a full account of discoveries up to 1942 in this field, for more recent work see Chaps. IX, X, and XI of "Atomic Energy for Military Purposes" by H. D. Smyth (Princeton University Press, 1945)

[5] The history of this discovery, for which the Nobel Prize was awarded to Dr. H. C. Urey, is given by Urey and Teal in *Rev. Modern Phys.*, **7,** 34 (1935). Concentration of the heavy isotope by fractional distillation of liquid hydrogen gave the first indication that successful isolation of it in a pure state might be possible, but its isolation as nearly pure deuterium oxide (somewhat inaptly called "heavy water") was accomplished by Washburn, who electrolyzed large quantities of water and obtained D_2O from the last por-

These experiments showed that hydrogen contains about 99.98 per cent of atoms of weight 1.0081 and only about 0.02 per cent of deuterium atoms of weight 2.0147. They do not show that hydrogen contains 0.8 per cent of the heavier element and that the lighter one is of mass 1.000, and thus they do not explain the mass changes that must be assumed if the atoms of other elements are made up of hydrogen nuclei or protons. (This "mass defect" will be discussed later in the chapter.) But the experiments confirm the results of the mass spectrograph in showing that natural elements are mixtures of particles of different masses and identical chemical properties.

Complete separations have been accomplished for lithium,[1] neon,[2] rubidium, potassium, and chlorine;[3] nearly complete separation of some other elements has also been attained, and, of course, the attempts are still being actively conducted. The chief methods are electrolysis, centrifuging, the mass spectrograph, fractional distillation, and gaseous diffusion.

Two minor facts will illustrate the very slight chance of separating isotopes except in experiments designed for the purpose.[4] (1) The residual brine in an electrolytic cell to which KCl and water had been added to produce $KClO_3$ for 30 years without refilling showed an apparent separation of the isotopes of chlorine about equal to the error of the experimental method, which was 0.01 per cent. (2) The residual chlorine in a still through which 2700 tons of liquid chlorine had been passed showed possible increase of 0.1 per cent of Cl^{37} at the most.

Isotopes and the Law of Definite Proportions.—Experiments quoted in the previous chapter have shown that the combining

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tion of the residue. In the reference given above, the work bearing upon deuterium through the end of 1934 is reviewed (279 papers). Later work on isotopic separation is given by Urey in *Pub. Am. Assoc. Advancement Sci.*, No. 7, 73 (1939).

[1] OLIPHANT, SHIRE, and CROWTHER, *Proc. Roy. Soc.* (*London*), (*A*) **146,** 922 (1934).

[2] HARMSEN, *Z. Physik.*, **82,** 589 (1933) (by using a high-intensity mass spectrograph); HERTZ, *ibid.*, **91,** 810 (1934) (by diffusion against mercury vapor).

[3] Hirschbold-Wittner, *Z. anorg. allgem. Chem.*, **242,** 222 (1939), using the thermal-diffusion method of Clusius and Dickel, *Naturwissenschaften*, **26,** 546 (1938).

[4] *Helv. Chim. Acta*, **22,** 805 (1939), through *Chem. Abst.*, **33,** 8064 (1939).

weight of lead from radioactive decomposition is not the same as that of ordinary lead. Thus, lead bromide may contain a variable proportion of "lead," depending on the source from which it was derived. This constitutes a real exception to the law of definite proportions, though one of no very great practical importance in view of the scarcity of radiogenic lead.

Since the atomic weight of deuterium is twice that of hydrogen, the fraction of oxygen in "water" will vary from about $^{16}/_{18}$ to about $^{16}/_{20}$, depending on the ratio of H^1 to H^2 (or of H to D) in the specimen. So long as we leave hydrogen (or the other elements) in the state in which nature made them, the law of definite proportions stands as a useful general law of chemistry. But it will be imperative to clarify our nomenclature with respect to the products of isotopic separation as, for example, by reference to the oxide $Li^6Li^7O^{16}$ rather than to "lithium oxide," which was adequate until isotopic separations were accomplished.

Models of Atomic Structure.—All the isotopes carry positive charges in the mass spectrograph, as do the mass-bearing products of radioactive change when they are expelled. Since atoms as a whole are not electrically charged, it follows that there must be an equal number of positive and negative charges in the atom structure. The experiments discussed so far do not show whether the positive electricity is on the outside of the atom and the negative electricity within it or whether the positive electricity is concentrated in the interior of the atom and the negative electric charges are on the outside. The latter arrangement is now considered to be the correct one, and several "models" or proposals for discussion have been suggested, of which those by Rutherford and Bohr are discussed briefly in this chapter.

Thomson Atom Model.—This model, which was proposed as a working hypothesis by Sir J. J. Thomson prior to 1907, assumed that the atom was a sphere over which the positive charge was uniformly distributed and within which the electrons were symmetrically arranged. Experiments on the scattering of alpha particles by thin metal foil could not be explained by a distribution of the positive charge over a sphere of radius 10^{-8} cm. as assumed in the Thomson model, and it was discarded. It is of interest only as the first clearly described model to be suggested.

✓**Scattering of Alpha Particles by Matter.**[1]—When a beam of swiftly moving alpha particles, or charged helium atoms, is made to fall on thin gold foil, most of the particles pass through it, showing that the greater part of the space within the gold is "empty" or that the mass is concentrated in a very small portion of the total volume. But while nearly all the particles pass through or are slightly deflected, an occasional particle is deflected through an angle greater than a right angle, presumably because of having entered into the very core of an atom and there encountered an intense electric field. In order to account for the intensity of this field it is necessary to suppose that the positive electricity is concentrated within a region less than 10^{-12} cm. in diameter. This led Sir Ernest Rutherford[2] to propose the model that forms the basis of the atomic structure now considered most probable.

✓**Rutherford Atom Model.**—It is now commonly accepted that an atom consists of a small nucleus with which are associated the mass of the atom and the positive charges; that this nucleus is at, or very near, the center of the space available for the whole atom; and that the exterior portion of this space contains the negative electrons. In Rutherford's model, it was assumed that the electrons form the outer layer of the atom. The material in the following pages relates (1) to the structure of this inner mass nucleus; (2) to the number and arrangement or behavior of the outer electrons, and the relation of this arrangement to chemical behavior; or, alternatively, to the rotation of electrons about the nucleus in orbits of different energy levels, and the relation of this to atomic spectra.

✓ **Nuclear Charge and Atomic Number.**—If we define the atomic number of an element as the *number of positive charges on its nucleus*, as determined in experiments on the scattering of alpha particles, the same order is obtained as in the periodic system. There is a simple relation between atomic number and the frequency of characteristic X-ray spectra, as determined by Moseley's experiments mentioned in the previous chapter. If

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[1] GEIGER and MARSDEN, *Proc. Roy. Soc.* (*London*), (*A*) **82,** 495 (1909), *Phil. Mag.*, **21,** 669 (1911); **27,** 488 (1914); see also RUTHERFORD, *Proc. Roy. Soc.* (*London*), (*A*) **97,** 378 (1920).

[2] *Phil. Mag.*, **21,** 669 (1911), **26,** 702 (1913), **27,** 488 (1914).

Z is the atomic number, which is the magnitude of the positive charge on the nucleus of an atom, and ν is the characteristic X-ray frequency, this relation is

$$\nu = a(Z - b)^2$$

where a and b are constants. The elements when arranged according to the atomic numbers fall into their proper places in the periodic table. Hence the atomic number of an element is a more fundamental property than its atomic weight.

Structure of Atomic Nuclei.[1]—The early experiments of Rutherford, in which hydrogen was obtained from nitrogen by bombardment with alpha particles, as well as natural radioactive decompositions that expel alpha particles, seemed to indicate that hydrogen and helium nuclei were the constituents of atomic nuclei responsible for the mass of these atoms. Among the abundant elements, carbon, oxygen, silicon, and calcium have atomic weights that are very close to multiples of 4, and aluminum and silicon have atomic weights that are nearly whole numbers, not divisible by 4. It seemed reasonable to assign the structure 3α to the carbon nucleus, 4α to oxygen, 7α to silicon, and 10α to calcium. Nitrogen was assigned the structure $3\alpha + 2\text{H}$; and there was the possibility that helium itself might be 4H, with the mass defects not explained Nuclear structures such as the last two indicate more positive charges on the nucleus than corresponded to the number of external electrons, and therefore "nuclear electrons" in sufficient number to make the atoms neutral were also assumed. There were serious difficulties in explaining the stability of a nucleus containing electrons to which no one was blind but from which there was no evident escape at the time. With the discovery of the neutron,[2] a particle with the mass of a hydrogen atom and no electric charge, these difficulties vanished, and a more reasonable theory of nuclear structure became available.[3]

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[1] For an excellent discussion of the material presented so briefly in this section, see Richtmyer and Kennard, "Introduction to Modern Physics," Chap. XI, McGraw-Hill Book Company, Inc., New York, 1942.

[2] Chadwick, Constable, and Pollard, *Proc. Roy Soc.* (*London*), **130**, 463, (1931); see also Chadwick, *ibid.*, **136**, 692 (1932).

[3] No more striking illustration could be found of the changing interpretation required by additional experimentation than the radical revision of ideas of nuclear structure that followed the discovery of the neutron.

If we denote a hydrogen nucleus or proton by p, a neutron by n, and an electron by e, the *nuclear* structures already given become $2p + 2n$ for He, $6p + 6n$ for C, $7p + 7n$ for N, $8p + 8n$ for O, etc., and the electron is not required in any nucleus. The *atomic* structures are $2p + 2n + 2e$ for He, $6p + 6n + 6e$ for C, etc. In general, an atom of atomic number Z has Z protons in the nucleus and enough neutrons to supply the remainder of the mass, with Z electrons outside the nucleus Thus Cl^{35} is supposed to be $17p + 18n + 17e$, and Cl^{37} is $17p + 20n + 17e$.

Of course, the carbon nucleus *may* contain 3α rather than $6p + 6n$; but, since one of the nuclear reactions to be given in a later section synthesizes alpha particles by a reaction that we shall write $Li^7 + H^1 = 2He^4$, it is unnecessary and possibly misleading to make this assumption. On the other hand, there is the fact that the decompositions of *naturally radioactive* elements expel alpha particles and never protons; and this seems to indicate that the alpha particle is a constituent of these elements stable enough to survive the violent atomic explosion which expels it from the nucleus. If an alpha particle consists of two protons and two neutrons, the decrease in mass attending its formation (0.03 gram per mole) indicates that the energy necessary for decomposing an alpha particle is 28×10^6 electron volts

The "Packing Effect" or Mass Defect.—There are some mass discrepancies in these assumed constitutions that are of the greatest importance and some others that are only apparent mass discrepancies. If we consider the helium nucleus first, its formation may be indicated by $2n + 2p = \alpha$, but the mass $2n + 2p$ exceeds the atomic weight of helium by about 0.034, which is at least a hundred times the error of the atomic-weight determinations. According to an important equation of the theory of relativity, mass is convertible into energy, and the ergs obtained by the conversion of m grams of mass into energy is mc^2, where c is the velocity of light in centimeters per second. Hence $0.034\ (3 \times 10^{10})^2$ c.g.s. units of energy, or 7×10^{11} cal., should be evolved by this synthesis, and this quantity of energy would be absorbed in decomposing 4 grams of helium into neutrons and protons. If these statements are accepted, it is easy to understand that helium nuclei are very stable indeed and that it will be difficult to decompose them. While this has never been accomplished in the laboratory, the *synthesis* of helium nuclei from lithium and hydrogen leaves no doubt that the helium nucleus is not a "fundamental" particle but only one of exceptional stability. Moreover, the decrease in mass attending this synthesis explains quantitatively the energy of the new products formed and thus confirms the belief that mass is converted into energy in these atomic reactions.

The decrease in mass that attends the formation of helium from two protons and two neutrons is called the mass defect, or the binding energy. A similar mass defect could be computed for the nitrogen nucleus or for any nucleus; but, since the standard reference mass is the O^{16} isotope of oxygen, a slightly different procedure is usually followed in computing the mass changes. It is assumed in calculating mass defects that the O^{16} nucleus contains 8 neutrons and 8 protons, each of $\frac{1}{16}$ the mass of O^{16}, and the fractional decrease in mass that results from the union of these fictitious particles is recorded as the "packing fraction." This has the advantage of retaining the same mass standard that is used in the mass spectrograph and for atomic weights, but it gives the largest packing fraction to H^1, which contains only one proton or hydrogen nucleus, and leads to negative packing fractions for certain elements. There is no known particle of the exact mass used as the basis of the packing fraction; the closest approach to it is the hydrogen nucleus of mass 1.0081.

Nuclear Reactions.—In addition to the formation of hydrogen from nitrogen by bombardment with alpha particles,[1] in which the projectiles came from a natural source, there are many reactions in which nuclei are synthesized or shattered by particles accelerated to suitable velocities in the laboratory. A cyclotron is one of the instruments for providing high-velocity particles for this purpose. The nature of the particles formed in these reactions is usually inferred from their penetration of air or other matter, since the quantities produced are usually too small for chemical identification.

Some elements from which *protons* have been derived by atomic shattering through their use as targets for alpha particles are B^{10}, N^{14}, F,^{19} Na^{23}, Al^{27}, P^{31}, and Mg^{25}, with Ne, S, Cl, A, and K doubtful. *Neutrons* have been derived from the alpha-particle bombardment of Li^7, Be^9, B^{10}, B^{11}, N^{14}, F^{19}, Na^{23}, Mg^{24}, Al^{27},

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[1] Rutherford, *Phil. Mag.*, **37**, 571 (1919) *Science*, **50**, 467 (1919); *Proc. Roy. Soc.* (*London*), (*A*) **97**, 374 (1920).

P^{31}, and others. When neutrons are produced by the bombardment of atoms with high-velocity alpha particles from the disintegration of polonium, the processes are atomic transmutations that may be shown by equations such as[1]

$$\mathrm{Li}^7 + \mathrm{He}^4 = \mathrm{B}^{10} + n^1$$
$$\mathrm{Be}^9 + \mathrm{He}^4 = \mathrm{C}^{12} + n^1$$

in which the small decreases in mass (the masses of isotopes are not quite whole numbers) account for extremely high energies of the neutrons formed Neutrons have also been produced by the impact of deuterons (H^2 nuclei of unit charge) upon metal targets and from other reactions.

One transmutation that seems to prove beyond doubt that the helium nucleus contains protons is the nuclear reaction[2]

$$\mathrm{Li}^7 + \mathrm{H}^1 = 2\mathrm{He}^4$$

The mass decrease in this reaction is about 0.018, which should (and did) give the alpha particles energy corresponding to over 8,000,000 electron volts, whereas the energy of the bombarding particles was less than 1,000,000 electron volts.[3] Since the bombarding protons here concerned were energized in the laboratory, this reaction constitutes atomic transmutation wholly by laboratory means.

Other nuclear reactions consist in adding neutrons to existing nuclei with no change in atomic number, ejecting neutrons from stable nuclei by gamma rays, adding protons to nuclei with an increase in atomic number, and proton emission by neutron bombardment. One typical example of each reaction is given for illustration, but many other examples are well known. In each equation the subscript preceding the symbol is the atomic number, and the superscript is the mass number of the nucleus.

$$_{11}\mathrm{Na}^{23} + {}_0n^1 = {}_{11}\mathrm{Na}^{24} \tag{1}$$
$$_{8}\mathrm{O}^{16} + \gamma = {}_{8}\mathrm{O}^{15} + {}_0n^1 \tag{2}$$
$$_{6}\mathrm{C}^{12} + {}_1\mathrm{H}^1 = {}_{7}\mathrm{N}^{13} \tag{3}$$
$$_{12}\mathrm{Mg}^{24} + {}_0n^1 = {}_{11}\mathrm{Na}^{24} + {}_1\mathrm{H}^1 \tag{4}$$

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[1] CHADWICK, *ibid*, (*A*) **142,** 1 (1933).

[2] COCKCROFT and WALTON, *ibid*, (*A*) **136,** 619 (1932).

[3] The energy that a particle of unit charge would acquire by falling through a field of 1,000,000 volts is equivalent to the disappearance of 0.001074 mass unit, or about 1,500,000 ergs for 6 × 10^{23} particles.

These reactions produce unstable nuclei that decompose at characteristic rates. They are artificial radioactive elements, but their important feature for this discussion is that they prove the presence of neutrons and protons in atomic nuclei. The complexity of the field is made evident by the fact that over 350 *artificial* nuclei, not known to exist in nature, have been added to the *natural* atomic nuclei, of which there are about 280.

The nuclear "chain reactions," which have recently attracted so much attention, form more than one neutron in a nuclear reaction initiated by one neutron, and some of them have comparatively large conversions of mass into energy An illustration of such a reaction is

$$_{92}U^{235} + _0n^1 = _{56}Ba^{140} + _{36}Kr^{93} + 3_0n^1$$

The actual reaction is much more complicated than this in that fission products other than barium and krypton may form and the number of neutrons may not be 3, but the simplified illustration will show the principle of self-perpetuating nuclear reactions. If the reaction can be so arranged that the efficiency of the generated neutrons in continuing the initial reaction (assuming 3 to be the number formed) is higher than one-third, the reaction "builds up," and an explosive reaction may result If the efficiency is less than one-third, the reaction stops when the supply of initiating electrons stops.

Since uranium has the highest atomic number (92) of any natural element now known, an artificial nucleus of higher atomic number is called a "trans-uranium" element. The unstable artificial element $_{92}U^{239}$, which is formed by the reaction

$$_{92}U^{238} + _0n^1 = _{92}U^{239}$$

gives off electrons in its decomposition and leads to trans-uranium elements as shown by the reactions

$$_{92}U^{239} = _{93}Np^{239} + e-$$
$$_{93}Np^{239} = _{94}Pu^{239} + e-$$

These reactions are similar to that given above for the formation of $_{11}Na^{24}$.

The possibility of a nuclear reaction arises whenever protons, neutrons, electrons, or alpha particles strike a nucleus with sufficient velocity to overcome the repulsive forces. Either shattering of a nucleus or synthesis may result. Some of the nuclei so produced are identical with natural nuclei, but about 350 nuclei not known to exist in nature have also been synthesized. Artificial nuclei may be "stable" or radioactive, with the emission of electrons or positrons Element 85, which is not known to exist in nature, has been synthesized, and it is the only "artificial" nucleus yet made that decomposes with the expulsion of an alpha particle. Polonium has been synthesized from bismuth and neutrons; of course, it gives off alpha particles, as does "natural" polonium.

Artificially radioactive elements may be mixed with their naturally occurring isotopes and made into compounds in which they still retain their radioactivity. Radioactive iron, iodine, carbon, sulfur, and other elements have long been used as tracers in studying animal metabolism; sodium, phosphorus, bromine, and other tracer elements have been used in plant metabolism; still others have been used in radiotherapy; and the possibility of other uses is fascinating.

Number and "Arrangement" of Electrons in Atoms.—The atomic number of an element is the net positive charge on its nucleus and hence also the number of electrons in the space surrounding the nucleus Since the radius of the nucleus is of the order 10^{-12} cm. and the minimum distance between atomic centers is about 10^{-8} cm , the volume available for the electrons is large relative to the volume of the nucleus. Interpretations based on spectroscopy seem to require orbits of different energy levels in which the electrons revolve about the nucleus. Such a picture is not well adapted to chemical interpretations, and for this purpose the electrons are treated as if they were in shells or layers of different quantum levels with "positions," which means average densities higher in some parts of the orbits than in others, for a reason that will presently appear. We consider the spectroscopic model first.

Bohr's Atom Model.—In order to explain the spectra of the elements, Bohr assumes orbits for the electrons, with radii restricted to certain discrete values, and that while revolving in these orbits the electrons do not radiate. An electron revolving in any one of these orbits is in a "stationary state"; *i.e.*, it possesses an integral number of quanta of energy. This is contrary to the classical electrodynamics, and there is experimental evidence that these laws are not applicable to atomic systems in these circumstances. The picture of this atom model that we shall present here is oversimplified in that only the "principal" quantum numbers are considered, but it is probably sufficient for a first consideration of the spectra. We discuss first the hydrogen atom, in which a single electron revolves about a nucleus of unit positive charge.

Bohr assumes that the rotating electron in the hydrogen atom is restricted to definite, stable orbits whose radii are proportional to 1^2, 2^2, 3^2, . . . within any one of which the electron rotates continuously without loss of energy (see Fig 69). These integers 1, 2, 3, . . . are called the principal quantum numbers of the orbits. It is further assumed that the electron may pass from one orbit to another and that the energy of the atomic system is greater for orbits of greater radius. Little is known as to how the electron passes or what causes it to pass to a "higher" orbit, but it is assumed that energy is absorbed in the transfer and radiated when the electron passes to a "lower" orbit. It may be calculated that the diameter of the innermost *orbit* for the hydrogen atom is very close to 1×10^{-8} cm., while the diameter of the nucleus is of the order 10^{-12} cm. or less. Thus the estimates of molecular diameter based on the kinetic theory correspond to those required for the orbits of the electrons. While the electron rotates in a given orbit, it radiates no energy and the atom is in a "stable state"; but when the atom passes from one stable state to another of lower energy, or when the

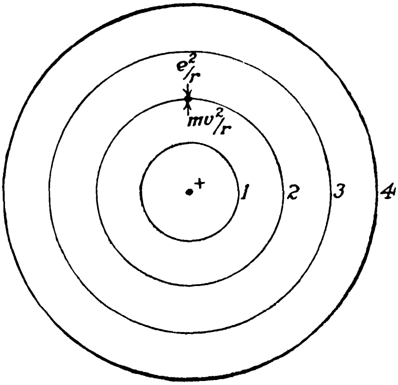

FIG 69—Orbits of the electron around a hydrogen nucleus.

electron falls to a lower energy level, energy must be lost by the atomic system. It may be shown that for the transition from the orbit of quantum number n_2 to that of number n_1 the energy lost is

$$E_2 - E_1 = k\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

and the numerical value of k may be calculated from physical constants.[1] The numbers n_1 and n_2 may be any integers, and so long as n_2 is greater than n_1 energy will be radiated by the atomic system.

If it be further assumed that the quantum theory is applicable, this lost energy appears as a quantum of frequency ν, and

$$h\nu = k\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

The spectrum of hydrogen has been carefully studied, and lines corresponding to many frequencies ($\nu = c/\lambda$) are known. Spectroscopic data are more commonly given in terms of the wave number $\tilde{\nu}$ rather than the frequency, where $\tilde{\nu}$ is the number of waves per centimeter and $\tilde{\nu}c = \nu$. The equation above may therefore be written in the form

$$\tilde{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

The value of R, calculated from physical constants not involving spectroscopic data, is 110,500, and that derived from spectroscopy is 109,737. This is usually called the Rydberg constant. By choosing the proper *whole* numbers for n_1 and n_2 it should be possible to calculate wave numbers for hydrogen spectrum lines from this equation that are in agreement with spectroscopically measured wave numbers, if the Bohr theory is correct.

A series of lines in the visible spectrum of hydrogen, discovered by Balmer, may be described *quantitatively* by the equation above, if $n_1 = 2$ and n_2 is successively 3, 4, 5, 6, ... Similarly, by taking $n_1 = 1$ and $n_2 = 2, 3, 4, 5$ . . . the Lyman

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[1] See RICHTMYER and KENNARD, *op. cit.* The quantity is

$$k = 2\pi^2 me^4/ch^3 = 1\ 105 \times 10^5 \text{ cm.}^{-1}$$

series (discovered later in the ultraviolet region) is accurately described; and the lines of the Paschen infrared series are in agreement with wave numbers calculated from $n_1 = 3$ and $n_2 = 4, 5, 6, 7, \ldots$, the *same* value for R being used in all three series. Brackett's series (or Bergman's series) follows similarly if $n_1 = 4$

It is evident that a fundamental truth is partly revealed by Bohr's model, which deserves serious attention. The theory has been applied successfully to ionized helium and somewhat less satisfactorily (owing to the complexity of the phenomena) to heavier elements as well. It has been necessary to assume elliptical orbits as well as circular orbits and to use more than one set of quantum numbers, in addition to other complications, to explain even the simplest spectra. Elements with several electrons, revolving in orbits that require four or more quantum numbers, necessarily present complications and are best excluded from a first consideration of atoms.

✓ **Electron "Shells."**—The Bohr atom model is less useful to chemists than another concept, in which the energy levels, or "shells," of electrons are considered. These shells are considered to be complete for the rare gases and incomplete in the outer layers for all other elements to an extent that offers a partial explanation of their chemical properties. The maximum number of electrons in the shells increases as twice the squares of natural numbers, $2(1^2, 2^2, 3^2, 4^2) = 2, 8, 18, 32$; and it will be recalled that in Bohr's arrangement of the elements in Table 86 the numbers of elements in the periods were 2, 8, 8, 18, 18, 32 (and 5 for the incomplete seventh period). Thus in each period after the first the maximum number of electrons in the main group is repeated once before going on to the next highest number in the series $2(1^2, 2^2, 3^2, 4^2)$. Through the first three periods the lowest shell is completed before any electrons are added at a higher level. In the language of spectroscopy these levels are designated K, L, M, N, O, P, and Q, with subdivisions in all the levels except K.

The elements that end the various periods are all rare gases of the zero group, elements numbered 2, 10, 18, 36, 54, and 86; and hence the elements containing these numbers of electrons are, respectively, He, Ne, A, Kr, Xe, and Rn. The simplified discussion of the distribution of electrons at the various levels that is now to be given is not, of course, a complete explanation of chemical properties, or even a close approach to completeness, and there are difficulties in applying the concept, even to simple systems. An attempt to present the experimental evidence on which the picture is based or to consider bonds that are neither polar nor covalent would be quite out of place in a first discussion such as we are attempting here. Nevertheless, the simplified concept is worthy of careful study, and we now turn to a discussion of it.

First Period.—The hydrogen atom consists of a single proton and a single *K* electron, or electron at the first quantum level, or one electron in the first shell, or one 1*s* electron. A helium atom consists of a nucleus of net charge +2 and two electrons at the first level. Thus a hydrogen atom must acquire an electron to complete the first shell, but the fact that H^- is not a familiar chemical substance indicates that a hydrogen atom has little tendency to acquire the electron.

The fact that H^+ is a familiar chemical substance shows that it has a greater tendency to lose its electron under favorable circumstances, and we shall soon come to a consideration of what these circumstances are First, we may consider the hydrogen molecule, in which the electron density between the two nuclei is at a maximum, causing a "covalent" or "nonpolar" bond. In the common terminology these atoms "share" a pair of electrons, and the bond is written H:H, in which the two dots indicate the pair of shared electrons. (This notation should not be confused with a double bond such as exists in ethylene and which is two pairs of shared electrons; such a bond would be written C: :C.)

The helium atom consists of two protons and two neutrons, with two 1*s* electrons, or *K* electrons, to complete its electrical neutrality. Since two is the number of electrons for the completed first shell, this is a very stable system. Helium has practically no tendency in the ordinary chemical sense to lose or acquire or share electrons, and thus there are no stable compounds of helium. The ionization potential of helium for removal of the first electron is 24.46 volts, which is the highest of any element and which indicates again that helium has very little tendency to lose an electron and become He^+. Helium has no tendency to share electrons, even with another helium atom, and it forms no chemical compounds. Thus it is indicated that an atom with a complete electron shell is an inert, stable atom. We shall soon see that neon and argon also have complete outer shells, though not shells of two electrons, and they are likewise chemically inert.

Second Period.—The elements of the second period in their normal states, considering only the isotope of mass number nearest the atomic weight, have the compositions shown in the following table, in which p is a proton and n a neutron·

Atomic number	Element	Mass number	Nuclear composition	Electrons
3	Li	7	$3p + 4n$	$2 + 1$
4	Be	9	$4p + 5n$	$2 + 2$
5	B	11	$5p + 6n$	$2 + 3$
6	C	12	$6p + 6n$	$2 + 4$
7	N	14	$7p + 7n$	$2 + 5$
8	O	16	$8p + 8n$	$2 + 6$
9	F	19	$9p + 10n$	$2 + 7$
10	Ne	20	$10p + 10n$	$2 + 8$

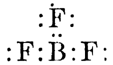
In a first consideration of atomic structure it seems advisable to omit the distinction between the electrons at the second level usually designated $2s$ and $2p$ and to list them all merely as of the second level, or in the second shell. The table above shows 2 electrons in the first shell and those of the second shell increasing from 1 to 8. Since neon, with eight in the second shell, has an ionization potential (21.47 volts) higher than any element except helium, it will be evident that 2 electrons in the first shell and eight in the second constitute also a very stable system, as was helium with two in the first shell and no others. Neither helium nor neon forms stable compounds or molecules.

A lithium atom could acquire the stable electron structure of helium by losing the electron in the second shell and becoming Li^+, and a fluorine atom could acquire the complete second shell that is possessed by neon if it accepted the electron lost by lithium and became F^-. We have already seen in Chap. V that NaCl crystals consist of ions and not of molecules of NaCl, and LiF has the same crystal structure. We customarily write Li^+ and F^- as the solutes in an aqueous solution of LiF, just as we write

Na^+ and Cl^- for an aqueous solution of NaCl. Thus the assumed electron structures of Li atoms and F atoms are in harmony with the known chemistry of these elements. Chemical union of Li and F is assumed to be attended by the transfer of an electron from one atom to the other; such a "bond" is called "polar," in contrast to the nonpolar bond in H_2.

Beryllium atoms have 2 external electrons, and become Be^{++} when these electrons are transferred, say, to 2 fluorine atoms. An aqueous solution of BeF_2 probably contains Be^{++} and F^-, but the salt is largely hydrolyzed. (The Be═F bond is not wholly polar, nor are the Be—Cl and Be—O bonds, but the distinction is best ignored at first.[1] The same statement applies to bonds between boron and the halogens and to a lesser extent to some of the other bonds.)

Boron, with 3 external electrons, has little tendency to lose them and become B^{+++} and a strong tendency to share them in forming compounds such as BF_3, even though no shell is completed by doing so The probable structure of BF_3 is indicated by the arrangement



$$\begin{array}{c} :\dot{F}: \\ :F:\ddot{B}:F: \end{array}$$

The halides of boron hydrolyze completely in aqueous solution, BF_3 forming boric acid and fluoboric acid, with no B^{+++} ions, and the other halides forming boric acid and the ions of hydrogen halides.

Carbon, with 4 external electrons, likewise has no tendency to lose them and form C^{++++}, but it readily completes its shell by sharing 4 pairs of electrons with any of several elements having incomplete shells. There are four covalent bonds in all the compounds CH_4, CH_2Cl_2, $CFCl_3$, CO_2, and CS_2. No single electron structure is satisfactory for carbon monoxide, and there may be several arrangements with resonance between them. The remarkable resemblance of CO to N_2 in many physical properties has often been cited as evidence that they have the same electron structure.

The next two elements, nitrogen and oxygen, commonly form compounds in which the bonds are covalent or nonpolar. The

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[1] See PAULING, "Nature of the Chemical Bond," 2d ed., Chap. II, Cornell University Press, Ithaca, N. Y., 1940.

arrangement of electrons in nitrogen molecules is not known, and there may be two arrangements as with CO; oxygen molecules are probably formed, not merely by sharing two pairs of electrons, but by some other arrangement that is uncertain.

Fluorine readily accepts an electron to complete its shell and become F^-, and it shares a pair of electrons in F_2.

Third Period.—Sodium begins this period, and argon ends the period. If we consider only the isotope with mass number nearest the atomic weight and ignore the distinction between *p* and *s* electrons, as was done for the second period, the elements in their normal states have the following compositions:

Atomic number	Element	Mass number	Nuclear composition	Electrons
11	Na	23	$11p + 12n$	$2 + 8 + 1$
12	Mg	24	$12p + 12n$	$2 + 8 + 2$
13	Al	27	$13p + 14n$	$2 + 8 + 3$
14	Si	28	$14p + 14n$	$2 + 8 + 4$
15	P	31	$15p + 16n$	$2 + 8 + 5$
16	S	32	$16p + 16n$	$2 + 8 + 6$
17	Cl	35	$17p + 18n$	$2 + 8 + 7$
18	A	40	$18p + 22n$	$2 + 8 + 8$

In general, the discussion for each element in this period is the same as that for the element above it in each column of Table 85. Sodium tends to lose its single outer electron, assume the electron arrangement of neon, and become Na^+ in solution or in a crystal. Chlorine tends to acquire an electron, assume the electron arrangement of argon, and become Cl^- in solution or in a crystal. Thus NaCl has a polar bond. The ions Mg^{++} and Al^{+++} similarly result from the loss of electrons and reversion to the stable electron arrangement of neon, and these ions are found in solution and in most of the crystals

Silicon, like carbon, does not lose 4 electrons and form positive ions, but it shares electrons to form compounds such as SiH_4, $SiCl_4$, and $SiHCl_3$ with covalent or nonpolar bonds. Phosphorus forms PH_3 and completes its shell just as nitrogen forms NH_3 Sulfur may complete its shell, as in H_2S with two covalent bonds, or become S^{--}. In HS^- it probably shares one *pair* of electrons and loses one electron. Polysulfides up to S_5^{--} are also known, and the electron arrangement for sulfur in all of them is probably close to that for covalent bonds.

Fourth Period.—Eighteen elements fall in this period, two each in groups I to VII (thus beginning the subgroups), three elements in group VIII, and one element in the zero group as shown in Table 85. In discussing the fourth period we cannot ignore the separation of electrons into *s* and *p* groups, and thus we must now refer briefly to the distinction in the second and third periods of the elements.

In the second period lithium has one 2*s* electron, beryllium and all the other elements in this period have two 2*s* electrons, boron has in addition one 2*p* electron, and the following elements have, successively, two, three, four, five, and six 2*p* electrons. Thus in neon, which has a complete shell, there are two 1*s*, two 2*s*, and six 2*p* electrons to form the "neon core."

The succession in the third period is the same for electrons outside the "neon core"; sodium has one 3*s* electron, magnesium has two 3*s* electrons, as do all the other elements in the third period, and the elements from aluminum to argon add one to six 3*p* electrons. Throughout the third period the "neon core" persists, throughout the fourth period the "argon core" persists, while outside of each core the electrons of the next shell are successively added.

Electron structures for the first four periods are shown in Table 94, which the student should study before reading the next section and to which he should refer while reading it.

Potassium (atomic number 19) begins the fourth period by adding a single 4*s* electron to the argon core of element 18, and calcium (atomic number 20) has two 4*s* electrons; but with scandium (21), titanium (22), and vanadium (23) a new circumstance is met. These three elements have two 4*s* electrons, and, respectively, one, two, and three electrons at the third level, designated 3*d*. Chromium (24) has not one additional 3*d* electron, but two more, or five altogether, and only one 4*s* electron. Manganese (25) adds one 4*s* electron to restore the number to two, and iron (26), cobalt (27), and nickel (28) retain two at the 4*s* level while increasing, respectively, to six, seven, and eight at the 3*d* level.

All the elements in the second line of the fourth period of the periodic table as shown in Table 85, the elements copper (29)

TABLE 94.—SOME ELECTRON STRUCTURES FOR ATOMS IN THEIR NORMAL STATES[1]

		K	*L*		*M*			*N*			
		1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*
H	1	1									
He	2	2									
Li	3	2	1								
Be	4	2	2								
B	5	2	2	1							
C	6	2	2	2							
N	7	2	2	3							
O	8	2	2	4							
F	9	2	2	5							
Ne	10	2	2	6							
Na	11				1						
Mg	12	2	2	6	2						
Al	13		neon		2	1					
Si	14		core		2	2					
P	15				2	3					
S	16				2	4					
Cl	17				2	5					
A	18				2	6					
K	19							1			
Ca	20	2	2	6	2	6		2			
Sc	21			argon			1	2			
Ti	22			core			2	2			
V	23						3	2			
Cr	24						5	1			
Mn	25						5	2			
Fe	26						6	2			
Co	27						7	2			
Ni	28						8	2			
Cu	29							1			
Zn	30	2	2	6	2	6	10	2			
Ga	31			copper				2	1		
Ge	32			core				2	2		
As	33							2	3		
Se	34							2	4		
Br	35							2	5		
Kr	36							2	6		

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[1] For a full table see Richtmyer and Kennard, *op. cit.*, Appendix III.

to krypton (36), have the same "copper core" of electrons, while the additional electrons increase as in the second and third periods. Copper has one 4*s* electron, zinc (30) has two 4*s*, gallium and all of the remainder have two 4*s* and successively one 4*p* for gallium, two 4*p* for germanium (32), up to six 4*p* for krypton (36) to complete the period, and a new stable "krypton core" that persists through the next 10 elements.

This detailed discussion of the elements of the fourth period is given to point out the fact that the addition of electrons at a fourth level does not exclude further additions at the third level. In the next period additions at the fifth level do not exclude further additions at the fourth level. It should also be noted that a number of electrons once reached at a given level is not always maintained. In the period beginning with cesium the first addition of an electron is at the sixth level, and subsequent additions at both the fourth and fifth levels are found.

The rare earths have the same number of electrons in all levels up through 6*s* and 6*p* except the 4*f*, with different numbers of 4*f* electrons, which is a partial explanation of their chemical similarity, since chemical behavior is largely determined by electrons in the outer levels.

As was said at the beginning of the chapter, the purpose of the discussion has been to give support to the belief that atoms consist of neutrons, protons, and electrons, to obtain a general picture of their structures, to point out that the electrons largely govern the properties of the elements while the protons and neutrons supply substantially all the mass, and to indicate the sources of the information on which these beliefs are based. It may be worth repeating that the concept of electron shells is not wholly free from objections, that, since the evidence regarding electrons is almost all spectroscopic, the conclusions apply to gaseous atoms, and that there is some danger of error in the literal acceptance of a simplified picture of a complicated situation.

References

For a discussion of nuclear reactions see Richtmyer and Kennard, "Introduction to Modern Physics," McGraw-Hill Book Company, Inc., New York, 1942; for the separation of isotopes see Aston, "Mass Spectra and Isotopes," Edward Arnold & Co , London, 1942; for a discussion of the chemical bonds see Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N.Y., 1940.

CHAPTER XVII

COLLOIDS. SURFACE CHEMISTRY

In this chapter we discuss very briefly some "heterogeneous" systems of a special type, systems in which a substance is so finely dispersed in a liquid that surface effects become of first importance. Any attempt to discuss such a vast field of chemistry in a few pages must necessarily be only a consideration of a few principles and their application to a few simple systems, with an almost total neglect of the complex experimental technique and the many important industrial applications. It must be remembered, however, that there are experimental techniques of preparation and study which are of the greatest importance and applications of the widest variety in plastics, adhesives, pharmacy, textiles, ceramics, and many other fields.

Colloidal systems are intermediate between true solutions, homogeneous dispersions of ionic or molecular solutes, and mixtures in which phase boundaries are evident and to which the principles of heterogeneous equilibrium apply. Since many colloidal systems are not at equilibrium, their study is complicated by a change of properties with time. There is no sharp dividing line between solutions, colloids, and gross suspensions except by arbitrary definition that would serve no useful purpose. As polymerization (for example) proceeds from single to double or triple or multiple molecules, to "low" polymers, to "high" polymers, to visible droplets or crystals, the change is attended by a gradual change of properties. One of the important problems in industry is control of such a process and its restraint in order to produce a polymer of the desired properties. Since the mechanism of the process is commonly not known, it is difficult to apply rate considerations such as were discussed in Chap. XII to them; and since the composition or structure of the colloid changes with time, it is also difficult to consider adsorption isotherms, intermolecular forces, oriented monolayers at interfaces, and other apparently applicable principles.

Of the eight possible types of disperse systems [(1) liquid in gas, (2) solid in gas, (3) gas in liquid, (4) liquid in liquid, (5) solid in liquid, (6) gas in solid, (7) liquid in solid, (8) solid in solid] only the fourth and fifth are of such general importance as to be considered in this brief discussion. While the word colloid, which is commonly applied to these systems, is derived from the Greek word for glue, it is now used to classify almost any system in which particles significantly larger than molecules but small enough to be invisible in a microscope are dispersed in a nearly stable form. Almost any liquid may be the dispersion medium, or "solvent," but we shall consider mostly aqueous dispersions; and almost any insoluble substance may be the "dispersed part" of a colloidal system.

As a rough classification, particles that are of greater diameter than 10^{-4} cm. or 1μ are considered coarse suspensions, and particles 10^{-5} to 10^{-7} cm. (100 to 1 $m\mu$) are called colloidal suspensions. Since molecular dimensions are about 10^{-8} cm., it will be clear that a particle of 10^{-7} cm. diameter might contain only a few molecules of a substance of high molecular weight. We have seen in an earlier chapter that the thickness of some of the monolayers exceeded 10Å or 1μ, and hence a particle of $1\mu^3$ volume might be a single molecule. Thus there is no sharp dividing line between colloids and true molecular dispersion of large molecules. We shall see presently that colloidal suspensions have some of the properties of dilute solutions of very large molecules.

Aqueous suspensions, or hydrosols, may be divided into two classes called hydrophobic, or electrocratic (when the attraction between water and the colloid is slight), and hydrophilic (when there is a strong attraction between water and the colloid); but since slight and strong are not precisely definable, there are colloidal systems whose classification in this way might be arbitrary or misleading. Typical examples of hydrophobic colloids are gold, platinum, ferric hydroxide, arsenious sulfide, sulfur, bentonite, silver iodide, and ferric ferrocyanide. Stable aqueous suspensions of these substances, when the particles are 10^{-5} cm. or less in diameter, appear transparent when viewed in transmitted light, but they may be opalescent or opaque when viewed at a right angle to the transmitted light. The viscosity or vapor pressure or surface tension of any of them would be almost the same as for pure water, but methods to which we shall come presently show that they are not true solutions. Through X-ray diffraction it has been shown that the particles of many colloids are small crystals presumably held in suspension because of the extreme fineness of subdivision and probably stabilized by selective adsorption on the large surface exposed Even such typically crystalline substances as sodium chloride have been prepared in colloidal form in nonaqueous dispersion media.

When the particle edge for a centimeter cube of material is reduced to 10^{-5} cm., the surface exposed is multiplied by 10^5, so that about 10 sq yd. of surface become exposed for each original square centimeter, and surface effects become of the first importance in determining the properties of these systems

Typical hydrophyllic colloids are aqueous gelatin, agar, starch, proteins, and soap. These systems at moderate dilutions would have almost the same vapor pressure as pure water, since the mole fraction of the colloid is very small, but the surface tension is usually much less, and the viscosity much greater, than for pure water.

Degree of Dispersion.—The diameter of particles concerned in suspension formation depends on the method of preparation; thus a gold suspension may be red, purple, violet, or black, according to the average size of particle produced, though the color also depends on the concentration of colloid and its method of preparation. The average diameter may be determined by counting the particles in a known volume of solution (by a method to be described presently), then evaporating a portion of sol, and weighing the resulting deposit. From the number of particles per cubic centimeter, their weight, and the density of the dispersed substance, the average diameter is readily calculated. It should be borne in mind that the diameters of individual particles in a sol may be very much larger and very much smaller than an average thus determined unless special precautions are taken to ensure a nearly uniform size This is accomplished by fractional settling, usually with the aid of a powerful centrifuge, or by the use of selective filters called ultrafilters. Diameters of particles may also be obtained from the density distribution of a sol under the influence of gravity and in another way that will be described in connection with Brownian movement in a later paragraph.

In this discussion the word diameter should not be taken too literally, for while some dispersed solids behave as if they were of approximately the same size in all directions others do not. Some "high polymers" made by condensation of molecules may be 100 or 1000 times as long as the dimensions of molecules and of approximately molecular cross section, and the cube root of the volume of such a particle would have little meaning as a diameter.

Surface Phenomena.—According to Langmuir's theory of the structure of a solid surface, outlined in Chap. V, an atom or molecule in the surface of a crystal has an attractive force reaching into space for a distance comparable to the diameter of a molecule and capable of holding molecules in adsorbed monolayers upon the surface. A dispersed solid, such as a hydrosol, exposes a very large surface per unit quantity of dispersed solid and is thus able to adsorb solvent molecules or whatever solute may be in the suspending medium to a much greater extent than the same quantity of gross matter. The adsorptive forces are selective in character; they may attract one kind of ion to the nearly total exclusion of others present in equivalent or greater concentration; they may hold only solvent molecules and ignore moderate concentrations of solutes. In the latter circumstance that part of the liquid in immediate contact with the dispersed part of the colloidal system may be wholly free of solute, and the effect of adding a solute may not be appreciable. If the adsorption is confined to a given ion, addition of very small quantities may alter the stability of the sol and cause coagulation, while the addition of a larger quantity of some other solute may produce almost no effect.

✓ **Dialysis.**—The existence of colloidal materials was first shown by their failure to diffuse through membranes of parchment paper, collodion films, and animal membranes, while salts, alcohol, sugar, and most "true" solutes passed through such membranes when they were used to separate a solution from pure water. Such a separation of solutes from colloids by allowing the former to pass through the membranes is called dialysis, and the process itself is still of common application in colloid chemistry whenever it is desired to free a hydrosol from dissolved salts or other solutes.

Dialysis is a slow process, requiring many days when a sol is to be freed from dissolved substances completely. It cannot, in general, be accelerated by immersing a sol in hot water, since this is likely to precipitate the sol. As dialysis depends on diffusion of a dissolved substance through a membrane into a region where its concentration is lower, the rate of dialysis depends on the area of membrane used and on the difference in concentration between the inside and outside liquid. Hence a vessel composed entirely of membrane is used to enclose the sol, and a stream of distilled water is sometimes passed into the outer vessel. Toward the end of such a dialyzing process the difference in concentration of diffusing substance becomes very small, and the rate very slow

Methods of Preparing Sols.[1]—Since the dispersed part of a colloidal system consists of particles that are smaller than ordinary crystals and larger than single molecules, the obvious methods of preparation are dispersion of larger particles and condensation of molecules. Dispersion by mechanical grinding in "colloid mills" usually fails to reach true colloidal dimensions These mills are shearing mills rather than grinders; they find application in decreasing the particle size of emulsions and thus increasing their stability. Electrical dispersion is accomplished by striking an arc between metal poles immersed in the suspending medium. Gold, platinum, silver, and other metals have been made into hydrosols by this procedure; electrodes of oxidizable metals form hydroxide or oxide hydrosols. Low-frequency alternating current or direct current gives similar sols, but high-frequency alternating current is said to produce smaller particles.

Condensation methods include precipitation by chemical reactions, as in the formation of As_2S_3 by passing H_2S into arsenious acid, of colloidal sulfur by pouring an alcoholic solution of sulfur into a large quantity of water, of ferric hydroxide by the hydrolysis and dialysis of ferric chloride, and of other substances by the ordinary reactions such as oxidation, reduction, and metathesis. The insoluble substances familiar in analytical chemistry are usually precipitated under conditions designed to

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[1] Stable colloids must be prepared with care by special methods, with attention to many details. Only a bare outline of the general methods can be included here, but there are several books readily available. Hauser and Lynn, "Experiments in Colloid Chemistry," McGraw-Hill Book Company, Inc., New York, 1940, gives many of these methods, with ample references to the literature.

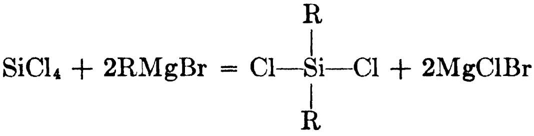
avoid the formation of colloids that are difficult to filter, but most of them may be prepared in colloidal form under other conditions of precipitation. Removal of electrolytes by dialysis usually increases the stability of these colloids up to a certain point, but complete removal may cause flocculation. The ferric hydroxide hydrosol formed by the hydrolysis of ferric chloride is more stable in the presence of some ferric chloride than after its nearly complete removal. Other colloids, such as platinum, silica, and some sulfides, are unstable if electrolytes are removed.

Certain solutes act on precipitates in such a way as to convert them into nearly stable hydrosols; the most common examples are inorganic salts of which the solute has an ion in common with the precipitate. Thus silver halides are converted into sols by dilute silver nitrate or the corresponding potassium halide; sulfides, such as cadmium sulfide, zinc sulfide, mercuric sulfide, and lead sulfide, are rendered colloidal by hydrogen sulfide; metallic oxides, by strong alkali hydroxides. In some sols this action, which is called peptizing, is reversible, as in that of metallic sulfides, which may be made into colloidal suspensions by hydrogen sulfide, thrown down by boiling it out, and taken up again by passing hydrogen sulfide into a suspension of the precipitate, and this process may be repeated over and over.

Another type of "colloidal" particle may be built up through the usual methods of organic chemistry, a chain such as

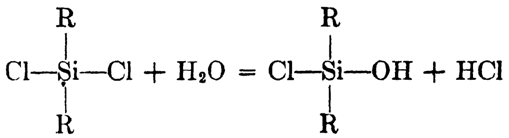
$$\text{—Si—O—Si—O—Si—O—}$$

being formed with organic radicals on the silicon atoms. The first step is shown by the equation



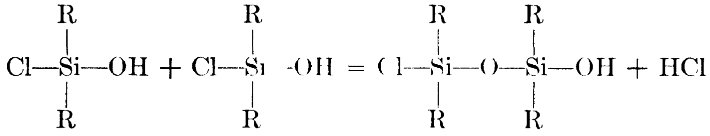
$$\mathrm{SiCl_4 + 2RMgBr = Cl{-}\overset{\displaystyle R}{\underset{\displaystyle R}{Si}}{-}Cl + 2MgClBr}$$

followed by partial hydrolysis



$$\mathrm{Cl{-}\overset{\displaystyle R}{\underset{\displaystyle R}{Si}}{-}Cl + H_2O = Cl{-}\overset{\displaystyle R}{\underset{\displaystyle R}{Si}}{-}OH + HCl}$$

Two of these molecules then split out HCl, uniting the silicon atoms and leaving a terminal —OH on which further condensation takes place, and this may be continued as long as desired The third step is



$$\mathrm{Cl{-}\underset{R}{\overset{R}{Si}}{-}OH + Cl{-}\underset{R}{\overset{R}{Si}}{-}OH = Cl{-}\underset{R}{\overset{R}{Si}}{-}O{-}\underset{R}{\overset{R}{Si}}{-}OH + HCl}$$

These "silicones" may contain only one organic radical or several, and "branched" chains may be formed by using $RSiCl_3$ as the starting material

Solutions of isobutylene in volatile solvents yield polyisobutylene when treated with BF_3, the number of molecules in the polymer depending on experimental conditions. These polymers are also probably chain molecules Other materials may likewise be polymerized under suitable conditions.

Determination of Molecular Weights.—Sols do not appreciably lower the vapor pressures or freezing points of the solvents in which they are dispersed; their osmotic pressures are very small, and their molecular weights are very high.

The diameters of colloidal particles in the finest suspensions are ten times those of molecules and much larger in the ordinary colloid; the "molecular weights" would be thousands of times those of molecules of ordinary solutes, and thus the mole fractions corresponding to small weight percentages would be very small Since the ordinary molecular-weight methods measure the mole fraction of the solute, it is uncertain whether the osmotic pressure or freezing-point measurements carried out on these substances really represent the osmotic pressure of the colloidal substance itself, and not that of some contaminating solute, in spite of great care used in purifying the sols. Molecular weights so determined are often many thousands and far from concordant. It will be clear from considerations to be given presently that colloidal particles are far larger than ordinary molecules, and that ordinary molecular-weight methods are quite unsuited to studying them. Molecular weights of certain colloidal substances may be determined from osmotic-pressure measurements in which the ratio of osmotic pressure to concentration is plotted against the concentration, as was explained in Chap. VI. This procedure has been particularly successful in studying some of the "high polymers."

Viscosity and Density.—Densities of colloidal suspensions, calculated on the assumption that the sol is a mixture of solid particles in suspension in a liquid, and without any effect upon it, agree with those based on experiment. This is not surprising in view of the small concentrations of suspended material usually encountered, as these are usually less than a tenth of 1 per cent. The viscosity of dilute suspensions is usually only slightly greater than that of the suspending medium, and the increase in viscosity depends on what fraction of the total volume is solid, rather than on its fineness of dispersion. A relation due to Einstein, $\eta = \eta_0(1 + \frac{5}{2}\phi)$, where ϕ is the volume of suspended material, is approximately true under certain restricted conditions, but greatly in error if the particles carry electric charges.

An approximate relation of some usefulness in following the extent of polymerization of long-chain molecules is[1]

$$\frac{\eta - \eta_0}{\eta_0} = kcn$$

in which $(\eta - \eta_0)/\eta_0$ is the fractional change in the viscosity of the solution produced by the solute, η_0 is the viscosity of the solvent and η is that of the solution, k is a constant, c is the concentration of the solution expressed as moles of single molecules, and n is the number of molecules in the chain. Other factors also influence the change in viscosity, so that the relation is only a rough guide. For instance, the viscosity change is not the same when "branched chains" are formed as when straight chains are formed, and thus the molecular weight of the condensation product is not n times that of the single molecule when n is determined from the viscosity change, unless proper allowance is made for the structure of the condensed molecule.

These polymers have "molecular" dimensions in two directions and "colloidal" dimensions in their length. Their solutions have some of the properties of "true" solutions and some of the properties of colloids, as is true of other organic compounds of high molecular weight.

Rate of Settling of Suspensions.—If it be assumed that a particle is a sphere of radius a and density d and that it is settling

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[1] STAUDINGER, *Kolloid Z.*, **82**, 129 (1938).

through a gaseous or liquid dispersing medium of density d' and viscosity η under the influence of gravity g, its rate of settling is given by Stokes's law,

$$v = \frac{2a^2(d - d')g}{9\eta}$$

Thus the rate at which a particle settles becomes slower as the density of the particle approaches that of the suspending medium Under the influence of a force greater than gravity (for example, in a centrifuge) the rate of settling can be correspondingly increased.

Experiments have shown that this equation describes the rate of settling of some dilute suspensions and that the radius of the particles as determined from the rate of settling agrees with that from other methods. "Very small" particles settle faster than Stokes's law requires, but particles 10^{-5} cm. in diameter or smaller remain permanently in suspension, probably because of their Brownian movement. In very concentrated suspensions the particles settle with a uniform velocity more slowly as the concentration increases. For example, in an aqueous suspension containing 25 per cent silica by volume, the rate of settling is about half that calculated from Stokes's law. The law also applies to fog or dust particles settling in air, provided that the particles are large compared with the mean free path of the gas molecules.

Electrical Properties.—Sols exert a slight effect on the electrical conductance, and part of this small increase is probably due to traces of electrolyte adsorbed by the particles. Either because of adsorbed ions, or from frictional electricity, suspensions bear charges that cause them to migrate in an electric field. Most colloidal metals, As_2S_3, and AgI are examples of colloids that move toward and precipitate upon the anode; most hydroxide sols move toward the cathode. The phenomenon is called cataphoresis, and it should not be confused with the movement of ions as in transference. There is no relation such as Faraday's law between the weight of colloid precipitated and the quantity of electricity. In other words, the charge upon a colloidal particle depends not on its weight, but on the amount and charge of adsorbed ions, which vary with the conditions under which the colloid is prepared.

The motion of water toward the cathode through a porous clay separator when a potential is applied to electrodes on opposite sides of it is called electroendosmosis. When a fine suspension of clay in water is placed between electrodes, the clay moves toward the anode. Thus the displacement of clay relative to water by the electric field is the same, whether the clay or the water moves. A similar effect is observed when any other suspension, such as arsenious sulfide, is held stationary in an electric field; water is displaced in the opposite direction This movement in an electric field is applied industrially in purifying china clay, in tanning, in medicine, for separating water from peat, and in several other ways. The mechanism of the process is probably similar to that in the Cottrell precipitator for smoke and dust, in which fine particles suspended in air are caused to precipitate on a charged netting or set of chains.

Electrical Double Layer.—This expression is commonly used to describe the condition around a colloid particle that has adsorbed ions of one charge, leaving the corresponding ions of opposite charge in the solution free to migrate as much as the electrical attractions permit. If to a suspension that has adsorbed positive ions one adds a small amount of an electrolyte whose negative ions are adsorbed, equal amounts of positive and negative ions may be acquired by the particles at a characteristic (small) concentration, and, when they have no net charge, flocculation usually results.

To account for the existence and formation of the electrical double layer at colloid surfaces, two theories have been proposed. The "adsorption theory" postulates that the ionic layer which confers the fundamental charge is firmly held at the surface by means of the preferential adsorption of ions from the dispersion medium, whereupon the ions of opposite charge form a diffuse system about the particle, owing to electrostatic attraction. The solubility, or "ionogenic complex," theory attributes the formation of the diffuse layer to ions dissociated from the colloidal particles, which themselves are considered as complex colloidal salts. The charge on the particles exists because of the free valence ions on the surface of the complex salt. The experimental evidence seems to favor the adsorption theory.[1]

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[1] See Hauser and Hirshon, *J. Phys. Chem.*, **43**, 1015 (1939), for a discussion of these theories and the interattraction of colloidal micelles.

In an attempt to go one step further in explaining the stability of colloidal suspensions, the interaction of "long-range" van der Waals' forces and electrostatic repulsions has been brought into the discussion; but the evidence so far accumulated is not very convincing, and direct proof is wholly lacking.

✓ **The Ultramicroscope.**—This instrument does not render particles *visible* that are invisible in an ordinary high-power microscope, but it shows that such particles are present by a bright spot of light radiated from each particle. Nothing whatever as to the size or color or shape of a particle is learned from its effect upon the eye when viewed through an ultramicroscope: yet the apparatus is justly entitled to its name, since it shows the presence of a particle that cannot be seen at all in an ordinary microscope A rough illustration of the principle on which it is based is afforded by the beam of light from a projection lantern in a darkened room, the so-called Tyndall effect. This shows particles of dust or smoke suspended in the air that are quite invisible when the room is thoroughly lighted but does not show the color of the particles. The ultramicroscope merely magnifies highly a small portion of such an illuminated volume of suspension in a liquid medium, which is made so dilute that light radiated from each particle reaches the eye without interference from some other particle, as shown in Fig. 70.[1] Under similar conditions a concentrated suspension gives only a uniformly bright field in which no individual particles are rendered visible.

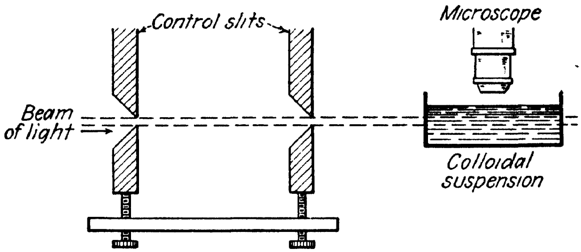

FIG. 70—Diagram of an ultramicroscope.

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[1] Special methods have been developed for accurate control of the slit, which governs the depth of liquid illuminated, and for intense illumination These are described in any of the larger reference books on colloids mentioned at the end of this chapter.

A particle 10^{-5} cm. in diameter is invisible under the highest power of a microscope, but the effect of such a particle is clearly seen under an ultramicroscope. Particles far smaller in diameter than a wave length of visible light are able to show their presence by radiating light in the ultramicroscope, and the number of such particles in an illuminated volume may be counted. When the area of field under the microscope is known and the depth of illuminated area is measured and regulated by a micrometer slit between the arc light and vessel containing a sol, a count of the spots of light in such a field gives the number of particles in a known volume Even with very dilute sols it is often necessary to dilute them with large quantities of pure water before a count is possible. For this dilution ordinary distilled water is quite unsuited, as it contains thousands of visible particles in a drop. Specially prepared "optically empty" water is required, and its preparation involves special methods.

The size of particle detected by an ultramicroscope depends chiefly on the intensity of illumination; the lower limit is not far from 10^{-7} cm., which is about 0.2 per cent of the wave length of visible light.

Brownian Movement.—The molecules in a liquid are in rapid though tumultuous motion of the kind outlined in connection with the kinetic theory of gases. A colloidal particle is very large compared with the diameter of a single molecule, and it is continuously bombarded on all sides by great numbers of molecules. Occasionally, the pressure due to this bombardment is for the moment greater on one side of the particle than on the other, and the particle is urged forward until a new distribution of impacts hurls it in another direction. The excursions due to these movements depend mainly on the size of the particles, and the movement corresponds exactly with that predicted by the molecular theory.

Here we have reproduced in a way visible to our eyes the random unordered continuous motion of molecules postulated in connection with the kinetic theory of gases. This motion takes place as a result of impacts with real molecules, but it makes a colloidal particle behave as if it were a single molecule. The motion was first observed by the botanist Brown on plant cells that were visible in an ordinary microscope; the movement was little more than an irregular oscillation, whose real cause remained long unsuspected From equations based on the kinetic theory it may be shown that the amplitude of this vibration is directly related to the diameter of the particle and the viscosity of the suspending medium. Thus what in an ordinary high-power microscope is a slow-oscillating effect produced on a plant cell or small bacillus becomes, for a much smaller colloidal particle, a lively zigzag motion, as shown by the cone of light radiated from it in an ultramicroscope.

A reliable method of determining the size of suspended particles is based on their Brownian movement, the equation for which is used in another way in the next paragraph. In this equation the radius of a particle may be determined if we assume a value for Avogadro's number of molecules in a gram-molecular weight of gas; or from counting particles and an analysis of the sol we may determine the radius, perform the reverse calculation, and compute a value of Avogadro's number. The latter procedure is more interesting.

✓**Brownian Movement and Avogadro's Number.**—A relation may be derived between the intensity of Brownian movement, the radius of the particle, the viscosity of the dispersing fluid, and the number of molecules of gas in a gram-molecular weight. Since colloidal particles are bombarded by molecules in a wholly random way, they will have the random motions of a large gas particle and will behave as such. Upon this assumption, the equation, in terms of the mean displacement d in a unit of time t, is

$$\frac{d^2}{t} = \frac{RT}{3N\pi r\eta}$$

where r is the radius of a particle, N is Avogadro's number, and η is the viscosity of the liquid suspending medium. Experiments based on observation of displacements in small time intervals lead to values of Avogadro's number between 6.2×10^{23} and 6.9×10^{23}, in fair agreement with other methods.

✓ **Distribution of Particles under the Influence of Gravity.**—A suspension of colloidal particles tends to separate out the solid under the influence of gravitational attraction and is partly prevented from doing so by the Brownian movement, in much the way that molecules of the atmosphere are attracted to the earth by gravity and prevented from settling upon it by the intensity of their molecular motion. The equation expressing the variation in density of the atmosphere with the altitude contains N, the number of molecules in a gram-molecular weight. A colloidal suspension of particles of uniform size that has reached settling equilibrium distributes itself in the way that the atmosphere is distributed under the action of gravity, thus reproducing within reasonable space the effect for which the atmosphere requires several miles of altitude. From determinations of the number of particles per milliliter at equilibrium, the variation of density with altitude may be established and used to calculate a value of Avogadro's number N. If n_1 is the number of particles per unit volume at a level that we may call zero height, and n_2 is the number at another level h cm. above the first one, the equation for change of concentration with h is

$$2.303 \log \frac{n_1}{n_2} = \frac{Nmgh}{RT}$$

where m is the difference in mass between a colloidal particle and the volume of solvent it displaces, g is the acceleration of gravity, and N is Avogadro's number. Investigations based on this equation lead to a value for N of 6.8×10^{23}.

The derivation is based on the assumption that the colloid particles exhibit the same behavior as molecules of an ideal gas. Let ρ be the density of colloidal particles in the mixture; then $\rho\, dh$ is the mass of an element of thickness The change of pressure with h is then shown by the equation on page 69, namely,

$$dp = -\rho g\, dh$$

For ρ substitute Nm/v, where N is Avogadro's number, v is the molecular volume, and m is the apparent mass of a particle, *i.e.*, the difference between its mass and that of the solvent it displaces. It should be noted that Nm is the molecular weight. If, now, we divide the above equation by $pv = RT$, we have

$$\frac{dp}{p} - \frac{-Nmg}{RT}\, dh$$

On integrating between limits and noting that the ratio of pressures is equal to the ratio of the number of particles per milliliter, we have

$$2.3 \log \frac{n_1}{n_2} = \frac{Nmg}{RT}(h_2 - h_1)$$

where $(h_2 - h_1)$ is the h of the equation in the above text.

Precipitation of Colloids.—As has been mentioned before, most suspensions are electrically charged, probably as a result of adsorbed ions on the surface of the particles. Ionic adsorption is a selective process, some ions being more strongly adsorbed than others When a solution containing readily adsorbed negative ions at low concentration is added to a positively charged sol, these ions are adsorbed and neutralize the electric charge of the particles, so that they no longer repel each other. Coagulation or precipitation takes place, and it has long been recognized that this ionic adsorption is highly specific, in regard to both the colloid and the ions. The significant ion in the precipitation of colloids by electrolytes is the one having a charge opposite in sign to that of the particle A general rule, to which there are occasional exceptions, is that ions of higher valence are more strongly adsorbed (and therefore more effective in producing precipitation) than ions of lower valence. Thus, for most negatively charged suspensions, ferric salts, aluminum salts, and trivalent cations in general are most effective as precipitants, *i.e.*, produce coagulation when added in the smallest concentrations; lead and barium salts come next, and then heavy monovalent ions, such as silver; finally, the alkali ions are least effective. The negative ions play only a minor part in these precipitations. Similarly, positively charged sols are more readily precipitated by sulfates or phosphates than by monovalent anions at equivalent concentrations, and the positive ion exerts a secondary effect or one that is negligible. Among anions the order of decreasing precipitating effect is sulfocyanate, iodide, chlorate, nitrate, chloride, acetate, phosphate, and sulfate for albumin and certain other colloids; but the precipitating power of these ions is in the reverse order for some colloids.

The term precipitation is not used in the same sense as in analytical chemistry, for there is no stoichiometric relation between the weight of "precipitate" and the quantity of salt producing it. There is rather an aggregation of the particles, which depends on the *concentration* of reagent to a greater degree than on its quantity. Ordinarily the salt, such as $MgSO_4$, that is used as the precipitant largely remains in solution after the suspension has settled out.

Precipitation also takes place when a positively charged sol is added in proper quantity to a negatively charged sol, each neutralizing the charge carried by the other. It does not follow that a chemical compound is formed, though the coagulated material may seem to be a compound. For example, ferric hydroxide sol precipitates arsenious sulfide sol but probably does not form ferric thioarsenite. It seems probable that precipitation is due to a reaction of the adsorbed stabilizing electrolyte. In general, suspensions are much more sensitive to electrolytes at very small concentrations than are emulsions.

Protective Colloids.—Certain substances have a conspicuous property of stabilizing colloidal suspensions. Thus a dispersion of silver chloride is maintained in a stable state by gelatin in a photographic film, and the success of a film is largely dependent on its retaining a uniform dispersion of this silver chloride. Lyophilic colloids such as gelatin, gum arabic, protein, starch, casein, and soap are among the common protective colloids; tannic acid stabilizes the aqueous suspensions of graphite used as commercial lubricants, though other substances are also effective. Electrolytes that stabilize colloids probably do not form a protective film but owe their effectiveness to the adsorption of a common ion, by which repulsive forces are set up between the particles that increase dispersion and thus increase stability. There is no reason to doubt that adsorption is also active in the mechanism of protective colloids, though a simple and quite plausible explanation is that the protective substance coats the suspended particles with a very thin layer of protecting colloid. Substances that are effective in this respect are themselves able to form stable gels.

Soap Solutions.—The extensive researches of McBain and his associates have brought to light another colloidal condition that seems to be characteristic of soaps in aqueous solution. These solutions conduct electricity to about the same extent as other salts at the same equivalent concentration but they produce a depression of the vapor pressure of solvent that would be expected of a nonionized solute.[1] His studies have shown that soaps are not hydrolyzed to the large extent formerly assumed but that a colloidal aggregate of the negative ions forms, which he calls an "ionic micelle." If we take sodium

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[1] McBain and others, *J. Chem. Soc.* (*London*), **101, 105, 113, 115, 117, 119, 121.** See especially pp. 1–31 of the "Report on Colloid Chemistry," *Brit. Assoc. Advancement Sci.* (1920), and pp. 244–263 of the 1922 *Report.*

palmitate as an example and let P^- denote the palmitate ion, $C_{15}H_{31}COO^-$, an important part of the effect produced when soap dissolves in water may be represented by the equation

$$x\text{NaP} = x\text{Na}^+ + P_x^{x-}$$

The chief difference between this condition and that of an ordinary ionized solute is the aggregation of negative ions into a large (colloidal) group possessing about the same *equivalent* conductance as a negative ion. There are also present in a soap solution simple sodium palmitate molecules, colloidal soap $(\text{NaP})_y$, and simple palmitate ions The proportion of these various solutes present in solution varies greatly with the concentration. In dilute solutions NaP and P^- predominate, and in a normal solution 50 per cent exists as $(\text{NaP})_y$ at 90° and about 30 per cent as the ionic micelle. Aqueous solutions of soaps when functioning as detergents are seldom at concentrations greater than 0.01*m*. or less, so that neither the colloidal soap nor the ionic micelle contributes very largely to the useful properties commonly associated with soap Probably the effect of simple sodium palmitate molecules upon the surface tension is chiefly responsible for the cleansing action of soap.

Experiments upon sodium laurate, $C_{11}H_{23}COONa$, which is abbreviated NaL, show the molecular species HL_2^-, $NaHL_2$, HL.3NaL, and L_6^{6-} are present[1], and it is probable that similar solutes exist in other soap solutions.

In a study[2] of the potassium salts of the long-chain acids containing 6 to 12 carbon atoms, the conductances and freezing points are said to show that only simple ions and simple molecules are present; and solutions up to 0.5*m*. contain very small amounts of micelles if any. The soaplike properties of salts are not important for chains much shorter than that of lauric acid, which is $C_{11}H_{23}COOH$, so that these statements are not applicable to the true soaps in common use.

Donnan Equilibrium.[3]—We may consider here the *equilibrium* that prevails on the two sides of a dialyzing membrane that

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[1] Ekwall and Lindblad, *Kolloid. Z.*, **94**, 42 (1941).

[2] McBain, *J. Phys. Chem.*, **43**, 671 (1939).

[3] *Z. Elektrochem.*, **17**, 572 (1911). For a detailed discussion of this equilibrium and its bearing on colloid chemistry, see Bolam, "The Donnan Equilibrium" (1932).

is permeable to ordinary ions but not to a colloid or its ion. If congo red is taken as an illustration, we may write its formula NaR to indicate that it is a sodium salt of a radical of colloidal character. We shall assume that a solution containing this salt and sodium chloride is separated from pure water by a membrane permeable to sodium chloride and its ions but not to NaR or to the colloidal ion R^- that is formed when congo red ionizes. It may be that this ion forms a micelle $(R^-)_x$, as in the case of soaps. Dialysis will proceed, and *at equilibrium* some of the sodium chloride and all of the congo red and its negative ion will be on the original side of the membrane and sodium chloride alone will have diffused through the membrane. The equilibrium condition may be shown as follows, if the dotted line represents the membrane:

$$\begin{array}{c|c} Na^+R^- & Na^+Cl^- \\ Na^+Cl^- & \\ (1) & (2) \end{array}$$

Since a positive ion may not diffuse through the membrane without a negative ion except by overcoming very large electrostatic forces, the ions of sodium chloride must diffuse through together. If $(Na^+)_1$ and $(Cl^-)_1$ represent the concentrations of sodium ions and chloride ions on the left-hand side at equilibrium, the rate of diffusion through the membrane into the right-hand side is proportional to the product of these concentrations, $(Na^+)_1(Cl^-)_1$. But since equilibrium prevails, diffusion in the reverse direction takes place at the same rate, this rate must be proportional to the product of the concentrations on the right, and the same proportionality constant applies. That is, at equilibrium

$$(Na^+)_1(Cl^-)_1 = (Na^+)_2(Cl^-)_2$$

The concentrations $(Na^+)_2$ and $(Cl^-)_2$ are necessarily equal, since only sodium chloride has diffused through the membrane, but $(Na^+)_1 = (Cl^-)_1 + (R^-)$. Thus the concentration of sodium chloride on the side of the membrane where it alone is present is greater than its concentration on the side with the colloid, but the *total solute* concentration is greater on the side containing the colloid.

This equilibrium may be applied to the swelling of gelatin immersed in an acid solution, for the proteins are amino acids that are combined with hydrogen ions (above a certain concentration) to form salts. If P denotes the protein molecule, $P + H^+Cl^- = PH^+Cl^-$. When the gelatin has swelled to equilibrium, the product $(H^+)(Cl^-)$ in the solution within the gelatin must be the same as in the external liquid. Denoting the concentration in the presence of the colloid by the subscript 1, in the inside solution we should have

$$(Cl^-)_1 = (H^+)_1 + (PH^+)$$

whence at equilibrium

$$(H^+)_1(Cl^-)_1 = (H^+)_2(Cl^-)_2$$

or

$$[(H^+)_1 + (PH^+)](H^+)_1 = (H^+)_2^2$$

It has been shown by Loeb that, when the hydrogen-ion concentration is greater than 2×10^{-5} (*i e.*, pH = 4.7, to use the original notation), gelatin combines with hydrogen ions and forms gelatin chloride; at a lower hydrogen-ion concentration metal proteinates form, and at pH = 4 7 protein combines equally with hydrogen ions and hydroxyl ions This is called the isoelectric point for gelatin. Thus, whether the gelatin combines to form a complex positive ion or a complex negative ion, the *total solute* concentration within it is greater than in the outer solution with which it is in equilibrium. In other words, the activity of water, as measured by its vapor pressure, is less within the gelatin, and water tends to pass into the gelatin. This is probably the explanation of the swelling of gelatin in water.

Isoelectric Point.—Gelatin and other proteins probably consist of complicated "molecules" having the character of amino acids that may be represented by $(NH_2RCOOH)_x$. In the presence of acids the protein particles become "neutralized" and function as cations such as $(NH_3RCOOH)_x^{x+}$. Of course, the electrical balance is maintained by xCl^-. These ions are positively charged and migrate toward the cathode. Similarly, in the presence of bases, proteins form negative ions such as $(NH_2RCOO)_x^{x-}$, and the opposite movement in an electric field is observed. The extensive researches of Loeb[1] and others

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[1] This work is described in detail in Loeb, "Proteins and the Theory of Colloidal Behavior," McGraw-Hill Book Company, Inc., 1927.

have shown that for proteins there is a certain characteristic acidity of the suspending medium, called an "isoelectric point," at which no migration takes place in either direction. It is probable that at this hydrogen-ion concentration the acidic and basic dissociations of the amino acids which make up the protein "molecules" are equal. This effect is observed when the hydrogen-ion concentration is 2×10^{-5}, or at pH = 4.7. Other substances also have characteristic isoelectric points.

When wool in a finely divided condition is suspended in a buffer solution of pH 2 or 3, it moves toward the cathode[1] but much more slowly in the pH 3 solution. When pH is increased to 3.4, no motion is perceptible. As pH changes from 3.6 to 5.5, the suspended wool particles move toward the anode at increasing velocities, indicating that the "isoelectric point" was passed at pH 3.4. Other experiments[2] indicate that the isoelectric pH may be nearer 4.8, and further work seems required before any more definite statement may be made. But, regardless of the numerical significance, it is evident that wool has amphoteric properties similar to simpler amino acids. Analogous behavior has been observed with silk.

Emulsions.—It is commonly, though not necessarily, true of emulsions that both parts are liquid, and the ratio of dispersed part to dispersing medium is much greater than in suspensions. In the hydrosols that we have been discussing, the dispersed part is usually not more than one-thousandth of the whole, but emulsions may be prepared in which as much as 99 per cent is the dispersed part and 1 per cent or less is dispersing medium or continuous part. But suspensions of liquid oil in water in which the dispersed part is only a small portion of the whole are properly considered suspensions and not emulsions. Stable emulsions usually require low surface tension between the parts of the system, which is commonly brought about by dissolving soap or some other "emulsifying agent" in the dispersing medium.

Such systems have also very large interfacial areas, and it is probable that the orientation which was found in the monolayers on liquids is established in emulsions. If soap is taken as a typical stabilizer, it is to be expected that the hydrocarbon portion of the soap will be toward the oil layer in the emulsion and

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[1] M. Harris, *Am. Dyestuff Reptr.*, **21**, 399 (1932).

[2] Speakman, *Trans. Faraday Soc.*, **30**, 539 (1934).

that the carboxyl group attached to sodium will be toward the aqueous layer. The experimental evidence seems to show also that the "concentration" of soap in the interface is very much greater than that in the bulk of either liquid part of the emulsion, probably forming a surface layer which is nearly saturated long before saturation is attained in the liquid as a whole.

Concentration in Surfaces.—It is a general law that substances which lower the surface tension of a solution accumulate in the surface, producing there a higher concentration of solute than is present in the bulk of liquid. Any substance that will lower the surface tension may act as an emulsifying agent. The relation between u, the excess of solute per unit of surface or interface; c, the concentration; and the rate at which surface tension changes with concentration, $d\gamma/dc$, is

$$u = -\frac{c}{RT}\frac{d\gamma}{dc}$$

which is called the "Gibbs adsorption equation." From this equation it will be seen that, if $d\gamma/dc$ is positive, surface tension is increased by the solute, u is negative, and there is no accumulation of solute in the surface, but a deficiency of it. When the solute lowers the surface tension, $d\gamma/dc$ is negative and u is positive; *i.e.*, solute accumulates in the surface in excess. If a froth is formed on such a liquid in which the surface tension has been lowered, excess solute will be found in the froth.

In moderately strong solutions of substances that depress the surface tension, the surface probably consists of a layer of the dissolved substance *one molecule deep*,[1] and there is no transition layer in which the concentration varies progressively at points farther from the surface into the solution. The amount of solute required to form this layer may be calculated from the Gibbs equation, and from this quantity of solute in the surface layer may be calculated the diameter and cross section of the molecules forming the layer. The data so found are in agreement with those obtained from other methods of measuring molecular diameters. For example, Langmuir found that the molecular cross section in the surface was 24 × 10^{-16} sq. cm. per molecule for palmitic acid. In Chap. IV, 21 × 10^{-16} was found from the spreading of a film of palmitic acid on the surface of water.

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[1] LANGMUIR, *Proc. Nat. Acad. Sci.*, **3**, 251 (1917).

Measurements of the surface tension of soap solutions against a benzene interface[1] have given 40 to 47 × 10^{-16} for the molecular cross section of sodium oleate adsorbed into the interface. With solutions of inorganic salts, in which the surface tension is greater than that of water and increases linearly with the concentration, the "concentration" of solute in the surface layer is less than in the solution as a whole. This does not explain the increase of surface tension; for if no solute at all were in the surface layer the interface tension would be that of pure water, and the surface tension of some salt solutions is greater than that of pure water.

Surface Tension and Emulsion Formation.—It has long been known[2] that a decrease of surface tension is produced by those substances which aid emulsification and that a lowering of surface tension is essential to the formation of most stable emulsions. The first sodium salt of the series of fatty acids to produce appreciable lowering of surface tension when it is added to water is sodium laurate, and this is the first salt in such a series to aid appreciably in forming emulsions of oil in water. It is the first to form a soap with marked froth formation and having cleansing properties. There is at least a rough proportionality between surface-tension decrease and emulsifying power so far as emulsions of oil in water are concerned.

When sodium oleate is dissolved in water, a very rapid decrease in surface tension takes place at the interface between solution and vapor with increasing concentration of the soap, until at 0.002 *N* the surface tension reaches its minimum value[3] of about 25 dynes per cm. Further additions of sodium oleate produce no significant change, from which it may be concluded that the *surface is saturated.* In other words, the interface contains all the soap it is capable of holding when the bulk of the solution is very far from saturated. The arrangement is probably similar to that assumed by oleic acid films spreading upon water; a monomolecular layer of soap exists at the interface, which is saturated with sodium oleate at any concentration over 0.002 *N*. Water and oil, when shaken together, do not form a stable emulsion; *i.e.*, the layers separate soon after shaking is discontinued. If a little sodium oleate is dissolved in the water layer

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[1] HARKINS and ZOLLMAN, *J. Am. Chem. Soc.*, **48**, 58 (1926).

[2] DONNAN and POTTS, *Kolloid-Z.*, **9**, 159 (1911).

[3] HARKINS, DAVIES, and CLARK, *J. Am. Chem. Soc.*, **39**, 541 (1917).

and this is then shaken with oil, a more stable emulsion forms in which droplets of oil are suspended in a continuous solution of dilute aqueous soap

If a solution of sodium oleate is 0.005*m.*, the interfacial tension between benzene and the solution is about 5 dynes per cm.; the interfacial tension between benzene and pure water is 35 dynes. Since the oleic group is highly soluble in benzene and the sodium or NaCOO— group is not, the molecules of soap in the interface probably arrange themselves with the latter group toward the aqueous layer and the oleic groups toward the benzene. Inversion of the emulsion takes place, and benzene becomes the continuous part in which droplets of water are suspended, when magnesium oleate (which is insoluble as a whole in water and soluble in benzene) is substituted for sodium oleate as the emulsifying agent.

Structure of Emulsions.—Emulsions of one liquid in another probably consist of microscopic droplets of the dispersed liquid in the continuous liquid. It is not necessary that the continuous part be present in greater quantity than the dispersed part, so long as there is enough of the continuous part to fill the voids between the droplets. Stiff, nonflowing emulsions have been prepared in which 99 per cent of mineral oil is dispersed in 1 per cent of dilute soap solution.[1] Probably in such a system a magnified cross section would look something like a section through a comb of honey, with thin films of soap solution represented by the wax and the oil droplets by the honey. The viscosity of such a system of droplets in a continuous liquid would probably be much higher than that of either liquid part in gross form; it is sometimes so high that a "jelly" is formed. But while it has been suggested that "gels" in general are emulsions of submicroscopic droplets, this has not been proved and there is evidence that it cannot be true of all gels. Another theory is that rodlike particles in a sol make contact with one another when the sol gels, an effect perhaps roughly analogous to that of a pile of matches strewn at random. The gelation of a bentonite suspension has been thus explained,[2] but another study[3]

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[1] PICKERING, *J. Chem. Soc.* (*London*), **92,** 2001 (1907).

[2] GOODEVE, *Trans. Faraday Soc.*, **35,** 3421 (1939).

[3] HAUSER and LEBEAU, *J. Phys. Chem.*, **42,** 961 (1938); HAUSER and HIRSHON, *ibid.*, **43,** 1015 (1939).

of bentonite suspensions has shown that after gelation the individual particles are separated from one another, which is incompatible with a mechanical theory of gelation assuming a continuous "scaffolding" structure.

Either theory might apply to the structure of the agar "jelly" used in bacterial culture. The usual solution is 1.5 per cent by weight; solution in water does not occur at a reasonable rate much below 100°C, but the solution so formed remains fluid until cooled to about 35°. After "solidification" is produced by cooling to room temperature, the culture medium does not again become fluid when incubated at 37° or even higher It has not been established that this system is either an emulsion of a more fluid liquid in a less fluid one or a scaffolding of comparatively rigid rods supporting a fluid portion by something like capillarity. Other rigid systems of high water content, such as silica gel or gelatin or table jellies, have also been studied, but no agreement as to a general theory of structure has yet been reached.[1]

Gels in the Ultramicroscope.—Gelatin and other gels show under the ultramicroscope a slight Tyndall effect that increases with concentration, but these gels do not show individual particles as in the case of sols. Such light as is seen in an ultramicroscope is probably due to a difference in index of refraction of the liquid parts forming a gel There is no Brownian movement of the droplets of disperse part. In very dilute dispersions of oil in water Brownian movement is observed, but these are not properly considered gels, since the quantity of disperse part is very small, and these emulsions have the properties of suspensions to a far greater extent than they resemble gels.

Viscosity of Emulsions.—Emulsions have viscosities which, even for very dilute gels, are much higher than that of the "solvent" and which seem to depend on the rate of shear within the fluid dispersing medium. No satisfactory theory relating to the viscosity of colloids has been developed; but it is known that very slight changes in a gel produce a marked effect upon its viscosity, and hence viscosity measurements are a delicate

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[1] Bogue, "Colloidal Behavior," Vol. I, p. 378. Chapter XV of this volume (by H. B Weiser) discusses at length the rather inconclusive evidence in support of the various views regarding gel structure and gives references to the voluminous literature devoted to it.

means of tracing such changes. About all that can be deduced, however, is that a change has taken place, the nature of which is matter for speculation or empirical interpretation. Use of such methods is extensive in the rubber and nitrocellulose laboratories, where the age of an emulsion is a very important factor in determining its properties. Lack of a satisfactory theory does not interfere with the use of these measurements as control methods.

References

A review of the field is given in "Surface Chemistry," edited by F R Moulton, *Am Assoc Advancement Sci*, Pub 21 (1943), containing papers by 15 leading investigators in the field Some of the many important texts in the field are as follows.

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KRUYT: "Colloids," translated by van Klooster, 2d ed , John Wiley & Sons, Inc., New York, 1930

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THOMAS: "Colloid Chemistry," McGraw-Hill Book Company, Inc., New York, 1934.

WEISER: "Inorganic Colloid Chemistry," John Wiley & Sons, Inc , New York, Vol. I, "The Colloidal Elements," 1933, Vol. II, "The Hydrous Oxides and Hydroxides," 1936.

CHAPTER XVIII

FREE ENERGY OF CHEMICAL CHANGES

In this chapter we consider some simple applications of thermodynamics to changes in state involving chemical reactions. Isothermal changes in state will be considered first and then the effect of changing temperature on the values of the thermodynamic properties. It should be remembered that changes in all the thermodynamic properties p, v, T, E, H, S, A, and $\mathbf{F}$ depend only on the change in state, that ΔH and ΔE may be evaluated along paths which are not thermodynamically reversible when convenient, and that ΔS, ΔA, and $\Delta \mathbf{F}$ must be evaluated along reversible paths. The definitions and most of the equations that are to be used have been developed in Chap. II, but it will be profitable to give some further discussion of them before entering upon the calculations.

Maximum Work of Isothermal Changes in State.[1]—The ideal reversible process is one in which the pressure (or temperature or potential or other property) of the working system differs only by an infinitesimal amount from the pressure (or temperature or potential or other property) of the system on which the work is done. Such a change may be reversed by an infinitesimal change in the pressure, and in a change in state taking place reversibly the work done is the maximum obtainable. Expenditure of this work upon the system will restore it to its original state. Although no actual process is reversible, yet by eliminating friction, electrical resistance, and other factors involved in inefficiency this ideal type of change may be closely approached.

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[1] This section and the following one are quoted from Lewis, *J. Am. Chem. Soc.*, **35**, 1 (913), with only minor changes. Readers of this chapter will not need to be reminded that this brief treatment makes no pretense of being complete. Its purpose is to illustrate a few of the simple operations that may be carried out with free-energy data and to stimulate students who find these calculations attractive to read further in the field. Five excellent books in which to do further reading are given on page 49.

The maximum work that can be obtained from a system on passing *reversibly* from state 1 to state 2 at the same temperature is of great importance, for it is independent of the particular reversible process employed. If this were not true, then by proceeding from 1 to 2 by one isothermal reversible process and returning from 2 to 1 by another isothermal reversible process requiring less work a certain net amount of work would be gained. This work could come only from heat absorbed from the surroundings according to the *first* law of thermodynamics, since the whole process is an isothermal cycle for which $\oint dE = 0$ and dq must be equal to dw. But the *second* law of thermodynamics asserts the impossibility of converting heat into work by an isothermal cycle of changes. Note that the second law does not say that $\oint dw = 0$ for an isothermal cycle, nor does it forbid the conversion of work into heat by an isothermal cycle. It says that the work done by the system in an isothermal cycle is zero or negative.

Since no work is obtainable from an isothermal reversible cycle, it follows that the reversible work done by a system in passing isothermally from state 1 to state 2 is the same by all paths. We may then consider the maximum work as the difference between two quantities that are properties of the system in the specified states. One of these, A_1, is completely determined by the initial state of the system, and the other, A_2, is determined by the final state of the system. These quantities A_1 and A_2 may be designated the *isothermal work contents* of the system before and after the change took place. Neither of the values is determinable for the system; we are to consider *changes* in A, just as we considered *changes* in H or E in earlier chapters. The maximum work to be derived from an isothermal change in state is

$$w_{\max} = -\Delta A = A_1 - A_2 \qquad (t \text{ const.})$$

It will not necessarily be true that $-\Delta A$ is the actual work performed in an isothermal change in state, for many changes take place while performing less work than the maximum that could be obtained in an ideally reversible process. Even if the work done were zero, $-\Delta A$ for the change would be equal to $w_{\max}$, and at least this amount of work would be required to reverse the change in state. The ratio of the actual to the maximum work is the efficiency of the process, but $-\Delta A$ is the decrease in the capacity of the system to do work at constant temperature and is independent of the work efficiency of the process, for there is no law of conservation of work. In conformity with the custom already followed for E and H, we write equations in terms of ΔA rather than $-\Delta A$, so that this equation is

$$\Delta A = A_2 - A_1 = -w_{\text{max}} \quad (t \text{ const.}) \qquad (1t)^1$$

The definition of the quantity A given on page 45 was

$$A = E - TS$$

For a reversible process at constant temperature

$$dA = dE - T\,dS$$

and the last term is equal to the heat absorbed, dq_{rev}. Hence by substituting $dq_{\text{rev}} - dw_{\text{max}}$ for dE above, we have

$$dA = dq_{\text{rev}} - dw_{\text{max}} - T\,dS = -dw_{\text{max}} \quad (t \text{ const.})$$

which upon integration gives equation (1t) above.

Free-energy Increase in Isothermal Changes in State.—For many calculations in chemistry there is another quantity that is more convenient to use than the isothermal work-content increase, especially since the tabulated data are in terms of this quantity. The quantity is related to A in the same way as H is related to E; but before giving a mathematical expression for it, its significance may be illustrated by a concrete example. Suppose that an electric cell operates isothermally and reversibly under atmospheric pressure, producing the electrical work w_e and at the same time undergoing a change in volume. The quantity of work w_e represents all the work reasonably available from the cell, for example, that which could be obtained by operating an electric motor. But it is not w_e that we have defined as $-\Delta A$, for a certain amount of mechanical work is also involved in the change in state, owing to the volume change against the atmospheric pressure. If Δv represents the increase in volume when chemical substances react isothermally and at constant

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[1] The letter t included with the number of an equation indicates the restriction of the equation to changes at constant temperature.

pressure through the operation of an electrical cell, the mechanical work done *by the system* is $p\ \Delta v$, whence

$$\Delta A = -w_e - p\ \Delta v$$

or

$$-w_e = \Delta A + p\ \Delta v \tag{2t}$$

This important quantity, which in general represents the work actually available from an isothermal change, is itself dependent only on the initial and final states of the system and is thus a property of the system in a specified state, for $-\Delta A$, p, and Δv depend only on the initial and final states. It is commonly called the free-energy change We shall write as our formal definition of the free energy

$$\mathbf{F} = A + pv \tag{3}$$

and for isothermal changes

$$\Delta\mathbf{F} = \Delta A + \Delta(pv) \tag{4t}$$

This definition of **F** is in no sense a retraction or a revision of the definition $\mathbf{F} = H - TS$ given in Chap. II, where the definition $A = E - TS$ was also given. Since H and E differ by pv, it will be seen that **F** and A must differ by the same quantity.

By substituting $\Delta A = -w_{\max}$ from equation (1*t*), we have another equation for isothermal free-energy increase,

$$\Delta\mathbf{F} = -w_{\max} + \Delta(pv) \tag{5t}$$

The quantity **F** will be called the free energy and $\Delta\mathbf{F}$ the free-energy increase accompanying a change in state.[1]

Electrical work is the product of potential and quantity of electricity, $w_e = ENF$, in which E is the potential, N is the number of faradays of electricity required to produce the change in state, and F is Faraday's constant. The maximum work obtainable from the isothermal operation of a cell at constant pressure has already been given as $\Delta A = -w_e - p\ \Delta v$, and on substituting

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[1] This is the definition of free energy given by Lewis and followed in "International Critical Tables" and in the publications of the American Chemical Society; it is the Gibbs ζ and is written G in some recent books Some European chemists call our A the free energy, following Helmholtz, but most American chemists call our **F** the free energy. Our E is Gibbs's ϵ, our H is his χ, and our A is his ψ.

this in equation (4*t*) we have another means of evaluating an isothermal free-energy increase,[1]

$$\Delta \mathbf{F} = -ENF \qquad (t \text{ const.}) \qquad (6t)$$

It will be recalled from Chap. VIII that the increase in enthalpy, ΔH, accompanying an isothermal change in state is the negative of the heat evolved. Similarly, the increase in free energy, $\Delta \mathbf{F}$, of an isothermal change in state is the negative of the available maximum work derived from it, other than that due to changes of p or v, and ΔA is the negative of reversible work of all kinds available from the change in state. When work (electrical work, for example) is done upon a system at constant temperature, its free-energy content increases, and it is capable of performing this work again when it is desired.

The condition of reversibility should be kept in mind constantly in connection with changes in A or $\mathbf{F}$. A system decreases its work content and its free-energy content during a spontaneous change in state by the maximum amount, whether it does the maximum amount of work or a smaller quantity. Thus $w_{\max}$ depends only on the change in state that takes place, but the actual work done may be any amount smaller than $w_{\max}$; it may even be zero. The least work that will reverse the change in state is $w_{\max}$, regardless of the work efficiency of the first change.

We have already seen that, because of the way free energy is defined, the work of reversible isothermal expansion at constant pressure is added to the work-content increase in evaluating $\Delta \mathbf{F}$, so that $\Delta \mathbf{F} = \Delta A + \Delta(pv)$ becomes

$$\Delta \mathbf{F} = -w_{\max} + p(v_2 - v_1) \qquad (t \text{ const.})$$

when the pressure remains constant, as required by equation (4*t*). If we apply this equation to the reversible isothermal evaporation of a liquid, p is the vapor pressure at the temperature of the evaporation, $(v_2 - v_1)$ is the difference between the volume of the saturated vapor and the liquid from which it forms, so that $p(v_2 - v_1)$ is equal to $w_{\max}$. Hence for such a change in state $\Delta \mathbf{F} = 0$, and the molal free-energy content of a liquid is

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[1] In these equations and throughout the book, the italic letter F denotes Faraday's constant, 96,500 amp.-sec.; and the bold-faced letter $\mathbf{F}$ denotes the free energy.

equal to that of its saturated vapor. For example, in the change in state,

$$H_2O(l,\ 100°,\ 1\ \text{atm}) = H_2O(g,\ 100°,\ 1\ \text{atm.}) \qquad \Delta F = 0$$

This is not to say that the free-energy contents of liquid water and water vapor at 1 atm. pressure are equal at any other temperature than 100° or that liquid water at 100° and water vapor at 100° and some pressure other than 1 atm. have the same free-energy contents, for these statements would be untrue. (Some illustrations are given in the next section.) But at 25° the free-energy contents of liquid water and water vapor at 0.0313 atm would be equal; for this is the vapor pressure of water at 25°, and evaporation at this temperature would be a reversible isothermal process for which $w_{\max} = p(v_2 - v_1)$. Hence, for the change in state,

$$H_2O(l,\ 25°,\ 0.0313\ \text{atm.}) = H_2O(g,\ 25°,\ 0.0313\ \text{atm.})$$
$$\Delta F = -w_{\max} + 0.0313(v_g - v_l) = 0$$

It will be true, in general, that ΔF is positive when an isothermal change in state requires the expenditure of work from an outside source in order to produce it; that $\Delta F = 0$ for any equilibrium change in state; and that ΔF is negative for spontaneous changes, *i.e.*, for changes that are capable of doing work in approaching equilibrium. Thus, a solute at a greater pressure than its equilibrium pressure above a solution may be expanded reversibly with the production of work and a decrease in its free-energy content and then pass into solution reversibly under its equilibrium pressure. But to remove a solute from a solution to a vapor phase in which its pressure is higher than its equilibrium pressure requires work from an outside source. The mechanism would consist in removing the solute at its equilibrium pressure, for which

$$\Delta F = -w_{\max} + p\,\Delta v = 0$$

followed by isothermal reversible compression, which would require work and increase the free-energy content of the substance.

Isothermal Change of Free Energy with Pressure.—Consider the change in free energy in an isothermal process, of which the net result is the expansion of n moles of a pure substance from the pressure p_1 to the pressure p_2. This may be done reversibly by allowing the substance to expand or contract under an external pressure that is always kept equal within an infinitesimal amount to the pressure of the substance. Then

$$\Delta A = -\int p\,dv$$

and, from equation (4*t*),

$$\Delta \mathbf{F} = -\int p\,dv + \int d(pv) = \int v\,dp \tag{7t}$$

This same relation follows from equation (31), page 47,

$$d\mathbf{F} = -S\,dT + v\,dp$$

for in an isothermal reversible process the first term on the right-hand side is zero, and thus

$$\left(\frac{\partial \mathbf{F}}{\partial p}\right)_T = v \qquad \text{or} \qquad d\mathbf{F} = v\,dp \qquad (t \text{ const.})$$

Over moderate pressure ranges the isothermal change in free-energy content of liquids and solids is very small. For example, in the change in state

$$H_2O(l,\ 25°,\ 5\ \text{atm.}) = H_2O(l,\ 25°,\ 1\ \text{atm.})$$

the volume is substantially constant at 18 ml. per mole;

$$\int v\,dp = v(p_2 - p_1) \qquad \text{and} \qquad \Delta \mathbf{F} = -72\ \text{ml.-atm. or } -1.7\ \text{cal.}$$

Hence in chemical changes, in which $\Delta \mathbf{F}$ is commonly several thousand calories, the change in free-energy content of a liquid phase or solid phase with changing pressure is usually negligible. But $\Delta \mathbf{F}$ would not be negligible for large pressure changes, and for such changes v must be expressed as a function of p before integrating equation (7*t*).

When an ideal gas undergoes isothermal reversible expansion, its volume is given as a function of the pressure by the relation $v = nRT/p$, and for this change equation (7*t*) becomes

$$\Delta \mathbf{F} = nRT \ln \frac{p_2}{p_1} \tag{8t}$$

For the isothermal expansion of a mole of nearly ideal gas as shown by a change in state such as

$$1O_2(g,\ 25°,\ 5\ \text{atm.}) = 1O_2(g,\ 25°,\ 1\ \text{atm.})$$

$\Delta\mathbf{F}$ is -954 cal., and since in this change $\Delta(pv)$ is nearly zero, ΔA is -954 cal. and $w_{\max}$ is 954 cal. At high pressures equation (8*t*) would be inaccurate, and some adequate means of expressing v as a function of the pressure must be found before performing the integration of equation (7*t*)

Free Energy and Activity.—It will be recalled from previous chapters that the activity a of an ideal solute is equal to its molality and that for one which is not ideal $a = m\gamma$, in which γ is the activity coefficient, a number by which the molality must be multiplied to correct it for deviation from the behavior of an ideal solute For an ideal solute that has a vapor pressure, the activity is proportional to the vapor pressure. Since $\Delta\mathbf{F}$ for any change must be the same by all paths, we may transfer a solute from an activity a_1 to an activity a_2 by the following isothermal reversible steps:

1 Evaporate n moles of solute from a large quantity of solution in which its activity is a_1 and over which its vapor pressure is p_1 The quantity of solution is assumed to be so large that the molality is substantially constant during removal of n moles of solute For this process the maximum work is $p_1(v_1 - v_{\text{solute}})$, in which v_1 is the volume of n moles of vapor at p_1 and v_{solute} is the change in volume of the solution caused by the removal of the solute; and for this change $\Delta(pv)$ is also $p_1(v_1 - v_{\text{solute}})$ Hence

$$\Delta\mathbf{F} = -w_{\max} + \Delta(pv) = 0$$

This calculation shows that the molal free-energy content of a solute is the same in a solution and in the vapor in equilibrium with the solution, as was shown in an earlier paragraph to be true of a pure liquid and its vapor. It is a general truth that the molal free-energy content of any substance is the same in two phases which are in equilibrium, and hence $\Delta\mathbf{F} = 0$ for the transfer of it from one phase to another phase with which it is in equilibrium.

2. Expand or compress the vapor from p_1 to p_2, for which $\Delta\mathbf{F}$ is $nRT \ln (p_2/p_1)$ by equation (8*t*).

3. Condense the solute into so large a quantity of solution of the solute at a_2 that the molality is substantially unchanged by the addition of n moles of solute. For this reversible process $w_{\max} = p_2(v_{\text{solute}} - v_2)$, and this is also the value of $\Delta(pv)$; hence

$\Delta F = 0$. The summation of free-energy changes for the entire isothermal change in state,

$$n \text{ moles of solute at } a_1 \rightarrow n \text{ moles of solute at } a_2$$

is $\Delta F = nRT \ln (p_2/p_1)$; and since the ratio p_2/p_1 is equal to a_2/a_1 (*i.e.*, since Henry's law applies to ideal solutes), we may write

$$\Delta F = nRT \ln \frac{a_2}{a_1} \tag{9t}$$

Though we have chosen a volatile solute for this illustration, we might have transferred a nonvolatile solute by an electrochemical reaction, as we shall do in the next chapter, to obtain the same equation. This equation (9*t*) is in fact applicable to the transfer of a solute by any reversible means, and regardless of whether it has a vapor pressure or not, since ΔF has the same value for any change in state by all paths

An ideal solute is one for which $a = m$. This relation is almost satisfied by nonionized solutes in water at moderate concentration, so that m_2/m_1 or C_2/C_1 may be used for nonionized solutes in place of a_2/a_1 in equation (9*t*), with little error. For ionized solutes the ratios m_2/m_1 and a_2/a_1 are not equal until extreme dilutions are reached, and thus $m_2\gamma_2/m_1\gamma_1$ is required for a_2/a_1 in exact calculations In solutions containing a single solute, activity coefficients may be estimated by means of the equations given at the end of Chap. VII, and we are to take up other means of obtaining them in the next chapter. While the *exact* calculation of activity coefficients in mixtures of electrolytes is too difficult for beginners, a suitable estimate may usually be made. For example, it will be better practice to use 0.8 for the activity coefficient in a mixture of uni-univalent solutes at 0.1*m*. and 0.9 for such a mixture at 0.01*m*. than to omit the correction entirely, though it will be still better practice to use the measured activity coefficients 0.796 for 0.10*m*. HCl, 0.778 for 0.10*m*. NaCl, 0.765 for 0.10*m*. KBr, etc. One must remember also that these estimated activity coefficients do not apply in solutions of other ionic types such as 0.1*m*. H_2SO_4, in which the activity coefficient is 0.27, 0.1*m*. $ZnCl_2$, in which it is 0.50, or 0.1*m*. $ZnSO_4$, in which it is 0.15. Students should refer to Table 98 on page 641 for data of this type.

Both of the equations (8*t*) and (9*t*) must be applied to a single molecular species. For example, if a mole of nitrous acid is to be transferred isothermally from a solution in which its molality is m_1 and the fractional ionization is α_1 to a solution in which its molality is m_2 and the fractional ionization is α_2, this may be accomplished by transferring a mole of HNO_2 from $m_1(1 - \alpha_1)$ to $m_2(1 - \alpha_2)$ or by transferring a mole of H^+ and a mole of NO_2^- from $m_1\alpha_1$ to $m_2\alpha_2$. The corresponding free-energy increases are

$$\Delta F = 1RT \ln \frac{m_2(1 - \alpha_2)}{m_1(1 - \alpha_1)} \quad \text{and} \quad \Delta F = 2RT \ln \frac{m_2\alpha_2}{m_1\alpha_1}$$

Since the same change in state is accomplished by either procedure, the free-energy increases must be equal, and on equating them we have

$$\frac{(m_1\alpha_1)^2}{m_1(1 - \alpha_1)} = \frac{(m_2\alpha_2)^2}{m_2(1 - \alpha_2)}$$

which is required by the ionization equilibrium. Since nitrous acid conforms rather closely to the requirement of the equation $K_c = (H^+)(NO_2^-)/(HNO_2)$, either procedure is satisfactory.

If hydrogen chloride, or H^+ and Cl^-, is to be transferred, the activity coefficients of the ions may not be canceled from equation (9*t*), as was done for nitrous acid above. Let the change in state at 25° be

$$1HCl\ (4m.) \rightarrow 1HCl\ (6m.)$$

The vapor pressure of $HCl(g)$ is 0.24×10^{-4} atm. above a 4*m.* solution of HCl, and so $HCl(g)$ at this pressure has the same molal free-energy content as $H^+ + Cl^-$ at 4*m.* But the activities of H^+ and Cl^- in 4*m.* HCl are not 4—they are about 7.0. Similarly, in 6*m.* HCl the activities of the ions are about 20.1, and $HCl(g)$ at 1.84×10^{-4} atm. (the vapor pressure) is in equilibrium with HCl (6*m.*) or with H^+ and Cl^- at activities of 20.1. If the transfer is brought about isothermally and reversibly through the vapor, we see from equation (8*t*) that

$$\Delta F = RT \ln \frac{1.84 \times 10^{-4}}{0.24 \times 10^{-4}}$$

and if it is brought about isothermally and reversibly by the transfer of the ions (for example, through the operation of two opposed electrolytic cells), equation (9*t*) applies, and

$$\Delta F = 2RT \ln \left(\frac{20.1}{7.0} = \frac{m_2\gamma_2}{m_1\gamma_1}\right)$$

These free-energy increases are equal, of course, but they do not lead to an ionization constant for HCl when equated, for this substance has no ionization constant. Activities in concentrated hydrochloric acid are obtained from the potentials of cells in a way explained in the next chapter.

Free-energy Increase and Chemical Equilibrium.—The free-energy increase for an isothermal change in state that involves a chemical reaction is related to the equilibrium constant of the reaction by an important equation that is now to be derived. It will be recalled that ΔF for a specified change in state is independent of the path or process by which the change occurs but that in order to evaluate this change we must proceed by some path which is reversible in the thermodynamic sense For our convenience we may choose any reversible path for which the calculation is readily performed. Let the chemical reaction be

$$aA + bB = dD + eE$$

and assume that the substances involved are ideal gases to which we may apply equation (8*t*) The equilibrium constant for this chemical reaction is

$$K_p = \frac{p_D{}^d p_E{}^e}{p_A{}^a p_B{}^b}$$

A chemical equation does not adequately specify a change in state, for the partial pressures of the substances and the temperature must also be given. The isothermal change in state at the temperature T is

$$aA(\text{at } p_A') + bB(\text{at } p_B') = dD(\text{at } p_D') + eE(\text{at } p_E')$$

For the ideal process by which this change in state is conceived to occur reversibly, we may assume an "equilibrium box" containing an equilibrium mixture of the substances and fitted with four cylinders. Each cylinder connects to the box through a membrane permeable to one substance only; each has an arrangement for closing the membrane and a movable piston for altering the pressure. At the start one cylinder contains a moles of substance A at a pressure p_A', a second contains b moles of substance B at a pressure p_B', and the membranes between these cylinders and the equilibrium mixture are closed. The pistons of the third and fourth cylinders are in contact with the membranes permeable to C and D, so that these cylinders are empty. The primed pressures p_A' and p_B' are the ones arbitrarily specified in the change in state, and they do not satisfy the equilibrium relation; the pressures without primes, p_A, etc., do satisfy this relation

As the first step of the reversible process, let a moles of A expand (or be compressed) isothermally and reversibly from p_A' to p_A, and let b moles of B expand (or be compressed) isothermally and reversibly from p_B' to p_B while the membranes remain closed. The free-energy increases for these processes are

$$\Delta \mathbf{F}_1 = aRT \ln \frac{p_A}{p_A'} \qquad \text{and} \qquad \Delta \mathbf{F}_2 = bRT \ln \frac{p_B}{p_B'}$$

Now open the membranes of these cylinders, and force A at p_A and B at p_B into the equilibrium mixture through their respective membranes; as they react, withdraw d moles of D through its membrane at the pressure p_D and e moles of E through its membrane at the pressure p_E. At the A cylinder, the maximum work performed by the system is $-p_A v_A$, and $\Delta(pv)$ is also $-p_A v_A$, whence $\Delta \mathbf{F} = -w_{\text{max}} + \Delta(pv) = 0$. It is also true of each of the other cylinders that the work performed is only that of a change of volume under constant pressure, so that $w_{\text{max}} = p\,\Delta v$ and $\Delta \mathbf{F} = 0$ for the entire second step.

The change in state is completed by closing the membranes of the D and E cylinders, compressing (or expanding) d moles of D isothermally and reversibly from p_D to p_D' and e moles of E isothermally and reversibly from p_E to p_E'. For these steps

$$\Delta \mathbf{F}_3 = dRT \ln \frac{p_D'}{p_D} \qquad \text{and} \qquad \Delta \mathbf{F}_4 = eRT \ln \frac{p_E'}{p_E}$$

Upon adding the free-energy increases for all the steps and rearranging so that all the initial or final pressures specified in the change in state appear in one term and all the equilibrium pressures appear in another term, the summation becomes

$$\Delta \mathbf{F} = RT \ln \frac{p_D'^{d} p_E'^{e}}{p_A'^{a} p_B'^{b}} - RT \ln \frac{p_D^{d} p_E^{e}}{p_A^{a} p_B^{b}} \qquad (10t)$$

This equation allows us to calculate ΔF for any gaseous isothermal change in state for which the equilibrium constant is known. We shall consider in the next section the use of tabulated data that allow the calculation of equilibrium constants at a single standard temperature in much the way that enthalpy changes at a standard temperature were calculated from molal enthalpy tables in Chap. VIII. We shall also have later in this chapter an equation for calculating ΔF at any temperature from its value at the standard temperature. Hence equation (10*t*) is an important one.

In order to save labor when equation (10*t*) is to be written often, it has become fairly common practice to write it

$$\Delta \mathrm{F} = RT \ln Q - RT \ln K$$

in which Q indicates a fraction containing the pressures appearing in the formulation of the change in state, and arranged according to the same conventions as in the equilibrium constants, and K is the equilibrium constant.

For changes in state involving solutes, an equation of similar form involving the activities of solutes may be derived. For the general change in state at T,

$$d\mathrm{D}(\text{at } a_{\mathrm{D}}') + e\mathrm{E}(\text{at } a_{\mathrm{E}}') \rightarrow g\mathrm{G}(\text{at } a_{\mathrm{G}}') + h\mathrm{H}(\text{at } a_{\mathrm{H}}')$$

the increase in free energy of the isothermal change is

$$\Delta \mathrm{F} = RT \ln \frac{a_{\mathrm{G}}'^{g} a_{\mathrm{H}}'^{h}}{a_{\mathrm{D}}'^{d} a_{\mathrm{E}}'^{e}} - RT \ln \frac{a_{\mathrm{G}}^{g} a_{\mathrm{H}}^{h}}{a_{\mathrm{D}}^{d} a_{\mathrm{E}}^{e}} \qquad (11t)$$

where the activities not primed satisfy the equation for equilibrium

$$K_a = \frac{a_{\mathrm{G}}^{g} a_{\mathrm{H}}^{h}}{a_{\mathrm{D}}^{d} a_{\mathrm{E}}^{e}}$$

Since the activities of nonionized solutes at moderate concentrations are nearly equal to their concentrations, equation (11*t*) may be altered by substituting concentrations or molalities for the activities. In some approximate calculations involving ions this may also be done. For example, it will matter little whether the equilibrium concentration of a substance is $10^{-6}m.$ or $10^{-7}m.$ if the object of a process is to precipitate it completely.

But there are also many equilibriums involving ionized solutes in which a rough approximation is inadequate, and for such calculations activities must be used in equation (11*t*).

Free Energy and the Third Law of Thermodynamics.—In Chap. II we defined the free energy as

$$\mathbf{F} = H - TS$$

and, for isothermal changes, this becomes

$$\Delta\mathbf{F} = \Delta H - T\,\Delta S \tag{12t}$$

Thus we may calculate $\Delta\mathbf{F}$ attending any isothermal change in state for which ΔH and ΔS are known.

It will be recalled that, according to the third law of thermodynamics, the entropy of any pure crystal is zero at the absolute zero of temperature. It will also be evident that at a standard temperature and pressure, such as 298°K. and 1 atm. pressure, entropies are not zero; they are $\int C_p d \ln T$ between 0° and 298°K. Both free energies and entropies at a given temperature change with pressure, and for liquids and solids the changes in entropy or free energy are small for moderate changes in pressure. For ideal gases the change of entropy with pressure at constant temperature is given by the equation

$$\Delta S = -nR \ln \frac{p_2}{p_1}$$

This equation follows from equations (8*t*) and (12*t*), since ΔH is zero for the isothermal expansion of an ideal gas. It also follows from the fourth "Maxwell relation" as shown in the footnote on page 607.

Entropies for elements or compounds are usually given in tables in calories per mole per degree at 298°K. and 1 atm. pressure for the state of aggregation stable under these conditions and are designated S^0_{298}. A few are given in Table 96, and many more are known. Since $\Delta S = S_2 - S_1$ for any change in state, an entropy table and an enthalpy table provide data for calculating $\Delta\mathbf{F}$.

Standard Isothermal Changes in State.—The changes in state with which we are to be concerned in this section and in the next three sections are called "standard changes in state." In such changes each substance, element or compound, appearing in the description of a change in state, is in its stable state of aggregation at 1 atm. pressure for the temperature concerned. Following the common custom, we take as our standard temperature 25°C. or 298°K., since this is the temperature for which tabulated data are available. Solutes in a standard change in state are used or formed at unit activity. Some illustrations of standard changes in state are

$$\begin{aligned}
\tfrac{1}{2}H_2(1\text{ atm.}) + \tfrac{1}{2}Cl_2(1\text{ atm.}) &= HCl(1\text{ atm.})\\
2Ag(s) + \tfrac{1}{2}O_2(1\text{ atm.}) &= Ag_2O(s)\\
Ag_2O(s) + 2H^+Cl^-(u.a.) &= 2AgCl(s) + H_2O(l)\\
H_2O_2(u.a. = 1m.) &= H_2O(l) + \tfrac{1}{2}O_2(1\text{ atm.})\\
\tfrac{1}{2}H_2(1\text{atm.}) + \tfrac{1}{2}Br_2(l) &= H^+Br^-(u.a.)
\end{aligned}$$

It has become common practice in physical chemistry to designate the changes in enthalpy, free energy, entropy, etc., for standard changes by a superscript zero attached to the symbol for the quantity, followed by specification of the temperature with a subscript, ΔH^0_{298}, $\Delta \mathbf{F}^0_{298}$, ΔS^0_{298}, etc. Standard changes in state may of course be subtracted or added, with addition or subtraction of the $\Delta \mathbf{F}^0$s, as is true of any other changes. They may be added to changes that are not standard; but the sum of a $\Delta \mathbf{F}$ and a $\Delta \mathbf{F}^0$ is a new $\Delta \mathbf{F}$ and not a new $\Delta \mathbf{F}^0$.

Standard Free-energy Contents of Elements.—In Chap. VIII we defined the enthalpy of an *elementary* substance at 1 atm. pressure and the standard temperature as zero and we compiled a table of molal enthalpies of compounds relative to this standard. For moderate changes in pressure the variation of H with pressure was negligible for liquids and solids, and for ideal gases $(\partial H/\partial p)_T = 0$, so that the enthalpies of the elements were substantially zero at any moderate pressure, and the enthalpies of compounds were substantially the same at any moderate pressure as at 1 atm. pressure. Enthalpies so calculated were relative and not absolute, since they were based on a standard arbitrarily defined as zero for the elements at the standard temperature.

For the purpose of preparing a table of *standard molal free energies of compounds* we shall also define the free energy as zero for an *elementary* substance in its stable state of aggregation at 1 atm. pressure and the standard temperature as zero. The molal free energies of compounds at 1 atm. and the standard temperature will thus be the free-energy increases attending their formation at 1 atm. pressure from the elements at 1 atm. pressure. Variations in pressure of a few atmospheres will cause negligible changes in the free energies of *liquids and solids*, as was shown on page 597. This will not be true of gaseous compounds, nor will the molal free energy of gaseous elements be zero at the standard temperature and any moderate pressure, since $(\partial \mathbf{F}/\partial p)_T = v$, from page 597. It may be seen from equation (8*t*) that, if the free energy of a mole of oxygen (for example) is zero at 1 atm. and 298°K., its free energy will be 1365 cal. at 10 atm., -410 cal. at 0.5 atm., -1365 cal. at 0.1 atm., and -2730 cal. at 0.01 atm., all for 298°K.

The molal free-energy content of $Br_2(g)$ at 25° and 1 atm is given in Table 95 as 755 cal. Since this is a positive free-energy content, bromine vapor does not assume this condition spontaneously, and it is a familiar fact that the vapor pressure of bromine is less than 1 atm. at 25°. The experimental fact recorded by this free-energy content is the vapor pressure of bromine at 25°. We shall use this molal free-energy content to calculate the vapor pressure, though it will be understood that this is the reverse of the actual procedure by which the free-energy content of bromine in the imaginary state of vapor at 1 atm. pressure at 25° was calculated from the measured vapor pressure.

Let the changes in state at 25° be

$$Br_2(l) \rightarrow Br_2(g, \text{satd vapor}, p \text{ atm.}) \rightarrow Br_2(g, 1 \text{ atm.})$$

Since bromine at 25° and 1 atm. is a liquid, the free-energy content of the system in its original state is zero by the convention we have adopted. When it evaporates isothermally to form saturated vapor, the only work done is $p\,\Delta v$, so that

$$\Delta \mathbf{F} = -w_{\max} + p\,\Delta v = 0$$

and the free-energy content of *saturated vapor* is also zero. For the second step $\Delta \mathbf{F}$ is $RT \ln (1/p)$ from equation (8*t*), which is 755 cal., whence $\log p = -0.553$ and $p = 0.280$ atm.

The molal free-energy content of $I_2(g, 1 \text{ atm.})$ is given as 4630 cal. in Table 95, and this is another example of a free-energy content ascribed to a substance in an imaginary state. It records the experimental fact that the sublimation pressure of iodine at 25° is 0.309 mm., and the entry itself is useful in making calculations which involve iodine vapor. There is no implication that iodine vapor has been observed in this condition.

Standard Entropies of Elements.—The standard entropy of oxygen gas at 298°K. and 1 atm. pressure is $S^0_{298} = 49.03$ cal. per mole per deg. Its molal entropy at 298°K. and some other pressure, such as 0.1 atm., will differ from 49.03 by an amount shown by the equation[1]

$$\Delta S = -R \ln \frac{p_2}{p_1}$$

which is 4.57 e.u. for the change in state

$$O_2(g,\ 298°\text{K.},\ 1\ \text{atm.}) = O_2(g,\ 298°\text{K.},\ 0.1\ \text{atm.})$$

whence the entropy of oxygen at 298°K. and 0.1 atm. is 53.6 e.u. The same result is obtained, of course, from the equation

$$\Delta \mathbf{F} = \Delta H - T\,\Delta S \qquad (12t)$$

From equation (8*t*) we calculate $\Delta\mathbf{F} = -1365$ cal. for the expansion of a mole of gas from 1 atm. to 0.1 atm. at 298°K., and since $\Delta H = 0$ for the expansion,

$$-1365\ \text{cal.} = 0 - 298\,\Delta S \qquad \Delta S = 4.57\ \text{e.u.}$$

As another illustration, we may calculate S^0_{298} for $I_2(g)$ in the imaginary state of vapor at 298°K. and 1 atm. from ΔS^0 for the standard change in state

$$I_2(s) = I_2(g,\ 1\ \text{atm.})$$

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[1] For the isothermal expansion of an ideal gas, $\Delta E = 0$, and if the expansion takes place reversibly as well, $q_{\text{rev}} = w_{\text{rev}}$. Since $q_{\text{rev}} = T\,\Delta S$ at constant temperature and $w_{\text{rev}} = nRT \ln (v_2/v_1) = -nRT \ln (p_2/p_1) = T\Delta S$,

$$\Delta S = -nR \ln \frac{p_2}{p_1}$$

This equation also follows from the fourth "Maxwell relation" given on p 48,

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$$

For an ideal gas $pv = nRT$ and $-(\partial v/\partial T)_p = -nR/p$, whence

$$dS = -\frac{nR}{p}\,dp \qquad \text{and} \qquad \Delta S = -nR \ln \frac{p_2}{p_1}$$

for isothermal changes in pressure.

for which $\Delta\mathbf{F}^0_{298} = 4630$ cal. was calculated on page 606. The heat of sublimation at 298°K. is $\Delta H = 14{,}877$ cal., and when these quantities are substituted in the equation

$$\Delta\mathbf{F}^0 = \Delta H^0 - T\,\Delta S^0$$
$$4630 = 14{,}877 - 298\,\Delta S^0$$

ΔS^0 is 34.4 e.u. Since the standard entropy of the solid is $S^0_{298} = 27.9$, $S^0_{298} = 62.3$ for $I_2(g)$.

At the risk of some repetition, it must be pointed out that $\Delta\mathbf{F}$ and ΔS for the sublimation to yield saturated vapor at 25°, *i.e.*, for the change in state

$$I_2(s) = I_2(g, 4.07 \times 10^{-4} \text{ atm.})$$

are not the same as $\Delta\mathbf{F}^0$ and ΔS^0 for the change in state which forms the vapor at 1 atm. pressure. For the formation of *saturated vapor*, at 298°K. $\Delta\mathbf{F} = 0$, $\Delta H = 14{,}877$ cal., $\Delta S = 49.9$, and the entropy of the saturated vapor is 77.8 e.u. For the compression of the vapor to 1 atm. from the saturation pressure,

$$I_2(g, 4.07 \times 10^{-4} \text{ atm.}) = I_2(g, 1 \text{ atm.})$$

$\Delta H = 0$, $\Delta\mathbf{F} = 4630$ cal., $\Delta S = -15.5$, and S^0_{298} is 62.3 as before. Since these last two changes in state are not standard ones, no values of $\Delta\mathbf{F}^0$ and ΔS^0 may be assigned to them.

Standard Free Energies of Compounds.—The standard free energy of a compound is defined as the free energy of its formation from the elements by a standard change in state. The fundamental equations for these calculations have all been given, and we have already seen that for the evaluation of free energy we must proceed along reversible paths. The standard free energy of an ion in aqueous solution is its free energy of formation from the elements in a standard change as well, and the standard for ions is unit activity.

For the special condition in a gaseous reaction that the pressure of *each reacting substance* is 1 atm. and the pressure of *each reaction product* is 1 atm., *i.e.*, for standard changes in state, equation (10*t*) reduces to

$$\Delta\mathbf{F}^0 = -RT \ln K_p \qquad (13t)$$

It must be understood that this equation applies, not if the total pressure of a mixture is 1 atm., but only when the pressure of each substance is 1 atm. The standard temperature for which free energies are recorded is 298°K., but equation (13*t*) may be used for any constant temperature, provided that the initial and final pressures of each substance involved are 1 atm. at this temperature.

A corresponding equation may be written for changes in state in which solutes are used or formed at unit activity. The general change in state is

$$d\mathrm{D}(a_{\mathrm{D}}' = 1) + e\mathrm{E}(a_{\mathrm{E}}' = 1) = g\mathrm{G}(a_{\mathrm{G}}' = 1) + h\mathrm{H}(a_{\mathrm{H}}' = 1)$$

and for this change the first logarithmic term in equation (11*t*) becomes zero, so that

$$\Delta \mathbf{F}^0 = -RT \ln K_a \qquad (13t)$$

For many approximate calculations molalities or concentrations may be used, and for standard changes in state in terms of these quantities the free-energy equation is

$$\Delta \mathbf{F}^0 = -RT \ln K_c \qquad (13t)$$

We designate by (13*t*) the equation in any terms. The superscript zero on the $\Delta \mathbf{F}^0$ is intended to indicate that the first term in equations (10*t*) or (11*t*) has been made zero by the way in which the change in state has been formulated, namely, by making it a standard one. This superscript should always be written for standard changes in state and omitted when the change in state is not standard, as is the usual custom in physical chemistry.

For standard changes in state taking place in an electrolytic cell, equation (6*t*) becomes

$$\Delta \mathbf{F}^0 = -E^0 NF \qquad (14t)$$

and the equation applies *only* to cells in which standard changes in state take place reversibly with the development of a maximum or reversible potential E^0.

For standard changes in state equation (12*t*) becomes

$$\Delta \mathbf{F}^0 = \Delta H^0 - T\,\Delta S^0 \qquad (15t)$$

and the equation likewise applies *only* when standard entropies are used. As has been pointed out so often before, the distinction between ΔH^0 and ΔH is usually not required, since enthalpy changes are small for moderate changes in pressure. Since we have used ΔH_0, written with a subscript of zero, as an integration constant in expressing ΔH as a function of the temperature, it must be observed that ΔH^0 with the superscript of zero is not this integration constant but ΔH for a standard change in state. When it is necessary to indicate the integration constant in a standard change in state, this is written with zero as both subscript and superscript, ΔH^0_0.

It is seldom possible to determine the free energy of formation of a given compound directly by all three of the equations (13*t*), (14*t*), and (15*t*), though free energies determined by two of them may usually be checked for the difference between them by the third method. Before making any calculations, we summarize the standard conventions for *elements*

$H = 0$ at any temperature and 1 atm. pressure for elements in the state of aggregation stable at that temperature (Changes in H with moderate changes in pressure may be neglected in all but the most precise calculations.)

$\mathbf{F} = 0$ at any temperature and 1 atm. pressure for elements in the state of aggregation stable at that temperature. [Changes in $\mathbf{F}$ with moderate changes in pressure are negligible for liquids and solids; they are given for gases by equation (8*t*).]

$S = 0$ only at absolute zero.

Some calculations of standard free energies of compounds at 298°K. will now be given to illustrate the methods.

Silver Oxide.—1. By plotting the logarithm of the dissociation pressures for silver oxide given on page 396 against $1/T$, we find that $\Delta H = -7250$ cal. and ΔC_p is zero or very small for the reaction

$$2\text{Ag}(s) + \tfrac{1}{2}\text{O}_2(g) = \text{Ag}_2\text{O}(s)$$

Through the van't Hoff equation we calculate the equilibrium pressure of oxygen at 298°K. to be 1.66×10^{-4} atm Since the equilibrium constant for the change in state as written is the reciprocal of the square root of this pressure, equation (13*t*) gives

$$\Delta\mathbf{F}^0_{298} = -RT \ln \frac{1}{\sqrt{p_{\text{O}_2}}} = -2580 \text{ cal.}$$

We define the free standard energies of the elements as zero, and thus the free energy of $Ag_2O(s)$ is -2580 cal. per mole at 298°K. from this calculation.

2. A cell of which the anode is silver and silver oxide, the electrolyte dilute sodium hydroxide, and the cathode oxygen gas bubbling over platinum would appear to be a means of determining the free energy of silver oxide, since the cell reaction is the formation of a mole of Ag_2O for 2 faradays. But it is a requirement in free-energy calculations that a *reversible* process be used, and neither of the electrode reactions is reversible in the thermodynamic sense. Operation of the cell forms silver oxide but does not form it reversibly, and thus the measured potential (which is erratic) is not the maximum potential. Accepting the free energy as determined by the other two methods, one may *calculate* that the reversible potential should be 0.055 volt, and such a potential is sometimes recorded for this cell in tables of oxidation potentials. No harm is done by such an entry if one understands that the potential has been calculated and is not a *measured reversible potential.*

3. The standard entropies at 298°K. are 10.2 for silver, 49.03 for oxygen, and 29 1 for silver oxide, from which we may calculate an entropy balance for the formation of silver oxide as follows:

$$\begin{aligned} 2\text{Ag}(s) + \tfrac{1}{2}\text{O}_2(g) &= \text{Ag}_2\text{O}(s) \\ 2(10.2) + \tfrac{1}{2}(49.03) &= 29.1 - \Delta S^0 \\ \Delta S^0 &= -15.81 \text{ cal. per deg.} \end{aligned}$$

Taking $\Delta H = -7250$ cal. for the reaction, as before, we have

$$\Delta \mathbf{F}^0_{298} = \Delta H - T\,\Delta S^0 = -7250 - 298(-15.81) = -2530 \text{ cal.}$$

If ΔH is taken from Table 58, where it is given as -7300 cal., $\Delta \mathbf{F}^0_{298}$ becomes -2580, which is substantially the value given in Table 95.[1]

Silver Chloride.—1. Direct equilibrium measurements are not available for calculating the free energy of formation of silver chloride, since the pressure of chlorine at equilibrium is too small for measurement. The theoretical equilibrium pressure for the reaction

$$\text{Ag}(s) + \tfrac{1}{2}\text{Cl}_2(g) = \text{AgCl}(s)$$

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[1] PITZER and SMITH, *J. Am. Chem. Soc.*, **59**, 2633 (1937).

may be calculated from the free energy derived from other methods through equation (13*t*),

$$\Delta F^0 = -RT \ln K = -RT \ln \frac{1}{\sqrt{p_{Cl_2}}} = -26{,}200 \text{ cal.}$$

to be $10^{-38.4}$ atm., but such a quantity has no meaning as a pressure. In a table of equilibrium constants this pressure might be given as a record of the molal free energy derived from other methods, and no harm is done in recording it so long as it understood that *no pressure measurement* is implied.

2. The potential of a cell in which silver chloride forms reversibly is 1.136 volts at 298°K. For 1 faraday the change in state and the free-energy increase are shown by the equations

$$\begin{gathered} Ag(s) + \tfrac{1}{2}Cl_2(1 \text{ atm.}) = AgCl(s) \\ \Delta F^0 = -E^0F = -109{,}600 \text{ joules} = -26{,}220 \text{ cal.} \end{gathered}$$

Details of the method will be given in the next chapter.

3. The standard entropies of all the substances involved are well known; therefore, through an entropy balance and the enthalpy of formation, which is −30.300 cal., we obtain

$$\begin{aligned} &Ag(s) + \tfrac{1}{2}Cl_2(1 \text{ atm.}) = AgCl(s) \\ &10.2 \quad + 26.65 \qquad\quad = 23.0 - \Delta S^0 \end{aligned}$$

and, on substituting $\Delta S^0 = -13.85$ in the equation (15*t*),

$$\begin{aligned} \Delta F^0_{298} &= \Delta H^0 - T\,\Delta S^0 \\ &= -30{,}300 - 298(-13.85) \\ &= -26{,}270 \text{ cal.} \end{aligned}$$

which agrees with the value derived from cell potential.

Chloride Ion.—The molal free energies of ions are mostly derived from the potentials of cells in which the ions are formed reversibly from the elements or from equilibrium reactions in which ions are involved. Since the procedures and conventions used in this type of work require some explanation and since some of the derived quantities are difficult to understand without this explanation, we shall postpone our consideration of cell potentials until the next chapter and be content to use the free energies of ions before studying the methods by which they are obtained. It will suffice to point out here that, when suitable conditions prevail, the potential of the cell

$$H_2(g,\ 1\ \text{atm.}),\ H^+Cl^-(\text{unit activity}),\ Cl_2(g,\ 1\ \text{atm.})$$

is 1.358 volts at 298°K. and that when 1 faraday passes through this cell the change in state and the free-energy increase are

$$\tfrac{1}{2}H_2(1\ \text{atm.}) + \tfrac{1}{2}Cl_2(1\ \text{atm.}) = H^+Cl^-(u.a.)$$
$$\Delta F^0 = -E^0F = -131{,}000\ \text{joules} = -31{,}350\ \text{cal.}$$

The free energy of hydrogen ion at unit activity is *defined* as zero by the convention that the hydrogen electrode H_2 (1 atm.), $H^+(u.a.)$, has zero potential, and the free energy of chlorine is zero for 1 atm. pressure by definition, so that the free energy of chloride ion at unit activity is given as −31,350 cal. by this cell potential.

Water.—Since the free energies of water and water vapor appear in many chemical calculations, they have been determined with care by several methods. The calculation for the vapor, based on high-temperature measurements of the dissociation, is complicated by the fact that two reactions take place simultaneously, namely,

$$H_2O(g) = H_2(g) + \tfrac{1}{2}O_2(g)$$

and

$$H_2O(g) = \tfrac{1}{2}H_2(g) + OH(g)$$

The older calculations, which did not take account of the second reaction, were almost correct through a curious compensation of errors. Since the oxygen electrode is not reversible, calculations based on the potential of an oxygen-hydrogen cell and the equation $\Delta F^0 = -E^0NF$ are not available.

An entropy balance and ΔH for the reaction

$$H_2(1\ \text{atm.}) + \tfrac{1}{2}O_2(1\ \text{atm.}) = H_2O(l)$$
$$31.23 + 24.51 = 16.75 - \Delta S^0$$

gives $\Delta S^0 = -38.99$ e.u., $T\,\Delta S^0 = -11{,}625$ cal.; and since $\Delta H = -68{,}318$ cal., $\Delta F^0 = -56{,}693$ cal. at 298°K. for the formation of liquid water.

Confirmation of this value is obtained by adding four standard reactions and their free-energy changes.[1]

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[1] Pitzer and Smith, *ibid.*, **59**, 2633 (1937).

$$H_2(1\text{ atm.}) + 2AgCl(s) = 2Ag(s) + 2H^+Cl^-(u.a.) \qquad \Delta F^0_{298} = -10{,}259\text{ cal.}$$
$$Ag_2O(s) + H_2O(l) + 2Cl^-(u.a.) = 2AgCl(s) + 2OH^-(u.a.) \qquad \Delta F^0_{298} = -5596\text{ cal.}$$
$$2H^+(u.a.) + 2OH^-(u.a.) = 2H_2O(l) \qquad \Delta F^0_{298} = -38{,}186\text{ cal.}$$
$$2Ag(s) + \tfrac{1}{2}O_2(1\text{ atm}) = Ag_2O(s) \qquad \Delta F^0_{298} = -2585\text{ cal}$$
$$\overline{H_2(1\text{ atm}) + \tfrac{1}{2}O_2(1\text{ atm}) = H_2O(l) \qquad \Delta F^0_{298} = -56{,}626\text{ cal}}$$

The first of these reactions takes place in an electrolytic cell that will be described on page 633, the second is from a measured chemical equilibrium quoted in Problem 7 on page 626, the third comes from K_w, which has been determined by several methods, and the fourth from the calculation given on page 611. Other means of confirming it are given in the next chapter.

The standard free energy of water vapor in the imaginary state of a gas at 1 atm. and 298°K. is obtained by the method used in calculating the standard free energy of bromine vapor. The changes in state and their free-energy increases are

$$H_2O(l) = H_2O(g, 0.0313\text{ atm}) \qquad \Delta F = 0$$
$$H_2O(g, 0.0313\text{ atm.}) = H_2O(g, 1\text{ atm}) \qquad \Delta F = RT\ln\frac{1}{0.0313} = 2057\text{ cal.}$$

and, upon addition,

$$H_2O(l) = H_2O(g, 1\text{ atm.}) \qquad \Delta F^0 = 2057\text{ cal.}$$

and the standard free energy of water vapor is

$$-56{,}693 + 2057 = -54{,}636\text{ cal.}$$

These calculations will suffice to show the methods used in measuring the standard free energies of substances. A short list to be used in problems is given in Table 95, and many others are known.[1] A short list of standard entropies is given in Table 96, and many others are likewise known.[2]

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[1] See, for example, LATIMER, "Oxidation Potentials," pp. 302–308, Prentice-Hall, Inc., New York, 1938.

[2] The best compilation of standard entropies is by Kelley, *U.S. Bur. Mines, Bull.*, **434**, (1941). All the entropies in Table 96 are from this publication.

TABLE 95.—SOME STANDARD FREE-ENERGY CONTENTS AT 298°K.[1]

Substance	ΔF^0_{298}	Substance	ΔF^0_{298}	Substance	ΔF^0_{298}
$H_2O(g)$	− 54,636	$HNO_2(u.a.)$	− 13,020	$Br^-(u.a.)$	− 24,568
$H_2O(l)$	− 56,690	$HCN(g)$	27,730	$I^-(u.a.)$	− 12,340
$H_2O_2(l)$	− 28,230	$HCN(u.a.)$	26,340	$I_3^-(u.a.)$	− 12,295
$H_2O_2(u.a.)$	− 31,470	$CO(g)$	− 32,787	$HS^-(u.a.)$	2,985
$O_3(g)$	39,400	$CO_2(g)$	− 94,239	$HSO_3^-(u.a.)$	−125,870
$Cl_2(l)$	1,146	$CO_2(u.a.)$	− 92,229	$SO_4^{--}(u.a.)$	−176,100
$Cl_2(u.a.)$	1,630	$COCl_2(g)$	− 48,960	$NH_4^+(u.a.)$	− 18,830
$HCl(g)$	− 22,770	$CH_4(g)$	− 12,085	$NO_2^-(u.a.)$	− 8,450
$HClO(u.a.)$	− 19,110	$C_2H_6(g)$	− 7,790	$NO_3^-(u.a.)$	− 26,345
$Br_2(g)$	755	$C_2H_4(g)$	16,280	$CN^-(u.a.)$	39,140
$Br_2(u.a.)$	977	$C_2H_2(g)$	50,030	$HCO_3^-(u.a.)$	−140,270
$HBr(g)$	− 12,540	$NaCl(s)$	− 91,770	$CO_3^{--}(u.a.)$	−126,170
$HBrO(u.a.)$	− 19,680	$KCl(s)$	− 97,555	$Li^+(u.a.)$	− 70,700
$I_2(g)$	4,630	$KClO_3(s)$	− 67,960	$Na^+(u.a.)$	− 62,590
$I_2(u.a.)$	3,926	$AgCl(s)$	− 26,200	$K^+(u.a.)$	− 67,430
$HI(g)$	315	$Ag_2O(s)$	− 2,585	$Cu^+(u.a.)$	12,040
$H_2S(g)$	− 7,865	$Cu_2O(s)$	− 35,150	$Cu^{++}(u.a.)$	15,910
$H_2S(u.a.)$	− 6,515	$CaCO_3(s)$	−269,940	$Ag^+(u.a.)$	18,441
$SO_2(g)$	− 71,750	$Hg_2Cl_2(s)$	− 50,310	$Ca^{++}(u.a.)$	−132,430
$SO_2(u.a.)$	− 71,870	$TlCl(s)$	− 44,190	$Zn^{++}(u.a.)$	− 35,110
$H_2SO_3(u.a.)$	−128,563	$PbCl_2(s)$	− 75,050	$Cd^{++}(u.a.)$	− 18,550
$NH_3(g)$	− 3,864	$CuCl(s)$	− 28,490	$Hg_2^{++}(u.a.)$	36,850
$NH_3(l)$	− 2,574	$HgO(s)$	− 13,940	$Tl^+(u.a.)$	− 7,760
$NH_3(u.a.)$	− 6,257	$H^+(u.a.)$	0	$Sn^{++}(u.a.)$	− 6,490
$NO(g)$	20,650	$OH^-(u.a.)$	− 37,585	$Pb^{++}(u.a.)$	− 5,840
$NO_2(g)$	12,275	$Cl^-(u.a.)$	− 31,340	$Fe^{++}(u.a.)$	− 20,310
$N_2O_4(g)$	23,440	$ClO^-(u.a.)$	− 9,200	$Fe^{+++}(u.a.)$	− 2,530

Calculation of Chemical Equilibrium.—Free-energy changes and entropy changes for isothermal changes in state, whether standard or not, may be evaluated by the procedure that was used in Chap. VIII for enthalpy changes, namely, $\Delta \mathbf{F} = \mathbf{F}_2 - \mathbf{F}_1$ and $\Delta S = S_2 - S_1$, and chemical equations may be added as was done there, with addition of $\Delta \mathbf{F}$ or ΔS. For standard changes, a free-energy balance gives the equilibrium constant at 298°K. for the reaction through equation (13*t*), and an entropy balance gives the equilibrium constant at 298°K. through equation (15*t*) when ΔH is known or can be calculated from tables. Thus a

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[1] In calories per mole, s = solid, l = liquid, g = gas, $u.a.$ = aqueous solution at unit activity. For additional free energies, see Latimer, *op. cit.*, Appendix II.

TABLE 96 — SOME STANDARD ENTROPIES AT 298°K.[1]

Substance	S^0_{298}	Substance	S^0_{298}	Substance	S^0_{298}
$H_2(g)$	31 23	$H_2O(g)$	45 13	$KCl(s)$	19 76
$O_2(g)$	49 03	$H_2O(l)$	16 75	$KClO_3(s)$	34 2
$N_2(g)$	45 79	$HCl(g)$	44 66	$KClO_4(s)$	36 1
$Cl_2(g)$	53 31	$HBr(g)$	47 48	$Ag_2O(s)$	29 1
$Br_2(g)$	58 63	$H_2S(g)$	49 1	$AgCl(s)$	23 0
$Br_2(l)$	36 7	$NH_3(g)$	46 03	$AgBr(s)$	26 1
$I_2(s)$	27 9	$CO(g)$	47 32	$HgO(s)$	17 6
C(diamond)	0 585	$CO_2(g)$	51 08	$Hg_2Cl_2(s)$	47 0
C(graphite)	1 36	$SO_2(g)$	59 2	$PbCl_2(s)$	32 6
$K(s)$	15 2	$CH_4(g)$	44 5	$MgO(s)$	6 66
$Na(s)$	12 2	$CH_3OH(g)$	56 66	$Mg(OH)_2(s)$	15 09
$S(s)$	7 62	$C_2H_4(g)$	52 3	$MgCO_3(s)$	15 7
$Mg(s)$	7 77	$C_2H_5OH(g)$	67 3	$CaO(s)$	9 5
$Ag(s)$	10 20	$NO(g)$	50 34	$CaCO_3(s)$	22 2
$Hg(l)$	18 5	$NO_2(g)$	57 47	$ZnO(s)$	10 4
$Pb(s)$	15 49				
$Zn(s)$	10 0				

table of free energies, or of entropies and enthalpies, provides a convenient means of recording a vast number of equilibrium constants through a reasonable number of entries. The equilibrium constants at 298°K. for the hundreds of chemical reactions involving the substances in Table 95 are all available from a simple calculation involving this table, and the addition of one more free-energy content to this list makes available the equilibrium constants for all possible reactions of that substance with all those in the table. A direct tabulation of all these equilibrium constants would fill many pages, and the constants for a single additional substance would fill more pages still.

The usefulness of these tables will be greatly extended by some simple equations to be given presently, which allow the calculation of $\Delta \mathbf{F}$ or $\Delta \mathbf{F}^0$ at any temperature from their values at a given temperature by means of enthalpies and heat capacities. We have already had one way of doing this through the van't Hoff equation; the new equations are only more convenient means for accomplishing the same end with a smaller number of intermediate calculations through the use of data tabulated in other forms. A few illustrations for constant temperature will be

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[1] In calories per mole per degree, s = solid, l = liquid, g = gas.

given before deriving the equations applicable to changing temperature.

The standard free energies of HCl(g) and of H^+ and Cl^- at unit activity enable us to calculate the activity $m\gamma$ and the activity coefficient γ in solutions of HCl for which vapor pressures have been measured. For example, the activity of the ions in 6*m.* HCl was given as 20.1 on page 600, which means an activity coefficient of 3.35. This coefficient is calculated through the following reversible path for the transfer of the gas to the solution:

$$\begin{array}{llll} HCl(g,\ 1\ \text{atm.}) & = HCl(g,\ 1.84 \times 10^{-4}\ \text{atm.}) & & \\ \mathbf{F}_1 = -22{,}692 & (1)\ \mathbf{F}_2 = -27{,}792 & & \\ & = \ H^+Cl^-(6m.) & = & H^+Cl^-(u.a.) \\ & (2)\ \mathbf{F}_3 = -27{,}792 & (3) & \mathbf{F}_4 = -31{,}340 \end{array}$$

$\Delta\mathbf{F}_1$ for the first change in state is $RT \ln 1.84 \times 10^{-4} = -5100$ cal., $\Delta\mathbf{F}_2$ for the passage of HCl into solution under the equilibrium pressure is zero, and $\Delta\mathbf{F}_3$ is -3553 cal., the difference between the calculated $\mathbf{F}_3$ and $\mathbf{F}_4$, the free energies of the ions from Table 95. From equation (9*t*), $-3553 = 2RT \ln 1/(m\gamma)$, we find $m\gamma = 20.1$ and $\gamma = 20.1/6.0 = 3.35$.

The standard free energy of lead ion at unit activity is -5840 cal. as calculated from its standard electrode potential. From Table 73 we see that the equlibrium constant for the reaction

$$Sn(s) + Pb^{++} = Pb(s) + Sn^{++}$$

is 3.0 at 298°K., and thus $\Delta\mathbf{F}^0$ for this reaction is -650 cal., which is the difference between the standard free energies of these ions. This gives -6490 cal., or $-27{,}200$ joules, as the standard free energy of stannous ion, which in turn gives E^0 for the electrode reaction $Sn(s) = Sn^{++} + 2e^-$ as $27{,}200/2 \times 96{,}500 = 0.140$ volt from equation (14*t*). Direct measurement of the standard electrode potential for tin is excluded by the hydrolysis of stannous ion in the absence of excess acid and by direct displacement of hydrogen ion by tin in the presence of acid. Since there are some calculations in which it is desirable to have this standard potential available, this calculated potential is an important one.

From the free energies of a solid salt and of its ions at unit activity one may calculate the activity product in a saturated solution, and for slightly soluble salts that do not hydrolyze K_a will be almost equal to K_c. When the molality in the saturated solution is high enough so that allowance for activity coefficients is required, the activity product and a solubility product in terms of molalities will not be the same. Calculations for silver chloride and for lead chloride will illustrate these two situations. For the former the free-energy balance is

$$\begin{aligned} \mathrm{AgCl}(s) &= \mathrm{Ag}^+\,(u.a.) + \mathrm{Cl}^-\,(u.a.) \\ -26{,}200 &= 18{,}441 - 31{,}340 - \Delta\mathbf{F}^0 \end{aligned}$$

whence $\Delta\mathbf{F}^0 = 13{,}301$ cal $= -RT \ln (a_{\mathrm{Ag}^+})(a_{\mathrm{Cl}^-})$, the activity product is 1.75×10^{-10}, and the square root of this product is 1.32×10^{-5}, which is the solubility of silver chloride in water at 298°K.

For lead chloride the free-energy balance is

$$\begin{aligned} \mathrm{PbCl_2}(s) &= \mathrm{Pb}^{++}\,(u.a.) + 2\mathrm{Cl}^-\,(u.a.) \\ -75{,}050 &= -5840 - 62{,}680 - \Delta\mathbf{F}^0 \end{aligned}$$

whence

$$\Delta\mathbf{F}^0 = 6530 \text{ cal} = -RT \ln (m_{\mathrm{Pb}^{++}}\gamma_{\mathrm{Pb}^{++}})(m_{\mathrm{Cl}^-}\gamma_{\mathrm{Cl}^-})^2 = -RT \ln 4m^3\gamma^3$$

and $m\gamma = 0.0158$. We are unable to calculate the molality without an activity coefficient or the activity coefficient without an experimental solubility; since the measured solubility at 298°K. is 0.039, we calculate the activity coefficient as $0.0158/0.039 = 0.41$ for the ions in a saturated solution of lead chloride. Without allowance for the activity coefficients, the "calculated" solubility would be more than double the actual one.

The solubility of CO_2 in water as a function of the pressure is recorded by the entries for $CO_2(g)$ and $CO_2(u.a.)$, as may be seen by calculating $\Delta\mathbf{F}^0$ for the standard change in state at 25°,

$$\begin{aligned} \mathrm{CO_2}(g) &= \mathrm{CO_2}(u.a.) \\ -94{,}239 &= -92{,}229 - \Delta\mathbf{F}^0 \end{aligned}$$

for which $K = m_{\mathrm{CO_2}}/p_{\mathrm{CO_2}}$ and $\Delta\mathbf{F}^0 = 2010$ cal. $= -RT \ln K$, whence $K = 0.034$, in agreement with the solubility used in earlier chapters. A word of caution regarding such tabulated free energies as $CO_2(u.a.)$ and $H_2CO_3(u.a.)$ will not be out of place at this point, and it will also apply to the difference between $NH_3(u.a.)$

and $NH_4OH(u.a.)$ or between $SO_2(u.a.)$ and $H_2SO_3(u.a.)$. There is no information on the fraction of the dissolved gas that is hydrated for any of these systems, and the notations $CO_2(u.a.)$ and $H_2CO_3(u.a.)$ both mean unit activity of the dissolved non-ionized gas in the two forms together. Hence for all three of the hydrates the free-energy content is merely that of the unhydrated solute plus −56,690 for a mole of liquid water. Thus for the two forms of equation expressing the ionization of carbonic acid,

$$CO_2(u.a.) + H_2O(l) = H^+(u.a.) + HCO_3^-(u.a.)$$

and

$$H_2CO_3(u.a.) = H^+(u.a.) + HCO_3^-(u.a.)$$

ΔF^0 will be the same, and the ion activities calculated from $\Delta F^0 = -RT \ln K$ will be the same, as they should be. But this does not mean that we may use these free energies for such a calculation as

$$CO_2(u.a.) + H_2O(l) = H_2CO_3(u.a.) \qquad \Delta F^0 = 0$$

from which $K = 1 = a_{H_2CO_3}/a_{CO_2}$ is justified; for this calculation leads to the fiction that half the CO_2 is in the hydrated form, and we have no information on this fraction.

A corresponding calculation for the solubility of chlorine in water gives the equilibrium concentration of Cl_2 molecules in water when the pressure of chlorine gas is 1 atm., but it does not give the total solubility of chlorine in water, for almost a third of the total dissolved chlorine is hydrolyzed. The concentrations of H^+, Cl^-, and HClO in equilibrium with chlorine gas at 1 atm. can of course be calculated from the free-energy tables; and since one mole of chlorine gives one mole of each of these solutes upon hydrolysis, the total dissolved chlorine is the sum of the hydrolyzed and unhydrolyzed quantities, or $(Cl_2) + (H^+)$.

A solubility product for $CaCO_3$ may be calculated from the standard free energies

$$\begin{aligned} CaCO_3(s) &= Ca^{++}(u.a.) + CO_3^{--}(u.a.) \\ -269{,}940 &= -132{,}430 \quad - \quad 126{,}170 \quad - \Delta F^0 \end{aligned}$$

from which $\Delta F^0 = 11{,}340$ cal. at 25° and the solubility product is $5 \times 10^{-9} = (Ca^{++})(CO_3^{--})$. The product of *these molalities* in a saturated solution of $CaCO_3$ is thus correctly given by the calculation, but the square root of the solubility product will not give the solubility of calcium carbonate in water, since more than half the dissolved material is in the form of hydrolysis products, as was explained on page 414.

Entropies and free energies may sometimes be used to determine enthalpies to advantage. For example, ΔH for the formation of PbS(*s*) is given by one source as $-24{,}800$ cal. and by another source as $-20{,}600$ cal., with little indication as to which is the better value. From the equilibrium

$$\mathrm{PbS} + \mathrm{H_2}(g) = \mathrm{Pb}(s) + \mathrm{H_2S}(g)$$

and the well-known free energy of H_2S one calculates the standard free energy of PbS(*s*) as $-21{,}735$ cal. at 298°K., and from entropy data one calculates $\mathrm{Pb}(s) + \mathrm{S}(s) = \mathrm{PbS}(s)$, $\Delta S^0_{298} = -1.3$ e.u., and $T\,\Delta S^0 = -390$ cal., whence from equation (15*t*)

$$\Delta H^0 = \Delta \mathbf{F}^0 + T\,\Delta S^0 = -21{,}735 - 390 = -22{,}125 \text{ cal.}$$

There are other reactions for which ΔH so determined will be a better value than the direct calorimetric determination for one reason or another. Precise calorimetry is difficult at temperatures much above room temperature, and there are many reactions that proceed too slowly for direct measurement of their heat effects until high temperatures are reached. The experimental difficulties of high-temperature equilibrium measurements and low-temperature heat capacities have been so completely solved as to open up a new means of determining enthalpies of reactions through the relation $\Delta \mathbf{F} = \Delta H - T\,\Delta S$.

Change of Free Energy with Temperature.—This important relation will be derived in two ways, first from a reversible cycle of changes in which a reacting system performs a Carnot cycle with the absorption of heat at one temperature, the conversion of part of the heat into work, and the rejection of the remainder of the heat at a lower temperature, and then from the defined relation $\mathbf{F} = H - TS$.

In the first derivation, the maximum work of the reversible cycle will be expressed in terms of the free-energy change, which will then be related to the heat absorbed at the higher temperature through the second law of thermodynamics.

1. We begin the cycle with a system in state 1 at the temperature T, where its volume is v_1 and its pressure p_1. The system

changes to state 2 at T for the first step in the cycle, by which its pressure becomes p_2 and its volume v_2; and for this change in state the heat absorbed is q, the enthalpy increase is ΔH, and the free-energy increase is $\Delta\mathbf{F}$. The maximum work done by the system in this step is $w_1 = -\Delta\mathbf{F} + p_2v_2 - p_1v_1$.

2. We cool the system under the constant pressure p_2 to $T - dT$, by which the volume becomes $v_2 - dv_2$ and for which the work done by the system is $w_2 = -p_2\,dv_2$.

3. We change the system back to state 1 at $T - dT$, where its volume is $v_1 - dv_1$ and its pressure p_1; for this change in state the free-energy increase is $-(\Delta\mathbf{F} - d\,\Delta\mathbf{F})$, since $\Delta\mathbf{F} - d\,\Delta\mathbf{F}$ is the smaller increase in $\Delta\mathbf{F}$ upon going from state 1 to state 2 at $T - dT$, and the free energy for the change from state 2 to state 1 has the opposite sign. The maximum work of this change is $w_3 = (\Delta\mathbf{F} - d\,\Delta\mathbf{F}) + p_1(v_1 - dv_1) - p_2(v_2 - dv_2)$.

4. Finally, we return the system to its original condition by heating it at the constant pressure p_1 to T, for which $w_4 = p_1\,dv_1$.

The summation of work quantities for the cycle is $-d\,\Delta\mathbf{F}$, which by the second law of thermodynamics is equal to $q\,dT/T$. This quantity q is equal to $\Delta H + [w - \Delta(pv)]$ in view of the definition $\Delta H = \Delta E + \Delta(pv) = q - w + \Delta(pv)$. But since the change in state at T took place *reversibly*, the quantity in square brackets is $-\Delta\mathbf{F}$ and hence $q = \Delta H - \Delta\mathbf{F}$. Thus, the desired relation is

$$-d\,\Delta\mathbf{F} = \frac{(\Delta H - \Delta\mathbf{F})}{T}\,dT$$

or

$$\frac{d\,\Delta\mathbf{F}}{dT} = \frac{\Delta\mathbf{F} - \Delta H}{T} \tag{16}$$

Upon rearranging and dividing through by T^2, this equation becomes

$$\frac{Td\,\Delta\mathbf{F} - \Delta\mathbf{F}\,dT}{T^2} = d\left(\frac{\Delta\mathbf{F}}{T}\right) = -\frac{\Delta H}{T^2}\,dT \tag{17}$$

The formal definition of free energy, $\mathbf{F} = H - TS$, given on page 45, may also be used to derive equation (16). Upon differentiating with respect to T at constant pressure, we have

$$\left(\frac{\partial\mathbf{F}}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p - T\left(\frac{\partial S}{\partial T}\right)_p - S$$

But at constant pressure $dH = T\,dS$ for a reversible process, and thus this equation becomes

$$\left(\frac{\partial \mathbf{F}}{\partial T}\right)_p = -S \tag{18}$$

Upon summation of free-energy changes for the following paths,

$$\begin{tikzcd}
\begin{matrix}\text{State 1 at } T + dT \\ \mathbf{F}_1 + d\mathbf{F}_1\end{matrix} \arrow[rr, "\Delta\mathbf{F} + d\,\Delta\mathbf{F}"] & & \begin{matrix}\text{State 2 at } T + dT \\ \mathbf{F}_2 + d\mathbf{F}_2\end{matrix} \\
\begin{matrix}\text{State 1 at } T \\ \mathbf{F}_1\end{matrix} \arrow[u, "d\mathbf{F}_1"'] \arrow[rr, "\Delta\mathbf{F}"] & & \begin{matrix}\text{State 2 at } T \\ \mathbf{F}_2\end{matrix} \arrow[u, "d\mathbf{F}_2"]
\end{tikzcd}$$

we see that, for the change at T followed by heating to $T + dT$, the free-energy change is $\Delta\mathbf{F} + d\mathbf{F}_2$ and, for heating first to $T + dT$ and then undergoing change, the free energy is $d\mathbf{F}_1 + \Delta\mathbf{F} + d\,\Delta\mathbf{F}$; upon equating these,

$$d\,\Delta\mathbf{F} = d\mathbf{F}_2 - d\mathbf{F}_1 = -S_2\,dT + S_1\,dT$$

whence

$$\frac{d\,\Delta\mathbf{F}}{dT} = -S_2 + S_1 = -\Delta S = \frac{\Delta\mathbf{F} - \Delta H}{T} \tag{16}$$

Before integrating equation (17), ΔH must be expressed as a function of the temperature by the method given on page 321. The equation for ΔH will usually have the form

$$\Delta H = \Delta H_0 + aT + bT^2 + cT^3$$

in which ΔH_0 is the integration constant that appears when $d(\Delta H) = \Delta C_p\,dT$ is integrated. Upon substituting this in equation (17), integrating, and multiplying through by T, we have

$$\Delta\mathbf{F}_T = \Delta H_0 - aT\ln T - bT^2 - \tfrac{1}{2}cT^3 + IT \tag{19}$$

If ΔH is independent of temperature or sufficiently constant over the temperature range involved, the simpler integral of equation (17) is

$$\Delta\mathbf{F}_T = \Delta H + IT \tag{20}$$

When $\Delta\mathbf{F}$ at a single temperature is to be calculated from $\Delta\mathbf{F}$ at the standard temperature and provided that ΔH is constant, one may, of course, integrate equation (17) between limits and obtain

$$\frac{\Delta\mathbf{F}_2}{T_2} - \frac{\Delta\mathbf{F}_1}{T_1} = -\Delta H \frac{T_2 - T_1}{T_2 T_1} \tag{21}$$

From the equation $d(\Delta H)/dT = \Delta C_p$ we see that, when ΔH is constant, ΔC_p is zero, and that the heat capacities of the system in its initial and final states are the same. And since the entropy increase on heating any system reversibly is $\int C_p\, d \ln T$ between the temperatures involved in the heating, it follows that the entropies of the system in its initial and final states increase by the same amount when heated through the same temperature range, if C_p is the same for both, and thus that ΔS for the isothermal change in state is the same at all temperatures. This fact shows that the integration constant I in equation (20) is $-\Delta S$ when ΔH is independent of temperature, since $\Delta\mathbf{F} = \Delta H - T\,\Delta S$ for an isothermal change.

Thus, for reactions in which ΔC_p is zero or negligible, equation (20) has the convenient forms

$$\Delta\mathbf{F}_T = \Delta H - T\,\Delta S \tag{22}$$

$$\Delta\mathbf{F}^0{}_T = \Delta H^0 - T\,\Delta S^0 \tag{23}$$

These equations are, respectively, (12*t*) and (15*t*) for *isothermal* changes in state, but when ΔH is constant they are also the equations for changing $\Delta\mathbf{F}$ with changing temperature. When ΔH is not constant, these equations may not be used and equation (19) must be used.

The van't Hoff Equation.—In order to show the relation of these equations to the van't Hoff equation for the change of equilibrium constant with temperature, equation (10*t*) on page 602 may be put in the form

$$\frac{\Delta\mathbf{F}}{T} = R \ln \frac{p_{\mathrm{D}}'^{d} p_{\mathrm{E}}'^{e}}{p_{\mathrm{A}}'^{a} p_{\mathrm{B}}'^{b}} - R \ln K \tag{24}$$

All the pressures in the first term on the right are the initial or final pressures appearing in the change in state; and since they are kept constant when the system changes temperature, the derivative of this term with respect to T is zero. By differentiating (24) and combining with (17), we have

$$d\left(\frac{\Delta F}{T}\right) = -R\, d \ln K = -\frac{\Delta H}{T^2}\, dT \tag{25}$$

which rearranges to give the van't Hoff equation

$$d \ln K = \frac{\Delta H}{RT^2}\, dT \tag{26}$$

Thus the equations derived in this section are only more convenient ones for calculating change of equilibrium with temperature from free-energy tables or entropy and enthalpy tables.

A few illustrations will not be out of place. The dissociation pressure of silver oxide is 1 atm. at 463°K., and ΔH is constant for the reaction

$$2\text{Ag}(s) + \tfrac{1}{2}\text{O}_2(g) = \text{Ag}_2\text{O}(s) \qquad \Delta H = -7300 \text{ cal.}$$

At 463°K., $\Delta \mathbf{F}^0 = 0$, and thus from the substitution

$$\begin{aligned} \Delta \mathbf{F}^0 &= \Delta H^0 - T\,\Delta S^0 \\ 0 &= -7300 - 463\,\Delta S^0 \end{aligned}$$

we find $\Delta S^0 = -15.8$ for all temperatures. From this we calculate the standard free energy at 298°K.,

$$\Delta \mathbf{F}^0_{298} = -7300 - 298(-15.8) = -2580 \text{ cal.}$$

which is the same as the result obtained on page 611 from equation (13*t*) and the van't Hoff equation.

From a standard entropy balance at 298°K. for the reaction

$$\begin{aligned} \text{HgO}(s) &= \text{Hg}(g) + \tfrac{1}{2}\text{O}_2(g) \\ 17.6 &= 41.8 + 24.5 - \Delta S^0 \end{aligned}$$

ΔS^0 is 48.7 e.u. The heat absorbed is $\Delta H = 36{,}200$ cal. at 298°K. It seems unlikely that ΔC_p is zero for this reaction, but there are no reliable data for the heat capacity of HgO as a temperature function. We may make an approximate calculation of $\Delta \mathbf{F}^0$ at 713°K., at which the measured dissociation pressure is 0.845 atm., $K = \tfrac{2}{3}p\sqrt{\tfrac{1}{3}p} = 0.30$, and $\Delta \mathbf{F}^0 = -RT \ln K = 1710$ cal. From equation (23) we calculate

$$\Delta \mathbf{F}^0_{713} = 36{,}200 - 713(48.7) = 1500 \text{ cal.}$$

from which $K_{713} = 0.35$ and the calculated dissociation pressure is 0.94 atm. Such a calculation is not very satisfactory, but it should be noted that ΔF^0_{713} is the small difference between two larger quantities, ΔH and $T\,\Delta S^0$, and small errors in either of them have a large effect upon the difference. The assumption that ΔH is constant is probably not the chief source of the error in the calculated dissociation pressure; for changing ΔH to 36,400 cal, which is a change of less than 1 per cent, changes ΔF^0_{713} to 1700 cal. and gives perfect agreement between the calculated and measured dissociation pressures. It is probable that the actual error in ΔH is as great as 200 cal., but this is not to say that an approximate calculation such as we have made above shows that this error exists.

It may be profitable to close this discussion of free-energy data with a word of caution based upon the calculation just given and other similar ones throughout the text, a word that is applicable to the data in any field. Tables often include entries of high accuracy with others of questionable accuracy but give no indication of their comparative reliability. Entries are sometimes admittedly uncertain but the only ones available. Actual errors are sometimes increased by the necessity of taking the small difference between two large quantities Under these circumstances one must do the best he can with the data he has, he must realize that the final result is no better than the data on which it is based and discard digits that are not truly significant, and above all he must maintain a sense of proportion tempered with patience. The quantity of good data is increasing rapidly; many of the older measurements are being repeated with better instruments and higher skill; and many new quantities are being measured. We have attempted to show how the data we have may be used; the appearance of new data will not change the method of use.

Problems

Numerical data should be sought in the tables in the text.

1. (*a*) Calculate ΔH for the evaporation of a mole of bromine at 298°K. from the data in Tables 95 and 96. (*b*) Calculate the entropy of saturated bromine vapor at 298°K. (*c*) The density of liquid bromine is 2.93 grams per ml. at 298°K. Estimate ΔF for the change in state $Br_2(l,\ 1\ \text{atm.}) = Br_2(l,\ 10\ \text{atm.})$ at 298°K.

2. (*a*) Calculate ΔF at 298°K for the change in state $Cl_2(g,$ 1 atm.) = $Cl_2(g,$ 7.0 atm.), neglecting the deviation of chlorine from ideal gas behavior. (*b*) The vapor pressure of chlorine at 298°K. is 7.0 atm. Calculate the molal free-energy content of $Cl_2(l)$

3. The partial pressure of $HBr(g)$ above an aqueous solution of HBr at 298°K changes with the molality as follows:

m	6	8	10
10^6p, atm	1 99	11 7	77 6

(*a*) Calculate the activity coefficients in these solutions from the data in Table 95. (In these solutions the activity *coefficient* will be greater than unity) (*b*) Calculate the pressure of HBr above a solution 1.0*m*. in HBr at 298°K., taking 0.80 as the activity coefficient for the ions

4. Calculate the free-energy increase at 298°K for the reaction $H_2O(l)$ + $\frac{1}{2}O_2(g,$ 1 atm.) = $H_2O_2(u\ a\ )$ and the pressure of oxygen in equilibrium with H_2O and $H_2O_2(u\ a\ )$

5. (*a*) Calculate the ionization constant for water at 298°K from free-energy data. (*b*) From ΔH for the ionization of water given on page 320, calculate K_w at 323°K

6. The ratio of $CO_2(g)$ to $CO(g)$ in equilibrium with $Zn(s)$ and $ZnO(s)$ at 693°K. is 5.5×10^{-5}, ΔH for the reaction $ZnO(s) + CO(g) = Zn(s) + CO_2(g)$ is 15,500 cal , and $\Delta C_p = 0$ (*a*) Calculate the standard free energy of $ZnO(s)$ at 298°K. (*b*) Calculate another value of the free energy of $ZnO(s)$ from the data in Tables 58 and 96.

7. Calculate the equilibrium constant at 298°K. for the reaction $AgCl(s)$ + NaOH = $\frac{1}{2}Ag_2O(s)$ + NaCl + $\frac{1}{2}H_2O$. [The measured ratio $(Cl^-)/(OH^-)$ is 0.00893. *J. Am. Chem. Soc.*, **50**, 3528 (1928).]

8. Using the free-energy data, calculate the pressure of oxygen required to make the reaction $KCl(s) + \frac{3}{2}O_2(g) = KClO_3(s)$ proceed. (*b*) Calculate the free energies of $KCl(s)$ and $KClO_3(s)$ from the entropies and enthalpy data, and recalculate the pressure of oxygen required for the first reaction

9. Calculate the standard free energy and standard entropy of $SO_3(g)$ at 298°K. from the following data: The equilibrium constants for the reaction $SO_2(g) + \frac{1}{2}O_2(g) = SO_3(g)$ are 31.3 at 800°K. and 6.56 at 900°K., and ΔC_p for the reaction is zero.

10. From the solubility data in Problem 20, page 425, calculate the molal free-energy content for the complex ion $CuCl_2^-(u.a.)$ at 298°K.

11. (*a*) Show by free-energy calculations whether a catalyst could cause the "fixation" of nitrogen as ammonia at 298°K (*b*) Show whether a catalyst could form NO or NO_2 in appreciable quantities from air at 298°K.

12. The chemical reaction $N_2(g) + C_2H_2(g) = 2HCN(g)$ is a possible one for the fixation of nitrogen. (*a*) Given $\Delta H_{298} = 7700$ cal., $\Delta S^0_{298} = 3\ 2$, and $\Delta C_p = 0$, calculate the equilibrium constant for this reaction and the fraction of nitrogen reacting in a mixture of 1 mole of N_2 and 1 mole of C_2H_2 at 700°K. and at 1100°K. (*b*) Recalculate ΔF^0_{700}, assuming $\Delta C_p = 2.6 - 0.002T$ for the reaction.

13. (*a*) Calculate the solubility of H_2S in water at 1 atm. pressure and 298°K. (*b*) Calculate the solubility of bromine in water at 298°K., neglecting the small hydrolysis. (*c*) Calculate the fraction of the dissolved bromine that is hydrolyzed.

14. (*a*) Calculate $\Delta \mathbf{F}^0$ as a function of the temperature for the reaction $CO(g) + 2H_2(g) = CH_3OH(g)$, $\Delta H_{298} = -21{,}660$ cal., taking $C_p = 2.0 + 0.030T$ for $CH_3OH(g)$ and $C_p = 6.5 + 0.001T$ for the other gases. (*b*) Calculate the equilibrium constant for the reaction at 473°K.

15. The solubility product of $Mg(OH)_2$ is 5.5×10^{-12} at 298°K. (*a*) Calculate the free energy of $Mg^{++}(u.a.)$. (*b*) Calculate the solubility product for $MgCO_3$ at 298°K. (Note that this should not agree with the solubility product for $MgCO_3.3H_2O$ given in Problem 16 on page 425.)

16. Calculate the hydrolysis constants for the ions CN^- and HCO_3^- from the free-energy data.

17. (*a*) Calculate the dissociation pressure of $MgCO_3$ at 612°K. and at 681°K., taking ΔH from Table 58 and assuming $\Delta C_p = 0$. (*b*) The recorded dissociation pressure at 681°K. is 1.00 atm. On the assumption that the entropy data are correct, what value of ΔH would be required to show a calculated dissociation pressure of 1 atm. at 681°K.? (The recorded ΔH for the dissociation is given as 28,300 ± 850 cal.)

18. Calculate the dissociation pressure of $Mg(OH)_2(s)$ at 485°K., assuming ΔH constant. (The measured dissociation pressure at 485°K. is 0.0717 atm.)

19. Show that $KClO_3$ is thermodynamically unstable with respect to its decomposition into $KClO_4$ and KCl at 298°K.

20. (*a*) Calculate the entropy of $H_2O(g)$ at 298°K. and 0.0313 atm. (which is the vapor pressure of water at this temperature) from the standard entropy. (*b*) Calculate ΔH for the evaporation of water at 298°K.

21. (*a*) Calculate the quantities ΔH, ΔE, ΔA, $\Delta \mathbf{F}$, and ΔS for the change in state $H_2O(l,$ 423°K., 4.7 atm.$) = H_2O(g,$ 423°K., 4.7 atm.$)$ from the experimental data on page 108. (*b*) Estimate these quantities for the change in state $H_2O(l,$ 423°K., 4.7 atm.$) = H_2O(g,$ 423°K., 1 atm.$)$ by devising a reversible path for the change and assuming the vapor an ideal gas.

22. Calculate the standard free energies of $I_2(g)$ and $I_2(l)$ at 114.15°C., taking $I_2(s) = 0$ at 114.14°C. (See page 146 for data.)

23. For the change in state $N_2(g,$ 1 atm.$) = N_2(g,$ 0.1 atm.$)$ at 25°C., calculate ΔH, ΔE, ΔA, ΔS, and $\Delta \mathbf{F}$, assuming nitrogen to be an ideal gas. What are the upper and lower limits of q and w for the isothermal process?

24. (*a*) Calculate the equilibrium constant at 25° for the reaction $CuCl(s) + \frac{1}{2}H_2O = \frac{1}{2}Cu_2O(s) + H^+Cl^-$. (*b*) Calculate the solubility product for cuprous chloride in aqueous solution at 25°. (*c*) The solubility of cuprous oxide in water is negligibly small. Calculate the concentration of cuprous ion in a solution made by saturating water with cuprous chloride. allowing for the hydrolysis shown in part (*a*). The activity coefficients may be assumed unity in these dilute solutions.

25. For the chemical reaction $2NaH(s) = 2Na(l) + H_2(g)$, $\Delta H = 30{,}500$ cal., and $\Delta C_p = 0$. The equilibrium pressure (in atmospheres) changes with the absolute temperature as follows:

T	573	593	613	633	653	673
p	0.0105	0.0245	0.0549	0.117	0.240	0.467

The vapor pressure of sodium is negligible in this temperature range. (*a*) Calculate ΔF^0 at 371°K. for the reaction. (*b*) The latent heat of fusion of sodium at 371°K. is 630 cal. per atomic weight Calculate ΔH for the reaction $2NaH(s) = 2Na(s) + H_2(g)$ at 371°K. and ΔF^0 for the reaction at 298°K., again assuming $\Delta C_p = 0$.

26. From the data on page 64 and in Tables 58 and 95, calculate an approximate value of the molal enthalpy of $COCl_2(g)$ at 25°, neglecting ΔC_p, for which there are no data

27. (*a*) Calculate the equilibrium concentration of chlorine molecules in a solution at 298°K. when the partial pressure of chlorine above the solution is 1 atm (*b*) The measured solubility of chlorine is 0 094*m*. at 298°K. for 1 atm. pressure. Calculate the fraction of chlorine hydrolyzed in the solution. (*c*) Calculate the standard free energy of HClO, taking 0.85 as the activity coefficient for the ions and neglecting the very small ionization of HClO in the solution. (*d*) Calculate the ionization constant of HClO.

28. The enthalpy of combustion of graphite is −94,030 cal. at 298°K , and that of diamond is −94,484 cal. (*a*) Calculate ΔF^0_{298} for the transition $C_{\text{graph}} = C_{\text{diam}}$. (*b*) Calculate roughly the pressure that would be required to give ΔF a negative sign at 298°K. for this transition, taking the density of diamond as 3.51 and that of graphite as 2 26 and neglecting the compressibilities. (Note that ΔF must be negative for a spontaneous process)

29. (*a*) Derive an expression for ΔF^0 as a function of the temperature for the reaction $C_2H_4(g) + H_2O(g) = C_2H_5OH(g)$, $\Delta H = -11{,}000$ cal., assuming $\Delta C_p = 0$. (*b*) Calculate the equilibrium constant for the reaction at 500°K. (*c*) Calculate the fraction of ethylene hydrated when a mixture of 2 moles of C_2H_4, 2 moles of $H_2O(g)$, and 6 moles of inert gas reach equilibrium at a total pressure of 10 atm. at 500°K. [Parks, *Ind. Eng. Chem.*, **29,** 845 (1937), estimates $\Delta C_p = -6\ 43 + 0\ 0133T$, $\Delta F^0 = -9674 + 6.43T \ln T - 0.006657T^2 - 9\ 01T$, and finds $\Delta F^0_{500} = 4139$ cal.]

30. (*a*) Calculate the equilibrium constant at 25° for the reaction $NOBr(g) = NO(g) + \frac{1}{2}Br_2(g)$, taking 19,260 cal. as the standard free energy of $NOBr(g)$. (*b*) What fraction of NO will be converted to NOBr at 25° in contact with liquid bromine?

31. Calculate the equilibrium constant for the reaction $2H_2S(g) + SO_2(g) = 2H_2O(g) + 3S(s)$ at 25°.

32. The molality of a solution in equilibrium with $CaSO_4(s)$ at 298°K. is 0.0202, and the activity coefficient in this solution is 0.32; the molality of a solution in equilibrium with $CaSO_4.2H_2O(s)$ at 298°K. is 0 0153, and the activity coefficient in this solution is 0.35. (*a*) Calculate ΔF^0_{298} for each of the reactions

$$\begin{aligned}CaSO_4(s) &= Ca^{++}(u.a.) + SO_4^{--}(u\ a.)\\ CaSO_4.2H_2O(s) &= Ca^{++}(u\ a\ ) + SO_4^{--}(u.a.) + 2H_2O(l)\\ CaSO_4(s) + 2H_2O(l) &= CaSO_4.2H_2O(s)\end{aligned}$$

taking the activity of water in the saturated solution equal to that of pure water. (*b*) For the reaction $CaSO_4(s) + 2H_2O(l) = CaSO_4.2H_2O(s)$, $\Delta H = -4040$ cal., and $\Delta C_p = 0$. Calculate the transition temperature of the dihydrate to anhydrous salt, this being the temperature at which $\Delta F^0 = 0$.

(*c*) The standard entropies at 298°K. are 25.5 for $CaSO_4$, 46.4 for $CaSO_4.2H_2O$, and 16.75 for $H_2O(l)$. Calculate ΔS^0_{298} for the reaction $CaSO_4(s) + 2H_2O(l) = CaSO_4.2H_2O(s)$, and calculate another value of ΔF^0_{298}.

33. From the data in Tables 58 and 96 calculate the standard free energies of $HCl(g)$, $KCl(s)$, $NH_3(g)$, and $KClO_4(s)$

34. (*a*) Calculate ΔF^0_{298} for the reaction $Na_2SO_4(s) + 10H_2O(l) = Na_2SO_4.10H_2O(s)$, for which $\Delta H_{298} = -19{,}400$ cal. and $\Delta S^0_{298} = -61.4$. (*b*) The vapor pressure of water at 298°K. is 0.0313 atm. Calculate ΔF^0_{298} for the reaction $Na_2SO_4(s) + 10H_2O(g) = Na_2SO_4(s)$. (*c*) Calculate the dissociation pressure of the hydrate at 298°K.

35. (*a*) The vapor of NH_4Cl is completely dissociated into NH_3 and HCl, and at 610°K. the equilibrium pressure is 1 0 atm. for the reaction $NH_4Cl(s) = NH_3(g) + HCl(g)$; $\Delta H = 40{,}000$ cal., $\Delta C_p = 0$. Calculate the standard free energy of $NH_4Cl(s)$ at 298°K. (*b*) The standard entropy of $NH_4Cl(s)$ at 298°K. is 22.6. Calculate the standard free energy of $NH_4Cl(s)$, using the same free energies for $NH_3(g)$ and $HCl(g)$ as in part (*a*).

36. The enthalpy of $PbS(s)$ is $-22{,}160$ cal. at 298°K., and the standard entropy is 21.8. (*a*) Assume $\Delta C_p = 0$, and calculate the equilibrium constant at 600°K for the reaction $PbS(s) + H_2(g) = Pb(s) + H_2S(g)$. (*b*) The heat of fusion of lead at 600°K is 1200 cal per atomic weight. Calculate ΔH, ΔF^0, and ΔS^0 at 600°K for the reaction $PbS(s) + H_2(g) = Pb(l) + H_2S(g)$.

37. (*a*) Calculate the standard free energy of S^{--}(*u a.*) from the data in Tables 63 and 95. (*b*) Calculate the solubility product for $PbS(s)$.

CHAPTER XIX

POTENTIALS OF ELECTROLYTIC CELLS

The purpose of this chapter is to consider the potentials of electrolytic cells in which chemical changes take place isothermally and reversibly and through these potentials to evaluate the free-energy changes of the chemical reactions. The equations and measurements will confirm some of the standard free energies of substances obtained in the previous chapter and furnish activity coefficients for ions, transference numbers, solubilities, ionization constants, equilibrium constants, and other important quantities. Cell potentials are one of the most important sources of precise data for the calculations of physical chemistry, and thus it is important to understand the underlying theory and the limitations of the theory, in order to make full use of the measurements.[1] Since cell potentials change with the nature of the electrodes, with the nature and molality of the solutes, and with the temperature, it is evident that a record of all cells at all molalities and all temperatures is not to be compiled in a limited space. The expedient used is one that has been used before, namely, a record of standard potentials at a standard temperature and some simple equations through which to calculate the change of potential with molality or temperature.

Electrode reactions such as were considered in Chap. VII will apply in this chapter also, as will Faraday's law and the law of transference. The passage of electricity through a cell will require chemical reactions in which one equivalent of chemical change is produced at each electrode for each faraday passing; and the ions in the solution will carry fractions of the total elec-

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[1] The precision of modern data is not to be judged from the fact that most of the potentials in this chapter are given to a millivolt or 0 1 mv.; for most of them are known with higher precision. In a first meeting with the subject it will not be important to know that the potential of a given cell is 0.46419 volt, and we have been content to state it as 0.4642 volt or as 0.464 volt The additional figures will be found in the original sources of data quoted for the cells.

tricity that are equal to their transference numbers in the solution. These transference numbers will be in the same ratio as the mobilities of the ions, so that

$$T_+ = \frac{N_+}{N_+ + N_-} = \frac{\Lambda_+}{\Lambda_+ + \Lambda_-}$$

The potential of an electric cell depends on the rate at which current is drawn from it, and experiment shows that the potential produced approaches a maximum value when the current drawn from the cell becomes very small. When electricity is passed through a cell to reverse the chemical change, the potential required decreases as the current decreases; and the maximum potential produced by the cell approaches the minimum potential required to reverse it when the smallest measurable currents are employed. This maximum potential is the one with which we shall be concerned in this chapter.

Such potentials are measured on a potentiometer, a device for opposing the potential of a cell with another which is slightly greater or slightly less and in which the difference decreases until the current flowing through the cell is no longer measurable. The opposing potential is regulated by a sliding contact along a wire of uniform resistance or through dial resistances, and the actual potential is derived from a similar procedure with a cell of standard potential. The common standard is the "Weston cell," whose potential is 1.0181 volts at 25°.

The electrical energy derived from a cell is the product of potential, current, and time For most of the cells we are to consider the quantity of electricity will be 96,500 amp.-sec., or 1 faraday, so that 96,500E joules will be produced. When N faradays passes through a cell, the electric energy is ENF joules.

The relation of the free-energy change to the electric energy produced in a cell in which a chemical change takes place isothermally and reversibly was given in the previous chapter, but it is repeated here, since we are to use it extensively.[1]

$$\Delta\mathbf{F} = -ENF \qquad (1t)$$

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[1] The italic letter F denotes Faraday's constant of 96,500 amp.-sec. per equivalent of reacting substance, the bold-faced letter $\mathbf{F}$ the free-energy content of a system, and $\Delta\mathbf{F}$ the free-energy increase attending a change in state, as was done in the previous chapter. The letter t with the number of an equation indicates its restriction to a process taking place at constant temperature.

A spontaneous process is one for which $\Delta\mathbf{F}$ is negative; and since $\Delta\mathbf{F} = -ENF$, a positive cell potential means a free-energy decrease and a spontaneously operating cell. A negative potential means a free-energy increase attending operation of the cell or that an opposing potential must be applied to the cell to cause it to operate.

Formulation of Cells.—It has become common practice to describe a cell in terms of the substances involved in the change in state, with those portions at which a potential difference exists separated by commas or vertical bars and with the *anode written at the left*. For example,

$$\mathrm{Ag} + \mathrm{AgCl},\ \mathrm{HCl}(0.1m.),\ \mathrm{Cl_2}(1\ \mathrm{atm.});\ E_{298} = 1.136\ \text{volts}$$

or

$$\mathrm{Ag} + \mathrm{AgCl}\,|\,\mathrm{HCl}(0.1m.)\,|\,\mathrm{Cl_2}(1\ \mathrm{atm.});\ E_{298} = 1.136\ \text{volts}$$

This notation means that an anode of silver coated with silver chloride is dipping into $0.1m.$ hydrochloric acid and that the cathode is a platinum or other inert metal plate dipping into $0.1m.$ hydrochloric acid saturated with chlorine at 1 atm. pressure and over which chlorine gas is bubbling. The subscript attached to E defines the temperature at which the potential was measured, and the positive sign of the potential means that the cell will operate and produce this maximum potential.

If the cell above were written

$$\mathrm{Cl_2}(1\ \mathrm{atm.}),\ \mathrm{HCl}(0.1m.),\ \mathrm{AgCl} + \mathrm{Ag};\ E_{298} = -1.136\ \text{volts}$$

with the chlorine electrode as the anode, the negative sign of the potential means that at least this potential must be applied to the cell to make it operate with the silver chloride electrode as a cathode.

In another type of cell the electrode materials are the same for anode and cathode, and two solutions are involved. An example is the cell

$$\mathrm{Ag} + \mathrm{AgCl},\ \mathrm{HCl}(0.10m.),\ \mathrm{HCl}(0.020m.),\ \mathrm{AgCl} + \mathrm{Ag};\quad E_{298} = 0.0645\ \text{volt}$$

to which we shall come later in the chapter. The notation means that a silver chloride electrode is in contact with $0.1m.$ HCl at the anode of the cell, another silver chloride electrode is in contact with 0.020*m.* HCl at the cathode, and the two solutions meet in a "liquid junction."

Throughout the chapter we shall follow the custom, which is now standard, of considering the left-hand electrode as the anode, which is to say that oxidation takes place at this electrode, or that negative charges are given to the metal electrode at this point, or that the electrode reaction is written with the symbol e^- for a faraday of electricity on the right-hand side of the chemical equation expressing the change in state. The cathode reaction is that one which occurs at the right-hand electrode, and the symbol e^- is written on the left side of the chemical equation to indicate the acceptance of negative charges from the metal at this electrode.

Cell Reactions.—Electrode reactions will be written in the same manner as in Chap. VII, with the additional specification of the molality at which ions are formed or used. So long as we were concerned only with Faraday's law, this specification was unnecessary, for the quantity of solute formed by an electrode reaction is independent of molality. But the potential of an electrode or a cell is the chief topic of the present discussion; and since potentials depend on the molality in some of the cells to be considered, we must always specify the molality of the solution in a cell. For example, in the cell

$$\mathrm{Ag} + \mathrm{AgCl},\ \mathrm{HCl}(0.10m.),\ \mathrm{Cl_2}(1\ \mathrm{atm.});\ E_{298} = 1.136\ \mathrm{volts}$$

the chemical change attending the passage of 1 faraday through the cell is the sum of two electrode reactions, as follows:

$$\begin{array}{rcl} \mathrm{Ag} + \mathrm{Cl^-}(0.10m.) & = & \mathrm{AgCl}(s) + e^- \\ e^- + \frac{1}{2}\mathrm{Cl_2}(1\ \mathrm{atm.}) & = & \mathrm{Cl^-}(0.10m.) \\ \hline \mathrm{Ag}(s) + \frac{1}{2}\mathrm{Cl_2}(1\ \mathrm{atm.}) & = & \mathrm{AgCl}(s) \end{array}$$

In this cell the potential is independent of molality, but this will not be true of cells in general. As examples, the cells

$$\mathrm{H_2}(1\ \mathrm{atm.}),\ \mathrm{HCl}(0.10m.),\ \mathrm{AgCl} + \mathrm{Ag};\ E_{298} = 0.3524\ \mathrm{volt}$$
$$\mathrm{H_2}(1\ \mathrm{atm.}),\ \mathrm{HCl}(0.01m.),\ \mathrm{AgCl} + \mathrm{Ag};\ E_{298} = 0.4642\ \mathrm{volt}$$

differ only in the molality of the acid. The cell reaction for the first one is again the sum of two electrode reactions:

$$\begin{array}{rcl} \tfrac{1}{2}H_2(1\text{ atm.}) & = & H^+(0.10m.) + e^- \\ AgCl(s) + e^- & = & Cl^-(0.10m.) + Ag(s) \\ \hline \tfrac{1}{2}H_2(1\text{ atm.}) + AgCl(s) & = & H^+Cl^-(0.10m.) + Ag(s) \end{array}$$

By writing the corresponding reactions for the second cell, it will be seen that it forms 0.010*m.* HCl from hydrogen gas and silver chloride. The free-energy changes in the two cells differ by the free energy of transferring a mole of H^+ and a mole of Cl^- from one molality to the other.

One further requirement in the operation of cells is illustrated by the difference between the potentials above, namely, that the molality of the acid must remain constant as the cell operates. In laboratory practice this is accomplished by passing such a small quantity of electricity through the cell that the change in acid molality is negligible. But it is convenient to write the cell reactions in terms of a faraday of electricity and to assume such large cells that the formation of a mole of solute produces no change in the molality. If this condition is not met, passage of electricity will cause a change in the molality, the measured potential will not apply to any particular molality of acid, and it will thus have no clear meaning. During the passage of 1 faraday through the cell

$$H_2,\ HCl(0.01m.),\ AgCl + Ag$$

if it contained a liter of 0.010*m.* HCl, the molality would increase to 1.01 and the cell potential would fall gradually from 0.4642 volt to about 0.23 volt; and it should be understood that while this is a possible occurrence in a laboratory it is *not* the procedure that is being discussed here.

A "standard" cell reaction is one that conforms to the definition of a "standard" change in state given in the previous chapter, namely, one in which all the reacting substances and all the reaction products are gases at 1 atm. pressure, pure liquids or pure solids, or solutes at unit activity. We shall write E^0 for the potential of a cell when the cell reaction is a standard one in the sense of the definition, in conformity to the use of $\Delta \mathbf{F}^0$ and ΔS^0 for standard changes in state. For such changes

$$\Delta \mathbf{F}^0 = -E^0 NF$$

Whether or not the cell reaction is a standard one, it should be written down fully and completely after the cell is completely described and before any discussion or calculation is attempted. Students are advised to make this a matter of rigid routine, both to promote their understanding of the cell reaction and to save needless labor in the solution of problems.

When two cells are connected in series, the potential of the pair is the sum of the individual potentials, the change in state is the sum of the individual changes in state, and the total ΔF is the sum of those for the two cells. For example, if the silver chloride electrodes of the cells

$$\begin{gathered} H_2(1 \text{ atm.}),\ HCl(0.10m.),\ AgCl + Ag;\ E_{298} = 0.3524 \text{ volt} \\ AgCl + Ag,\ HCl(0.10m.),\ Cl_2(1 \text{ atm.});\ E_{298} = 1\ 136 \text{ volts} \end{gathered}$$

are connected together, the total potential is 1.488 volts at 298°K. and the total change in state in the pair of cells for 1 faraday is

$$\tfrac{1}{2}H_2(1 \text{ atm.}) + \tfrac{1}{2}Cl_2(1 \text{ atm.}) = H^+Cl^-(0.10m.)$$

The same change in state would be produced by the passage of 1 faraday through the cell

$$H_2(1 \text{ atm.}),\ HCl(0.1m.),\ Cl_2(1 \text{ atm.})$$

and thus the potential of this cell is also 1.488 volts at 25°C. For this particular cell the potential derived from the other two is a better value than could be obtained by direct measurement, since the first cell is accurately known and the second one is independent of the molality of the acid so that no correction for the hydrolysis of chlorine is required. There are serious experimental difficulties in working with a chlorine electrode, most of which are avoided by using silver chloride or mercurous chloride electrodes when chloride ions are involved. Since these electrodes are the ones commonly used in cells reversible to chloride ions, their potentials have been determined with particular care.

The cells that we have been discussing also change potential when the partial pressure of the gas at the electrode changes; for the potential is a measure of the free-energy increase attending the operation of the cell, and the free-energy content of a gas changes with pressure at constant temperature. A cell in which the potential is due only to a difference in the pressure of a gas is

$$H_2(1 \text{ atm.}),\ HCl(0.1m.),\ H_2(0.1 \text{ atm.})$$

for which the electrode reactions on a basis of 1 faraday are

$$\begin{array}{ll} \text{(Anode)} & \tfrac{1}{2}H_2(1 \text{ atm.}) = H^+(0.1m.) + e^- \\ \text{(Cathode)} & \underline{H^+(0.1m.) + e^- = \tfrac{1}{2}H_2(0.1 \text{ atm.})} \\ \text{Change in state:} & \tfrac{1}{2}H_2(1 \text{ atm.}) = \tfrac{1}{2}H_2(0.1 \text{ atm.}) \end{array}$$

The sum of the electrode reactions, which gives the net change in state, shows that when 1 faraday passes through the cell ½ mole of hydrogen gas is expanded by a reversible process from 1 atm. pressure to 0.1 atm., and this is a change in state to which the equation

$$\Delta F_{298} = nRT \ln \frac{p_2}{p_1} = -ENF \qquad (2t)$$

applies. In this equation R must be expressed in joules. The free-energy increase for this change in state is thus −2855 joules, and $E = 2855/96{,}500 = 0.0296$ volt. We shall have occasion to use this equation later in making corrections for the partial pressures of gas electrodes when the total pressure is given. The potential of a hydrogen electrode, for example, depends on the partial pressure of the hydrogen, and when the atmospheric pressure is 1 atm. the partial pressure of hydrogen will be less than 1 atm. by the pressure of water vapor from the solution. At an electrode such as H_2, $HCl(14m.)$, the partial pressure of $HCl(g)$ would also have to be subtracted from the barometric pressure to give the partial pressure of hydrogen gas.

Standard Free Energies from Cell Potentials.—The isothermal reversible operation of a cell in which a single substance forms from its elements gives through the measured potential the free energy of formation of the compound. As an illustration, the cell[1]

$$Ag + AgCl,\ HCl(1.0m.),\ Cl_2(1 \text{ atm.});\ E_{298} = 1.1362 \text{ volts}$$

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[1] All the cells quoted in this section were measured by Gerke, *J. Am. Chem. Soc.*, **44**, 1684 (1922).

forms silver chloride by its reversible operation, as shown by the sum of the electrode reactions.

$$\begin{array}{l} Ag(s) + Cl^-(1.0m.) = AgCl(s) + e^- \\ \frac{1}{2}Cl_2(1\ \text{atm.}) + e^- = Cl^-(1.0m.) \\ \hline Ag(s) + \frac{1}{2}Cl_2(1\ \text{atm.}) = AgCl(s) \end{array}$$

Since this is a "standard" change in state, E is also E^0 and $\Delta F^0 = -E^0NF = -109{,}640$ joules, or $-26{,}220$ cal. This is the free-energy content of silver chloride calculated on page 612

Another cell, from which we obtain the free energy of formation of mercurous chloride,[1] is

$$Hg(l) + Hg_2Cl_2(s),\ HCl(0.1m.),\ Cl_2(1\ \text{atm.});\ E_{298} = 1.0904\ \text{volts}$$

The chemical reaction that attends the passage of 2 faradays through this cell is

$$2Hg(l) + Cl_2(1\ \text{atm.}) = Hg_2Cl_2(s)$$

for which E is again E^0, since this is a standard change in state. Then $\Delta F^0 = -2E^0F = -210{,}460$ joules $= -50{,}290$ cal. This free energy is readily confirmed by the enthalpy data in Table 58 and the entropy data in Table 96 through the equation

$$\Delta F^0 = \Delta H^0 - T\,\Delta S^0 \tag{3t}$$

Writing the chemical equation, appending ΔH, and making an entropy balance below the equation we have

$$\begin{array}{lclcl} 2Hg(l) & + & Cl_2(1\ \text{atm.}) & = & Hg_2Cl_2(s); \qquad \Delta H = -63{,}150\ \text{cal.} \\ 37.0 & + & 53.3 & = & 47.0 - \Delta S^0 \end{array}$$

from which $\Delta S^0 = -43.3$, $T\,\Delta S^0 = -12{,}900$ cal., and

$$\Delta F^0_{298} = -63{,}150 - (-12{,}900) = -50{,}250\ \text{cal.}$$

Later in the chapter we shall come to yet another means of obtaining ΔS^0 for this and other reactions through the temperature coefficient of the cell potential. Since the calomel and

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[1] The evidence that mercurous chloride is Hg_2Cl_2 rather than HgCl comes from the X-ray diffraction pattern, which shows a linear molecule ClHgHgCl, with the distance between mercury atoms smaller (by about 35 per cent) than other atomic distances in the crystal. Mercurous ion is shown to be Hg_2^{++} and not Hg^+ from the potentials of concentration cells [LINHART, *ibid.*, **38,** 2356 (1916)] in which Hg_2^{++} is transferred from one molality to another. These cells are described on p. 653.

silver chloride electrodes are so extensively used, a further check on their potentials has been obtained from the cell

$$\text{Ag} + \text{AgCl}(s),\ \text{KCl}(1m.),\ \text{Hg}_2\text{Cl}_2(s) + \text{Hg};\ E_{298} = 0.0455 \text{ volt}$$

for which E is equal to E^0, since the change in state is the standard one

$$\text{Ag}(s) + \tfrac{1}{2}\text{Hg}_2\text{Cl}_2(s) = \text{AgCl}(s) + \text{Hg}(l)$$

for which $\Delta\mathbf{F}^0 = -E^0F/4.18 = -1050$ cal. If $-26{,}220$ cal. is accepted as the free-energy content of AgCl(s), that of $\text{Hg}_2\text{Cl}_2(s)$ is $2(-26{,}220 + 1050) = -50{,}340$ cal.

One more illustration of cells of this particular type will suffice, though there are of course many more available. The standard free energy of lead chloride is measured in the cell

$$\text{Pb} + \text{PbCl}_2(s),\ \text{HCl}(1.0m\ ),\ \text{AgCl} + \text{Ag};\ E^0_{298} = 0.4900 \text{ volt}$$

in which the cell reaction and the free-energy balance are

$$\begin{array}{lcll} \text{Pb}(s) + 2\text{AgCl}(s) & = & \text{PbCl}_2(s) + 2\text{Ag}(s); & \Delta\mathbf{F}^0_{\text{cell}} = -2E^0F \\ 0 \quad + 2(-26{,}220) & = & \Delta\mathbf{F}^0_{\text{PbCl}_2} + \quad 0 - \Delta\mathbf{F}^0_{\text{cell}} & \end{array}$$

and, since $\Delta\mathbf{F}^0_{\text{cell}} = -2 \times 0.4900 \times 96{,}500/4.18 = -22{,}600$ cal., the standard free energy of $\text{PbCl}_2(s)$ is $-75{,}040$ cal. as calculated from the potential of this cell.

In order to calculate the standard free energies of ions we shall first need a means of determining their activity coefficients at different molalities, and we now turn to a means of determining them from the potentials of cells.

Activity Coefficients from Concentration Cells.—One of the most direct means of determining activity coefficients for ions is through the free-energy changes attending the operation of cells that transfer the solute isothermally and reversibly from one molality to another. Such a cell is

$$\text{H}_2(1 \text{ atm.}),\ \text{HCl}(m_2),\ \text{AgCl} + \text{Ag—Ag} + \text{AgCl},\ \text{HCl}(m_1),\ \text{H}_2(1 \text{ atm.})$$

When 1 faraday passes through the whole combination considered as a single cell, the net effect is the transfer of two moles of solute from m_1 to m_2, one mole of hydrogen ion and one mole of chloride ion. The free-energy relation that applies is

$$\Delta F = -ENF = nRT \ln \frac{a_2}{a_1} = nRT \ln \frac{m_2\gamma_2}{m_1\gamma_1} \qquad (4t)$$

In this equation n is the number of moles of solute transferred from m_1 to m_2 when N faradays passes through the cell.

It should be remembered that an activity has the dimensions of a molality and that, since $a = m\gamma$, the activity coefficient γ is a number. For a given solute this coefficient varies with the molality, the temperature, and the molality of any other solutes present in the solution with it.

A "concentration cell without transference," such as the one we are now considering, is really two opposed cells with identical electrodes and a solute at different molalities, of which the net effect is the transfer of a solute from one molality to another. The name is a somewhat unfortunate choice but the one commonly applied to these cells. (A cell "with transference" is one in which the transference numbers of the ions are involved in the formulation of the change in state. We shall come to them later in this chapter.) Data are commonly reported as in Table 97. Thus the potential for the cell above is the difference between E for m_2 and E for m_1 in this table. The change in state for the passage of 1 faraday through the whole cell is obtained by adding the four electrode reactions, as follows:

$$\begin{aligned}
\tfrac{1}{2}H_2(1\text{ atm.}) &= H^+(m_2) + e^- \\
AgCl(s) + e^- &= Ag(s) + Cl^-(m_2) \\
Ag(s) + Cl^-(m_1) &= AgCl(s) + e^- \\
H^+(m_1) + e^- &= \tfrac{1}{2}H_2(1\text{ atm.}) \\
\hline
\text{Net change in state: } H^+Cl^-(m_1) &= H^+Cl^-(m_2)
\end{aligned}$$

We shall use the data of Table 97 and the potentials at 25° first to show how the activity coefficient at any molality may be calculated if a "reference" value of γ is assumed for one molality, such as $\gamma = 0.796$ for $0.1m.$ at 25° and then to show how this standard is itself obtained. In the above cell let $m_1 = 0.10$ and $m_2 = 0.4897$, and assume $\gamma = 0.796$ in $0.1m.$ HCl at 25°. The potential of the "concentration cell" is the difference between the tenth and seventh cells in the fourth column of Table 97, $0.27342 - 0.35240 = -0.07898$ volt, and the net change in state for 1 faraday is

$$H^+Cl^-(0.1m.) = H^+Cl^-(0.4897m.)$$

for which the free-energy change is

$$\Delta F = -EF = 2RT \ln \frac{(0.4897\gamma)}{0.0796} = 7622 \text{ joules}$$

TABLE 97.—CHANGE OF POTENTIAL WITH MOLALITY IN THE CELL H_2, (1 atm), HCl(m), AgCl + Ag[1]

m	Electromotive force at			
	0°	15°	25°	35°
0.0050	0.48916	0.49521	0.49844	0.50109
0.0070	0.47390	0.47910	0.48178	0.48389
0.0100	0.45780	0.46207	0.46419	0.46565
0.020	0.42669	0.42925	0.43022	0.43058
0.050	0.38586	0.38631	0.38589	0.38484
0.070	0.37093	0.37061	0.36965	0.36808
0.100	0.35507	0.35394	0.35240	0.35031
0.2030	0.32330	0.32057	0.31803	
0.3189	0.30239	0.29862	0.29545	
0.4897	0.28193	0.27727	0.27342	
0.6702	0.26616	0.26076	0.25644	
0.9699	0.24623	0.23998	0.23513	
1.2045	0.23362	0.22691	0.22174	
1.4407	0.22253	0.21536	0.20992	
2.3802	0.18684	0.17858	0.17245	
4.0875	0.13594	0.12648	0.11968	

Upon solving for γ, we find 0.756 for 0.4897m. HCl at 25°, and similar treatment of the other cells yields a table of activity coefficients for the several molalities. The activity coefficients thus obtained are given for HCl in Table 53 and repeated with coefficients for other solutes in Table 98, which will be useful in solving problems.[2]

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[1] HARNED and EHLERS, *ibid.*, **54**, 1350 (1932), **55**, 2179 (1933); for data at higher molalities see Åkerlof and Teare, *ibid.*, **59**, 1855 (1937); for other cells see "International Critical Tables," Vol. VI, p. 321, and the current chemical literature.

[2] For an extensive table of activity coefficients, see Latimer, "Oxidation Potentials," pp. 323*ff*., Prentice-Hall, Inc., New York, 1938.

Of the many determinations of this type, we quote one more for sodium hydroxide concentration cells "without transference" at 25°, in which the potential of the whole concentration cell was directly measured[1] and γ was taken as 0.920 in 0.010*m*. NaOH. The cell measured was

H_2(1 atm.), NaOH(m_1), $NaHg_x$—$NaHg_x$, NaOH(0.010*m*.), H_2(1 atm.)

and some of the data are as follows:

E_{298}.	−0 0315	+0 0338	0 0796	0 1116	0 1416	0 1672	0 2103	0.2221
m_1..	0 0053	0 0202	0.0527	0 1047	0 1934	0 3975	0 807	1 020
γ_{298}.	0 951	0 880	0.822	0 768	0 748	0 714	0 678	0 680

In both illustrations, all the activity coefficients depend on a single one assigned to a "reference" solution. This is not an arbitrary choice, but a quantity derived from the experimental data, which are so treated as to provide a means of determining E^0 for a cell in which the activity of the ions is unity (though the molality is not unity), as shown in the following section.

TABLE 98 —SOME ACTIVITY COEFFICIENTS AT 25°

m	0 001	0.01	0 05	0 10	0 50	1.0	2 0	3 0
HBr	0 966	0 906	0 838	0 804	0.79	0 87	1 17	1 7
HCl	0 966	0 904	0 823	0 796	0.758	0 809	1 01	1 32
NaOH	. ..	0 92	0.82	0 77	0 69	0 68	0.74	0 84
KOH	. .	0.90	0 82	0 80	0 73	0 76	0 89	1 08
NaCl	0 966	0 904	0 82	0 78	0.68	0 66	0 67	0 71
KCl	0 964	0.90	0 81	0 77	0.65	0 61	0 58	0 57
H_2SO_4	0 83	0 54	0 34	0 27	0 15	0 13	0 12	0 14
$Mg(NO_3)_2$	0 88	0 71	0 55	0 51	0 44	0 50	0 69	0 93
$PbCl_2$	0 86	0 71						
$ZnCl_2$	0 88	0 71	0.56	0 50	0 38	0 33		
$CuSO_4$	0 74	0.41	0.21	0 16	0 068	0 047		
$ZnSO_4$	0 70	0.39	.	0 15	0 065	0 045	0.036	

"Standard" Cell Potentials.—We have already considered some cell potentials in which the cell reaction was a "standard" one not involving solutes. But in many cells the reaction forms or uses ions, and for these cells a "standard" reaction requires the

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[1] HARNED, *J. Am. Chem. Soc.*, **47**, 676 (1925).

formation or use of ions at unit activity. In order to evaluate E^0 for a cell of this type, such as

$$H_2(1\text{ atm.}),\ H^+Cl^-(u.a.),\ AgCl + Ag$$

in which (*u.a.*) indicates unit activity of the ions, and at the same time determine the chemical composition of the solution in which the activities are unity, we consider a concentration cell in which this cell is opposed to another in which the molality of the acid is m and the activity of the ions is $m\gamma$, as follows:

$$H_2(1\text{ atm.}),\ H^+Cl^-(u.a.),\ AgCl + Ag\text{—}Ag + AgCl,\ H^+Cl^-(m),\ H_2(1\text{ atm.})$$

The potential of this concentration cell is obviously $E^0 - E_m$, the difference between the potential of the cell containing ions at unit activity and that of the cell

$$H_2(1\text{ atm.}),\ H^+Cl^-(m\text{ molal}),\ AgCl + Ag$$

The change in state and the free-energy increase for 1 faraday passing through the whole concentration cell are

$$1H^+Cl^-(m\text{ molal}) = 1\ H^+Cl^-(u\ a.)$$

$$\Delta F = -(E^0 - E_m)F = 2RT \ln \frac{1}{m\gamma} \qquad (5t)$$

This equation may be rearranged with the experimentally determined quantities E_m and m on the left-hand side as follows:

$$E_m + \frac{2RT}{F} \ln m = E^0 - \frac{2RT}{F} \ln \gamma \qquad (6t)$$

By plotting the left-hand side of this equation against some function of the molality suitable for extrapolation and by extending the curve to zero molality the potential E^0 is evaluated, since γ becomes unity and $\ln \gamma$ becomes zero at zero molality by definition. There are theoretical as well as practical advantages (see page 286) in plotting $E_m + 0.1183 \log m$ against the square root of the molality, of which the important one for our purpose is that the plot for dilute solutions is almost a straight line. Figure 71 shows such a plot for the potentials at 25° given in Table 97, from which we find $E^0_{298} = 0.2224$ volt, in close agreement with the value obtained by others.[1] Upon substituting this value in equation (5*t*) and rearranging, we have

$$E_m = 0.2224 - \frac{2RT}{F} \ln m\gamma \tag{7t}$$

Application of this equation to the cells at 25° yields the activity coefficients given in Table 98, including the coefficient 0.796 used in the previous section for 0.1*m*. HCl.

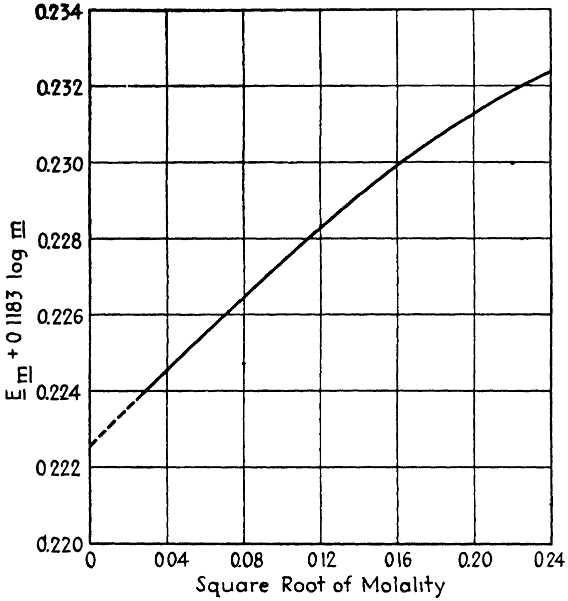

Fig 71 —Determination of E^0_{298} for H_2, HCl(*u.a.*), AgCl + Ag.

It will be noted that no cell whose potential is 0.2224 volt at 25° appears in Table 97, and it will seldom be required to prepare a solution in which the activities of the ions are unity. By plotting *E* against *m*, one may determine that *m* = 1.19 when *E* = 0.2224 and *a* = 1.00 for HCl at 25°C., but it must be noted that because of the definition of activity there is no assurance that 1.19*m*. HCl will have ions of unit activity at any temperature

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[1] For example, Prentiss and Scatchard, *Chem. Rev.*, **13,** 139 (1933); Shedlovsky and MacInnes, *J. Am. Chem. Soc.*, **58,** 1970 (1936); Carmody, *ibid.*, **54,** 188 (1932).

other than 25° or that any other solute will be at unit activity for this molality at 25°.

The same procedure may be applied to other cells. When ions of valence higher than 1 are involved, the expression derived for plotting has a slightly different form, but the method is otherwise the same An illustration is the cell

$$\mathrm{Pb}(s),\ \mathrm{PbCl_2}(m\ ),\ \mathrm{AgCl} + \mathrm{Ag}$$

for which the electrode reactions for 2 faradays and the cell reaction obtained by adding them are

$$\begin{aligned} \mathrm{Pb}(s) &= \mathrm{Pb^{++}}(m\ ) + 2e^- \\ \underline{2\mathrm{AgCl}(s) + 2e^-} &\underline{= 2\mathrm{Ag}(s) + 2\mathrm{Cl^-}(2m.)} \\ \mathrm{Pb}(s) + 2\mathrm{AgCl}(s) &= 2\mathrm{Ag}(s) + \mathrm{Pb^{++}}(m.) + 2\mathrm{Cl^-}(2m\ ) \end{aligned}$$

In such solutions the molality of the chloride ion is twice the molality of lead ion, and thus the equivalent of equation (7*t*) for this cell is

$$E_m = E^0 - \frac{RT}{2F}\ln\,(m\gamma)(2m\gamma)^2 = E^0 - \frac{RT}{2F}\ln\,4m^3\gamma^3 \qquad (8t)$$

Rearrangement with the experimental quantities on the left as before and the substitution of numerical values of the constants for 25° give *s* as the equivalent of equation (6*t*)

$$E_m + 0.0887\log m + 0.0178 = E^0 - 0.0887\log\gamma \qquad (9t)$$

The measured potential at 298°K. changes with the molality of lead chloride as follows:[1]

m	0.0390	0.0296	0.0205	0.0104	0.00516	0.00262
E_{298} . . .	0.490	0.496	0.507	0.526	0.548	0.570

Extrapolation to zero molality gives E^0 for the cell as 0.348 volt.

This method may be applied to any cell in which the potential varies with the molality of the solution, such as

$\mathrm{Pb},\ \mathrm{PbCl_2}(m.),\ \mathrm{Hg_2Cl_2} + \mathrm{Hg}$
$\mathrm{Pb} + \mathrm{PbSO_4}(s),\ \mathrm{H_2SO_4}(m.),\ \mathrm{H_2}$
$\mathrm{Zn},\ \mathrm{ZnCl_2}(m.),\ \mathrm{AgCl}(s) + \mathrm{Ag}$
$\mathrm{Tl} + \mathrm{TlCl}(s),\ \mathrm{HCl}(m.),\ \mathrm{H_2}$

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[1] CARMODY, *ibid*, **51**, 2905 (1929).

to determine E^0 for the cell; and it is unnecessary for cells such as

$$\begin{gathered}\mathrm{Pb} + \mathrm{PbCl_2}(s),\ \mathrm{HCl}(m.),\ \mathrm{Hg_2Cl_2}(s) + \mathrm{Hg}\\ \mathrm{Tl} + \mathrm{TlCl}(s),\ \mathrm{KCl}(m.),\ \mathrm{AgCl}(s) + \mathrm{Ag}\end{gathered}$$

in which the potential is independent of the molality of the solution. However, the custom in physical chemistry is to record not the standard potentials of cells but the standard potentials of single electrodes, all of them being written as anodes. Then in a given cell $E^0 = E^0{}_1 - E^0{}_2$, the difference between the anodic potentials of the first and second electrodes. Since it is impossible to determine the potential of a single electrode, the expedient is to define one arbitrarily and to express all the others in terms of this defined potential, as explained in the next section.

Standard Electrode Potentials.—In conformity to the usual custom in physical chemistry, the potential of the single electrode H_2(1 atm.), H^+(*u.a.*) is taken as zero. This definition was contained in the specification that the standard free energy of hydrogen ion at unit activity is zero. The potential of a whole cell of which this standard is a part is thus the potential of the other electrode; but since all electrode potentials are listed as anodes, the standard potential of the cell

$$\mathrm{H_2}(1\ \mathrm{atm.}),\ \mathrm{H^+Cl^-}(u.a.),\ \mathrm{AgCl} + \mathrm{Ag};\ E^0{}_{298} = 0.2224\ \mathrm{volt}$$

of which the hydrogen electrode is the anode, is given by the relation $E^0{}_{\mathrm{cell}} = E^0{}_1 - E^0{}_2$, for which $E^0{}_1$ is zero, and thus $E^0{}_2$ is -0.2224 volt.

The standard potential for chlorine[1] may be calculated from the potential of the cell

$$\mathrm{Ag}(s) + \mathrm{AgCl}(s),\ \mathrm{HCl}(0.1m.),\ \mathrm{Cl_2}(1\ \mathrm{atm.});\ E_{298} = 1.136\ \mathrm{volts}$$

The change in state for 1 faraday is the sum of the anode and cathode reactions.

$$\begin{array}{rcl}\mathrm{Ag}(s) + \mathrm{Cl^-}(0.1m.) & = & \mathrm{AgCl}(s) + e^-\\ \tfrac{1}{2}\mathrm{Cl_2}(1\ \mathrm{atm.}) + e^- & = & \mathrm{Cl^-}(0.1m.)\\ \hline \mathrm{Ag}(s) + \tfrac{1}{2}\mathrm{Cl_2}(1\ \mathrm{atm.}) & = & \mathrm{AgCl}(s)\end{array}$$

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[1] The electrode Cl_2(1 atm.), Cl^-(*u.a.*) might also be described as Cl_2-(0.062*m.*), Cl^-(*u.a.*), since this is the equilibrium molality for a chlorine pressure of 1 atm. But the electrode potential Cl_2(*u.a.*), Cl^-(*u.a.*) is not -1.358 volts at 25°, for chlorine gas at 1 atm. is not in equilibrium with chlorine as a solute at unit activity.

Since this is a standard change in state, in which the molality of the acid solution cancels when the total change in state is written, E^0 for the cell is $E^0{}_1 - E^0{}_2$, and $E^0{}_1$ is -0.2224, whence $E^0{}_{\mathrm{Cl}}$ is $-1.136 - 0.222 = -1.358$ volts.

The standard potential of the lead electrode may be determined from the cell

$$\mathrm{Pb}(s) + \mathrm{PbCl_2}(m.),\ \mathrm{AgCl}(s) + \mathrm{Ag}$$

for which $E^0{}_{298}$ was found to be 0.348 volt on page 644. Since $E^0{}_{\mathrm{cell}} = E^0{}_{\mathrm{Pb}} - (-0.222)$, $E^0{}_{\mathrm{Pb}} = 0.348 - 0.222 = 0.126$ volt at 298°K.

The standard potential of $\mathrm{Hg} + \mathrm{Hg_2Cl_2},\ \mathrm{Cl^-}(u.a\ )$ is obtainable from the cell

$$\mathrm{Ag} + \mathrm{AgCl}(s),\ \mathrm{HCl}(0.1m.),\ \mathrm{Hg_2Cl_2} + \mathrm{Hg};\ E_{298} = 0.0455 \text{ volt}$$

for which the change in state for 1 faraday is

$$\begin{array}{rcl} \mathrm{Ag} + \mathrm{Cl^-}(0.1m\ ) &=& \mathrm{AgCl}(s) + e^- \\ \tfrac{1}{2}\mathrm{Hg_2Cl_2} + e^- &=& \mathrm{Hg}(l) + \mathrm{Cl^-}(0.1m.) \\ \hline \mathrm{Ag} + \tfrac{1}{2}\mathrm{Hg_2Cl_2}(s) &=& \mathrm{AgCl}(s) + \mathrm{Hg}(l) \end{array}$$

These equations show that the potential of the cell is independent of the molality[1] and that E° would be 0.0455 volt for the cell

$$\mathrm{Ag}(s) + \mathrm{AgCl}(s),\ \mathrm{H^+Cl^-}(u\ a\ ),\ \mathrm{Hg_2Cl_2}(s) + \mathrm{Hg}(l)$$

whence $0.0455 = E^0{}_{\mathrm{AgCl}} - E^0{}_{\mathrm{Hg_2Cl_2}}$, or

$$E^0{}_{\mathrm{Hg_2Cl_2}} = -0.2224 - 0.0455 = -0.2679 \text{ volt}$$

A brief list of standard potentials for 25°C. is given in Table 99, and many others are available. Not all of them are derived from cells in which standard changes take place, as will be seen in the next section. They are useful for calculating the potentials of cells in which cell reactions are not standard, through a relation that we now derive.

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[1] Experiment likewise shows that the potential of this cell is independent of the molality of the acid. The data of Randall and Young, *ibid.*, **50**, 989 (1928), at 25° are

m.	0.0974	0.1233	4.095
E	0.0456	0.0455	0.0455

TABLE 99.—SOME STANDARD ELECTRODE POTENTIALS AT 25°[1]

Electrode reaction	E^0_{298}	Electrode reaction	E^0_{298}
$Li = Li^+ + e^-$	3 024	$I^- = \frac{1}{2}I_2(s) + e^-$	−0 535
$K = K^+ + e^-$	2 924	$Br^- = \frac{1}{2}Br_2(l) + e^-$	−1 065
$Na = Na^+ + e^-$	2 715	$Cl^- = \frac{1}{2}Cl_2(g) + e^-$	−1 358
$Zn = Zn^{++} + 2e^-$	0 762	$Ag + I^- = AgI + e^-$	0 151
$Fe = Fe^{++} + 2e^-$	0 440	$Ag + Br^- = AgBr + e^-$	−0 073
$Cd = Cd^{++} + 2e^-$	0 402	$Ag + Cl^- = AgCl + e^-$	−0 222
$Sn = Sn^{++} + 2e^-$	0 140	$Cu + Cl^- = CuCl + e^-$	−0 124
$Pb = Pb^{++} + 2e$	0 126	$Hg + Cl^- = \frac{1}{2}Hg_2Cl_2 + e^-$	−0 268
$\frac{1}{2}H_2 = H^+ + e^-$	0 000	Normal calomel electrode	−0 280
$Cu = Cu^{++} + 2e^-$	−0 347	$Cu^+ = Cu^{++} + e^-$	−0 167
$Cu = Cu^+ + e^-$	−0 522	$Fe^{++} = Fe^{+++} + e^-$	−0 771
$Ag = Ag^+ + e^-$	−0 799	$Sn^{++} = Sn^{++++} + 2e^-$	−1 256
$Hg = \frac{1}{2}Hg_2^{++} + e^-$	−0 799	$OH^- + \frac{1}{2}Hg =$ $\frac{1}{2}HgO + \frac{1}{2}H_2O + e^-$	−0 098

Change of Potential with Molality.—Since the free energy of hydrogen gas is not zero at a pressure other than 1 atm. and since the free energy of hydrogen ion is not zero at a molality other than unity, it will be evident that the potential of the electrode

$$H_2(p \text{ atm.}),\ H^+(m \text{ molal})$$

is not zero In order to show the relation of E for this electrode to E^0 for the electrode at which the reaction is

$$\frac{1}{2}H_2(1 \text{ atm.}) = H^+(u.a.) + e^-$$

we note that $\Delta F = -EF$ for the first electrode and $\Delta F = -E^0F$ for the standard electrode. Since the free-energy increases for a series of changes add to that of a single step causing the same net change in state, we may calculate them for the three following steps and their sum as follows:

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[1] Compiled from various sources; for example, Li, Li^+ is from MacInnes, "Principles of Electrochemistry," p. 256, Reinhold Publishing Corporation, 1939, New York, where values for several other potentials will be found, Pb, Pb^{++} is by Lingane, *J. Am. Chem. Soc.*, **60,** 724 (1938); Ag + AgI, I^- is from Cann and Taylor, *ibid.*, **59,** 1484 (1937); Cu, Cu^{++} is from Adams and Brown, *ibid.*, **59,** 1387 (1937). A compilation of about 400 potentials is given in Latimer, *op. cit.*

$$\begin{array}{ll}
\tfrac{1}{2}H_2(p \text{ atm.}) = \tfrac{1}{2}H_2(1 \text{ atm.}) & \Delta F_1 = \tfrac{1}{2}RT \ln \frac{1}{p} \\
\tfrac{1}{2}H_2(1 \text{ atm.}) = H^+(u.a.) + e^- & \Delta F_2 = -E^0F \\
H^+(u.a.) = H^+(m \text{ molal}) & \Delta F_3 = RT \ln m\gamma \\
\hline
\tfrac{1}{2}H_2(p \text{ atm.}) = H^+(m \text{ molal}) + e^- & \Delta F = -EF
\end{array}$$

Upon equating ΔF to the sum of the other three and rearranging, we obtain the relation of E to E^0,

$$E_{\text{H}} = E^0_{\text{H}} - \frac{RT}{F} \ln \frac{m\gamma}{p^{1/2}} \tag{10t}$$

A corresponding relation is readily derived for the potential of any electrode at which the reaction is not a standard one, for example,

$$AgCl(s) + e^- = Ag(s) + Cl^-(m \text{ molal}) \qquad \Delta F_1 = -EF$$

This reaction may be treated as the sum of two, of which one involves the standard potential of the silver chloride electrode and the other a transfer of ions from unit activity to an activity $m\gamma$ as follows:

$$\begin{array}{ll}
AgCl(s) + e^- = Ag(s) + Cl^-(u.a.) & \Delta F_2 = -E^0F \\
Cl^-(u.a.) = Cl^-(a = m\gamma) & \Delta F_3 = RT \ln (m\gamma)
\end{array}$$

Since $\Delta F_1 = \Delta F_2 + \Delta F_3$, we add them and solve for E, which gives

$$E_{\text{AgCl}} = E^0_{\text{AgCl}} - \frac{RT}{F} \ln (m\gamma) \tag{11t}$$

The potential of any single electrode is related to the standard potential by a similar equation. The routine procedure is to write the reaction for the electrode as an anode and to obtain E by subtracting from E^0 a term that is RT/NF times the natural logarithm of a fraction in which the activities (or pressures) of the reaction products appear in the numerator raised to the powers that are the coefficients in the electrode reaction and the reacting substances appear in the denominator under the same restriction. This term is thus similar to the Q used in the previous chapter for the relation of ΔF to ΔF⁰. The potential will of course be independent of the quantity of electricity passing, and the calculated potential will be the same whether the electrode reaction is written for 1 faraday or 2 faradays. As an illustration, we may calculate the potential of a zinc electrode, writing the reaction first for 1 faraday and then for 2 faradays. The electrode is

$$\mathrm{Zn}(s),\ \mathrm{Zn}^{++}(m\ \text{molal})$$

and the anode reactions and anode potentials are

$$\left.\begin{aligned}&\tfrac{1}{2}\mathrm{Zn}(s) = \tfrac{1}{2}\mathrm{Zn}^{++}(m.) + e^- \\ &\qquad\qquad E_{\mathrm{Zn}} = E^0_{\mathrm{Zn}} - \frac{RT}{F}\ln (m\gamma)^{\frac{1}{2}} \\ &\mathrm{Zn}(s) = \mathrm{Zn}^{++}(m.) + 2e^- \\ &\qquad\qquad E_{\mathrm{Zn}} = E^0_{\mathrm{Zn}} - \frac{RT}{2F}\ln (m\gamma)\end{aligned}\right\} \quad . \qquad (12t)$$

It is common practice to write the reaction for the number of faradays that corresponds to the valence of the ion involved, but in cells such as

$$\mathrm{Zn}(s),\ \mathrm{ZnCl_2}(m.),\ \mathrm{AgCl} + \mathrm{Ag}$$

it will make no difference whether the cell reactions are written for 1 faraday or 2 faradays so far as the *potential* is concerned.

It will usually be more convenient to calculate the cell potential in a single step, rather than to use equations such as (10*t*) and (11*t*) for the individual potentials and then obtain that of the cell from $E_{\mathrm{cell}} = E_1 - E_2$. Thus the potential of the cell

$$\mathrm{H_2}(p\ \text{atm.}),\ \mathrm{HCl}(m\ \text{molal}),\ \mathrm{AgCl} + \mathrm{Ag}$$

follows directly from the difference between E_{H} calculated in equation (10*t*) and E_{AgCl} in equation (11*t*), namely,

$$E_{\mathrm{cell}} = (E^0_{\mathrm{H}} - E^0_{\mathrm{AgCl}}) - \frac{RT}{F}\ln\frac{(m\gamma)^2}{p_{\mathrm{H_2}}} \qquad (13t)$$

It will be seen by writing the cell reaction for the whole cell, which is the difference between the two anode reactions or the sum of an anode reaction and a cathode reaction,

$$\begin{aligned}\tfrac{1}{2}\mathrm{H_2}(p\ \text{atm.}) &= \mathrm{H^+}(m\ \text{molal}) + e^- \\ \mathrm{AgCl} + e^- &= \mathrm{Cl^-}(m\ \text{molal}) + \mathrm{Ag} \\ \hline \tfrac{1}{2}\mathrm{H_2}(p\ \text{atm.}) + \mathrm{AgCl} &= \mathrm{H^+Cl^-}(m\ \text{molal}) + \mathrm{Ag}\end{aligned}$$

that the logarithmic term contains the reaction products in the numerator, each raised to the power that is the coefficient in the cell reaction (that is, $m\gamma$ for H^+ and $m\gamma$ for Cl^-, since each is a separate solute), and the reacting substances in the denominator, similarly treated. The solids are given unit activity as usual, and thus equation (13*t*) is only a special form of the general equation

$$E_{\text{cell}} = (E^0{}_1 - E^0{}_2) - \frac{RT}{NF}\ln Q \qquad (14t)$$

which applies to any cell reaction. A few illustrations of the use of this important equation will not be out of place, for it may be used to calculate cell potentials when the quantities in Q are known or may be estimated or to obtain E^0 values from the measured potentials of cells.

In any cell involving gases at the electrodes the partial pressure of the gas will be lower than the barometric pressure by the pressure of water vapor and that of any volatile solute. Thus if a hydrogen electrode and a chlorine electrode in 0.1*m*. HCl form a cell and if the barometric pressure is 1 atm., the cell at 25° will be

$$H_2(0.967\text{ atm.}),\ HCl(0.1m.),\ Cl_2(0.967\text{ atm.})$$

in which each gas pressure is 1 atm. minus the vapor pressure of water at 25°. The cell reaction and the potential of the cell as calculated from equation (14*t*) are

$$\tfrac{1}{2}H_2(0.967\text{ atm.}) + \tfrac{1}{2}Cl_2(0.967\text{ atm.}) = H^+Cl^-(0.1m.)$$

$$E_{\text{cell}} = (E^0{}_{\text{H}} - E^0{}_{\text{Cl}}) - \frac{RT}{F}\ln\frac{(0.0796)^2}{(0.967)} \qquad (15t)$$

If the gas at the cathode were a mixture of 1 mole of chlorine and 9 moles of nitrogen and the remainder of the cell were the same, the potential would then be

$$E_{\text{cell}} = (E^0{}_{\text{H}} - E^0{}_{\text{Cl}}) - \frac{RT}{F}\ln\frac{(0.0796)^2}{(0.967)^{\frac{1}{2}}(0.0967)^{\frac{1}{2}}}$$

The reduction of silver chloride to silver and chloride ion by zinc takes place in the cell

$$Zn(s),\ ZnCl_2(0.01m.),\ AgCl(s) + Ag$$

for which the change in state for 2 faradays is the sum of the electrode reactions

$$\begin{array}{rcl} \text{Zn}(s) & = & \text{Zn}^{++}(0.01m.) + 2e^- \\ 2\text{AgCl}(s) + 2e^- & = & 2\text{Cl}^-(0.02m.) + 2\text{Ag} \\ \hline \text{Zn}(s) + 2\text{AgCl}(s) & = & \text{Zn}^{++}(0.01m.) + 2\text{Cl}^-(0.02m.) + 2\text{Ag} \end{array}$$

The potential of this cell is

$$E = (E^0_{\text{Zn}} - E^0_{\text{AgCl}}) - \frac{RT}{2F} \ln (0.01\gamma)(0.02\gamma)^2 \tag{16t}$$

It should be noted that in 0.01*m.* $ZnCl_2$ the molality of chloride ion is 0.02 and not 0.01.

Standard Potential and Standard Free Energy.—The standard potential of silver against silver ion may be obtained from the potential of the cell

$$H_2(1 \text{ atm.}), \text{HCl}(0.1m.), \text{AgCl} + \text{Ag}; E_{298} = 0.3524 \text{ volt}$$

through the solubility product of silver chloride. This product[1] is 1.77×10^{-10} at 25°, and in 0.1*m.* HCl the equilibrium

$$a_{\text{Ag}}(0.0796) = 1.77 \times 10^{-10}$$

requires that $a_{\text{Ag}} = 2.22 \times 10^{-9}$. We may then describe the same cell in terms of this activity as follows:

$$H_2(1 \text{ atm.}), \left\{\begin{matrix} \text{HCl}(0.1m.) \\ \text{Ag}^+(a = 2.22 \times 10^{-9}) \end{matrix}\right\}, \text{Ag}; E = 0.3524 \text{ volt}$$

in which the cell reaction is

$$\tfrac{1}{2}H_2(1 \text{ atm.}) + \text{Ag}^+(a = 2.22 \times 10^{-9}) = \text{Ag}(s) + \text{H}^+(a = 0.0796)$$

and upon substituting the measured cell potential and these quantities into equation (14*t*) and taking $E^0 = 0$ for the hydrogen electrode,

$$0.3524 = (0 - E^0_{\text{Ag}}) - \frac{RT}{F} \ln \frac{0.0796}{2.22 \times 10^{-9}}$$

we obtain an expression from which to calculate $E^0_{\text{Ag}} = -0.799$ volt. The standard free energy of silver ion is given as 18,441 cal. in Table 95, which is merely another way of recording this

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[1] PITZER and SMITH, *J. Am. Chem. Soc.*, **59**, 2633 (1937).

standard potential, as may be seen by calculating the free-energy change for the standard reaction

$$\mathrm{Ag}(s) = \mathrm{Ag}^+(u.a.) + e^-$$
$$\Delta\mathrm{F}^0 = -E^0F = 77{,}190 \text{ joules} = 18{,}448 \text{ cal.}$$

This statement also applies to the other standard free energies of the ions, for they are mostly from cell-potential measurements [1]

The standard potential $E^0_{298} = -1.358$ volts for the chlorine electrode, which was obtained on page 646, corresponds to the electrode reaction

$$\mathrm{Cl}^-(u.a.) = \tfrac{1}{2}\mathrm{Cl}_2(1 \text{ atm}) + e^-$$

and since the free energy of chlorine gas at 1 atm. is zero by definition, the standard free energy of chloride ion results from $\Delta\mathrm{F}^0 = -E^0F = +1.358 \times 96{,}500/4.18 = 31{,}310$ cal., which requires $-31{,}310$ cal. for the standard free-energy content of chloride ion. (The entry $-31{,}340$ cal. in Table 95 corresponds to a derived $E^0 = -1.3583$ volts, but we have not attempted to carry so many significant figures in the calculations in this text. Similar slight differences between other calculated potentials or free energies in other parts of the text arise from the same source.)

Substantially the same standard free-energy content of chloride ion may be derived from E^0 for Ag + AgCl, $\mathrm{Cl}^-(u.a.)$, for which $-E^0F/4.18$ gives the difference in calories between the standard free energies of AgCl(s) and $\mathrm{Cl}^-(u.a.)$. If we accept $-26{,}200$ cal. for AgCl(s), the standard free energy of chloride ion is

$$\mathrm{Cl}^-(u.a.) = -26{,}200 - (0.222 \times 96{,}500/4.18 = 5130)$$
$$= -31{,}330 \text{ cal.}$$

For further illustration, the formation of cupric ion from copper as shown by the reaction

$$\mathrm{Cu} = \mathrm{Cu}^{++} + 2e^-; \qquad E^0 = -0.345 \text{ volt}$$

gives $\Delta\mathrm{F}^0 = -2E^0F = 66{,}600$ joules, or 15,900 cal., for a change in state in which the free energy of the initial system is zero, and thus 15,900 cal. is the standard free energy of cupric ion.

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[1] They may also be calculated through the third law of thermodynamics from solubility measurements and activity coefficients based on vapor pressures or freezing points.

It will be seen from these examples that the potentials in Table 99 are only another record of the free energies in Table 95 and that many of the entries in one table could have been derived from the other.

The Composition of Mercurous Ion.—Concentration cells without transference supply the best reason for writing mercurous ion as Hg_2^{++}, rather than the apparently simpler Hg^+. Consider, for example, two cells containing perchloric acid of uniform concentration throughout but small concentrations of mercurous perchlorate in the ratio 2:1. Two such cells are[1]

$$H_2(1\text{ atm.}),\ HClO_4(0.0817m.),\ \left\{\begin{matrix} HClO_4(0.0817m.) \\ Hg_2(ClO_4)_2(0.00275m.)\end{matrix}\right\},\ Hg(l);\qquad E_{298} = 0.7777\text{ volt}$$

and

$$H_2(1\text{ atm.}),\ HClO_4(0.0817m.),\ \left\{\begin{matrix} HClO_4(0.0817m.) \\ Hg_2(ClO_4)_2(0.001375m.)\end{matrix}\right\},\ Hg(l);\qquad E_{298} = 0.7688\text{ volt}$$

Let these cells be opposed to one another by connecting the two mercury electrodes, and consider the change in state resulting when 1 faraday passes through the opposed cells. The four separate electrode reactions are

$$\begin{aligned} \tfrac{1}{2}H_2(1\text{ atm.}) &= H^+(0.0817m.) + e^- \\ e^- + \tfrac{1}{2}Hg_2^{++}(0.00275m.) &= Hg(l) \\ Hg(l) &= \tfrac{1}{2}Hg_2^{++}(0.001375m.) + e^- \\ e^- + H^+(0.0817m.) &= \tfrac{1}{2}H_2(1\text{ atm.}) \end{aligned}$$

It will be seen upon addition of these equations that the net change in state per faraday is

$$\tfrac{1}{2}Hg_2^{++}(0.00275m.) = \tfrac{1}{2}Hg_2^{++}(0.001375m.)$$

upon the assumption that the mercurous ion is Hg_2^{++}. The potential of the whole concentration cell, calculated from the free-energy increase attending this change in state,

$$\Delta F = \tfrac{1}{2}RT \ln \frac{0.001375\gamma_2}{0.00275\gamma_1} = -EF \qquad (17t)$$

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[1] Linhart, *ibid.*, **38**, 2356 (1916), records these cells with others in which the molalities of $HClO_4$ and $Hg_2(ClO_4)_2$ are varied over wide ranges, while for each pair of cells the ratio of $Hg_2(ClO_4)_2$ remains 2:1. All these data support the formula Hg_2^{++} for mercurous ion.

is 0.0089 volt, which is the difference between the measured potentials of the cells. Since the mercurous-ion concentration is a small part of the *total* ion concentration on which the activity coefficient depends, we may assume $\gamma_2 = \gamma_1$ without appreciable error in calculating the potential of the concentration cell. When this is done, the calculated and observed potential differences agree.

If the mercury electrode reactions are written upon the assumption that the mercurous ion is Hg^+, the second and third equations above become

$$e^- + Hg^+(0.0055m.) = Hg(l)$$
$$Hg(l) = Hg^+(0.00275m\,) + e^-$$

and 1 mole of Hg^+ is transferred per faraday Upon this assumption,

$$\Delta F = -EF = RT \ln \frac{0.00275\gamma_2}{0.0055\gamma_1} \qquad (18l)$$

and $E = 0.0178$ volt, which is twice the measured difference in the cells. Thus it is indicated that Hg_2^{++} represents the composition and charge of the mercurous ion.

Relation of Electrode Potential to Electrolysis.—The standard potentials in Table 99 are arranged in the order of decreasing anode potential, which is the same order as in the "electromotive series." The maximum potential of the cell at 25°

$$H_2(1 \text{ atm.}),\ H^+Cl^-(u.a.),\ AgCl + Ag$$

is 0.2224 volt, and the application of a higher opposing potential would cause the silver chloride electrode to function as an anode, with the electrode reaction $Ag + Cl^- = AgCl + e^-$ taking place, and with the evolution of hydrogen gas at the cathode. But the evolution of chlorine gas at the silver chloride electrode does not take place and could not take place until the opposing potential exceeded that of the cell

$$H_2(1 \text{ atm.}),\ H^+Cl^-(u.a.),\ Cl_2(1 \text{ atm.});\ E^0 = 1.358 \text{ volts}$$

It is true of this cell, as it is true of cells in general, that the electrode reactions requiring the lowest opposing potentials take place first during electrolysis. Since the formation of silver chloride from silver and chloride ions requires a potential about 1.14 volts less than that required for the evolution of chlorine, no chlorine is evolved. If the silver chloride electrode were replaced by platinum or any other inert metal, the evolution of chlorine in this cell would require an opposing potential exceeding 1 358 volts.

As another illustration, consider a cell composed of sodium chloride at unit activity (1.53*m*) with two platinum electrodes. When electricity is passed between these electrodes, hydrogen gas is evolved at the cathode and chlorine gas at the anode. We may calculate the minimum opposing potential required to *start* this electrolysis, which is that of a cell

$$H_2(1 \text{ atm }), \begin{Bmatrix} H^+(10^{-7}m.) \text{ from water} \\ Na^+Cl^-(u.a\ ) \end{Bmatrix}, Cl_2(1 \text{ atm.})$$

for which E_1 is 0.414 volt, E_2 is -1.358 volts, and E is 1.762 volts. Hence, if the opposing potential is greater than 1.762 volts, electrolysis will begin, chlorine gas will be evolved at the anode, hydrogen gas will be evolved at the cathode, and hydroxide ion forms in solution around the cathode. The use of an opposing potential of 2.2 volts (to overcome the extra hydrogen potential required as the solution around the cathode becomes more alkaline) would continue the electrolysis until the sodium hydroxide becomes about 2*m*. But the deposition of sodium upon the cathode would require a potential of at least

$$2.713 + 1.358 = 4.071 \text{ volts}$$

for this is the back potential of the cell Na, Na^+Cl^-(*u.a.*), Cl_2(1 atm.). Since the actual potential required to electrolyze aqueous sodium chloride with the evolution of hydrogen gas at a platinum electrode is less than half of this potential, it will be clear that there is no call for the "explanation" that sodium deposits and then reacts with water to form sodium hydroxide and hydrogen when salt brine is electrolyzed.

In certain commercial cells, sodium *amalgam*, which is a dilute solution of sodium in mercury, is formed when sodium chloride is electrolyzed with a mercury cathode, but there are several circumstances that prevent direct comparison of this process with the one discussed in the previous paragraph. In the first place, the potential of the cell

Na(*s*), NaI in ethylamine, $NaHg_x$ (0.2 per cent Na in Hg)

is about 0.85 volt,[1] and the amalgams are usually kept below this sodium content; in the second place, the potential required for the evolution of hydrogen gas upon mercury is 0.8 volt or more above that for hydrogen upon platinum, depending on the current density; and, in the third place, the actual potential applied to the commercial cells exceeds 4 volts. The potentials of these cells are no reflections on the statement in the previous paragraph that sodium metal does not deposit during the electrolysis of aqueous sodium chloride with inert electrodes; they make this statement more probable.

Concentration Cells with Transference.—Cells that consist of two identical electrodes dipping into solutions of the same electrolyte at different molalities, and with the two solutions in contact, are called cells "with transference." An example is the cell

$$\text{Ag} + \text{AgCl},\ \text{HCl}(0.10m.),\ \text{HCl}(0.020m\ ),\ \text{AgCl} + \text{Ag}$$

for which the measured potential is $E_{298} = 0.0645$ volt. The potential of this cell is not $E_1 - E_2$, when the potentials for the separate electrodes are computed in the way already explained, for the liquid junction is also a source of potential. We shall see the calculation of liquid junction potentials in the next section, but the cell will first be used for another purpose. The transference number T_H being assumed constant over the concentration range 0.10 to 0.020, the change in state for 1 faraday through the cell is the sum of the effects at the anode, the liquid junction, and the cathode, as shown by the equations

$$\begin{array}{lrcl}
\text{(Anode)} & \text{Ag}(s) + \text{Cl}^-(0.10m.) & = & \text{AgCl}(s) + e^- \\
\text{(Liquid junction)} & \left\{\begin{array}{r} T_H\text{H}^+(0.10m.) \\ T_{Cl}\text{Cl}^-(0.02m.) \end{array}\right. & \begin{array}{c} = \\ = \end{array} & \begin{array}{l} T_H\text{H}^+(0.02m.) \\ T_{Cl}\text{Cl}^-(0.10m.) \end{array} \\
\text{(Cathode)} & \text{AgCl}(s) + e^- & = & \text{Ag}(s) + \text{Cl}^-(0.02m.) \\
\hline
\text{Net change in state:} & T_H\text{H}^+\text{Cl}^-(0.10m.) & = & T_H\text{H}^+\text{Cl}^-(0.02m.)
\end{array}$$

For this change, $\Delta F = -E_tF = 2T_HRT \ln (0.02\gamma_2)/(0.10\gamma_1)$, and this gives for the potential of the cell with transference

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[1] Lewis and Kraus, *ibid.*, **32**, 1459 (1910).

$$E_t = \frac{2T_{\mathrm{H}}RT}{F} \ln \frac{0.10\gamma_1}{0.02\gamma_2} \tag{19t}$$

In the corresponding cell "without transference,"

$$\mathrm{Ag} + \mathrm{AgCl},\ \mathrm{HCl}(0.10m.),\ \mathrm{H_2}\text{—}\mathrm{H_2},\ \mathrm{HCl}(0.02m.),\ \mathrm{AgCl} + \mathrm{Ag};\quad E_{298} = 0.0778 \text{ volt}$$

(of which the potential is the difference between the fourth and seventh cells in Table 97), the net change in state is

$$\mathrm{H^+Cl^-}(0.10m.) = \mathrm{H^+Cl^-}(0.02m.)$$

The free-energy change is $\Delta F = 2RT \ln (0.02\gamma_2)/(0.10\gamma_1)$, from which the potential of the cell is seen to be

$$E = \frac{2RT}{F} \ln \frac{0.10\gamma_1}{0.02\gamma_2} \tag{20t}$$

Upon dividing the expression for E_t by that for E of the cell without transference and inserting the measured potentials we have

$$\frac{E_t}{E} = \frac{0.0645}{0.0778} = T_{\mathrm{H}} = 0.829 \tag{21t}$$

The transference number for hydrogen ion was given on page 266 as 0.827 at $0.02m$ and 0.831 at $0.10m.$, based upon the moving-boundary method, and it will be seen that the value derived from the cells is in agreement with these figures.

This is the third method of determining transference numbers that we have had, the others being a gravimetric method in which the actual quantities of ions gained or lost near the electrodes are determined, and the moving-boundary method in which the relative velocities of the ions in a solution are measured.

If in the cell with transference the left-hand solution is kept $0.1m.$ HCl and m_2 is the molality of HCl on the right, the potential of the concentration cell at 25° changes with m_2 as follows:[1]

m_2	0.00526	0.0100	0.02004	0.0598	0.0781
E_{298}	0.118	0.0925	0.06446	0.0206	0.00995

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[1] SHEDLOVSKY and MACINNES, *ibid.*, **58**, 1970 (1936).

Corresponding data for cells with the same electrodes, with 0.1*m.* KCl on the left and m_2 molal KCl on the right are[1]

m_2	0 0100	0 0200	0 0500	0 200	0 500
E_{298}	0 0540	0 0375	0 01591	−0 01576	−0.03645

Liquid-junction Potentials.—The potential at a liquid junction depends upon the nature and concentration of the ions on the two sides of the boundary and upon the temperature. In order to show the relation of the sources of potential in cells with transference to that of the whole cell, consider another cell similar to the one in the previous section,

$$\begin{array}{llll} \text{Ag+AgCl, HCl}(0.10m.), & \text{HCl}(0.01m.), & \text{AgCl+Ag}; & E_{298}=0.0925\,v \\ \quad E_1 & \quad + E_L & \quad - E_2 & \quad = E \end{array}$$

in which the separate sources of potential are indicated. The values of E_1 and E_2 are computed in the usual way, and that of E_L is, of course, $E - E_1 + E_2$. At the liquid junction, as through all parts of the cell, electricity is carried by the ions in proportion to their transference numbers. The transference number being assumed constant over the concentration range involved, the change in state at the liquid junction is shown by the two equations

$$T_H\text{H}^+(0.10m.) = T_H\text{H}^+(0.01m.)$$
$$T_{Cl}\text{Cl}^-(0.01m\ ) = T_{Cl}\text{Cl}^-(0.10m.)$$

The free-energy increase is

$$\Delta F = T_H RT \ln \frac{0.01\gamma_2}{0.10\gamma_1} + T_{Cl} RT \ln \frac{0.10\gamma_1}{0.01\gamma_2} = -E_L F \quad (22t)$$

Upon rearranging and solving for E_L,

$$E_L = (T_H - T_{Cl}) \frac{RT}{F} \ln \frac{0.10\gamma_1}{0.01\gamma_2} \quad (23t)$$

Substitution of the numerical quantities $T_H = 0.83$, $T_{Cl} = 0.17$, $\gamma_1 = 0.796$, $\gamma_2 = 0.904$ yields $E_L = 0.0367$. From the values

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[1] SHEDLOVSKY and MACINNES, *ibid.*, **59,** 503 (1937) Data for NaCl cells with transference are given by Brown and MacInnes, *ibid.*, **57,** 1356 (1935), and by Janz and Gordon, *ibid.*, **65,** 218 (1943).

$E_1 = -0.2874$ and $E_2 = -0.3432$, computed in the standard way, we confirm the computed value of the liquid junction, since

$$E_{\text{cell}} = -0.2874 + 0.0367 - (-0.3432) = 0.0925$$

which is the measured potential of the cell.

The recorded potentials of cells with liquid junctions are sometimes "corrected for liquid potential" by subtracting the calculated liquid potential from the measured potential. When this has been done, the common notation is to insert a double bar between the solutions written in the cell, as follows:

$$\text{Ag} + \text{AgCl},\ \text{HCl}(0.1m.)\|\text{HCl}(0\ 01m\ ),\ \text{AgCl} + \text{Ag};\ E = 0.0558$$

This indicates that the recorded potential is $E_1 - E_2$, and the notation

$$\text{Ag} + \text{AgCl},\ \text{HCl}(0.1m.),\ \text{HCl}(0.01m.),\ \text{AgCl} + \text{Ag};\ E = 0.0925$$

with a comma separating the two solutions, indicates that the recorded potential has not been so corrected and that it is $E_1 + E_L - E_2$.

Liquid junctions are also found in cells that are not merely concentration cells with transference, of course; and thus their calculation is desirable. It will usually be true that such junctions are avoided when possible, but in some types of work this is difficult or impossible. When the junction is between two solutions of the same solute at different concentrations, the liquid potential is independent of the way in which the junction is made or whether the boundary is sharp or not. If the transference number is sufficiently constant over the concentration range involved, the general expression for this type of junction is

$$E_L = (T_+ - T_-)\frac{RT}{NF}\ln\frac{m_1\gamma_1}{m_2\gamma_2} \tag{24t}$$

where m_1 is the molality on the left-hand side of the junction.

There is another type of junction in which the solutes on the two sides are not the same and for which the junction potential depends on the way in which the junction is made. When both the molality and the solute are different, the calculation is uncertain at best, and such junctions are usually avoided in experimental work by the expedient of two junctions. For example, HCl(0.1*m.*), KCl(0.1*m*), KCl(1.0*m.*) shows the way in which the first and third solutions would be connected. For the junction in which all the ions are univalent, the concentrations are the same on both sides, and one of the ions is common to both sides while the other is not, the liquid potential is given by equations such as

$$E_L = \frac{RT}{F} \ln \frac{\Lambda_{\text{HCl}}}{\Lambda_{\text{KCl}}} \tag{25t}$$

which applies to the first junction listed above.[1] When the ions have valences other than unity, when both ions are different on the sides of the junction, or when one ion is different and the molalities are not the same, the relations for calculating junction potentials are complicated and best not considered by beginners.

Ionization Constant of Water.—The potential of a hydrogen electrode is determined by the partial pressure of the hydrogen gas and by the activity of hydrogen ion in the solution, even if the solution is alkaline. Hence a properly designed cell may be used to determine the ion product for water, and a suitable one for the purpose is[2]

$$\text{H}_2(1\text{ atm.}),\ \left\{\begin{matrix}\text{KOH}(0.01m.)\\ \text{KCl}(0.10m\ )\end{matrix}\right\},\ \text{AgCl} + \text{Ag};\ E_{298} = 0.9916\text{ volt}$$

For this cell $E_1 = -0.0592 \log (a_{\text{H}^+}$ in 0.01*m.* KOH) and $E_2 = -0.222 - 0.0592 \log (1/a_{\text{Cl}^-})$. In this solution the activity coefficient is determined by the total molality and is very close to 0.80. Upon equating the measured potential of the cell to $E_1 - E_2$, we find $\log a_{\text{H}^+} = -11.90$; and since $\log a_{\text{OH}^-}$ is -2.097, $\log K_w$ is the sum of these quantities, or -13.99, and K_w is 1.03×10^{-14}. In the paper from which this cell is quoted, the measurements were upon a series of cells in which bath molalities varied over considerable ranges,

$$\text{H}_2(1\text{ atm.}),\ \left\{\begin{matrix}\text{KOH}(m_1)\\ \text{KCl}(m_2)\end{matrix}\right\},\ \text{AgCl} + \text{Ag}$$

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[1] LEWIS and SARGENT, *ibid.*, **31**, 363 (1909). For the general equations for liquid junctions and their integration, see MacInnes, *op. cit.*, Chap. 13.

[2] HARNED and HAMER, *J. Am. Chem. Soc.*, **55**, 2194 (1933). This paper gives data for a series of KCl molalities, for temperatures from 0 to 60°, and data for other cells from which K_w may be determined.

In place of assuming activity coefficients in any solution, the potentials were expressed as

$$E = E_0 - \frac{RT}{NF}\ln \gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}m_{\mathrm{H}}m_{\mathrm{Cl}}; \qquad K_w = \frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{OH}}}{a_{\mathrm{H_2O}}}\, m_{\mathrm{H}}m_{\mathrm{OH}}$$

Eliminating m_{H} and rearranging,

$$E - E^0 + \frac{RT}{NF}\ln\frac{m_{\mathrm{Cl}}}{m_{\mathrm{OH}}} = \frac{RT}{NF}\ln\frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{OH}}}{a_{\mathrm{H_2O}}} - \frac{RT}{NF}\ln K_w - \frac{RT}{NF}\ln \gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}$$

The left-hand side of this equation being plotted against the ionic strength μ, its intercept at $\mu = 0$ is $(-RT/NF)\ln K_w$, since, at $\mu = 0$, $a_{\mathrm{H_2O}} = 1$, and by reason of the definition of activity coefficients, the two other members on the right-hand side of the equation vanish

From such a procedure for the data at several temperatures, the value of K_w was determined over the range 0 to 60°. Finally, from the data and equation (30), which will be given on page 666, the value of ΔH for the ionization of water as a function of the temperature was calculated. The results given in Table 100 agree with those determined directly in a calorimeter. For example, the figures on page 318 are 13,610 for 20° and 13,360 for 25°, an agreement as close as is ordinarily found.

TABLE 100.—IONIZATION CONSTANT OF WATER

t, °C.	$K_w \times 10^{14}$	ΔH_i, cal.
0	0.115	14,513
10	0.293	14,109
20	0.681	13,692
25	1.008	13,481
30	1.471	13,267
40	2.916	12,833
50	5.476	12,390
60	9.614	11,936

Ionization Constants of Weak Acids.—Cells without liquid junction, containing mixtures of a weak acid and its salt, may also be used to determine the ionization constants of weak acids. As an illustration, the ionization constant of acetic acid has been measured[1] through the potential of a cell in which the solution

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[1] BATES, SIEGAL, and ACREE, *J Research Natl. Bur. Standards*, **30**, 347 (1943).

is 0.049*m.* in sodium acetate and 0.050*m.* in sodium chloride, with hydrogen and Ag + AgCl for electrodes. Addition of standard nitric acid (containing 0.05*m.* NaCl and 0.049*m.* $NaNO_3$) in known quantity displaces acetic acid from its salt and keeps the ionic strength and chloride molality constant; and the activity of hydrogen ion is determined from the potential of the cell. In effect, the cell is

$$H_2(1\ \text{atm.}),\ \left\{\begin{matrix} H^+\ (\text{variable}\ a) \\ Cl^-(0.050m.) \end{matrix}\right\},\ AgCl + Ag$$

With a constant chloride-ion molality and constant total-ion molality the activity coefficient is constant, E_2 for the silver chloride electrode is constant, and the cell potential is

$$E_{\text{cell}} = (E^0{}_{\text{H}} - E^0{}_{\text{AgCl}}) - \frac{RT}{F}\ln 0.05\gamma_{\text{Cl}^-} - \frac{RT}{F}\ln a_{\text{H}^+}$$

By assuming 0.78 for the activity coefficient, substituting the required numerical quantities, and rearranging, we have for 25°

$$\log a_{\text{H}^+} = \frac{0.305 - E_{\text{cell}}}{0.0592} \tag{26t}$$

The activity of acetate ion is $m\gamma$, and that of acetic acid is substantially equal to its molality; thus all the quantities necessary for computing K_a for the weak acid are at hand. Some of the measured potentials of this cell and the derived ionization constant K_a are shown in Table 101.

TABLE 101.—IONIZATION CONSTANT OF ACETIC ACID

E_{298}	$\log a_{\text{H}^+}$	m_{HAc}	m_{Ac^-}	$\log K_a$	$K_a \times 10^5$
0.6026	−5.014	0.00149	0.00305	−4.75	1.8
0.5803	−4.638	0.00250	0.00248	−4.75	1.8
0.5439	−4.021	0.00402	0.00096	−4.75	1.8
0.5231	−3.670	0.00450	0.00049	−4.75	1.8

These figures confirm the ionization constant of acetic acid used in Chap. IX. Application of the same method to other acids also yields ionization constants that are satisfactory.

Solubility Product of Lead Sulfate.—The potential at 25° for the cell

$$Pb(s) + PbSO_4(s),\ H_2SO_4(m \text{ molal}),\ H_2(1 \text{ atm.})$$

in which the cell reaction for 2 faradays is

$$Pb(s) + H_2SO_4(m \text{ molal}) = PbSO_4(s) + H_2(1 \text{ atm.})$$

changes with the molality of sulfuric acid as follows:[1]

m	0.001	0.002	0.005	0.010	0.020
E_{298}	0.1017	0.1248	0.1533	0.1732	0.1922

Extrapolation of these potentials in the way already explained gives $E^0 = 0.356$ volt for this cell; and since $E^0_H = 0$, $E^0 = 0.356$ volt for the electrode $Pb(s) + PbSO_4(s),\ SO_4^{--}(u.a.)$. This potential may be considered as that of an electrode at which the reaction is $Pb(s) = Pb^{++}$ (in SO_4^{--} *u.a.*) $+ 2e^-$, and to which the equation $E = E^0_{Pb} - (RT/2F) \ln a_{Pb^{++}}$ applies. Upon equating these potentials and substituting $E^0_{Pb} = 0.126$, we find

$$a_{Pb^{++}} = 1.6 \times 10^{-8}$$

in a solution containing $SO_4^{--}(u.a.)$, and therefore this is the activity product for lead sulfate. The square root of this activity product is not the solubility in pure water, for even in solutions $10^{-4}m$. of this ionic type the activity coefficient is about 0.9, and thus it is $(0.9S)^2$ which is equal to 1.6×10^{-8}, or $S = 1.5 \times 10^{-4}$.

Electrometric Titration and pH Measurement.—It will be recalled from Chap. IX that there is some confusion in the use of the term "pH," which is sometimes defined as $pH = -\log m_{H^+}$ and sometimes as $pH = -\log a_{H^+}$, which is $-\log m_{H^+}\gamma_{H^+}$. These definitions obviously differ by $-\log \gamma$, which is usually 0.05 or less for solutions in which the total ion molality is 0.1 or

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[1] Shrawder and Cowperthwaite, *J. Am. Chem. Soc.*, **56**, 2340 (1934), measured this cell with a two-phase lead-mercury amalgam. Their potentials have been increased by 0.0058 volt, which is the potential of the cell $Pb(s)$, $PbCl_2$, $PbHg_x$ (two-phase) to give the potentials above. Since the phases in the amalgam are a liquid solution and a solid solution, the potential of $Pb(s)$ and $PbHg_x$ cannot be the same. The phases in an electrode Zn-Hg (two-phase) are solid zinc and a liquid solution, and thus the potentials of $Zn(s)$ and $ZnHg_x$ (two-phase) are the same. The potential 0.0058 is given by Carmody, *ibid.*, **51**, 2905 (1929).

less, and in which the ions have unit valence; but $-\log \gamma$ may be a much larger quantity in strong salt solutions or in the presence of ions of higher valence. For some purposes the distinction between $-\log m_{H^+}$ and $-\log a_{H^+}$ is not important; for some it is less than other errors inherent in the measurements and calculation, and for some it requires attention.[1]

When a titration of acid with base is being made through the equivalent of a hydrogen electrode and another reference electrode dipping into the solution, the change of cell potential as base is added will often be a sufficient indication of the end point. In a cell such as

$$H_2(1 \text{ atm.}), \begin{Bmatrix} H^+ \text{ (variable } a) \\ Cl^- \text{ (constant } a) \end{Bmatrix}, AgCl + Ag$$

the relation of E to pH on an activity scale is

$$\text{pH} = \frac{E - E^0}{2.3RT/F} \tag{27t}$$

and the cell potential changes as base is added in the way shown in Fig. 72. As the end point is approached, small additions of base produce large changes in the hydrogen-ion activity. For example, in the titration of HCl, pH changes from 4 to 7 and the cell potential changes about 0.18 volt when the fraction of acid titrated changes from 0.998 to 1.000, and a similar change is produced by the addition of 0.2 per cent more base, so that the end point is determined without considering an activity coefficient. But in precise determinations of ionization constants, like the one described on page 662, it was desirable to keep the activity coefficient constant or to allow for its influence on the cell potential.

It should be observed that the above definition of pH in terms of a cell potential is valid *only* when the electrode reaction is $\frac{1}{2}H_2 = H^+ + e^-$, and hence any other substance that oxidizes or reduces at the electrodes will "interfere" if it is present in the solution. This important qualification is sometimes overlooked, and it may lead to serious errors in pH evaluations. Among the substances that must not be present at a hydrogen electrode are dissolved air, H_2S, organic substances, ions of metals below

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[1] See MacInnes, Belcher, and Shedlovsky, *ibid.*, **60**, 1094 (1938).

hydrogen in the potential scale, and oxidizing or reducing substances in general. Exclusion of air is especially troublesome from an experimental point of view, but it is quite necessary if precision is desired. The use of KCl "salt bridges" or other means of separating the reference electrode from the unknown solution is a further complication that is sometimes difficult to avoid and always difficult to interpret.

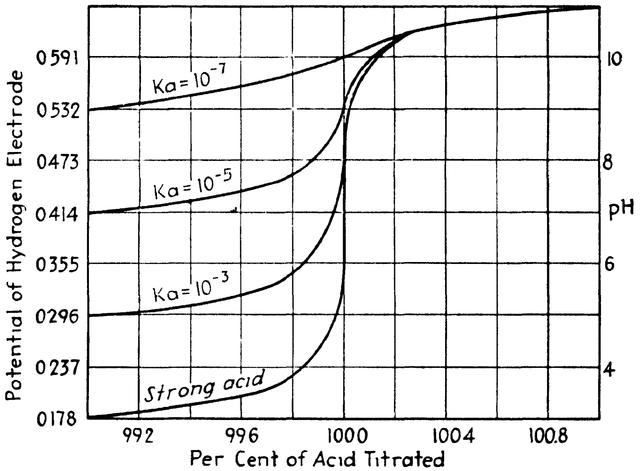

FIG. 72—Change of hydrogen electrode potential and pH with progress of a titration of acid.

Some equivalents of a hydrogen electrode will be briefly discussed, and it may be said that all of them have their own peculiar virtues and restrictions For details, the student is referred to the special works devoted to the topic.[1] The "antimony electrode" is a metal + oxide electrode for which the reaction is $2Sb + 3H_2O = Sb_2O_2 + 6H^+ + 6e^-$. Statements as to its use are a little conflicting, but it is commonly said to be of moderate but not high precision in the presence of air over the pH range 2 to 7 if oxidizing and reducing substances are absent. The "quinhydrone electrode" consists of a gold plate in contact with a molecular compound of 1 mole of quinone and 1 mole of hydro-

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[1] See KOLTHOFF and LAITINEN, "Electrometric Titrations," John Wiley & Sons, New York, 1941; DOLE, "The Glass Electrode," John Wiley & Sons, New York, 1941; MACINNES, *op. cit.*, Chap. XV. A review of pH methods with bibliography (630 references) is given by Furman in *Ind. Eng. Chem.*, Anal. Ed., **14**, 367 (1942).

quinone in the unknown solution, for which the electrode reaction is $C_6H_4O_2H_2(s) = C_6H_4O_2(s) + 2H^+ + 2e^-$. The unknown solution is connected to the reference electrode through a "salt bridge" of KCl, so that it is better suited to measuring changes in pH than to their precise determination unless a standard buffer is used for calibration. Interfering substances include amines, oxidizing and reducing agents, phenols, and other substances, and the pH must be below 7 when this electrode is used.

Another common device is the so-called "glass electrode," in which a silver chloride electrode in 0.1*m*. HCl is separated from the unknown solution by a glass barrier about 0.001 mm. thick, and with a calomel or other reference electrode in the unknown solution. The assembly functions as a concentration cell without transference, and the equation

$$\text{pH} = \frac{E - 0.352}{2.3RT/F} \qquad (28t)$$

applies.[1] The chief virtue of the glass electrode is that it permits pH determinations in the presence of air, organic matter, oxidizing or reducing agents, and metals below hydrogen in the potential series over a pH range of 1 to 9, with the widest general applicability of any method. Like any other method, it has its restrictions, and there are some experimental difficulties that require attention. In alkaline solutions it requires large corrections for sodium ions and less important corrections for other substances. It is probably the best means of determining hydrogen-ion activities available at the present time.

Change of Potential with Temperature.—The equations derived in the previous chapter for the change of free energy with temperature become the equations for the change of potential with temperature when the relation $\Delta F = -ENF$ is combined with them. By making this change in equations (16) and (17) on page 621, we have the necessary relations

$$\frac{ENF + \Delta H}{T} = NF\frac{dE}{dT} \qquad (29)$$

$$NFd\left(\frac{E}{T}\right) = \frac{\Delta H}{T^2}\,dT \qquad (30)$$

$$NF\frac{dE}{dT} = \Delta S \qquad (31)$$

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[1] MACINNES and LONGSWORTH, *Trans. Electrochem. Soc.*, **1937, 73.**

As a direct check upon equation (31), we return to the cells quoted on page 637, one of which was

$$\mathrm{Hg} + \mathrm{Hg_2Cl_2},\ \mathrm{HCl}(1.0m.),\ \mathrm{Cl_2}(1\ \mathrm{atm.});\ E^0_{298} = 1.0904\ \mathrm{volts}$$

for which $dE/dT = -0.000945$ volt per deg.[1] By substituting the numerical quantities into equation (31), we find $\Delta S^0_{298} = -43.6$ cal. per mole per deg. for the cell reaction

$$2\mathrm{Hg}(l) + \mathrm{Cl_2}(1\ \mathrm{atm.}) = \mathrm{Hg_2Cl_2}(s)$$

and from the entropy data we calculated $\Delta S^0_{298} = -43.3$ for this reaction on page 637.

Another confirmation of equation (31) is obtained from the cell

$$\mathrm{Ag} + \mathrm{AgCl},\ \mathrm{HCl}(1.0m.),\ \mathrm{Cl_2}(1\ \mathrm{atm.});\ E^0_{298} = 1.1362\ \mathrm{volts}$$

for which $dE/dT = -0.000595$ volt per deg. These measured quantities give $\Delta S^0_{298} = -13.7$ for the cell reaction

$$\mathrm{Ag}(s) + \tfrac{1}{2}\mathrm{Cl_2}(1\ \mathrm{atm.}) = \mathrm{AgCl}(s)$$

in confirmation of $\Delta S^0 = -13.8$ calculated on page 612.

Application of equation (29) to these same cells leads to the values $\Delta H = -63{,}200$ cal. for the enthalpy of mercurous chloride and $\Delta H = -30{,}300$ for silver chloride, and these are very close to the entries in Table 58

When ΔH is sufficiently constant, equation (30) may be integrated between limits to yield

$$\frac{E_2}{T_2} - \frac{E_1}{T_1} = \frac{\Delta H}{NF}\left(\frac{T_2 - T_1}{T_2 T_1}\right) \tag{32}$$

and equation (31) may be integrated to yield

$$ENF = T\,\Delta S + \text{const.} \tag{33}$$

By comparison with equation (22) on page 623, which is

$$\Delta F = \Delta H - T\,\Delta S$$

it is at once evident that the integration constant in equation (33) is $-\Delta H$, and thus the equation may be written

$$ENF = -\Delta H + T\,\Delta S \tag{34}$$

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[1] GERKE, *J. Am Chem Soc.*, **44,** 1684 (1922).

We may illustrate the use of equation (32) by applying it to the seventh cell in Table 97, taking the potentials at 15° and 35°. The cell reaction for 2 faradays is

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

for which we obtain ΔH by substituting the cell potentials in equation (32), finding $\Delta H = -18{,}730$ cal. The cell reaction consists in forming two moles of HCl from hydrogen and AgCl and introducing them into 0.1*m*. HCl. If ΔH is calculated from the data in Table 58 and the partial molal heat of solution based on the data on page 314, the result is −18,820 cal., which is a satisfactory check. For dilute solutions, such as the 0.1*m*. HCl in this cell, the difference between the partial molal heat of solution and ΔH for the change in state $HCl(g) + 555H_2O = 0.1m.$ HCl is small (about 100 cal. in this case) and is perhaps best ignored by beginners. But if the temperature coefficient of potential for a cell such as

$$H_2(1 \text{ atm}),\ HCl(10m.),\ AgCl + Ag$$

is used in the calculation of ΔH, the difference between a partial molal heat of solution and the "integral" heat of solution is an important one. It should be understood that ΔH calculated from the cell potentials involves this partial molal heat of solution, and not the integral heat of solution. Partial molal heat quantities and the partial molal entropies of ions derived from them are better reserved for more advanced courses.

Problems

Numerical data should be obtained from tables in the text.

1. The potential of the cell Zn(*s*), $ZnCl_2$(*m* molal), AgCl(*s*) + Ag(*s*) changes with the molality as follows:

E_{298}...	1.1650	1.1495	1.1310	1.1090	1.0844	1.0556	1.0327	0.9978
m	0.00781	0.01236	0.02144	0.04242	0.0905	0.2211	0.4500	1.4802

(*a*) Calculate the mean activity coefficients for the ions in the first, third, and last of these cells from the standard potentials in Table 99. (*b*) Show that the relation of E_m to E^0 for the cell is $E^0 - (RT/2F)\ln\gamma^3 = E_m + 0.0886 \log m + 0.0178$. (*c*) Plot the right-hand side of this equation against $\sqrt{m}$ for the first four cells, extrapolate the curve to zero molality, and obtain a confirmation of the value of $E^0_{Zn} - E^0_{AgCl}$ used in the first part of the problem. [Scatchard and Tefft, *J. Am. Chem. Soc.*, **52**, 2272(1930).]

2. For the cell H_2(1 atm.), HBr(0.100*m.*), Hg_2Br_2 + Hg, E_{298} = 0.2684 volt. Calculate E^0_{298} for the electrode Hg + Hg_2Br_2, Br^-(*u.a.*). [CROWELL, MERTES, and BURKE, *J. Am. Chem. Soc.*, **64**, 3021 (1942).]

3. The potential of the cell H_2(1 atm.), HCl(*m* molal), AgCl + Ag at 298°K. changes with the molality of HCl as follows:

m .	4	6	8	10	12	14
E_{298}	0.1299	0.0704	0.0241	−0.0166	−0.0525	−0.0839

(*a*) Calculate the standard free energy of HCl(*g*) from some of these potentials and the vapor-pressure data on page 188, taking −26,200 cal. for the standard free energy of AgCl(*s*). (*b*) Calculate the partial pressure of HCl(*g*) above the 12*m.* solution. (*c*) Calculate the activity coefficient for the ions in the 10*m* solution.

4. Calculate the potential of the cell H_2(0.1 atm.), HCl(0.001*m.*), Cl_2(0.2 atm.) at 25°.

5. Calculate the equilibrium constant for the chemical reaction $ZnSO_4$ + Cd = $CdSO_4$ + Zn at 25° from the electrode potentials.

6. Compute the potential of the concentration cell H_2(1 atm.), HCl(0.1*m.*), Hg_2Cl_2 + Hg—Hg + Hg_2Cl_2, HCl(0.001*m.*), H_2(1 atm.) at 25°.

7. (*a*) Compute the potential of the concentration cell H_2(1 atm.), HCl(0.1*m.*), HCl(0.001*m.*), H_2(1 atm.) at 25°. (*b*) Compute the potential of the cell Hg + Hg_2Cl_2, HCl(0.1*m.*), HCl(0.001*m.*), Hg_2Cl_2 + Hg at 25°.

8. The potential of the cell Zn(*s*), $ZnSO_4$(0.010*m.*), $PbSO_4$(*s*) + Pb(*s*) is 0.5477 volt at 25°, and the activity coefficient in 0.010*m* $ZnSO_4$ is 0.38. (*a*) Calculate the standard electrode potential for Pb(*s*) + SO_4^{--}(*u.a.*) = $PbSO_4$(*s*) + *e*− (*b*) The activity product $(a_{Pb^{++}})(a_{SO_4^{--}}) = 1.58 \times 10^{-8}$ at 25° in saturated $PbSO_4$ solution. Calculate the standard for potential Pb(*s*) = Pb^{++}(*u.a.*) + $2e^-$ (*c*) The potential of the cell becomes 0.5230 volt when the $ZnSO_4$ is 0.050*m.* Calculate the activity coefficient for this solution. [Data from Cowperthwaite and LaMer, *J. Am. Chem. Soc.*, **53**, 4333 (1931).]

9. The cell Cu(*s*) + CuCl(*s*), K^+Cl^-(0.1*m.*), Cl_2(1 atm.) has a potential of 1.234 volts at 25°. (*a*) Calculate the solubility product for CuCl in water at 25°. (*b*) What is the concentration of cuprous ion at the anode of this cell?

10. Calculate the standard electrode potential Br_2(*l*), Br^-(*u.a.*) from the cell H_2(1 atm.), HBr(0.02*m.*), Br_2(*l*); E_{298} = 1.287 volts

11. Given E_{298} = 0.1116 for the cell

H_2(1 atm.), NaOH(0.105*m.*), $NaHg_x$—$NaHg_x$, NaOH(0.010*m.*), H_2(1 atm.)

calculate E_{298} for the cells

(*a*) Hg+HgO,NaOH(0.105*m.*),$NaHg_x$−$NaHg_x$,NaOH(0.010*m.*),Hg+HgO

(*b*) H_2(1 atm.), NaOH(0.105*m.*), NaOH(0.010*m.*), H_2(1 atm.)

(*c*) $NaHg_x$, NaOH(0.105*m.*), NaOH(0.010*m.*), $NaHg_x$

In all these cells the activity of water may be assumed equal in the two solutions, and the transference number of sodium ion may be assumed constant at 0.20.

12. The cell Ag + AgCl(*s*), NaCl(0.050*m.*), NaCl(0.010*m.*), AgCl(*s*) + Ag has a potential of 0.0304 volt at 25°C., and in this range of molality the transference number of the sodium ion is 0.390. (*a*) Calculate the potential at 25° of the cell $Ag + AgCl(s), NaCl(0.050m.), NaHg_x—NaHg_x, NaCl(0.010m.), AgCl(s) + Ag$. (*b*) Calculate another value of the potential from the data in Table 98.

13. The potential at 298°K. of the cell $Ag + AgBr(s), KBr(0.050m.), KBr(0.010m.), AgBr(s) + Ag$ is 0.0375 volt. Write the change in state per faraday for the cell, and calculate the transference number of potassium ion, assuming it constant in this concentration range, and assuming the activity coefficients for KBr the same as those for KCl. [MACWILLIAM and GORDON, *J. Am. Chem. Soc.*, **65**, 984 (1943).]

14. Calculate the standard potential $Cl_2(1m.), Cl^-(u.a.)$ discussed in footnote 1 on page 645 from the entries in Tables 95 and 99.

15. The potential at 298°K of the cell $Hg + HgO, NaOH(m.), H_2(1\text{ atm.})$ for some molalities of NaOH is as follows:

E_{298}	−0.9255	−0.9255	−0.9255	−0.9255
m	0.0487	0.2000	0.2737	0.5000

Calculate K_w, the ion product for water, from this potential and the standard potentials in Table 99.

16. Calculate the potential at 25° of the cell $ZnHg$(amalg., 0.001m.), $ZnCl_2(0.1m.)$, $ZnHg$(amalg., 0.003m.). In the amalgams containing 0.001 and 0.003 mole of zinc per 1000 grams of mercury, zinc is an ideal monatomic solute.

17. (*a*) The activity coefficient for all the ions in the cell

$$H_2(1\text{ atm.}), \left\{\begin{matrix}KOH(0.01m.)\\ KCl(0.10m.)\end{matrix}\right\}, AgCl + Ag;\ E_{298} = 0.992\text{ volt}$$

is 0.80. Calculate E^0 for this cell with both negative ions at unit activity. (*b*) Calculate the potential of this cell with unit activities in series with the cell $Ag + AgCl, HCl(u.a.), H_2(1\text{ atm.})$, write the change in state for the two cells, and calculate K_w.

18. The potential of the cell $H_2(1\text{ atm.}), NaOH(0.02m.), ZnO(s) + Zn(s)$ is −0.420 volt at 298°K. Calculate the standard free energy of $ZnO(s)$, taking −56,690 cal. as the standard free energy of $H_2O(l)$. [The answer should check that of Problem 6, page 626.]

19. Calculate the potential at 25° of the cell $Ag + AgCl(s), NaCl(0.10m.), NaCl(0.010m.), AgCl + Ag$. (The measured potential is 0.0430 volt.)

20. The potential of the cell $Tl + TlCl(s), KCl, (0.02m.), Cl_2(g, 1\text{ atm.})$ is 1.91 volts at 25°. (*a*) Calculate ΔF for the change in state occurring in the cell and the standard free energy of $TlCl(s)$ at 25°. (*b*) Calculate the solubility of TlCl in water at 25°. (*c*) Calculate E for the electrode $TlCl(s) + Tl(s), HCl^-(0.10m.)$, taking γ as 0.80.

21. For the cell $Pb, PbCl_2(s), HCl(1m.), AgCl + Ag$; $E_{298} = 0.4900$ and $dE/dT = -0.000186$ volt per deg. (*a*) Calculate ΔH and ΔS for the cell reaction. (*b*) Calculate ΔH and ΔS for the cell reaction from the data in Tables 58 and 96.

22. Calculate the temperature coefficient of potential for the cell Ag + AgCl, KCl(1*m*.), Hg_2Cl_2 + Hg, $E_{298} = 0.0455$ volt from the data in Table 96

23. At 25° the cell Ag + AgCl, NaCl(m_2), $NaHg_x$—$NaHg_x$, NaCl(0.10*m*), AgCl + Ag changes with m_2 as follows:

m_2	0 200	0 500	1 000	2 000	3 000	4.000
E_{298}	0.03252	0 07584	0 10955	0 14627	0 17070	0.19036

(*a*) Given the activity coefficient 0 773 in 0.1*m* NaCl, calculate the activity coefficients for 0 2 and 3 0*m* NaCl (*b*) Calculate the potential of the cell, at 25°, $NaHg_x$, NaCl (0.20*m*), NaCl (0 10*m*.), $NaHg_x$, using the transference numbers in Table 48. [HARNED and NIMS, *J. Am. Chem. Soc.*, **54,** 423 (1932)]

24. Calculate the potential of the cell Hg + Hg_2Cl_2, HCl(0 01*m*), H_2(1 atm) at 298°K., first from the free-energy table and again from the standard electrode potentials.

25. Calculate the potential of the cell H_2, HCl(0 1*m*), AgCl + Ag if it operates under a barometric pressure of 700 mm., taking 23 mm as the vapor pressure of water above the solution

26. Write the change in state for 1 faraday passing through the sodium hydroxide concentration cell described on page 641 when m_1 is 0 1934, and confirm the calculated activity coefficient for this solution

27. Write the cell reactions for the six cells described on pages 644–645.

28. The potential of the cell

$$H_2(1\text{ atm }),\ \begin{Bmatrix}NH_3(0\ 05m\ ) \\ NH_4Cl\ (\text{satd. soln.})\end{Bmatrix},\ Hg_2Cl_2 + Hg$$

is 0 699 volt at 25°C. (*a*) Calculate ΔF and ΔF^0 for the cell reaction. (*b*) Note that the free energy of NH_4Cl in its saturated solution is the same as that of $NH_4Cl(s)$, refer to Table 95 for additional data, and calculate the standard free energy of $NH_4Cl(s)$ at 298°K. (Compare the result with that of Problem 35 on page 629.

29. Calculate the standard free energy of ferrous hydroxide from the cell Fe(*s*) + $Fe(OH)_2(s)$, $Ba(OH)_2$(0.05*m*.), HgO(*s*) + Hg; $E_{298} = 0.973$ volt and such other data as are required.

30. Calculate E^0 for the cell H_2(1 atm.), HCl(*u.a*), AgCl(*s*) + Ag at 273°K. from the data in Table 97.

31. Confirm the potential of the electrode Pb(*s*) + $PbSO_4(s)$, SO_4^{--}(*u.a.*) given on page 646 from a suitable plot of the data for the cell Pb + $PbSO_4$, H_2SO_4, H_2 given on page 663.

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