SEVENTH EDITION

of Chemistry

HILDEBRAND AND POWELL

Principles of Chemistry

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E7963530



The Macmillan Company, New York Collier-Macmillan Limited, London

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Fourth Printing, 1965

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Library of Congress catalog card number: 64-10965

The Macmillan Company, New York Collier-Macmillan Canada, Ltd., Toronto, Ontario

Printed in the United States of America

DESIGNED BY RONALD FARBER

PRINCIPLES OF CHEMISTRY

Preface to the Seventh Edition

Although hardly a paragraph of the previous edition has escaped revision, this seventh edition is an easily recognizable descendant of the senior author's first *Principles of Chemistry* of 1918. We are convinced as firmly as ever of the soundness of the philosophy of teaching general chemistry upon which it was based.

In the first place, the separation of a textbook of principles from one of descriptive chemistry gives the teacher a great deal of flexibility in planning his course. He can take up topics in any reasonable order, interspersing descriptive material wherever he thinks best, and adding his own favorite examples to supplement those we have given in illustration of each new principle as it is taken up. The text is designed to be used alongside a compilation such as Latimer and Hildebrand's Reference Book of Inorganic Chemistry.

Secondly, a textbook ought to be written so as to take into account the wide variation in intellectual appetite of students. Some wish to master thoroughly only the simplest principles. For them, we have provided numerous worked-out examples of various sorts of problems, as well as answers to all the numerical problems at the ends of chapters. Other

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students, with superior aptitude and background in chemistry, are ready to learn something of the more powerful techniques and the more complex relations of chemistry. For them, we have included several optional chapters (e.g., Chap. 16 on solubility of nonelectrolytes, 18 on valence theory, and 21 on Avogadro's number), as well as many individual paragraphs scattered throughout the text. In presenting these more advanced topics we have stressed their qualitative aspects rather than their mathematical formalisms, in the conviction that a beginner in a subject profits most from learning how to make sound qualitative predictions. For instance, although we have, in this edition, consistently emphasized the language and methods of thermodynamics, we have relied on heuristic arguments in lieu of formal thermodynamic proofs.

Finally, we have retained a sequence of chapters by which chemistry is presented in what can be called a "genetic" order. That is, topics are taken up more or less in their historical sequence. This is not to say we adhere to a strictly historical order, for the most elegant and persuasive solution to a problem has often arisen long after the first solution was found; in such cases, we have felt free to collect into a single chapter lines of evidence that came to light at different periods of chemical history. It is our opinion that the principles of chemistry are more comfortably assimilated when taught in this genetic sequence than in the opposite sequence, which begins with electrons, nuclei, and Schrödinger's equation in the first paragraph of the first chapter and works its way up by strictly logical steps until it eventually comes to actual substances in test tubes.

In making this revision, we have taken advantage of the opportunity to introduce a number of didactic devices that have proved to work well in our own classes during recent years. We have also removed a few scientific blunders that had crept into the previous edition (although it is not entirely unlikely that we have introduced some new ones). The changes are, in general, those that have survived the scrutiny of the able colleagues who participate in the teaching of general chemistry at the University of California, whose criticisms, though occasionally embarrassing, have always been valuable.

JOEL H. HILDEBRAND RICHARD E. POWELL

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$\it 1$. Kinds of Matter

1. Chemistry Is a Vast Subject

Just how vast, a simple computation will show: There are 103 known elements; they combine with one another to make something like ten thousand separate compounds, not counting the compounds of carbon; if the compounds of carbon be included in the count, the total number now approaches a million. To memorize the properties of more than a small part of the known compounds would be long, hard work. Then truly

The lyffe so short; the craft so long to lerne; Th'assay so harde, so sharp the conquering.

But comparatively little memorization is necessary. Chemistry has progressed far beyond the era of mere description and classification. Like physics and astronomy, it has profited by the discovery of certain systematizing principles which gather together a vast wealth of experimental data. The chemist of today is not so much the man who knows the answers, as the man who knows how to find the answers. The number of major systematizing principles in chemistry is not large—say a couple of

dozen—and it is our intention to treat each of these in a chapter of this book. Hence our title, *Principles of Chemistry*.

We welcome to the study of chemistry not only those students who will make it their profession, not only those who will find it useful to them in agriculture, engineering, medicine, or the biological sciences; but all those who feel a lively curiosity concerning their environment. Chemistry offers unsurpassed examples of science as exploration, of science as systematization. We believe that those who have had even a glimpse at its methods will be more inclined as well as more able to look at all problems, whether chemical or others, as susceptible to scientific treatment.

2. What Is Chemistry?

This question, appropriate at the beginning of a book or a course, might be answered by saying, "Chemistry is what chemists do." On the face of it this is a tautology, but it does serve to convey the idea of chemistry as an enterprise, and not merely as a stockpile of knowledge. The question might be answered by a dictionary definition such as "Chemistry is the science that treats of the composition of substances, and of the transformations they undergo," but this means very little until the words in it have been enriched, by examples or experience. The root of the difficulty is that one-sentence definitions are not at all adequate for big subjects, especially those that grade into one another (as chemistry grades into physics) with only a hazy or arbitrary boundary between them. We distrust such definitions. There is no adequate single, short definition. Chemistry is best defined by examples of the problems which chemists attack and the methods they use. A reasonably adequate idea of these requires a book or a whole course. We can make a sort of aerial reconnaissance of the domain of chemistry, but we must be aware that the view will now be preliminary and partial; the satisfactory view comes at the end of the course, not at its beginning.

Chemistry is concerned with substances, with kinds of matter, the materials of which things are made. It is concerned with wood but not the log, with glass but not the bottle, with copper but not the coin, with clay but not the brick. Chemistry is concerned with identifying or characterizing properties of substances, such as color, density, melting and boiling temperatures. The chemist now has at his disposal an array of properties, accurately measurable, that serve to identify particular substances.

In order that properties may be known accurately, the substances that serve for their determination must be pure, that is, reproducible. The chemist must know how to separate the pure constituents of heterogeneous mixtures and solutions.

One of the most important of all the facts about a pure substance is its composition: the kinds, number and arrangement of the atoms of which it is composed.

And finally, chemistry deals with the processes in which substances are transformed into other substances. These are called *chemical reactions*. The chemical reactions that a substance may undergo are its *chemical properties*. These often afford the most useful means of identification. Acids, for example, have the property of turning blue litmus red (a far safer test in general than sour taste). Sugar will char and burn, salt will not.

Some reactions permit us to break substances into simpler ones (for example, the reduction of iron oxide into iron, or the chemical analysis of an unknown mixture of salts, or the discovery of the structure of a vitamin by degrading it into simpler substances). Still more valuable and interesting are "synthetic" reactions that lead to the preparation of substances, even of many not occurring in nature.

In brief then, chemistry is concerned with substances: their characterization, their structure, and their interconversion.

3. Chemistry as the Study of Properties

The number of properties of substances that can be observed, measured, and used for identification is constantly increasing. We list a number of them in the following paragraphs.

(a) First, there is a group of properties which, like fingerprints, permit the quick and accurate identification of any compound, provided it is one which is previously known and tabulated (in a "fingerprint file" of that particular property). This kind of identification has the merit that it is nondestructive, i.e., the sample is unharmed by the test.

melting point boiling point index of refraction color (absorption or emission spectrum) density crystal angles solubility, in a specified solvent

It has been said that a chemist can tell what compound he has by a sniff and a melting point. Certainly the melting point and the boiling point are extremely valuable for identification of organic compounds, as witness the extensive tabulations in increasing order of m.p. or b.p. in textbooks of qualitative organic analysis, as well as in handbooks such as Lange's Handbook of Chemistry or the Chemical Rubber Company's Handbook of Chemistry and Physics. The melting point, boiling point, and solubility offer one further advantage: they are very sensitive to impurities, and therefore serve as criteria of purity. If a substance is pure it will entirely melt at a constant temperature, but if impure the melting will take place over a range of temperature, and the more the impurity the broader the melting range. Likewise, a pure substance has a constant boiling point, while an impure substance has a boiling point which is not sharp, but varies over a range as the liquid evaporates. Again, if a pure solid is added to a particular solvent until the first bit of solid remains undissolved, the solution is said to be saturated, and no additional solid will dissolve, no matter how much extra solid be added; if the same experiment is repeated with an impure solid, it is observed that even after the first bit of solid remains undissolved, the further addition of solid brings about an increase in the amount dissolved.

The index of refraction, the density, and the crystal angles are helpful in the identification of organic substances, but much more useful for inorganic crystals and especially for minerals. Tabulations of these properties will be found in textbooks of mineralogy.

Color as an identifying property is obviously most useful for identifying intensely colored substances such as dyes. Its usefulness has been greatly extended by spectroscopic measurements, which not only permit the quantitative measurement of the light absorption at each wavelength, but also extend the range of observation far beyond the limits of human vision. For example, the color of a copper sulfate solution is simply "blue" to the human eye; but as the spectrophotometer reveals it, it has a characteristic absorption of light at each wavelength. As Fig. 1-1 shows, it has a strong absorption peak in the near infrared, tailing into the red part of the visible spectrum (the absorption of the red light makes the solution appear to be blue, the complementary color, to the naked eye), and then another strong absorption in the ultraviolet. The color of a flame or hot body, or the material in an electrical discharge, arises from

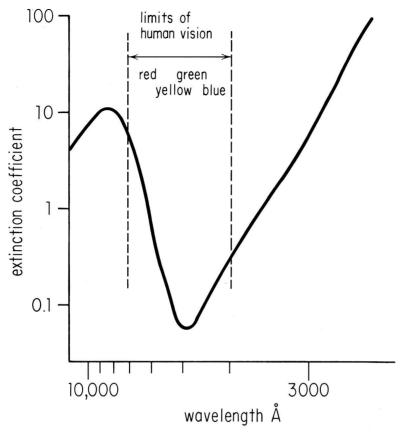


Fig. 1-1. The absorption spectrum of copper sulfate solution. The extinction coefficient is the fraction of light absorbed per centimeter of light path. The angstrom (abbreviated Å) is a unit of distance equal to 10^{-8} centimeters, named after the Swedish physicist A. J. Ångström, 1814-1874.

the emission of light; thus the yellow sodium flame, the red neon sign. So sensitive is emission spectroscopy that it permits the chemist to identify elements in alloys, even when present in the smallest traces; it also permits him to make a chemical analysis of the stars.

(b) "Structural" properties constitute another group. These depend, more or less directly, upon the properties of the individual atoms or molecules. We postpone to the chapters that follow the discussion of the atomic-molecular structure of matter; nevertheless most readers have already sufficient acquaintance with atoms and molecules to be aware that they have properties of their own—masses, dimensions, vibrations, electrical and magnetic properties. The properties in this list can be used (and occasionally are) for routine identification of known substances;

but their greatest value is that they give clues to the structure of the substance, even if it has never before been identified:

X-ray spectrum
infrared spectrum
microwave spectrum
nuclear magnetic resonance spectrum
X-ray diffraction pattern
electron diffraction pattern
molecular weight by gas density
molecular weight by mass spectrometry
molecular weight by freezing point depression,
boiling point elevation, osmotic pressure

We shall later take up in more detail the techniques for measurement of these properties. By X-ray spectroscopy one can analyze for the elements present. Infrared spectroscopy measures the molecular vibrations, and nuclear magnetic resonance the oscillations of magnetic nuclei in a magnetic field; both of these are sensitive to the types of chemical bonds present, and therefore give clues to the nature of the bonds. X-ray diffraction, electron diffraction, and microwave spectroscopy serve to measure the spacing between atoms in a molecule—the molecular dimensions. The various molecular weight methods reveal the mass of the molecule. An example of the effectiveness of physical methods in identifying hitherto unknown substances is the fact that the structure of vitamin B₁₂, very difficult and complicated, was elucidated by X-ray diffraction before the problem could be solved by the classical methods of organic chemistry.

(c) There are also biological properties, e.g.,

odor taste pharmacological properties, such as toxicity (50% lethal dose)

Although no one has discovered how to systematize it, "smell-o-metric analysis" is a common art among chemists. The value of the second property is largely nullified by the third; that is, any unknown chemical is likely to be poisonous, and the prudent chemist will keep it out of his mouth.

(d) There are a number of properties which are useful in the choice of materials for practical applications, for engineering and other technical uses. Although these properties can usually be interpreted in terms of

atomic and molecular properties, they are not themselves used much for identification or structural information:

elastic modulus
tensile strength
hardness
viscosity
diffusion coefficient
thermal conductivity
electrical conductivity
surface tension
dielectric constant
magnetic susceptibility

(e) Finally, we list a group of energy (or thermodynamic) properties. Strictly speaking, these are properties of processes rather than substances; they are measured because they permit the chemist to predict which processes will take place, which will not, and the conditions for chemical equilibrium:

heat of reaction (of fusion, of vaporization, of combustion, of ionization, etc.) entropy of reaction (of fusion, etc.) heat capacity critical temperature (pressure, volume) compressibility coefficient of thermal expansion standard potential

In later chapters we shall return to the application of thermodynamic properties to chemical problems.

4. Chemistry as the Study of Separations: Heterogeneous Mixtures

As soon as one tries to investigate the properties of any mixture, a new variable makes its appearance: namely, the composition of the mixture. Suppose; for example, the question is "What is the electrical conductivity of salt water?" The chemist is not content to measure one single sample of salt water; instead, he starts with pure salt and pure water, makes up a whole series of salt solutions with different amounts of salt,

and measures the conductivity as a function of composition. Again, suppose the question is "What is the melting point of solder?" Solder is a mixture of lead and tin, in indefinite proportions. So the chemist can answer the question only by getting hold of some pure lead and some pure tin, making up a series of different mixtures, and measuring the melting point as a function of composition. Since the study of mixtures has forced us, as a necessary first step, to their separation into their constituents, let us examine some of the standard techniques useful for separations.

Before going any further, we should point out that it is not wise to reserve the word *mixture* to a limited technical sense; chemists in general use "mixture" in its everyday sense. A housewife may mix baking powder, sugar, flour, salt, and lard for biscuit batter while her husband mixes a cocktail; to the chemist, as to anyone else, both the batter and the cocktail are mixtures. If a word is wanted for the kind of mixture whose properties change abruptly at the boundary between one small region and another, the word is *heterogeneous*. Granite is a heterogeneous mixture of quartz, mica, and feldspar; a mixture of chopped ice and liquid water is likewise heterogeneous. Since each region of the same kind of material is called a *phase*, it is equally proper to say that granite is a three-phase system, and that the mixture of ice with water is a two-phase system.

The heterogeneity of some materials may be detected by the naked eye: a rock, a slurry of sand suspended in water, kerosene floating on water, a foam of gas bubbles in a liquid. For others, a microscope is needed: paint, milk, smoke, cast iron are heterogeneous on a microscopic scale. Still another technique for detecting heterogeneity in solids is offered by X-ray diffraction; because, fortunately, the identifying X-ray pattern of each solid appears regardless of others that may be present in the mixture.

If we wish to separate a rock into its several minerals, we might crush a sample and pick out the individual fragments by hand. A suspended solid is commonly separated from its liquid by filtration: what is more common in the laboratory than to filter out a precipitate? Another practical technique makes use of "float-and-sink" behavior, i.e., takes advantage of differences in density. Gases float to the top of liquids and can be pumped off. Since liquids which do not mix will stand in layers, they can be separated in a "separatory funnel" which has a stopcock in the bottom for draining off the denser layer. Precipitates will settle to the bottom, and the supernatant liquid poured off ("decanted"); or,

instead of relying on the force of gravity, we may use centrifugal force as does the "cream separator" or the centrifuge which is used in the analytical laboratory. Two solids can also be separated by float-and-sink methods; for example, in the panning of gold the solid gold (density 19) remains in the pan while the agitated water carries away the sand (density 2.65).

Problem: How would you separate salt from sugar, without dissolving either of them? The density of salt is 2.16 and the density of sugar is 1.59.

Answer: Find some organic liquid whose density is between the two figures; then the sugar will float and the salt will sink. One possibility is ethyl iodide, density 1.92.

5. Chemistry as the Study of Separations: Homogeneous Mixtures

Let us dissolve a teaspoonful of sugar in a glass of water. The resulting mixture is a single phase to the eye, even under a microscope; the sugar does not settle out, nor can it be filtered out. This kind of mixture is called a *solution* or a *homogeneous mixture*, and is exemplified not only by liquid mixtures such as sugar-water, but also by some solid mixtures (the alloy of silver with gold, for example), and by all mixtures of gases with one another.

What experiments will serve to distinguish a pure substance from a solution? And what techniques can we use to separate a solution into its pure constituents? In practice, there is but a single answer to the two questions, because the best evidence for a solution is that it can be separated into its constituents! There are three widely used laboratory techniques for separating solutions: distillation, fractional freezing or melting, and extraction. All three are based on the same general idea, which is to convert a part of the sample into a different phase; if the original sample was a solution, it will thereby be separated * into two fractions of different chemical and physical properties from each other. By a systematic repetition of these fractional phase changes, the solution can eventually be separated into its components with any desired degree of purity.

^{*}Upon distillation, certain mixtures approach a composition called azeotropic, at which no further separation occurs. Certain others, upon fractional freezing, reach a composition called eutectic, after which the composition does not change. The solid separating at the eutectic point is readily identified as heterogeneous. When one method of separation fails, the chemist turns to another.