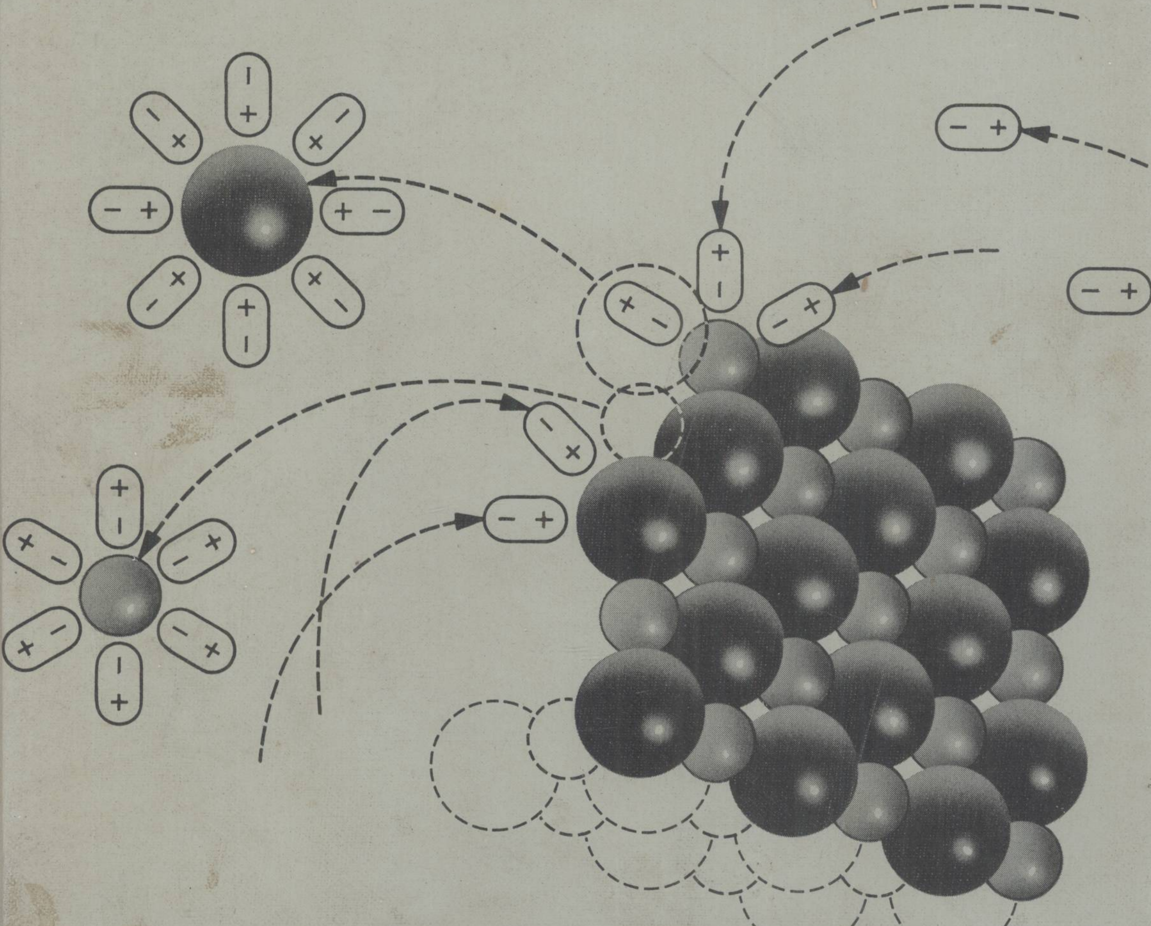
SELWOOD

CHEMICAL PRINCIPLES



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Preface

This book was written for the first-year college chemistry student whose preparation has included at least two years of preparatory mathematics and one of chemistry. A year of physics, though not essential, is certainly to be desired.

The plan of the book is to present the basic principles of chemistry in the first half, and descriptive inorganic chemistry in the second. The first half follows the general pattern that has proved to be successful in several recent texts, and the approach to general chemistry has been this: A student of science should not be asked to accept anything on faith. Now it is true that no matter how able a student may be, and no matter how long his educational career, he cannot possibly test for himself every statement in science. Nevertheless, I believe that he should be able to see how, in principle, he could make such tests, time and patience permitting. Failing this, we give up the very essence of science; we make of it a discipline where proof is abandoned and substituted by faith in the statements of higher authority.

There has, of recent years, been an increasing tendency to introduce modern valence bond theory to students of elementary chemistry. This has consisted in part of presenting the Schröedinger equation, and explaining how solution of the equation leads to quantum numbers and interaction energies. This has not been attempted in the present text. I believe that no student can understand the covalent bond until he has had a course in quantum mechanics; and to understand quantum mechanics he must first understand differential equations. Few first-year college students have mastered differential equations, and most of them never do. For this reason, I have treated the covalent bond descriptively, so far as this is possible, but I have not asked the student to accept, on faith, much that he cannot verify for himself—if not by actual test, then at least in principle.

Treatment of the inorganic half of the text deviates sharply from the current practice of many authors. Some thirty years of lecturing on general and inorganic chemistry at various levels has convinced me that the Periodic Table is not the most satisfactory plan of organization for presentation of the chemical elements and their properties. Too often the course has a tendency to bog down in a dreary recital of groups, trends, and exceptions. And this is likely to occur at the very moment in the spring when the lecturer must redouble his efforts to maintain the interest of his class.

The idea that an alternative approach to inorganic chemistry is preferable is certainly not new. An alternative was tried by Ephraim some fifty years ago. But, although his textbooks were widely used, his method was abandoned because the unifying principles especially applicable to inorganic chemistry had not at that time been fully developed.

The situation is quite different now. Inorganic chemistry has not only moved to an important position in science, but the wealth of experience, which a study of *all* the chemical elements can provide, makes it virtually imperative to place a generous part of descriptive inorganic chemistry in the first year. The method of presentation I have chosen is to consider first the chemical elements, then the binary compounds and, finally, more complex compounds. Full use, in so far as possible in an elementary presentation, has been made of modern structural chemistry, and emphasis has been placed on the separation, the synthesis, and the purification of the elements and their compounds.

All this material having been covered, it then becomes quite easy to present in a final chapter some examples of molecular structure and properties of organic compounds, without which no treatment of general chemistry can be considered complete.

No author of a book such as this can fail to be awed by the swift march of science. More than once I have found it best to illustrate a point by reference to a compound, or even to an element, that was unknown when I started writing the text. Even as the final chapters were being written I had to go back and change the words "inert gas" to read "group zero gas." Some of the "inert" gases are no longer inert. Other corrections will doubtless prove to have been required after the book goes to press. But if no author had the courage to write a text, no student would gain the knowledge to prove the text wrong.

SANTA BARBARA, CALIFORNIA
FEBRUARY, 1964

P. W. S.

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Gases

1.1 States of Matter

Chemistry is the science of matter and its transformations, and matter is anything that has mass and occupies space. Matter may exist in one or more of three states: gas, liquid, and solid.

A gas has the unique property that it may completely and uniformly fill any vessel in which it may be contained. The volume and shape of the container become the volume and shape of the gas. The gas will not only penetrate to all parts of the vessel, but equal weights of the gas will be found in equal portions of the volume.

A sample of matter in the liquid state may have a volume that is independent of the container. In this the liquid state is in contrast to the gaseous, but a sample of liquid will assume the shape of any vessel in which it may be placed so far as the vessel may be filled. A liquid is like a gas in adapting itself, at least in part, to the shape of the container; but it is unlike a gas in that any given sample of liquid has a definite volume which is not necessarily the volume of the container.

A sample of matter in the solid state always possesses both a volume and a shape that are characteristic of the particular sample but which are independent of the container, if any. It is true that a powdered solid may tend, in part, to assume the shape of the container, but this is true only because the powdered particles possess to some degree the properties of a liquid in that the particles are free to move with respect to each other.

Matter in the gaseous state is somewhat less complex than is the case when it becomes a liquid or a solid. The natural laws describing the behavior of gases are comparatively simple, and they yield a wealth of information concerning the molecules and atoms of which matter is composed. It is, therefore, to this state that our attention will be first directed.

Gases have three properties of special importance for our present purposes. These properties are compressibility, thermal expansion, and diffusibility. By *compressibility* is meant the property of a gas to change its volume when the pressure exerted on, and by, the sample is changed. The gas may be thought of as having a sort of elastic quality, its volume responding rapidly to changes in pressure; as the pressure increases, the volume decreases. This property of gases is described by Boyle's law.

The *thermal expansion* of gases is a matter of common experience. If a gas sample is heated, it tends to expand; if cooled, it tends to contract. Ultimately, all gases may be converted to liquids or to solids, although some gases do so only at astonishingly low temperatures. The thermal expansion of gases is described by Charles' law.

By *diffusibility* is meant the ability of a gas to permeate any space in which it may be put. If a gas sample is placed in an otherwise empty container, the gas almost instantly diffuses throughout the container, filling it completely. Or, if the container is already filled with air or some other gas, diffusion of an added gas, although much slower nevertheless reaches the same final stage of filling the container completely and uniformly. The gas is said to diffuse through the space, or through another gas. The diffusibility of gases is described by Graham's law.

1.2 Boyle's Law

If the pressure P_1 exerted by, and on, a gas sample is changed to P_2, it will be found that the new volume V_2 is related to the old volume V_1 by the expression

$$P_1V_1 = P_2V_2 \tag{1.1}$$

This is the mathematical expression for **Boyle's law** which may, in words, be stated as follows:

The volume of a fixed mass of gas varies inversely as the pressure, provided the temperature does not change.

Boyle's law is based on the experimental observation that for a given mass of gas at a fixed temperature, the product of volume and pressure is approximately constant over a considerable range of pressure.

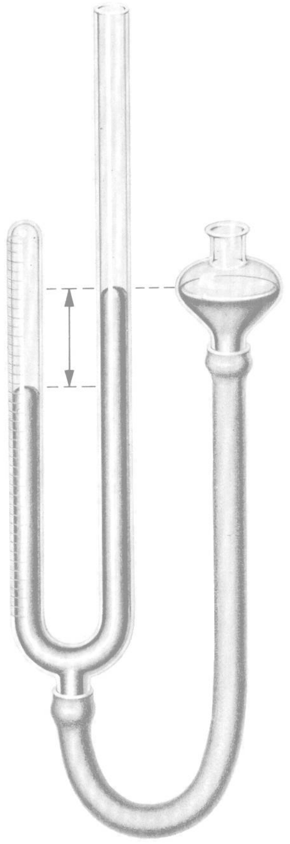

Fig. 1.1 Apparatus for demonstrating Boyle's law. A quantity of gas is trapped in the tube at left. This is subjected to greater or less pressure by raising or lowering the mercury reservoir which is attached to the rest of the apparatus by a flexible rubber tube. The volume of the gas is read directly. The pressure in millimeters of mercury is the difference in level of mercury in closed and open sides plus the barometric pressure of the atmosphere.

TABLE 1.1 TYPICAL EFFECT OF PRESSURE ON GAS VOLUME
(Data obtained on a sample of hydrogen at 25° C)

Pressure, P, mm mercury	Volume, V, ml	$P \times V$, mm $\times$ ml
50.0	884	44,200
170	260	44,200
310	143	44,200
498	88.8	44,200
760	58.1	44,100
1000	44.1	44,100

An experimental arrangement for investigating this relationship between volume and pressure is shown in Fig. 1.1, and some typical data so obtained are given in Table 1.1. It will be observed that over the range of pressure given, the product of pressure times volume is constant within the limits of probable experimental error, with due regard for an appropriate number of significant figures.

Boyle's law may be used to find the effect of changing pressure on the volume of a gas sample, as shown in the following problem.

PROBLEM: A given mass of nitrogen has a volume of 280 ml at a pressure of 845 mm of mercury. What volume will this sample occupy if the pressure is changed to 330 mm and the temperature remains unchanged?

SOLUTION: Boyle's law, as stated in Eq. 1.1, may be written as

$$V_2 = V_1 \times \frac{P_1}{P_2}$$

in which the new volume V_2 is equal to the old volume V_1 corrected for the change of pressure from P_1 to P_2. Substituting in the preceding equation,[1]

$$\begin{aligned} V_2 &= 280 \text{ ml} \times \frac{845 \text{ mm}}{330 \text{ mm}} \\ &= 718 \text{ ml} \end{aligned}$$

1.3 *Pressure Measurement*

The fundamental unit of pressure in the cgs system is the dyne per square centimeter. By definition, 1.013250×10^6 dyne cm^{-2} is said to be 1 atmosphere. One atmosphere (1 atm) so defined is very close to the pressure necessary to support a column of mercury 760 mm high, and is often referred to as standard pressure. It is convenient to use the height of a mercury column as a measure of pressure, and it will be so used throughout this book. A pressure designated as being h millimeters is thus actually $h/760$ atm.

Gas pressures are often measured with the aid of a U-shaped tube partially filled with mercury as shown in Fig. 1.2. One end of the tube is connected to the gas sample under investigation; the other, to the air. If the mercury in the open side of the tube stands higher than that in the

[1] Hereafter, when we encounter a fraction involving (as above) the same units in both numerator and denominator, we shall omit the units. The fraction 845 mm/330 mm will be written 845/330.

closed end, then the pressure exerted by, and on, the gas sample is given by the difference in heights of the mercury in open and closed sides plus the pressure exerted by the air on the open side. Such a device is called a *manometer*. The pressure of the air is not necessarily equal to one defined atmosphere, but may vary somewhat with the elevation above sea level and with atmospheric conditions.

It is possible to construct a manometer that is open to the air on one side, but completely sealed off under vacuum on the other. Two forms of this device are shown in Fig. 1.3. Under these conditions, it is the pressure exerted by the air itself that is being measured. Such a device is called a *barometer*. The pressure exerted by the air is given by the difference in heights of mercury in open and closed sides of the barometer. Corrections of various kinds must generally be applied for very precise measurements.

The use of a manometer may be illustrated by the following simple example: Suppose that on the side of the manometer open to the atmosphere, the mercury stands 43 mm lower than that on the closed side. The

Fig. 1.2 Simple mercury manometer attached to a flask containing a gas sample.

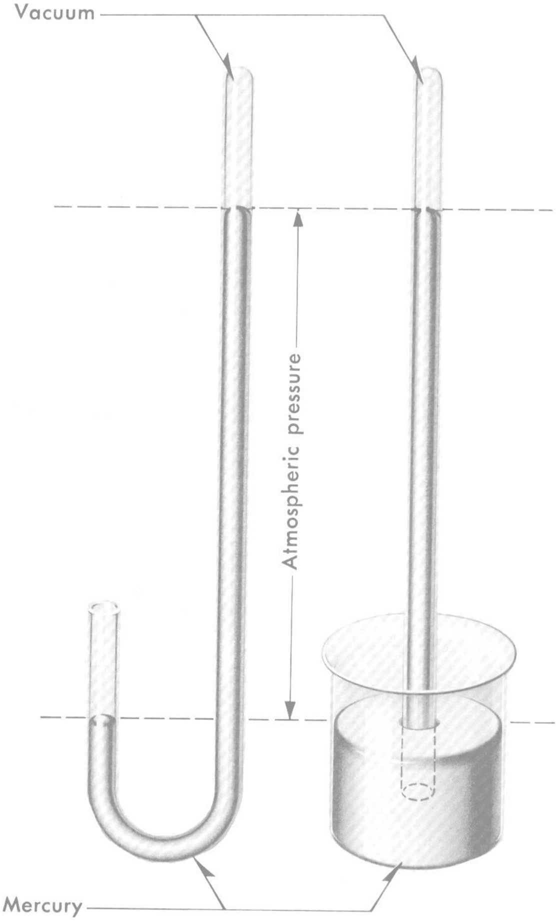

Fig. 1.3 Simple mercury barometers. Two forms are shown.

atmospheric pressure is found to be 738 mm. The pressure on the gas sample is obviously less than that exerted by the air. The actual pressure on the gas is 738 mm − 43 mm = 695 mm.

It is convenient in dealing with gases to designate a standard pressure. *Standard pressure* is 1 atm, or very nearly 760 mm of mercury.

1.4 Partial Pressure

If two or more gases are mixed, their total pressure is the sum of the pressures that each gas would exert if it were alone.

The pressure exerted by each gas in a mixture of gases is said