AN EXPERIENCE APPROACH TO EXPERIMENTAL CHEMISTRY

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An Experience Approach to Experimental Chemistry

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Experimental Chemistry

Chemistry is an experimental science. Laboratory work is an essential part of applied chemistry and is, therefore, the basis from which most of our modern high standards of living were developed.

There is no quick and easy way to become a chemist. Simply reading books and learning chemical theories can no more produce a true chemist than learning the theory of music can produce a real musician. A true chemist must do hundreds of experiments and make countless observations to gain the experience that will provide the necessary experimental background and intuition to use chemistry successfully. The situation is analogous to that of the professional golfer who must spend countless hours learning how to make different kinds of shots so that he can judge when and where given kinds of shots should be attempted. Similarly, it is only through practice and experience that one can become a concert pianist, a commercial pilot, or a physician.

In writing this book, we have endeavored to make the study of chemical reactions an enjoyable experience. We have tried to take boredom out of the laboratory by setting a fast pace for the experimental studies. We have also attempted to relate experiments to current problems such as crime detection, studies of medicine, application to industry, and the study of environmental problems. It is important to realize that, almost without fail, experiment

precedes theory. Because of the broad experiences that will be gained from these laboratory studies, the subsequent introduction to chemical theories will be easier and more exciting; the theories can be related to observations and experiences that have already been met.

This experience approach to experimental chemistry offers you the challenge of exploring the unknown, the thrill of discovery, and the satisfaction of accomplishment. These experimental studies should stimulate you to make careful observations, critically reflect upon the significance of observed phenomena, and establish the ability to seek reasons and conclusions. In the laboratory, you should observe many things that cause you to wonder. Although none of us will ever find answers to all of our questions, we all find satisfaction as we grow, learn, and finally understand.

As mentioned before, experiment almost always precedes theory. Theories are developed to explain experimentally observed phenomena. In practice, theory is learned to provide guidance in the solution of problems. Where theory may lead to the solution, it is only after experimental verification that the answer derived can be accepted in good faith.

From antiquity comes the classic story of the king who furnished his artisans with gold for a new crown but became suspicious that they were substituting cheaper metals. He assigned Archimedes the task of determining whether the crown was pure gold or an inferior alloy. After a great deal of searching and experimenting, Archimedes happened to notice the buoyancy of his own body in water. From this observation, he evolved the solution to the king's problem. The simple answer to this problem so excited him that he was overjoyed and ran through the streets shouting "Eureka! Eureka!" Although it would be quite optimistic to expect students to leave the laboratory in such an extreme state of elation, it is hoped that this experience approach to experimental chemistry will be fun as well as intellectually rewarding.

P. W. W.
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Contents

List of Figures

chapter 1

Reaction Chemistry

A knowledge of chemical reactions and the ability to conduct and interpret experiments are basic requirements for those who need chemistry as a tool or for those who choose chemistry as their profession. This basic knowledge is necessary because the chemical properties of matter determine how such matter can be studied and utilized.

The electron configurations of the calcium, carbon, and oxygen in a piece of chalk may fascinate a chemist or physicist. Likewise, the crystal structure of the chalk may intrigue a chemist, physicist, or geologist. From the practical standpoint, however, the chemical significance of calcium carbonate, whether it be chalk, limestone, oyster shell, calcite, or marble, derives from reactions it may undergo. When heated, calcium carbonate is converted to calcium oxide (lime) and carbon dioxide.

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (1\text{-}1)$$

calcium   calcium   carbon
carbonate   oxide   dioxide

The lime so produced finds many uses as such or is slaked (hydrated) for agricultural, construction, or chemical uses.

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad (1\text{-}2)$$

calcium oxide   calcium hydroxide
lime   slaked lime

1

When exposed to an acid, calcium carbonate reacts to neutralize the acid. For example, it reacts with hydrochloric acid to form a salt, calcium chloride, and carbonic acid.

$$CaCO_3 \; + \; 2HCl \; \rightarrow \; CaCl_2 \; + \; H_2CO_3 \qquad (1-3)$$

calcium   hydrochloric   calcium   carbonic
carbonate   acid   chloride   acid

This reaction is used industrially to neutralize spent acids in factory effluents. It is also the classic qualitative test to determine whether a rock sample is limestone. The carbonic acid produced in reaction (1-3) decomposes, forming carbon dioxide and water. Thus, when acid is added to limestone, bubbling or foaming is seen as a result of the carbon dioxide liberated.

The study of the interactions of matter encompasses a broad spectrum of activities. Reaction chemistry is the basis of simple oxidation processes such as rusting of iron or burning of coal as well as more complicated procedures such as those involved in the isolation of natural products and manufacture of synthetic materials. A knowledge of reactions is essential in understanding the processes involved in body metabolism and in developing better methods of treating physical and mental disorders.

Chemical reactions are represented by equations (the chemist's shorthand) which show the reactants used and the products formed. An equation summarizes what takes place and is incorrect, even though properly balanced, unless the products indicated are actually formed. In order to refresh your memory, exercises in writing formulas, naming compounds, and balancing equations are included at the end of the chapter.

The reactions included here fall into several categories, beginning with the well known acid-base reactions and proceeding through precipitation, complexation, oxidation-reduction (redox), catalyzed, and topochemical reactions.

Acid-Base Reactions

In your daily activities you have noticed that different types of substances have different physical properties. For example, vinegar and lemon juice taste sour, a typical characteristic of acids. Liquid detergents and household ammonia feel "soapy," a common property of bases. In order to determine what causes such differences in behavior, we need to examine the structures of some typical acids and bases.

Figure 1 shows the Lewis structures of three bases. These structures have one common characteristic, an unshared electron pair. Thus, Lewis defined a base as a substance that can donate an electron pair. On the other hand, an acid is a species that can accept an electron pair. The proton, H^+, acts as an acid when it accepts an electron pair in reactions such as (1-4).

$$H^+ \; + \; \left[:\ddot{O}:H \right]^- \rightarrow H:\ddot{O}:H \qquad (1-4)$$

In this reaction a covalent bond is formed. Many other ions and molecules can act as acids by accepting an electron pair.

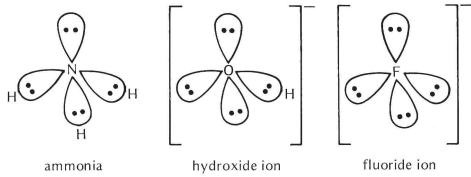ammonia   hydroxide ion   fluoride ion

Figure 1. Lewis structures of typical bases.

Acids and bases may be identified in various ways. Perhaps the simplest method is based on the fact that certain organic dyes exhibit different colors in acidic and basic solutions. One of the most familiar of these indicators is litmus, which is red in an acidic medium and blue in a basic medium. Although an introduction to the use of indicators is given in the experimental section, a more detailed explanation of the theory can be found in Chapter 6.

Because an acid is any substance that can accept an electron pair donated by a base, according to the Lewis concept any reaction leading to the formation of a coordinate covalent bond is an acid-base reaction. A common example is the reaction between the proton and the hydroxide ion usually referred to as neutralization. As sodium hydroxide is added to a solution of hydrochloric acid, the hydroxide ions react with the protons from the acid until finally a point is reached at which the solution is neutral. The acid and base react to form a salt, sodium chloride, and water.

$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + H_2O \qquad (1-5)$$

As implied by equation (1–5), the sodium and chloride ions do not really participate in the reaction; it is, therefore, customary to omit them and to write (1–6)

$$H^+ + OH^- \longrightarrow H_2O \qquad (1-6)$$

as a summary of the neutralization reaction. The salt is included in the equation only if it is insoluble. This discussion is intended only to be introductory in nature. A more detailed study of neutralization can be found in the section on titrimetry (Chapter 6).

Acids that ionize completely in water are called strong acids. In the reaction of other hydrogen-containing substances with water, a comparatively small fraction of the molecules dissociate, and the concentrations of the ionic species are, therefore, low compared to those of the undissociated molecules. Such species are referred to as weak acids. The terms strong and weak are not to be confused with concentrated and dilute. The latter expressions refer simply to the amount of the compound dissolved in water and are not related to the degree of ionization.

acid-base reactions   **3**

We have seen that, in water solution, common acidic properties are due to hydrogen ions and that the greater the degree of ionization (hence, the larger the number of hydrogen ions), the stronger is the given acid. Thus, by specifying the hydrogen ion concentration, it is possible to describe quantitatively the acidity or basicity of a solution. In 1909, Sørensen proposed the use of a term known as pH (power of hydrogen) defined as in (1-7)

$$pH = -\log_{10} [H^+] = \log_{10} \frac{1}{[H^+]} \qquad (1-7)$$

where $[H^+]$ represents the concentration of the hydrogen ion.

It has been determined experimentally that, in any water solution, the product of the concentrations of the hydrogen and hydroxide ions is 1×10^{-14} molar (M). In a neutral solution,

$$[H^+] = [OH^-] = 1 \times 10^{-7} \, M \qquad (1-8)$$

From the definition in (1-8)

$$pH = -\log_{10} [H^+] = -\log_{10} (1 \times 10^{-7}) = 7 \qquad (1-9)$$

In an acidic solution the hydrogen ion concentration is greater than 1×10^{-7}; hence, the pH is less than 7. Accordingly, the pH of a basic solution is greater than 7. (See Figure 2.)

acidic							basic						
1	2	3	4	5	6	7	8	9	10	11	12	13	14
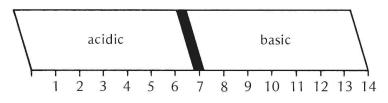
Figure 2. pH scale.

The pH of a solution can be determined accurately by use of an instrument called a pH meter. However, for many laboratory purposes it is sufficient to use pH test paper, impregnated with a mixture of indicators designed to give various colors over a wide pH range.

Precipitation Reactions

Precipitation is one of the simplest and most widely used techniques in reaction chemistry. In precipitation, a dissolved substance is converted into one that is insoluble and is thus separated from solution. People often refer to rain

or snow as precipitation. It rains when the water vapor in air exceeds the saturation limit. The same situation exists where a solid separates from solution. A precipitate forms when the concentration of a solute in a solution exceeds the saturation limit. This can occur through a physical change, such as a change in temperature, or because of the formation of an insoluble species that results from some chemical reaction.

The concept of precipitation is not new. The terms "precipitate" and "precipitation" appeared in a monograph by Basilius Valentinus in 1603. Later in the seventeenth century Robert Boyle made a detailed study of the process of precipitation[1].

There is no material that is completely insoluble. A striking example of solubility is the case of glass. We all think of glass as an ideal substance for making bottles, flasks, and other containers. It is considered inert except when in contact with hydrofluoric acid or strong alkali and is universally used for storage of chemicals and drugs without concern about possible contamination due to its dissolution. That it will dissolve in water can be demonstrated by grinding some soft glass tubing with a mortar and pestle; enough of the powdered material will dissolve in distilled water to give a pink color in the presence of phenolphthalein indicator.

Even a slightly soluble salt dissolves enough to produce a saturated solution of its ions. When the solid salt is in contact with the solution, an equilibrium exists between the ions and the solid. For example, when an excess of silver chloride is present in a water solution, the equilibrium is expressed by equation (1–10).

$$AgCl \rightleftharpoons Ag^+ + Cl^- \tag{1-10}$$

The product of the concentrations of the ions, raised to powers corresponding to their respective coefficients in the ionic equation, is a constant called the solubility product constant, denoted by K_{sp}. For silver chloride,

$$K_{sp} = [Ag^+][Cl^-] \tag{1-11}$$

where the brackets denote concentrations. A precipitate forms when the concentrations of the ions are large enough that the product mentioned above is greater than the value of the solubility product constant. A knowledge of solubility products is beneficial in developing proper reaction conditions for separation by precipitation.

The size and nature of the particles composing a precipitate depend upon the individual characteristics of the particular substance, the conditions under which the precipitate is formed, and its treatment after precipitation. A great deal of information can be gained by a study of the crystalline structure of precipitates. Some have beautiful, easily recognizable crystalline patterns. It is often easy to distinguish between two precipitates by knowing the crystal morphology of each. With the aid of a microscope it is possible to determine

the optical character, the index of refraction, and the crystal system to which a given substance belongs. This helps to elucidate the structure and identify the substance.

Complexation Reactions

In the experiment illustrating precipitation, the hydroxides of some metals dissolve upon addition of excess hydroxide ion. As an example, consider aluminum hydroxide.

$$Al^{3+} + 3\ OH^- \longrightarrow Al(OH)_3 \downarrow \xrightarrow{\text{excess } OH^-} [Al(OH)_4]^- \qquad (1\text{-}12)$$

The final product is a complex ion,

The hydroxyl groups are called ligands or coordinating groups; each ligand has an electron pair that it shares with the central metal atom.

In principle, any molecule or ion possessing an unshared pair of electrons can donate them to a metal to form a complex species; the ligands most frequently encountered in a beginning chemistry course are ammonia, water, hydroxide, chloride, fluoride, iodide, and tartrate. The metal ions that form the most stable complexes are those with unfilled d orbitals.

Complexation is such an important topic that an entire chapter is devoted to it. Chapter IV on coordination chemistry gives a more thorough discussion of complexation reactions and their significance in analytical chemistry.

Redox Reactions

In electroplating processes, such as gold plating of jewelry, an electron current is obtained from an electric circuit. The supply of electrons comes from an external source such as a power plant. However, it is not essential to use an external source; the electrons could be supplied within the system by some substance willing to give up electrons. Such a substance is called a reducing agent and is said to be oxidized; the element that picks up the electrons is reduced. Thus, oxidation is defined as a loss of electrons; reduction is a gain of electrons.

In oxidation-reduction, there is a transfer of electrons from one species to another. Hence, reduction never occurs by itself but is always coupled with a simultaneous oxidation. Likewise, oxidation occurs only where there is an

associated reduction of some other substance. The chemistry of reduction and oxidation reactions cannot be considered separately; in the designation for such reactions, the names have been combined and contracted, giving us the term "redox" reactions. Such reactions may take a variety of forms, but the underlying principle remains the same.

Air oxidation is perhaps the most familiar of the redox reactions, the rusting of iron being the most common example. In the laboratory you will see the ease with which Mn(II) is oxidized in reaction (1–13).

$$2 \, \text{Mn (OH)}_2 + \text{O}_2 \longrightarrow 2 \, \text{MnO (OH)}_2 \qquad (1\text{–}13)$$

One of the chemical properties of an acid is its ability to react with metals, liberating hydrogen. Such transformations can be considered redox reactions because there is a transfer of electrons between the metal and the proton of the acid.

A commercial process that involves an oxidation-reduction reaction is photography. The light-sensitive layer that coats a photographic film consists of an emulsion of a silver halide, usually silver bromide, in gelatin. When a film is exposed to light, a few of the silver ions are reduced to silver atoms, forming the latent image.

Although a great deal of research has been devoted to the subject, the mechanism of photochemical reduction is not well established. A photon of light knocks an electron from a bromide ion,

$$\text{Br}^- \xrightarrow{\;hv\;} \text{Br} + e \qquad (1\text{–}14)$$

This electron migrates through the crystal until it encounters an electron trap such as a defect in the lattice where an anion is missing. Since a trapped electron is not free to migrate, it tends to react with an adjacent silver ion, causing it to be reduced to a silver atom.

$$\text{Ag}^+ + e \longrightarrow \text{Ag} \qquad (1\text{–}15)$$

Silver atoms formed in this manner constitute the latent image.

After exposure, the film is treated, in the dark, with a solution of a weak reducing agent, referred to as a developer. The silver bromide grains sensitized by light during exposure are easily reduced to metallic silver; the reaction is catalyzed by the small number of silver atoms in the latent image. In the region of the film that was not exposed to light, there are no silver atoms and the reduction reaction occurs much more slowly.

After development the film is dipped in a solution called a fixing bath to remove the unreduced silver bromide, and the negative is ready for preparation of the positive print. The changes taking place in the photochemical reduction of silver will be studied in the experimental section.