Acid-Base Chemistry

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Preface

First and second year college chemistry courses are necessarily limited in depth of treatment; one such limited area is acid-base chemistry. Typically, first year students are rushed through the Brønsted-Lowry treatment and given a definition, but little more, of Lewis acids and bases. Yet these topics are of central importance as students progress in their study of chemistry. At the second year level the beginning student of quantitative analysis is presumed to have mastered subjects such as ionic equilibra, the effect of pH on solubility, and buffers. In our experience the mastery is far from complete. The student of organic chemistry is required to memorize a vast array of reactions, which may appear to be unrelated to one another. The task is much easier for those students with a firm grasp of the unifying principles of charge distribution in molecules, but the first year treatment of charge distribution is usually cursory at best. Our text, *Acid-Base Chemistry*, was written in an attempt to meet these needs. Specifically, the book:

1. is a mix of qualitative and quantitative approaches, well separated in the chapters. In the quantitative sections, no details are omitted from the worked examples; even good students do not like to be told "it can easily be shown that .... ."
2. includes a treatment of errors in pH calculations, as well as methods for exact solutions; these are rarely seen in other textbooks. Rules are developed for deciding when the exact method must be used. Programs written in BASIC are appended for student use.
3. provides many examples of numerical problems, completely worked, as well as end-of-chapter problems suitable for homework or exams.
4. can be used to ease the transition between first and second year chemistry. One example: introductory texts rarely use the concept of formal charge, yet organic texts use formal charge extensively, sometimes without good explanations. Our text includes a section explaining the concept and the rules, together with their significance and usefulness.
5. provides many examples of reaction mechanisms, taken primarily from organic chemistry. In all of these the importance of charge distribution is stressed. It is only a slight exaggeration to say that electron distribution within molecules is what determines the course of chemical reactions. That's what this book is about.
6. provides helpful supplementary material for three groups of students. The concepts and examples are simple enough for the first year student; there is a good review as

well as additional mathematical sophistication for the quantitative analysis student; there is, as has been pointed out by our reviewers, excellent material for the organic student.

Most projects have unsung heroes, and this is no exception. As a live-in editor, Dr. Elli O. Hand was a constant source of detailed critical analysis, suggestions for improvement, and ideas for additional topics. She deserves a great deal of credit. We are grateful also to those people who reviewed the manuscript in detail: Wayne Dunbar, I. C. Hisatsune, Alan Pribula, and especially Charles U. Pittman, Jr., and Joe Murphy. Finally, we would like to thank Nancie, Laura, Larry, Lance, Linda, Lisa, Alex, and Peggy—and each other for having a friendship strong enough to endure the rigors of coauthorship.

C. W. H.
H. L. B.

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Chapter 1

Introduction to the Study of Acid-Base Chemistry

1.1 WHAT IS ACID-BASE CHEMISTRY?

The area of acid-base chemistry is probably not a completely unfamiliar one. Most people, for instance, have heard that acids "turn litmus red" and know in general that acids and bases neutralize each other. However, there is no single, commonly used definition that adequately describes all the phenomena included under the heading "acid-base chemistry." The three best known approaches are the Arrhenius, the Brønsted-Lowry, and the Lewis theories. These define a *base* as a source of hydroxide ions, a proton acceptor, or an electron-pair donor, respectively, and an *acid* as a source of protons, a proton donor, or an electron-pair acceptor. Each of these theories has some limitations, and each emphasizes a different aspect of acid-base behavior. Of the three, the Lewis concept is the most widely applicable. These concepts are discussed in detail in Chapters 2 and 4.

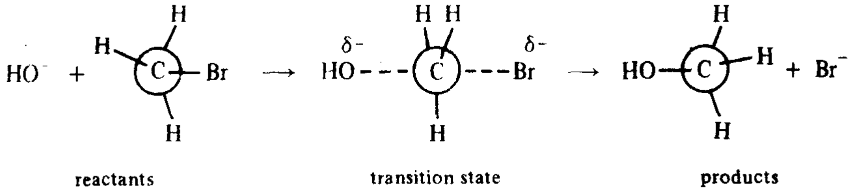
In the broadest sense, *acid-base chemistry* includes any interaction that takes place between electron-rich species (bases) and electron-poor species (acids). In this context *electron-rich* means a capability for giving up or sharing electrons with another species, and *electron-poor* means a capability for accepting or sharing electrons from another species. Many bases are negative ions or neutral molecules, and many acids are positive ions or neutral species. Free radicals and radical ions[1] are included in this definition, although radical reactions are often discussed separately from acid-base reactions. Most chemical reactions, in fact, occur between electron-rich and electron-poor species, and therefore may be categorized as acid-base reactions. The attraction and interaction between such species are discussed in detail in this text; the principles derived in the discussion give insight into *how* chemical reactions occur and aid in understanding *why* they occur.

1.2 CHEMICAL REACTIONS

In general, when a chemical reaction occurs, one or more chemical bonds are broken and/or one or more new chemical bonds are formed. Both bond breaking and bond formation are important aspects of reactions, although in most reactions these processes do not occur as separate sequential steps. There is instead a gradual, continuous transition between reactants and products; the bond-making and bond-breaking processes occur simultaneously, or nearly so. Such processes may be analyzed in terms of acid-base principles. For example, in reaction (1-1) methyl bromide (an acid) reacts with hydroxide ion (a base) to form methanol and bromide ion.

---

[1] A *free radical* is any atom or molecule containing one or more unpaired electron(s). Examples include highly reactive molecular fragments such as Cl or CH_3, as well as more stable species such as nitric oxide (NO) and molecular oxygen (O_2). A positive or negative ion having unpaired electrons is called a *radical ion*.



(1-1)

The dashed lines represent partial bonds: the Br–C bond is breaking while simultaneously the C–O bond is forming. The symbols δ− represent a partial negative charge and imply a continuous transfer of charge from oxygen to bromine. A significant portion of the driving force for this reaction can be attributed to the attraction between an electron-rich species (the oxygen atom in OH^-) and an electron-deficient species (the carbon atom in CH_3Br). If we know the relative base strength of Br^- and OH^-, we can predict the direction in which the reaction proceeds. The reaction goes to the right and not to the left because a strong (OH^-) displaces a weaker base (Br^-) from the carbon atom in CH_3Br.

If a reaction does not involve bond breaking or bond making, but rather the transfer of an electron from one species to another, it is called an *oxidation-reduction* or *redox reaction*. Since electron transfer from one species to another necessarily involves electron-rich and electron-poor species, the principles of acid-base interactions are applicable to redox reactions as well. Many reactions involving catalysts can be discussed with acid-base principles in mind. In short, acid-base concepts can be applied to most reactions; they provide a valuable tool for understanding chemical mechanisms.

1.3 BOND CLEAVAGE PROCESSES

A covalent chemical bond consists of a pair of electrons, located between and shared by two atoms. Such a bond can be broken in three ways, shown in reactions (1-2), (1-3), and (1-4).

$$\mathrm{A}{:}\mathrm{B} \longrightarrow \mathrm{A}^{+} + {:}\mathrm{B}^{-} \tag{1-2}$$

$$\mathrm{A}{:}\mathrm{B} \longrightarrow \mathrm{A}{:}^{-} + \mathrm{B}^{+} \tag{1-3}$$

$$\mathrm{A}{:}\mathrm{B} \longrightarrow \mathrm{A}\cdot + \mathrm{B}\cdot \tag{1-4}$$

The electrons of the bond remain paired in the first two of these cleavage modes and reside on one or the other of the products. This process is called *heterolytic cleavage*. In reaction (1-4), on the other hand, the bonding electrons become unpaired. One electron goes with each of the product fragments, in a process called *homolytic cleavage*. Homolytic cleavage in a neutral molecule leads to uncharged free radicals, whereas heterolytic cleavage leads to two oppositely charged ionic species.

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1.4 ENERGY AND STABILITY

It is usually helpful to think about energy relationships, because the energy absorbed or released during a process is an important factor determining whether or not the process takes place. Most spontaneous processes, including most spontaneous chemical reactions, move in the direction of decreasing energy. In such a reaction, illustrated in Figure 1.1, the products are at a lower energy than the reactants. As the reaction proceeds, the arrangement of the atoms in space changes continuously from the configuration of the reactants to the configuration of the products. The energy of the configuration rises, reaches a maximum, and then decreases again. At the energy maximum, the atoms are clustered in a configuration known as the *transition state*. The energy increase from reactants to transition state, called the *activation energy* (E_a), exerts a controlling influence on the *rate* of the reaction. The energy change from reactants to products, the *reaction energy* (ΔE_{rxn}) helps to determine the *extent* of reaction. When ΔE_{rxn} is a negative quantity, as in Figure 1.1, the reaction is *exothermic* and gives off heat to the environment. In *endothermic* reactions, ΔE_{rxn} is positive, and the reaction absorbs heat from the environment. Both reaction types are common. In an equilibrium reaction ΔE_{rxn} is usually small, although it may be either positive or negative.

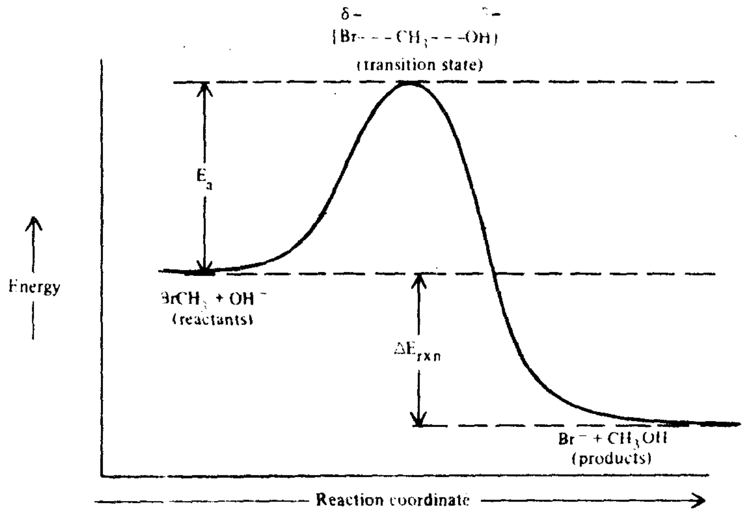

Figure 1.1 Potential energy changes during the basic hydrolysis of methyl bromide. The energy change of the reaction is indicated by ΔE_{rxn}; E_a is the energy of activation. The term "reaction coordinate" refers to the change in geometrical configuration as the seven atoms involved are transformed from the separate $BrCH_3$ and OH^- species to the separate CH_3OH and Br^- species. It does not refer to fraction of reactant species consumed.

The *stability* of a species refers to its energy. A stable species is low in energy, and a species that is more stable than another has lower energy. The stability of a species is closely related to the energy of the process in which the species was formed. A species formed in a highly exothermic reaction is in general more stable than those formed in less exothermic, thermoneutral, or endothermic reactions. The energy of the formation reaction can be divided into two components—the energy inherent in the process, and the energy resulting from interaction of the species with solvent. For example, the energies of the three possible cleavage reactions of hydrogen chloride are given in reactions (1-5), (1-6), and (1-7), in order of increasing energy. Note that the energies given are for

$$HCl(g) \longrightarrow H\cdot(g) + Cl\cdot(g) \qquad \Delta E_{rxn} = 431 \text{ kJ/mol} \tag{1-5}$$

$$HCl(g) \longrightarrow H^+(g) + Cl^-(g) \qquad \Delta E_{rxn} = 1393 \text{ kJ/mol} \tag{1-6}$$

$$HCl(g) \longrightarrow H^-(g) + Cl^+(g) \qquad \Delta E_{rxn} = 1610 \text{ kJ/mol} \tag{1-7}$$

processes taking place in the gas phase. Since there are no solvent interactions in the gas phase, these are the inherent energies of the cleavage reactions. Not one of these reactions takes place spontaneously; all involve an increase in energy. That is, H^- and Cl^+, H^+ and Cl^-, and $H\cdot$ and $Cl\cdot$ are less stable than HCl in the gas phase. Furthermore, the heterolytic reactions require more energy than the homolytic reaction, by a considerable margin: the ionic cleavage products are inherently less stable than the free radicals. When comparisons are made between gas-phase species, it is in general true that free radicals are more stable than the corresponding ions. Finally, we note that the pair (H^+, Cl^-) is more stable than the pair (H^-, Cl^+).

The relationships are different when the species are in solution. The solvent plays a crucial role, and the solvent interaction energy or *solvation energy* is usually the dominant factor. This is especially true for ions dissolved in polar solvents such as water. Solvation energies of ions in water are large, so that aqueous ionic species are quite stable. Thus although HCl shows no tendency to separate into fragments in the gas phase, it does so when dissolved in water. The dissociation reaction (1-8) is spontaneous and exothermic. The species $H^+(aq)$ and $Cl^-(aq)$ are considerably more stable than the undissociated

$$HCl(g) \longrightarrow H^+(aq) + Cl^-(aq) \qquad \Delta E_{rxn} \approx -70 \text{ kJ/mol} \tag{1-8}$$

molecule HCl. In general, a solvated species has lower energy and greater stability than it has when in the pure state.

In reactions that take place in solution, the reactant molecules as well as the product species are stabilized by interaction with the solvent. Whether the reaction is helped or hindered by the solvent hinges on whether products or reactants are stabilized more. If the products are stabilized more than the reactants, the reaction proceeds to a greater extent in solution than it would if there were no solvent present. In reaction (1-5) neither product nor reactant is charged, and therefore neither interacts particularly strongly with solvent. The reaction proceeds (or in this case fails to proceed) to about the same extent in solution as in the gas phase. Since in reaction (1-6) the products are charged, they can be stabilized considerably by solvation. When HCl is dissolved in water, reaction (1-8) proceeds essentially to completion. [Reaction (1-7) does not take place in solution, because H^- and Cl^+ are inherently much less stable than H^+ and Cl^-]. In contrast to the situation in the gas phase, ions are more stable than the corresponding free radicals when dissolved in a polar solvent such as water.

These considerations lead to a useful general rule. Processes involving ions are facilitated in polar solvents, even though the *inherent* stability of ions is less than that of free radicals. In nonpolar solvents no special stabilization is available for charged species, and the greater inherent stability of free radicals facilitates free-radical processes compared to ionic processes.

A cleavage reaction is usually not the final step, however, as the product fragments may undergo further reaction with other species present in solution. Consider the heterolytic cleavage of a molecule A–B, which forms ions according to reaction (1-9):

$$A{-}B \rightleftharpoons A^+ + B^- \qquad (1\text{-}9)$$

The subsequent reactions of A^+ and B^- to form the final products [reactions (1-10) and (1-11)], should be considered according to acid-base principles. The interaction of A^+ with reagent_1 depends on the electron-rich nature, that is, the basicity, of reagent_1.

$$A^+ + \text{reagent}_1 \longrightarrow \text{product}_1 \qquad (1\text{-}10)$$

$$B^- + \text{reagent}_2 \longrightarrow \text{product}_2 \qquad (1\text{-}11)$$

Similarly, the reaction of B^- depends on the electron-poor nature of reagent_2. Acid-base principles are useful tools for understanding both of these processes.

1.5 IMPORTANCE OF ACID-BASE CHEMISTRY

Perhaps the most significant feature of this introduction is the idea that acid-base principles have broad applicability in chemical thinking. Most chemical interactions occur between electron-rich and electron-poor species, and can be discussed in terms of the tendency to acquire or release electrons. It is both possible and useful to extend the reach of acid-base thinking to such topics as inorganic, organic, and biochemical (enzymatic) catalysis; oxidation-reduction reactions; and free-radical reactions.

Chapter 2

General Concepts of Acids and Bases

2.1 HISTORICAL BACKGROUND

Many different kinds of acids and bases have been known for centuries. The name *acid* is derived from the Latin *acidus*, which means sour, and describes the characteristic taste of acids. The terms *alkali* and *alkaline*, which refer to inorganic bases, are derived from the Arabic word *al-qili* (meaning "ashes of a plant"; a related English word is "potash"[1]).

Perhaps the earliest known acidic substance was vinegar, which the ancient Egyptians produced by exposing wine to air. When treated in this way, wine can contain as much as 3 to 6% acid. We now know that acetic acid is formed by the air oxidation of ethyl alcohol, one of the constituents of wine, and that bacteria present in fermenting fruit juices produce an enzyme that catalyzes the oxidation. During the Middle Ages, the alchemists first prepared the strongly acidic substances nitric acid, hydrochloric acid, and sulfuric acid. The acid *aqua regia* was prepared by mixing hydrochloric acid and nitric acid. The Latin name means "royal water," so called because of its ability to dissolve the precious metals platinum, silver, and gold.

The base potash, obtained by slowly leaching wood ashes with water, has been used for centuries in the manufacture of soap. The base calcium oxide (CaO) can be prepared by roasting ground seashells, which consist largely of calcium carbonate, $CaCO_3$ [reaction (2-1)]. Calcium oxide is sometimes referred to as "quicklime" or "unslaked lime" and can be converted to "slaked lime" by the addition of water [reaction (2-2)].

$$CaCO_3 \xrightarrow{\text{heat}} CaO + CO_2 \qquad (2\text{-}1)$$

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

As the scope of activity in chemistry grew, so did the understanding of these compounds and their properties. It was known even in medieval times that if acidic and basic substances were mixed, a solution was produced which had neither the characteristic properties of acids nor those of bases. Acids and bases were said to *neutralize* each other. This was an important discovery, and attempts were made to classify *all* chemicals as either acids or bases. It was hoped that all of chemistry could be understood in terms of acid-base interactions. Robert Boyle, who lived in the seventeenth century, was among the first to realize that all materials were not either acids or bases; his experiments proved that many materials do not fit into either category.

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[1] The term *potash* is not precisely defined in the chemical sense; it can refer to potassium oxide, potassium hydroxide, or potassium carbonate. All three of these substances are bases.

The fact that all acids exhibit certain similar physical and chemical properties prompted a search for the *acidifying principle,* believed to be a substance common to all acids. An important early theory of acids was proposed by Antoine Lavoisier (1743-1794). He thought that the acidifying principle was oxygen, that is, that all acids must contain oxygen. Hydrochloric acid (HCl), which was known at the time, contains no oxygen and should therefore have disproved the theory. However, the element chlorine had not yet been discovered and Lavoisier thought that the chlorine part of the molecule was really a mixture of elements, one of which was oxygen. Chemists of the time generally supported the oxygen theory; not until much later was it realized that Lavoisier's idea was incorrect.

The successor to Lavoisier's theory was the *hydrogen theory of acids*, in which the acidifying principle was identified as hydrogen rather than oxygen. The work of Humphry Davy in the early nineteenth century presented convincing evidence against Lavoisier's theory. Davy established that hydrochloric acid did not contain oxygen, but only hydrogen and chlorine. The work of Justus von Liebig and Jon Jakob Berzelius also provided support for the hydrogen theory. In the late nineteenth century Svante Arrhenius developed his theory (Section 2.3), which is accepted today as essentially correct, although limfted in scope.

2.2 PROPERTIES OF ACIDS AND BASES

Early chemists classified substances as either acids or bases according to the chemical and physical properties of their aqueous solutions.

Acids are substances which:

1. Have a sour taste.
2. React with many metals to liberate a flammable gas (hydrogen), and with limestone and some other minerals to produce a nonflammable gas (carbon dioxide).
3. Change the color of litmus (a vegetable dye) from blue to red.
4. Cause inflammation of the skin, or severe burns if the acid is concentrated.
5. Conduct electricity.
6. React with bases, causing the disappearance of acidic as well as basic properties.

Bases are substances which:

1. Have a slippery or soapy feel.
2. Have a bitter taste.
3. Change the color of litmus from red to blue.
4. Cause inflammation of the skin, or severe burns if the base is concentrated.
5. Conduct electricity.
6. React with acids, causing the disappearance of basic as well as acidic properties.

2.3 ARRHENIUS'S CONCEPT

The first modern approach to acid-base chemistry was offered in 1887 by Svante Arrhenius. His ideas evolved from his doctoral work on the electrical conductance of solutions, particularly of acid solutions. The prevailing belief at the time was that the passage of an electric current creates charged species, called *ions,* in solutions of certain substances. In contrast, Arrhenius suggested that ions exist in solutions even in the absence of an electric current. Specifically, he proposed that certain substances, as they dissolve in water, *dissociate* spontaneously into positive and negative ions. Arrhenius defined an acid as a substance capable of producing hydrogen ions (protons) by dissociation in water solution, according to reaction (2-3). In this reaction A refers to the remainder of the molecule (i.e., to all parts other than hydrogen). We use this notation throughout the text.

$$HA \xrightarrow{H_2O\ (\text{solvent})} H^+ + A^- \qquad (2\text{-}3)$$

The theory provides a satisfactory explanation of the fact that all acid solutions have similar properties. Acidic properties, according to Arrhenius, are due entirely to H^+, which is present in all acids. He defined a base as a substance capable of producing hydroxide ions by dissociation in water solution. This is illustrated in reaction (2-4), in

$$MOH \xrightarrow{H_2O\ (\text{solvent})} M^+ + OH^- \qquad (2\text{-}4)$$

which M refers to all parts of the base except OH. Basic properties are attributed to hydroxide ion, which is present in all solutions of bases. *Neutralization,* which causes the disappearance of both acidic and basic properties, results from the reaction of a proton and a hydroxide ion to produce a molecule of water:

$$H^+ + OH^- \longrightarrow H_2O \qquad (2\text{-}5)$$

Although the Arrhenius acid-base theory is generally useful, there are two features that restrict its use. One limitation arises from the fact that the theory requires dissociation into ions prior to undergoing any characteristic reaction of acids or bases. Since, for example, the gas-phase reaction (2-6) between hydrochloric acid and ammonia takes

$$HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s) \qquad (2\text{-}6)$$

place without dissociation into ions, it cannot be regarded as a neutralization reaction in the framework of Arrhenius theory. This is in spite of the fact that HCl has all the properties of acids, NH_3 has all the properties of bases, and NH_4Cl has the properties of neither. Furthermore, there are many commonly used solvents in which dissociation does not occur. Arrhenius theory does not permit us to regard as an acid-base reaction any interaction taking place in such a solvent.

A second limitation is that the theory does not explain why some substances, such as $AlCl_3$, have acidic properties and yet lack hydrogen, and some substances, such as NH_3, lack hydroxide and yet have basic properties. As examples, consider the compounds ammonia, sodium amide ($NaNH_2$), and sodium carbonate (Na_2CO_3). All these materials

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