

Reactions in Solutions

There are many gaseous materials that react, and there are a large number of reactions that take place in the solid state. In spite of this, most chemical reactions are carried out in solutions, with a large fraction of chemistry taking place in aqueous solutions. The study of chemical kinetics must, of necessity, include a consideration of the nature of solutions and the role of the solvent in chemical processes. However, before one undertakes a description of the effects of the solvent on a reaction, it is necessary to describe some of the characteristics of liquids and solutions.

5.1 THE NATURE OF LIQUIDS

It is a relatively simple process to model many aspects of the behavior of most gases satisfactorily (except at high pressure or low temperature) using kinetic theory. For many gases, the interactions between molecules can even be ignored. The interactions between ions in ionic solids are adequately treated using Coulomb's law because the interactions are electrostatic in nature. While molecular motions in gases are random, solids have units (ions, atoms, or molecules) that are localized to fixed positions except for vibrations. Part of the problem in dealing with the liquid state is that there are intermolecular forces that are too strong to ignore, but that are not strong enough to restrict molecular motion completely. There is some local structure that results in clusters of molecules, but there is rather extensive interchange between clusters. This view of the nature of a liquid has sometimes been called the *significant structure theory* of liquids, although this term is not as frequently encountered today.

While the problem of dealing with structure and order in the liquid state is very difficult, an associated problem is that of which force law to use to

describe the intermolecular interactions. Overall, the molecules are neutral, but there may be charge separations within the molecules. Therefore, dipole-dipole forces may be the dominant type of interaction between the molecules of some liquids. On the other hand, molecules such as CCl_4 are nonpolar, so there must be an other type of force responsible for the properties of the liquid. Because the interactions between molecules in liquids provide a basis for describing the nature of solutions, we will begin this chapter with a brief discussion of intermolecular forces.

5.1.1 Intermolecular Forces

If a diatomic molecule is composed of two atoms having different electronegativities, the molecule will be polar. The shared electrons will spend a greater fraction of time in the vicinity of the atom having the higher electronegativity (CO is an exception). A measure of this charge separation is μ , the *dipole moment*, which is defined by the relationship

$$\mu = q \cdot r \quad (5.1)$$

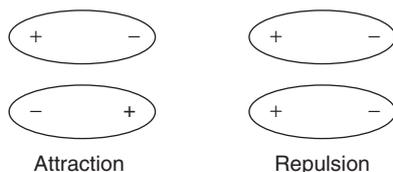
where q is the quantity of charge separated and r is the distance of separation. The quantity of charge separated will be a fraction of the electron charge (4.8×10^{-10} esu or 1.6×10^{-19} C), and the distance of separation will be on the order of 10^{-8} cm. Therefore, $q \cdot r$ will be on the order of 10^{-18} esu · cm, and it is convenient to measure μ in units of this size. This unit is known as 1 Debye in honor of Peter Debye, who did a great deal of work on polar molecules. Therefore, 10^{-18} esu · cm = 1 Debye (abbreviated as D), and these units are frequently encountered. However, when the standard units of coulombs and meters are used for charges and distances, $1 \text{ D} = 3.33 \times 10^{-30}$ C m.

In 1912, Keesom considered polar molecules to be assemblies of charges, although there is no *net* charge. The assembly of positive and negative charges generates an electric field that depends on the distribution of charge within the molecule. The potential energy of the interaction of the dipoles depends on their orientations. For two polar molecules having dipole moments μ_1 and μ_2 , the interaction energy is given by

$$E_D = -\frac{\mu_1 \mu_2}{r^3} (2 \cos \theta_1 \cos \theta_2 - \sin \phi_1 \sin \phi_2 \cos (\phi_1 - \phi_2)) \quad (5.2)$$

where θ_1 , θ_2 , ϕ_1 , and ϕ_2 are the angular coordinates (in polar coordinates) giving the orientations of the two dipoles, and r is the average distance of

separation. The extremes of interaction (orientation) of two dipoles can be shown as



These two extremes give rise to factors of $+2$ and -2 for repulsion and attraction, respectively. However, there is an effect of thermal energy that prevents all of the molecules from populating the lower energy (attraction) state. The two states of unequal energy will be populated according to the Boltzmann Distribution Law. At sufficiently high temperature, the attraction is completely overcome, and the orientation of the dipoles is random. If all possible orientations between these two extremes are considered, no net attraction results. At intermediate temperatures, there is a greater population of the orientation leading to attraction, which results in some *average* preferred orientation, and a net attraction results. The orientation energy, ΔE , involves a Boltzmann population of two states of different energy, and it is, therefore, temperature dependent. It involves a factor of $e^{-E/kT}$ where \mathbf{k} is Boltzmann's constant (written here in bold to distinguish it from a rate constant). It can be shown that this energy varies as μ^2/r^3 , and assuming that ΔE is $< kT$, the equation that describes the energy of interaction of two molecules having dipole moments μ_1 and μ_2 can be written as

$$E_D = -\frac{2\mu_1^2\mu_2^2}{3r^6\mathbf{k}T} \quad (5.3)$$

If the two dipoles are identical, $\mu_1 = \mu_2$ and the equation reduces to

$$E_D = -\frac{2\mu^4}{3r^6\mathbf{k}T} \quad (5.4)$$

If the energy per mole is considered, \mathbf{k} is replaced by R since \mathbf{k} is R/N_o where N_o is Avogadro's number and R is the molar gas constant.

In solutions containing solutes consisting of polar molecules, the solvent strongly affects the association of the dipoles. In general, if the solvent has low polarity and/or dielectric constant, the dipoles will be more strongly associated. If the solvent is also polar, it is likely that the solvation of each polar solute molecule will be strong enough that solute molecules will be

unable to interact with each other. In other words, the interaction between molecules of the solute and solvent will compete with interactions between the solute molecules. Thus, the association of a polar solute can be shown as



for which the equilibrium constant $K = [D_2]/[D]^2$ will be strongly solvent dependent. In the same way that interactions between ions are governed by Coulomb's law, the dielectric constant of the solvent will affect the attraction between dipoles. Species that are of extreme difference in polarity may not be completely miscible owing to each type of molecule interacting strongly with molecules of its own kind. Although they are weak compared to chemical bonds, dipole-dipole forces are of considerable importance in determining chemical properties.

A permanent dipole, $\mu = q \times r$ can induce a charge separation in a neighboring nonpolar molecule that is proportional to the polarizability of the molecule. If the polarizability of the molecule is represented as α , the energy of the interaction between the permanent dipole and the nonpolar molecule with an induced dipole moment can be expressed as

$$E_I = -\frac{2\alpha\mu^2}{r^6} \quad (5.6)$$

These forces between polar molecules and those having a dipole induced in them are called *dipole-induced dipole forces*, and they are essentially temperature independent.

It should be apparent that there must be *some* force between molecules that are nonpolar because CH_4 , He, CO_2 , and similar molecules can be liquefied. These forces must also be electrical in nature but cannot be the result of an overall charge separation within the molecules. If we consider two helium atoms as shown in Figure 5.1, it is possible that at some instant both of the electrons in one atom will be on the same side of the atom. There is an *instantaneous* dipole that will cause an instantaneous change in

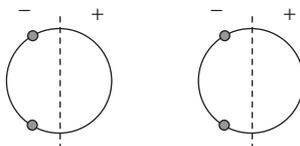


FIGURE 5.1 Two helium atoms showing the instantaneous dipoles that result in a weak force of attraction.

the electron distribution in the neighboring atom. There will exist, then, a weak force of attraction between the two atoms. Such forces between instantaneous dipoles are the *London forces* (sometimes called *dispersion forces*). They can be considered as weak forces between the nuclei in one molecule and the electrons in another.

The energy of interaction of molecules by London forces can be described by the equation

$$E_L = -\frac{3h\nu_0\alpha^2}{4r^6} \quad (5.7)$$

where ν_0 is the frequency of the zero-point vibration and α is the polarizability of the molecule. Because $h\nu_0$ is approximately equal to the ionization energy of the molecule, I, Eq. (5.7) becomes

$$E_L = -\frac{3I\alpha^2}{4r^6} \quad (5.8)$$

If two different types of molecules are involved in the interaction, the energy is

$$E_L = -\frac{3}{2} \frac{h\alpha_1\alpha_2\nu_1\nu_2}{r^6(\nu_1 + \nu_2)} \quad (5.9)$$

When expressed in terms of the ionization potentials, this equation can be written as

$$E_L = -\frac{3}{2} \frac{I_1I_2\alpha_1\alpha_2}{r^6(I_1 + I_2)} \quad (5.10)$$

Although it may be somewhat surprising, many molecules of greatly differing structures have ionization potentials that are approximately the same. The examples shown in Table 5.1 include molecules of many types, but the ionization potentials do not vary much. Therefore, the product of I_1 and I_2 is sometimes replaced by a constant.

TABLE 5.1 Ionization Potentials for Selected Molecules.

Molecule	I.P. (ev)	Molecule	I.P. (ev)
Acetone	9.69	Methanol	10.85
Benzene	9.24	3-Methylpentane	10.06
n-Butane	10.63	Pyrazine	10.00
1,4-Dioxane	9.13	Sulfur dioxide	11.7

Slater and Kirkwood have derived an expression for the London energy that makes use of the number of outermost electrons in the molecule. This is possible because the polarizability of the electrons in a molecule is generally dependent on the number of electrons present. The expression derived by Slater and Kirkwood can be written as

$$E_L = -\frac{3he\alpha^2}{8\pi r^6 m^{1/2}} \left(\frac{n}{\alpha}\right)^2 \quad (5.11)$$

where e is the charge on the electron, n is the number of electrons in the outermost shell, and m is the mass of the electron.

Because the London attraction energy depends on the magnitude of α , it shows a general relationship to molecular size and number of electrons. For example, the boiling point of a liquid involves the separation of molecules from their nearest neighbors. Thus, the boiling points of a given series of compounds (e.g., the hydrocarbons, C_nH_{2n+2}) show a general increase in boiling point as n (and, hence, α) increases. Similarly, the halogens reflect this trend with F_2 and Cl_2 being gases at room temperature while Br_2 is a liquid, and I_2 is a solid. All are nonpolar, but the number of electrons increases for the series, and the polarizability depends on the ability to distort the electron cloud of the molecule. Generally, the polarizability of molecules increases as the number of electrons increases, but it is important to note that molecules that have delocalized electron density have mobile electrons. Such electron clouds can be distorted, which gives rise to a larger polarizability. These effects are generally reflected in the boiling points of the liquids. Because of this, the boiling point of benzene (C_6H_6 , a total of 42 electrons and a molecular weight of 78) is very close to that of carbon tetrachloride (CCl_4 , a total of 74 electrons and a molecular weight of 154). Both are nonpolar, but the π -electron system in benzene results in a relatively large polarizability while the electrons in the CCl_4 molecule are more localized.

It is also important to note that London forces also play an important role in contributing to the overall stability of crystal lattices. Even though the dominant force is the Coulombic force between oppositely charged ions, the London forces are significant in the case of large, polarizable (*soft* in terms of the hard-soft interaction principle) ions. For example, in AgI the Coulombic attraction is 808 kJ/mol and the London attraction amounts to 128.7 kJ/mol. As expected, London forces are much less important for crystals like NaF because the ions are much less polarizable. Because the London energy varies as $1/r^6$, the force decreases rapidly as r increases, and only the interactions between nearest neighbors are significant.

Various equations have been used to represent the repulsion that also exists between molecules when they are separated by short distances. One such equation is

$$E_r = a e^{-br} \quad (5.12)$$

where a and b are constants. One type of potential function that includes both attraction and repulsion is known as the Mie potential, which is represented by

$$E = \frac{A}{r^n} - \frac{B}{r^m} \quad (5.13)$$

where A , B , m , and n are constants. The repulsion (positive) term is often written as

$$E_r = \frac{j}{r^n} \quad (5.14)$$

where j is a constant and n has values that range from 9 to 12. The Lennard–Jones potential combines this form with a term involving $1/r^6$ for the attraction and usually uses $n = 12$ as the exponent in the repulsion term. The resulting equation is

$$E = \frac{j}{r^{12}} - \frac{k}{r^6} \quad (5.15)$$

where j and k are constants, and is referred to as the “6–12” or Lennard–Jones potential. The discussion presented here should show that London forces are important in determining properties of liquids and are significant in certain types of crystals. We can also see that there are several ways of expressing the interaction energies mathematically. In some of the discussions presented in later sections of this book, we will have opportunities to make use of qualitative applications of the ideas presented here.

5.1.2 The Solubility Parameter

It is intuitively obvious that a liquid has a certain amount of cohesion that holds the liquid together. It should also be apparent that the energy with which the liquid is held together is related to the heat necessary to vaporize it, which separates the molecules. In fact, the cohesion energy, E_c , is given by

$$E_c = \Delta H_v - RT \quad (5.16)$$

The work done as the vapor expands against the external (atmospheric) pressure is $P \Delta V$. The quantity E_c/V , where V is the molar volume, is called the *cohesion energy density* because it is the cohesion energy per unit volume. A basic thermodynamic relationship,

$$\Delta E = T \, dS - P \, dV \quad (5.17)$$

provides a way of interpreting the cohesion energy. From Eq. (5.17), we obtain

$$\frac{\partial E}{\partial V} = T \left(\frac{\partial S}{\partial V} \right)_T - P = T \left(\frac{\partial P}{\partial T} \right)_V - P \quad (5.18)$$

where P is the *external pressure*. The *internal pressure* is given by

$$P_i = T \left(\frac{\partial P}{\partial T} \right)_V \quad (5.19)$$

However, we can also express the change in pressure with temperature at constant volume by making use of a well-known thermodynamic relationship,

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{\left(\frac{\partial V}{\partial T} \right)_P}{\left(\frac{\partial V}{\partial P} \right)_T} \quad (5.20)$$

The numerator on the right-hand side of this equation represents the coefficient of thermal expansion, α . The denominator of the equation represents the change in volume with pressure at constant temperature, which is the coefficient of compressibility, β . Therefore, the internal pressure is given by

$$P_i = T \frac{\alpha}{\beta} \quad (5.21)$$

For most liquids, the internal pressure ranges from 2000 to 8000 atm. As we will see, this has important ramifications with regard to the formation of transition states in which there is a volume change. From the foregoing development, we can now write the cohesion energy as

$$E_c = P_i - P \approx P_i \quad (5.22)$$

because the internal pressure is normally much greater than the external pressure, $P_i \gg P$. In a general way, the cohesion energy and internal pressure reflect the strength of intermolecular interactions in the liquid.

The cohesion energy (*energy* of vaporization) per unit volume is obtained from E_c/V , where V is the molar volume. It can be shown that if two liquids have the same value of E_c/V , the heat of mixing is zero because they form an ideal solution. If the E_c/V values are not equal, the heat of mixing will be positive (the solution will be nonideal). However, in developing the theory of solutions, the quantity $(E_c/V)^{1/2}$ is often encountered. This quantity is known as the *solubility parameter*, δ . The solubility parameter is given in $(\text{cal}/\text{cm}^3)^{1/2}$ or in $(\text{J}/\text{cm}^3)^{1/2}$. The unit of $1 \text{ cal}^{1/2}/\text{cm}^{3/2}$ is called 1 Hildebrand, (h) in honor of Joel Hildebrand who did extensive work on the nature of solutions. Table 5.2 shows solubility parameters for several common solvents. It can be seen that the values for δ range from about 7 $(\text{cal}/\text{cm}^3)^{1/2}$ for hexane (in which only London forces exist) to about 4 times that value for a strongly associated liquid such as water where there are hydrogen bonding, dipole-dipole, and London forces.

Since the cohesion energy is given by the relationship

$$E_c = \Delta H_v - RT \quad (5.23)$$

TABLE 5.2 Solubility Parameters for Selected Liquids.

Liquid	Solubility parameter (h)	Liquid	Solubility parameter (h)
<i>n</i> -C ₆ H ₁₄	7.3	CS ₂	10.0
<i>n</i> -C ₇ H ₁₆	7.5	CH ₃ CN	11.9
(C ₂ H ₅) ₂ O	7.66	Br ₂	11.5
<i>cyclo</i> -C ₆ H ₁₂	8.2	C ₃ H ₈ CN	20.0
CCl ₄	8.6	CH ₃ NO ₂	12.6
C ₆ H ₆	9.1	C ₆ H ₅ NO ₂	11.6
C ₆ H ₅ CH ₃	8.9	CH ₃ COOH	10.4
Tetrahydrofuran	9.5	<i>o</i> -C ₆ H ₄ (CH ₃) ₂	8.84
CHCl ₃	9.3	CH ₂ Cl ₂	9.9
CH ₃ COOC ₂ H ₅	9.0	HCON(CH ₃) ₂	12.1
CHCl ₃	9.3	C ₂ H ₅ OH	12.7
(CH ₃) ₂ CO	9.76	CH ₃ OH	14.5
1,4-dioxane	10.0	C ₆ H ₅ CN	9.7
HOC ₂ H ₄ OH	16.1	H ₂ O	26.0

we can calculate it when ΔH_v is known. Values for the heat of vaporization of many liquids are tabulated in handbooks. However, the heat of vaporization can be obtained by using the relationship

$$\frac{d \ln P}{d(1/T)} = \Delta H_v \quad (5.24)$$

if we have the vapor pressure expressed as a function of temperature. Although there are many equations that have been used to relate vapor pressure to temperature, one of the most convenient for this use is the Antoine equation,

$$\log P = A - \frac{B}{C + t} \quad (5.25)$$

where A , B , and C are constants characteristic of the liquid and t is the temperature in $^{\circ}\text{C}$. Antoine constants have been tabulated for a large number of liquids. However, if the vapor pressure of a liquid is known as several temperatures, the Antoine constants can be calculated. Using the Antoine equation and Eqs. (5.23) and (5.24), we find that the cohesion energy can be expressed as (the -1 term inside the parentheses provides for a subtraction of RT to correct for expansion work against atmospheric pressure)

$$E_c = RT \left(\frac{2.303BT}{(C + t)^2} - 1 \right) \quad (5.26)$$

Therefore, having determined the cohesion energy, the solubility parameter can be calculated if the molar volume is known. Calculating the molar volume requires knowing the density of the liquid at the desired temperature, and the density data are usually available for most liquids. If the density, ρ , at the desired temperature is unavailable but it is available at other temperatures, the data can be fitted to the equation

$$\rho = a + bT + cT^2 \quad (5.27)$$

and the constants a , b , and c can be evaluated using a least squares method. The calculated density at the desired temperature and the molar volume can then be determined.

The cohesion of mixed solvents can be calculated by making use of the sum of the contributions of each component. Those individual contributions are determined by the product of the solubility parameter of each liquid multiplied by the mole fraction of that component. The sum of the individual contributions gives the solubility parameter for the solution.

Because the solubility parameter reflects the intermolecular forces in a liquid, it is a very useful parameter. The total interaction between molecules in a liquid may be the result of dipole-dipole, London, and hydrogen-bonding interactions. Therefore, it is possible to separate the contributions from each type of interaction and express the solubility parameter as though it were a vector sum. The result is

$$\delta^2 = \delta_L^2 + \delta_D^2 + \delta_H^2 \quad (5.28)$$

where δ_D , δ_L , and δ_H are contributions to the solubility parameter from dipole-dipole, London, and hydrogen-bonding interactions, respectively.

5.1.3 Solvation of Ions and Molecules

When an ionic compound dissolves in a polar solvent such as water, the ions become strongly solvated. The ion-dipole forces produce a layer of solvent molecules (the primary solvation sphere) surrounding each ion. This layer can cause other solvent molecules in the immediate vicinity to become oriented as well. Although the primary solvation sphere may seem to be rather firmly attached to the ion, there is considerable interchange between these molecules and the bulk solvent in a dynamic process in most cases. For strongly solvated ions like $[\text{Cr}(\text{H}_2\text{O}_6)]^{3+}$, the exchange of coordinated water molecules and those of the bulk solvent is very slow. As we shall describe later, some desolvation of ionic species may be required before a reaction of the ion can take place.

The nature of solvated species is often an important consideration. For example, the symbol for the solvated proton in acidic solutions is written as H_3O^+ , but the H^+ is solvated by more than one water molecule. In fact, the predominant species is probably H_9O_4^+ , which is $\text{H}^+ \cdot 4\text{H}_2\text{O}$, and this ion has been identified in vapors above concentrated acids as well as a cation in solids, so it has some stability. Other species (e.g., H_7O_3^+ , which is H^+ solvated by three H_2O molecules) can also exist in equilibrium with H_9O_4^+ . In general, the average number of water molecules solvating an ion depends on the concentration of the ion in the solution as well as the size and charge of the ion.

Theoretical treatment of the solvation of ions is quite difficult. If we could use a simple electrostatic approach in which polar molecules interact with a charged ion, the problem would be much simpler. However, the fact that the polar solvent molecules interact with an ion causes their

character to change somewhat, and the polarity of the molecules is increased due to the induced charge separation resulting from the ion-dipole forces. Consequently, solvent molecules that are bound to an ion have a different dipole moment and dielectric constant from the bulk of the solvent. Moreover, the magnitude of the changes depends on the nature of the ion being solvated. The bound solvent molecules are essentially restricted in their ability to respond to an applied electric field, which is the phenomenon that provides the basis for measuring the electrical properties of the solvent. Therefore, the dielectric constant of the water attached to an ion is smaller than that of the bulk solvent.

When an electrostatic approach to the interaction between an ion and a polar solvent is used and the dielectric constant, ϵ , is assumed to be the same as the bulk solvent, the free energy of hydration (ΔG_h) of an ion of radius r can be shown to be

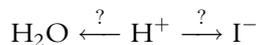
$$\Delta G_h = -\frac{N_o Z^2 e^2}{2r} \left(1 - \frac{1}{\epsilon}\right) \quad (5.29)$$

where Z is the charge on the ion, e is the charge on the electron, and N_o is Avogadro's number. However, agreement between calculated and experimental values of ΔG_h is usually poor. One way around this is to use an "effective" ionic radius, which is the radius of the ion plus the radius of a water molecule (about 0.75 Å or 75 nm). Another way to improve the calculation is to correct for the change in the dielectric constant that occurs when water surrounds an ion. When this approach is used, the dielectric constant is expressed as a function of the ionic radius. This is done because smaller, more highly charged ions are more strongly solvated and restrict the motion of the water molecules to a greater extent. The effective dielectric constant of a liquid changes around an ion in solution, and the higher the charge on the ion, the greater the change. This effect occurs because the dielectric constant is a measure of the ability of a molecule to orient itself in aligning with an applied electric field. Because the solvent molecules become strongly attached to an ion, they have a reduced ability to orient themselves in the electric field, so the dielectric constant is smaller than it is for the bulk solvent. Consequently, the reduction in dielectric constant is greater the closer the solvent molecules get to the ion and the higher the charge on the ion. The principles related to solvation are important in interpreting the role of the solvent in kinetic studies because solvation of both reactants and the transition state must be considered.

5.1.4 The Hard-Soft Interaction Principle (HSIP)

We have already alluded to one of the most useful and pervasive principles in all of chemistry, that being the hard-soft interaction principle (HSIP). This principle relates to many areas, but it is most directly applicable to interactions in which there is electron pair donation and acceptance (Lewis acid-base interactions). The terms *hard* and *soft* relate essentially to the polarizability of the interacting species. For example, I^- has a large size, so its electron cloud is much more distortable than that of F^- . Likewise, Hg^{2+} is a large metal ion having a low charge, while Be^{2+} is a very small ion. The result is that Hg^{2+} is considered to be a soft Lewis acid while Be^{2+} is considered to be a hard Lewis acid. As a result of these characteristics, Hg^{2+} interacts preferentially with I^- rather than F^- , while Be^{2+} interacts preferentially with F^- . The hard-soft interaction principle indicates that *species of similar electronic character (hard or soft) interact best*. It does *not* say that hard Lewis acids will *not* interact with soft Lewis bases, but the interaction is *more favorable* when the acid and base are similar in hard-soft character.

The applications of the hard-soft interaction principle are numerous. For example, if we consider the potential interaction of H^+ with either H_2O or I^- , where does H^+ go?



We find that H^+ , being a hard acid (electron pair acceptor), interacts preferentially with a pair of electrons in a small orbital on the oxygen atom rather than the pair of electrons in a large orbital on I^- . Accordingly, HI is completely ionized in dilute aqueous solutions as a result of the protons being transferred to H_2O . However, it must be emphasized that such a proton transfer from HI to H_2O is energetically unfavorable in the gas phase. The extremely high heat of solvation of H^+ makes this reaction take place in solutions, so the process is not quite as simple as shown earlier.

If we consider the competition between F^- and H_2O for H^+ ,



we find that the pairs of electrons on F^- and those on the oxygen atom in a water molecule are contained in orbitals of similar size. Furthermore, the negative charge on the F^- increases the attraction between H^+ and F^- . As a result, in aqueous solution, H^+ interacts more strongly with F^- than with H_2O , and, therefore, HF ionizes only slightly in water and behaves as a weak acid. Further, if we consider the complex formed between Pt^{2+}

(low charge, large size, soft electron pair acceptor) and SCN^- , it is found that the bonding is $\text{Pt}^{2+}-\text{SCN}$. The complex of Cr^{3+} (small size, high charge, hard electron pair acceptor) has the bonding arrangement $\text{Cr}^{3+}-\text{NCS}$. These results arise because the sulfur end of SCN^- is considered to be a soft electron pair donor, while the nitrogen end behaves as a hard electron pair donor.

The primary reason for discussing the hard-soft interaction principle at this time is because of its usefulness in dealing with solubility and solvation. Certainly, the principle “like dissolves like” has been known for a very long time. We will mention here only a few aspects of the HSIP and its relationship to solubility. As an example, we can consider that NaCl is essentially insoluble in nitrobenzene ($\mu = 4.27\text{D}$). Even though nitrobenzene is quite polar, it can not solvate ions like Na^+ or Cl^- because of the size of the molecules. It is polar, but μ depends on both the quantity of charge separated and the distance of separation. Since nitrobenzene is a large molecule, its size causes the dipole moment to be large, but it also limits the ability of the molecules to solvate small ions.

The solubility of NaCl in water and alcohols also shows an interesting trend and allows us to see the effects of solvent properties. The relevant data are shown in Table 5.3. As the size of the solvent molecules increases and the dielectric constant decreases, the solubility of NaCl decreases. The size and character of the alkyl group becomes dominant over that of the polar OH group. Accordingly, the solubility of ionic solids such as NaCl decreases with increasing size of the alkyl group.

It has long been known (and utilized) that liquid SO_2 will dissolve aromatic hydrocarbons. The resonance structures for SO_2 can be shown as

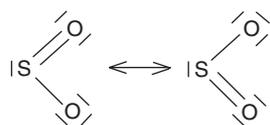


TABLE 5.3 Solubility of NaCl in Water and Alcohols.

Solvent	H_2O	CH_3OH	$\text{C}_2\text{H}_5\text{OH}$	$n\text{-C}_3\text{H}_7\text{OH}$
Solubility, mole percent	10.0	0.772	0.115	0.00446
Dipole moment, D	1.84	1.66	1.66	1.68
Dielectric constant, ϵ	78.5	24.6	20.1	18.3

and they show that the molecule has delocalized electron density due to the π -bonding. There is also delocalized electron density in aromatic hydrocarbon molecules. Therefore, the similarity between the electronic character of SO_2 and aromatic hydrocarbon molecules results in the hydrocarbons being soluble in liquid SO_2 . In contrast, aliphatic hydrocarbons are essentially insoluble in liquid SO_2 , so the difference in solubility allows aliphatic and aromatic hydrocarbons to be separated by an extraction process using liquid SO_2 as the solvent.

While we have barely introduced the applications of the HSIP (often referred to as HSAB when acid-base chemistry is the focus), the suggested readings at the end of this chapter can be consulted for additional details. A great deal of what will be discussed later about the solvation of reactants and transition states can be reduced to applications of this very important and versatile principle, which was first systematized by Ralph G. Pearson in the 1960s.

5.2 EFFECTS OF SOLVENT POLARITY ON RATES

We have already described briefly some of the effects of dipole-dipole association. For example, the more strongly solvated an ion or molecule is, the more difficult it is for desolvation to occur so that an active site is exposed. Reactions in which ions are *produced* as the transition state forms from reactants will usually *be accelerated as the solvent dielectric constant and dipole moment increase for a series of solvents*. The increased solvation of the ions that constitute the transition state will cause this effect. In contrast, *reactions that involve the combination of ions to produce a transition state of low charge will be retarded by solvents that strongly solvate ions*. In order for the ions to combine, they must be separated from the solvent molecules, which is energetically unfavorable.

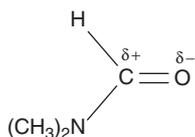
It is generally true that the formation of a transition state involves some change in the distribution of charges in the reactants. Neutral molecules frequently have charge separations induced (see Section 1.5.3), but in other cases forming a transition state during the reaction of ionic species involves cancellation or rearrangement of some portion of the charges.

An early attempt to explain these factors was put forth by Sir Christopher Ingold and his coworkers in 1935. The cases considered involve *charge neutralization* as positive and negative ions react and *charge dispersion* as a

positive or negative ion has part or all of its charge spread over the transition state. In cases involving charge neutralization, the rate of the reaction *decreases* when the reaction is carried out in a series of solvents of *increasing* polarity. It is more favorable energetically for the ions to remain separated and solvated by the polar solvent than to form a transition state that has the charges dispersed or cancelled.

On the other hand, a reaction in which a molecule having a symmetric charge distribution forms a transition state having some charge separation will have a rate that *increases* with solvent polarity. As the charged regions are formed, they interact favorably with the polar molecules of the solvent. This is sometimes referred to as *solvent-assisted formation of the transition state*. It must be remembered, however, that dipole moment alone is not always a good predictor of solvent behavior toward ions. For example, nitrobenzene is quite polar, but it is a very poor solvent for materials containing small ions (e.g., NaCl) because of the size of the nitrobenzene molecules. The dipole moment is the product of the amount of charge separated and the distance of separation. Therefore, a rather large value for μ could be the result of a small amount of charge being separated by a rather large distance. Molecules having those characteristics would not be good solvents for ionic salts containing small ions.

Some solvents consisting of polar molecules solvate anions and cations to different degrees because of their molecule structure. For example, *N,N*-dimethylformamide is polar,

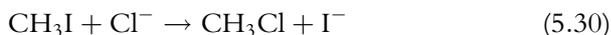


but the positive end of the dipole is shielded to the extent that it is not as accessible for solvating anions as is the negative end for solvating cations. This is also true for solvents such as $(\text{CH}_3)_2\text{SO}$ and CH_3CN . All are fairly good solvents for polar or ionic compounds. Because the negative end of the dipole is less shielded than is the positive end, cations tend to be more strongly solvated than are anions in these solvents. The weaker solvation of the anions results in their being able to react readily in reactions such as nucleophilic substitution in those solvents, and the rates are usually higher than when a solvent such as CH_3OH is used. Methanol can solvate both cations and anions about equally well.

TABLE 5.4 Relative Rates of the Reaction Shown in Eq. (5.30) in Several Solvents (Ege, 1994).

Solvent	Relative rate
CH ₃ OH	1
HCONH ₂	1.25
HCON(CH ₃) ₂	1.2 × 10 ⁶
(CH ₃)CON(CH ₃) ₂	7.4 × 10 ⁶

The rate of the reaction



shows such a dependence, and the relative rates of the reactions in several solvents are shown in Table 5.4. For the series of solvents shown, the reaction rate increases as the ability of the solvent to solvate anions decreases. Since the reaction involves an anion, strongly solvating the anion decreases the rate of substitution.

The data show that as the size of the solvent molecule increases, the solvent is less able to solvate the ion that is the entering group and the rate of the reaction increases. The number of cases where similar observations on solvent effects are encountered is enormous. Later in this chapter, those principles will be extended to include the effects that result from using solvents that have different solubility parameters.

5.3 IDEAL SOLUTIONS

The thermodynamic behavior of *real* solutions, such as those in which most reactions take place, is based on a description of *ideal* solutions. The model of an ideal solution is based on Raoult's law. While we can measure the concentration of a species in solution by its mole fraction, X_i , the fact that the solution is not ideal tells us that thermodynamic behavior must be based on fugacity, f_i . In this development, we will use f_i as the fugacity of the pure component i and \mathbf{f}_i as the fugacity of component i in the solution. When X_i approaches unity, its fugacity is given by

$$\mathbf{f}_i = X_i f_i \quad (5.31)$$

This is expressed by the relationship known as the *Lewis and Randall rule* which can be stated as,

$$\lim_{X_i \rightarrow 1} \left(\frac{f_i}{X_i} \right) = f_i \quad (5.32)$$

When X_i approaches zero, the limit of f_i/X_i approaches a constant, C , which is known as Henry's constant.

$$\lim_{X_i \rightarrow 0} \left(\frac{f_i}{X_i} \right) = C_i \quad (5.33)$$

When a solution behaves ideally, $f_i = C_i$ for all values of X_i . This means that we can write

$$f_i = X_i f_i^\circ \quad (5.34)$$

where f_i° is the fugacity of the standard state of component i . Usually, f_i° is taken as the fugacity of the pure component i at the temperature and pressure of the solution.

When a solution is formed by mixing two components, the properties of the mixture (the solution) are related to those of the individual components and the composition of the solution. For example, the change in volume is described as

$$\Delta V = V_{\text{actual}} - \sum X_i V_i^\circ \quad (5.35)$$

where V_i° is the molar volume of pure component i in its standard state. If we represent some property, \mathbf{P} , in terms of the molar properties of the components, P_i , we obtain

$$\mathbf{P} = \sum X_i P_i \quad (5.36)$$

Therefore, the *change* in the property upon mixing the components can be represented by the equation

$$\Delta \mathbf{P} = \sum X_i (P_i - P_i^\circ) \quad (5.37)$$

where P_i° is the property of the standard state of component i . When the property considered is the free energy, the equation becomes

$$\Delta G = \sum X_i (G_i - G_i^\circ) \quad (5.38)$$

Using the relationship that

$$\Delta G = RT \ln \left(\frac{f_i}{f_i^\circ} \right) \quad (5.39)$$

we see that mixing causes a change in free energy that is given by

$$\Delta G = RT \sum X_i \ln \left(\frac{f_i}{f_i^\circ} \right) \quad (5.40)$$

The ratio (f_i/f_i°) is the *activity* of component i in the solution. For a pure component ($X_i = 1$), the activity of the component in its standard state is given by

$$a_i = \frac{f_i}{f_i^\circ} \quad (5.41)$$

Since the fugacity of component i in an ideal solution is $f_i = X_i f_i^\circ$, we can write

$$a_i = \frac{f_i}{f_i^\circ} = \frac{X_i f_i^\circ}{f_i^\circ} = X_i \quad (5.42)$$

which shows that the activity of component i can be approximated as the mole fraction of i , which is equal to X_i . Therefore, Eq. (5.40) becomes

$$\Delta G = RT \sum X_i \ln X_i \quad (5.43)$$

or

$$\frac{\Delta G}{RT} = \sum X_i \ln X_i \quad (5.44)$$

In a similar way, it can be shown that because the composition of an *ideal* solution is independent of temperature,

$$\frac{\Delta H}{RT} = -\sum X_i \left(\frac{\partial \ln X_i}{\partial T} \right)_{P,X} = 0 \quad (5.45)$$

The subscript X after the partial derivative is for $X \neq X_i$. This equation indicates that the heat of solution for an *ideal* solution is zero. The entropy of solution can be shown to be

$$\frac{\Delta S}{R} = -\sum X_i \ln X_i \quad (5.46)$$

It is apparent that one of the criteria for the mixture being ideal is that $\Delta H_{\text{mixing}} = 0$. However, ΔG_{mixing} and $T\Delta S_{\text{mixing}}$ are not zero, but they are equal and opposite in sign because $\Delta G = \Delta H - T\Delta S$. The relationships of the thermodynamic quantities to composition for an ideal solution are shown in Figure 5.2.

Real solutions are described in terms of the *difference* between the experimental value for a property and that which would result for an

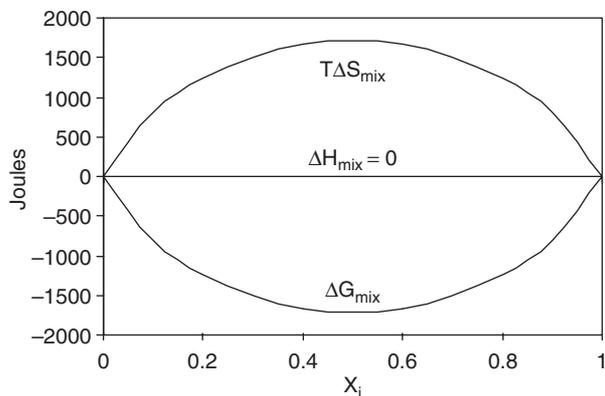


FIGURE 5.2 Relationship between the composition of an ideal solution and the thermodynamic quantities.

ideal solution at the same conditions. These differences are referred to as the *excess property*, P^E

$$P^E = P_{\text{measured}} - P_{\text{ideal}} \quad (5.47)$$

or

$$\Delta P^E = \Delta P_{\text{measured}} - \Delta P_{\text{ideal}} \quad (5.48)$$

The excess properties (such as excess volume) are important in describing solutions in thermodynamic terms.

5.4 COHESION ENERGIES OF IDEAL SOLUTIONS

If the forces between molecules are of the van der Waals type, it can be shown that the internal pressure, P_i , is given by the change in energy with volume at constant temperature.

$$\left(\frac{\partial E}{\partial V}\right)_T = P_i = \frac{a}{V^2} \quad (5.49)$$

where a/V^2 is the same quantity that appears in the van der Waals equation,

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \quad (5.50)$$

Although the terms *cohesion energy density* and *internal pressure* refer to the same characteristic of a liquid, they are not identical. The cohesion energy density (E_c/V) is equivalent to the energy of vaporization per mole of liquid and it is calculated in that way. The internal pressure, P_i , is given by

$$P_i = \left(\frac{\partial E}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T - P \quad (5.51)$$

Since it can be shown from thermodynamics that

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \quad (5.52)$$

the internal pressure is determined from measurements of the change in pressure with temperature at constant volume. Although P_i and E_c/V are not identical, they produce similar effects on the rates of reactions, so the terms are used somewhat interchangeably. For conditions where the internal pressure and the cohesion energy density are of equal magnitudes,

$$\frac{E_c}{V} = P_i = \frac{a}{V^2} \quad (5.53)$$

For a mixture of components 1 and 2, the cohesion energy for the mixture, E_{cm} , will be given by

$$E_{cm} = \frac{a_m}{V_m} \quad (5.54)$$

If we represent the mole fraction of component 1 as X_1 , then $X_2 = (1 - X_1)$ and the value of a_m is

$$a_m = X_1^2 a_1 + 2X_1(1 - X_1)a_{12} + (1 - X_1)^2 a_2 \quad (5.55)$$

where the interaction between components 1 and 2 is given in terms of the van der Waals constants by

$$a_{12} = (a_1 a_2)^{1/2} \quad (5.56)$$

This relationship is often referred to as the Bertholet geometric mean. If no change in volume occurs when the mixture is formed,

$$V_m = X_1 V_1 + (1 - X_1) V_2 \quad (5.57)$$

The cohesion energy of the mixture, E_{cm} , is given in terms of the mole fractions (X) and cohesion energies of the two components by

$$E_{cm} = X_1 E_{c1} + (1 - X_1) E_{c2} \quad (5.58)$$

The change in cohesion energy when the mixture forms compared to the cohesion energy of the two components is

$$\Delta E_c = \frac{X_1(1 - X_1)V_1V_2}{X_1V_1 + (1 - X_1)V_2} \left(\frac{\sqrt{a_1}}{V_1} - \frac{\sqrt{a_2}}{V_2} \right)^2 \quad (5.59)$$

This equation is known as the *Van Laar equation*. Considering the interaction between the molecules of the liquids as resulting from van der Waals forces, the cohesion energy density is

$$\frac{E_c}{V} = \frac{a}{V^2} \quad (5.60)$$

Therefore,

$$\Delta E_c = \frac{X_1(1 - X_1)V_1V_2}{X_1V_1 + (1 - X_1)V_2} \left[\left(\frac{E_{c1}}{V_1} \right)^{1/2} - \left(\frac{E_{c2}}{V_2} \right)^{1/2} \right]^2 \quad (5.61)$$

This equation is known as the *Hildebrand–Scatchard equation*. Of course $(E_c/V)^{1/2}$ is the solubility parameter, δ , so we can write this equation as

$$\Delta E_c = \frac{X_1(1 - X_1)V_1V_2}{X_1V_1 + (1 - X_1)V_2} [\delta_1 - \delta_2]^2 \quad (5.62)$$

Thus, the difference in solubility parameters between the solvent and solute determines a great deal about the character of the solution. For example, water and carbon tetrachloride have cohesion energies that are approximately equal. However, the cohesion in water is the result of dipole-dipole forces and hydrogen bonding, while that in carbon tetrachloride is due to London forces. Mixing the two liquids would result in a heat of mixing being positive because the strong interactions within the two components is not offset by forces that result between the polar and nonpolar molecules. Therefore, the two liquids do not mix. In some cases, the failure of the liquids to mix is due to an unfavorable change in entropy.

We need now to consider other aspects of the process of forming a solution from two components. We will represent the partial molar quantities of the pure components as G_i° , H_i° , and E_i° and those of the same components in solution as G_i , H_i , and E_i . The partial molar free energy, G_i , is related to that of the component in an *ideal* solution, G_i° , by the relationship

$$G_i - G_i^\circ = RT \ln a_i \quad (5.63)$$

where a_i is the activity of component i . By using the analogous relationship for a *real* solution, we obtain

$$G_i - G_i^\circ = RT \ln \frac{a_i}{X_i} = RT \ln \gamma_i \quad (5.64)$$

where X_i is the mole fraction of component i and γ is the activity coefficient. Therefore, because

$$\Delta G = \Delta H - T\Delta S \quad (5.65)$$

we can separate the free energy into the enthalpy and entropy components,

$$(H_i - H_i^\circ) - T(S_i - S_i^\circ) = RT \ln \gamma_i \quad (5.66)$$

If molecular clustering does not occur and the orientation of each component is random in both the pure component and in the solution, the entropy of component i will be approximately the same in the solution as it is in the pure component. Therefore,

$$S_i = S_i^\circ \quad (5.67)$$

The change in volume of mixing the liquids is usually small, so

$$\Delta H = \Delta E + \Delta(PV) \approx \Delta E \quad (5.68)$$

If the activity coefficient is approximately unity, the energy of one mole of component i is approximately the same in the solution as it is in the pure component. A relationship of this form is of great use in describing the thermodynamics of constituents of a solution. Although we have delved rather deeply into the nature of solutions and the related thermodynamics, these topics form the basis for understanding how solvents affect the kinetics of reactions. There is a great deal of similarity between how two components interact when they form a solution and how a solvent and a transition state interact as the reaction occurs.

5.5 EFFECTS OF SOLVENT COHESION ENERGY ON RATES

If the behavior of a reaction is considered in terms of the volume change, the formation of the transition state can be viewed as the formation of a state having a different volume than that of the reactants. The change in volume can be written as

$$\Delta V^\ddagger = V^\ddagger - V_R \quad (5.69)$$

where V_R is the volume of the reactants and V^\ddagger is the volume of the transition state. It is important to note that the *internal* pressure caused by the cohesion of the liquid results in an effect that is analogous to that produced by an *external* pressure (see Section 3.6). Accordingly, if the volume of activation is negative, the formation of the transition state will be enhanced when the solvent has a high internal pressure. Conversely, if the reaction has a positive volume of activation, the reaction will proceed faster in solvents having low internal pressure.

The effects of cohesion energy density or solubility parameter (δ) can be explained by considering a model in which cavities in the solution are altered as the reaction takes place. Cavity formation is hindered in solvents having large δ values. Moreover, the species having smaller volume (either the reactants or the transition state) will be favored in such solvents. If the reactants exist in cavities having a larger total volume than that of the transition state, a solvent of high cohesion energy will favor the formation of the transition state. These effects can be viewed in terms of a Boltzmann population of states having different energies with the energies of the states being altered by the solvent.

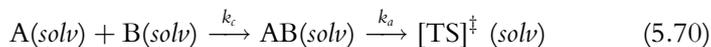
In terms of an overall chemical reaction, the cohesion energy density can often be used as a predictor of solvent effects on the rate. If the products have greater cohesion energy density than the reactants, the process will be favored when the solvent has a larger value for δ . Conversely, if the reactants have high cohesion energy density, a solvent having a large δ value retards the reaction. Predictably, if the reactants and products have similar cohesion energy densities, the δ value of the solvent will be relatively unimportant in its influence on the reaction. The cavities in a solution depend on the sizes of the species and the ability of the solvent to “compress” the cavity. Actually, if the solvent molecules are spherical, there will be free space in the pure solvent. We can see an analogy by considering a body-centered cubic structure similar to that found in solids. If a sphere is surrounded by eight others in a body-centered arrangement, it is easy to show there is 32% free space in the structure. When the interactions are of the “strong” dipole-dipole or hydrogen-bonding type, a solvent having a large δ value causes greater compression of the free space. Compression of this type is known as *electrostriction* of the free space. The effects of using solvents having different solubility parameters on reaction rates will be explored in more detail in Section 5.10.

5.6 SOLVATION AND ITS EFFECTS ON RATES

The complexity of reactions in solution has already been described briefly. However, many unimolecular reactions have rates in solutions that are approximately equal to those in the gas phase. The population of the transition state depends on the number of critical vibrational states populated, which is a function of temperature rather than the environment of the reacting molecule. The localization of the required energy in a vibrational mode for a bond to be broken is often somewhat independent of the environment of the molecule.

Generally, reacting molecules must come together and collide, form a transition state and react, and allow the products to be removed by diffusion from the reaction zone. In viscous media, the collision frequency of the reactants may limit the rate of formation of the transition state as a result of slow diffusion.

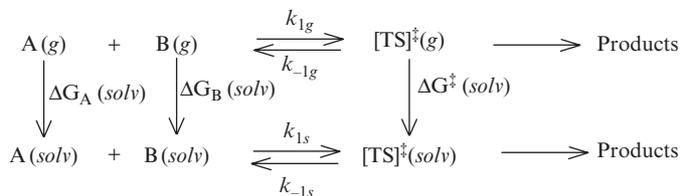
Consider a process in which two solvated reactant molecules A and B must come together to form a transition state. This process can be considered as requiring close proximity of A and B (sometimes called a *collision complex*) followed by the formation of the actual critical configuration in space, which is the reactive transition state. This process can be shown as follows.



In this scheme, $AB(soln)$ is the solvated collision complex of A and B, while $[TS]^\ddagger(soln)$ is the solvated transition state. We can characterize the rate of formation of the collision complex by the rate constant k_c and that of the formation of the transition state by k_a . The rate of diffusion of A and B in the solution determines k_c , and there is an activation energy associated with that process. In an approximate way, the activation energy for diffusion can be considered as having a lower limit that is on the order of the activation energy for viscous flow of the solvent. Such energies are generally lower than those required to form transition states during chemical reactions. Therefore, $k_c \gg k_a$, and the formation of the transition state is the rate-determining process. In the case of very viscous solvents and strong solvation of reactants A and B, the formation of the collision complex of A and B may be the rate-determining factor. In this case, the rate of the reaction is limited by the rate of formation of the collision complex, and the reaction is said to be *diffusion controlled*.

Although diffusion controlled reactions constitute a difficult special case, a general comparison of the behavior of gas phase reactions with those taking place in solution needs to be made. A problem with doing this is that few reactions that occur in the gas phase can be studied in solution under conditions that are otherwise the same with respect to temperature, concentration, etc. In some cases, even the products of the reaction may be different. The majority of studies on solvent effects have dealt with investigating the differences in kinetics of a reaction when different solvents are used rather than comparing the rates of gas phase reactions with those taking place in a solvent.

Let us consider the reaction between A and B that takes place in the gas phase and in some solvent to form the same products. We will write the process in the two phases as follows.



If the transition states formed under the two sets of conditions are identical except for solvation and have equal probabilities for reaction, the rate of the reaction in each case will be determined only by the concentration of the transition state. Therefore,

$$\text{Rate} \sim [\text{TS}]^\ddagger \quad (5.71)$$

For the reaction in the gas phase,

$$R_g \sim [\text{TS}]_g^\ddagger = K_g^\ddagger [\text{A}]_g [\text{B}]_g \quad (5.72)$$

and for the reaction in solution,

$$R_s \sim [\text{TS}]_s^\ddagger = K_s^\ddagger [\text{A}]_s [\text{B}]_s \quad (5.73)$$

where K_g^\ddagger and K_s^\ddagger are the equilibrium constants for the formation of the transition states in the gas phase and in solution. Therefore, when the concentrations of A and B are identical in the two phases, the ratio of the rates is given by the ratio of the equilibrium constants,

$$\frac{R_g}{R_s} = \frac{K_g^\ddagger}{K_s^\ddagger} \quad (5.74)$$

The equilibrium constants for the formation of the transition states in the two phases can be written in terms of the rate constants as

$$K_g^\ddagger = \frac{k_{1g}}{k_{-1g}} \quad \text{and} \quad K_s^\ddagger = \frac{k_{1s}}{k_{-1s}} \quad (5.75)$$

Consequently, making use of the principles illustrated in Chapter 2, we obtain

$$\frac{R_g}{R_s} = \frac{K_g^\ddagger}{K_s^\ddagger} = \frac{e^{-\Delta G_g^\ddagger/RT}}{e^{-\Delta G_s^\ddagger/RT}} \quad (5.76)$$

This equation can be written in logarithmic form as

$$\ln \frac{R_g}{R_s} = \frac{\Delta G_s^\ddagger - \Delta G_g^\ddagger}{RT} \quad (5.77)$$

This equation shows that the difference in free energy of activation in the gas phase and in the solvent determines any difference in reaction rate. We can also write Eq. (5.76) in terms of the enthalpy and entropy of activation as

$$\frac{R_g}{R_s} = \frac{e^{\Delta S_g^\ddagger/R} e^{-\Delta H_g^\ddagger/RT}}{e^{\Delta S_s^\ddagger/R} e^{-\Delta H_s^\ddagger/RT}} \quad (5.78)$$

which can be simplified to give

$$\frac{R_g}{R_s} = e^{(\Delta S_g^\ddagger - \Delta S_s^\ddagger)/R} e^{(\Delta H_s^\ddagger - \Delta H_g^\ddagger)/RT} \quad (5.79)$$

It is readily apparent that when solvation effects on forming the transition state in solution are negligible compared to those on forming the transition state in the gas phase, $\Delta S_g^\ddagger = \Delta S_s^\ddagger$ and $\Delta H_g^\ddagger = \Delta H_s^\ddagger$, so $R_g = R_s$ and the rate of the reaction will be the same in the gas phase and in solution.

In a general way, we can see the effect of the choice of solvent on a reaction by considering the free energy of activation. Figure 5.3 shows the cases that might be expected to arise when a reaction is studied in the gas phase and in four different solvents. In solvent 1, the reactants are strongly solvated so they reside at a lower free energy than they do in the gas phase. However, in this case the solvent is one that strongly solvates the transition state so it too resides at a lower free energy in the solvent than it does in the gas phase, and by a greater amount than do the reactants. Therefore, solvent

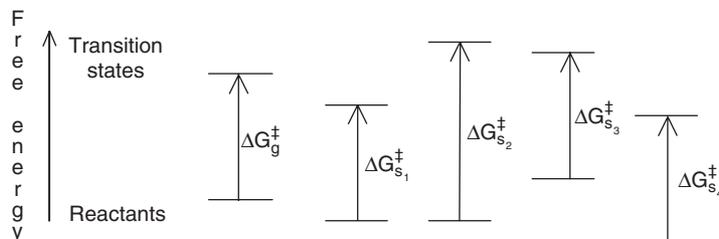


FIGURE 5.3 Effects of solvation of reactants and transition states on the free energy of activation. See text for explanation of the various cases. Subscripts indicate gas and solvents 1, 2, 3, and 4.

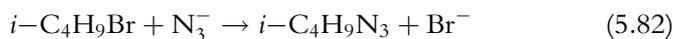
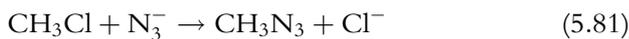
1 will increase the rate of reaction relative to that of the gas phase reaction because $\Delta G_{s1}^{\ddagger} < \Delta G_g^{\ddagger}$.

In solvent 2, solvation of the reactants leads to the reactants residing at a lower free energy, but the transition state is not solvated strongly and is destabilized compared to the gas phase transition state. Therefore, $\Delta G_{s2}^{\ddagger} > \Delta G_g^{\ddagger}$ and the reaction will proceed at a lower rate than it will in the gas phase. In solvent 3, neither the reactants nor the transition state is well solvated. In this case, the reactants and the transition state have higher free energies than they do for the gas phase reaction, but ΔG^{\ddagger} is unchanged. Therefore, the reaction should take place at about the same rate in solvent 3 as it does in the gas phase. Finally, in solvent 4, a solvent that strongly solvates both the transition state and the reactants, the rate should also be about the same as it is in the gas phase because $\Delta G_{s4}^{\ddagger} \approx \Delta G_g^{\ddagger}$.

The foregoing discussion is based on the effects of solvation of reactants and transition states on ΔG^{\ddagger} . However, because of the relationship

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \quad (5.80)$$

it is apparent that an effect on ΔG^{\ddagger} could arise from a change in ΔH^{\ddagger} or ΔS^{\ddagger} (assuming that they do not change in a compensating manner as described in Section 5.9). For example, when the reactions



were studied by Alexander and coworkers (1968) in methanol and DMF ($\text{HCON}(\text{CH}_3)_2$), the ΔH^{\ddagger} and ΔS^{\ddagger} values were found to reflect the difference in the influence of the solvent. For these reactions, $\Delta H_{\text{M}}^{\ddagger}$ and $\Delta S_{\text{M}}^{\ddagger}$ are the activation parameters in methanol and $\Delta H_{\text{DMF}}^{\ddagger}$ and $\Delta S_{\text{DMF}}^{\ddagger}$ are the same parameters in DMF.

When $(\Delta H_M^\ddagger - \Delta H_{DMF}^\ddagger)/2.303RT$ and $(\Delta S_M^\ddagger - \Delta S_{DMF}^\ddagger)/R$ are compared for the reaction shown in Eq. (5.82) at 25°C, the values are 4.3 and 1.0, respectively. The value of $\Delta H_M^\ddagger - \Delta H_{DMF}^\ddagger$ being positive indicates that formation of the transition state is more difficult in methanol than it is when the solvent is DMF. When expressed in the conventional way, $\Delta H_M^\ddagger - \Delta H_{DMF}^\ddagger = 24.5$ kJ/mol, while $\Delta S_M^\ddagger - \Delta S_{DMF}^\ddagger = 19$ J/mol (which is 0.019 kJ/mol). It is apparent that the effect of changing solvents is due predominantly to the effect on ΔH^\ddagger and that entropy differences are only minor.

The origin of the solvent effect just described has been explored in the following way. The enthalpies of transfer (the difference in the heats of solution), ΔH_{tr} , of $(C_2H_5)_4NX$ ($X = Cl, Br, \text{ or } I$) from water to dimethyl sulfoxide (DMSO) were determined, and they were expressed relative to the value for the iodide compound. The free energies associated with changing solvents, ΔG_{tr} , of the corresponding silver compounds were measured and expressed relative to AgI. By comparison of the values of ΔH_{tr} for the $(C_2H_5)_4NX$ compounds with the ΔG_{tr} values for the AgX compounds, the effects of cation cancel, so the differences in ΔG_{tr} and ΔH_{tr} can be compared. The results given by Parker and coworkers (1968) are as follows for the anions listed (given as the anion: ΔG_{tr} (kJ/mol): ΔH_{tr} (kJ/mol)): Cl^- : 29 : 31; Br^- : 16 : 16; I^- : 0 : 0 (the reference). The fact that $\Delta H_{tr} \approx \Delta G_{tr}$ indicates that the entropy effects caused by changing solvent are negligible. Further, it is clear that the differences in behavior of ΔG_{tr} when changing solvents are primarily due, at least for Cl^- , Br^- , and I^- , to differences in solvation enthalpies. In the case of these ions, the trend in solvation enthalpies from H_2O to DMSO is what would be expected because Cl^- is a rather small and hard species, and it is more strongly solvated in water, so ΔH_{tr} is more positive when Cl^- is transferred to DMSO. The bromide ion, being large and softer, is not much more strongly solvated by water than it is by DMSO. One could also expect that I^- might be about equally well solvated by the two solvents.

When a transition state is formed from a reactant molecule, the electrostatic charge distribution is changed. As a result, solvation factors are not static. A reactant may become a better electron donor or acceptor as the transition state forms, which may result in increased or decreased interactions with the solvent. Consequently, Hammett σ constants that are obtained in one type of solvent (say a protic, polar solvent such as CH_3OH) may not apply quantitatively in a solvent such as DMSO or CH_3CN (see Section 5.8).

5.7 EFFECTS OF IONIC STRENGTH

When ions react in solution, their charges result in electrostatic forces that affect the kinetics of the reactions. We can see how this situation arises in the following way. If a reaction occurs between a cation having a charge Z_A and an anion having a charge of Z_B , the transition state will be $[AB]^{Z_A+Z_B}$. The equilibrium constant for the formation of the transition state can be written in terms of the activities of the species as

$$K^\ddagger = \frac{a^\ddagger}{a_A a_B} = \frac{[\text{TS}]^\ddagger \gamma_\ddagger}{[\text{A}] \gamma_A [\text{B}] \gamma_B} \quad (5.83)$$

where a is an activity and γ is an activity coefficient. From this equation, we obtain

$$[\text{TS}]^\ddagger = \frac{K^\ddagger \gamma_A \gamma_B [\text{A}][\text{B}]}{\gamma_\ddagger} \quad (5.84)$$

For the reaction $A \rightarrow B$, the rate of the reaction can be written as

$$-\frac{d[\text{A}]}{dt} = k[\text{TS}]^\ddagger = kK^\ddagger [\text{A}][\text{B}] \frac{\gamma_A \gamma_B}{\gamma_\ddagger} \quad (5.85)$$

When written in terms of the frequency of the decomposition of the transition state, ν , which is equal to kT/h , the rate equation becomes

$$-\frac{d[\text{A}]}{dt} = \frac{kT}{h} \cdot \frac{\gamma_A \gamma_B}{\gamma_\ddagger} \quad (5.86)$$

If the solution is sufficiently dilute so that the Debye-Hückel limiting law applies,

$$\log \gamma_i = -0.509 Z_i^2 I^{1/2} \quad (5.87)$$

where Z_i is the charge on the species and I is the ionic strength of the solution. Therefore,

$$\log k = \log \frac{kT}{h} K^\ddagger + \log \frac{\gamma_A \gamma_B}{\gamma_\ddagger} \quad (5.88)$$

which by expanding the term containing the activity coefficients can be written as

$$\log k = \log \frac{kT}{h} K^\ddagger + \log \gamma_A + \log \gamma_B - \log \gamma_\ddagger \quad (5.89)$$

Substituting for the terms containing $\log \gamma$ gives

$$\log k = \log \frac{\mathbf{kT}}{h} K^\ddagger - 0.509(Z_A^2 + Z_B^2 - Z_\ddagger^2)I^{1/2} \quad (5.90)$$

The charge on the transition state $[\text{TS}]^\ddagger$ is $Z_A + Z_B$, so

$$Z_\ddagger^2 = (Z_A + Z_B)^2 = Z_A^2 + Z_B^2 + 2Z_A Z_B \quad (5.91)$$

Therefore, when this result is substituted in Eq. (5.90), after simplification we obtain

$$\log k = \log \frac{\mathbf{kT}}{h} K^\ddagger + 1.018Z_A Z_B I^{1/2} \quad (5.92)$$

When the first term on the right-hand side of this equation is represented as k_o , this equation can be written in logarithmic form as

$$\log \frac{k}{k_o} = 1.018Z_A Z_B I^{1/2} \quad (5.93)$$

At constant temperature, the first term on the right-hand side of Eq. (5.92) is a constant, so it is apparent that a plot of $\log k$ versus $I^{1/2}$ should be linear. If at least one reactant is not a charged species, Z_A or Z_B will be zero, and the ionic strength of the reaction medium should have little or no effect on the rate of the reaction. However, if A and B are both positive or both negative, the rate of the reaction should increase linearly with $I^{1/2}$. If A and B are oppositely charged, the rate of the reaction should decrease linearly with $I^{1/2}$. In these cases, the slope of the plot of $\log k$ versus $I^{1/2}$ is directly proportional to the magnitude of $Z_A Z_B$. Observations on many reactions carried out in dilute solutions are in accord with these predictions. Figure 5.4 shows the expected variation in rate constant as ionic strength of the solution varies.

The explanation for the observations when the product $Z_A Z_B$ is positive lies in the fact that when the ionic strength is *high*, the solvated ions change the dielectric behavior of the solution so that ions of like charge do not repel each other as greatly. This allows them to approach more closely, which causes an increase in collision frequency and an *increased* reaction rate. When the ions are of *opposite* charge, an increase in the concentration of ions in the solvent causes a decrease in the attraction between the ions so that the rate of the reaction between them is *decreased*. Deviations from predicted behavior are common even when the solutions are quite dilute because the Debye-Hückel limiting law applies only to very dilute

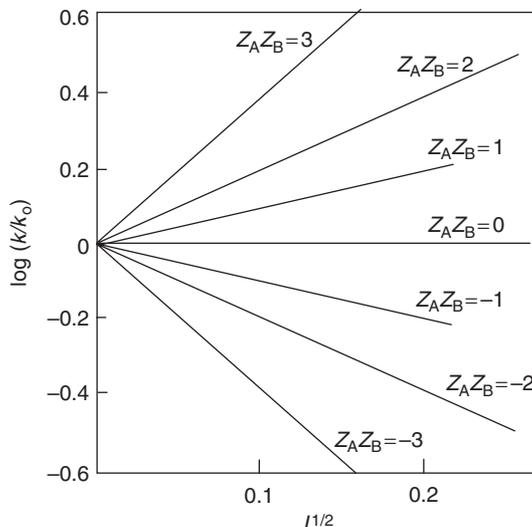


FIGURE 5.4 The effect of ionic strength on the rates of reactions between ions as a function of ionic strength of the solution (k_0 is the rate constant at $I=0$).

solutions. It should also be mentioned that ion pairing and complex formation can cause the relationship to be far from exact.

For reactions that involve uncharged reactants, the ionic strength of the solution should be expected to have little effect on the reaction rate. If the reaction is one in which ions are consumed or generated, the overall ionic strength of the medium will change as the reaction progresses. Such a situation will alter the kinetic course of the reaction. In order to avoid this situation, one of two approaches must be used. First, the change in ionic strength that occurs during the reaction can be determined and the results can be adjusted to compensate for the change. A more common approach is to carry out the reaction at a relatively high and essentially constant ionic strength by preparing a reaction medium that contains a large concentration of an "inert" salt to provide "ionic ballast." For many substitution reactions, the choice of salt is relatively easy since ions like ClO_4^- , NO_3^- , BF_4^- , or PF_6^- are not good nucleophiles and do not compete with most entering groups. If the reaction is one in which the electrophilic character of the cation is important, salts such as $\text{R}_4\text{N}^+\text{Cl}^-$ may be used because tetraalkylammonium ions are not electrophiles. Obviously, some discretion must be exercised in the choice of "inert" salt in light of the reaction being studied. A realistic approach is to carry out the reaction by

making duplicate runs with different salts present at identical concentrations. If the rate of the reaction is the same in both cases, the salt being tested is actually inert.

5.8 LINEAR FREE ENERGY RELATIONSHIPS

The term *linear free energy relationship* (LFER) applies to a variety of relationships between kinetic and thermodynamic quantities that are important in both organic and inorganic reactions. About 80 years ago, J. N. Brønsted found a relationship between the dissociation constant of an acid, K_a , and its ability to function as a catalyst in reactions that have rates that are accelerated by an acid. The Brønsted relationship can be written in the form

$$k = CK_a^n \quad (5.94)$$

where k is the rate constant, K_a is the dissociation constant for the acid, and C and n are constants. Taking the logarithm of both sides of this equation gives

$$\ln k = n \ln K_a + \ln C \quad (5.95)$$

or when common logarithms are used,

$$\log k = n \log K_a + \log C \quad (5.96)$$

Recalling the definition

$$\text{p}K_a = -\log K_a \quad (5.97)$$

allows Eq. (5.95) to be written as

$$\log k = -n \text{p}K_a + \log C \quad (5.98)$$

From this equation, we can see that a plot of $\log k$ versus $\text{p}K_a$ should be linear. However, the anion, A^- , of the acid HA is capable of functioning as a base that reacts with water.



Therefore, we can write the equilibrium constant for this reaction, K_b , as

$$K_b = \frac{[HA][OH^-]}{[A^-]} \quad (5.100)$$

Some reactions are catalyzed by bases so we can obtain relationships that are analogous to Eqs. (5.95) and (5.96), and the first is written as

$$\log k' = n' \log K_b + \log C' \quad (5.101)$$

In aqueous solutions, K_b can be written as K_w/K_a where K_w is the ion product constant for water. Therefore, Eq. (5.101) can also be written as

$$\log k' = n' \log \left(\frac{K_w}{K_a} \right) + \log C' \quad (5.102)$$

In base catalysis, the rate of the reaction is directly dependent on the strength of the base, but it is inversely related to the strength of the conjugate acid.

Because the equilibrium constant for dissociation of an acid is related to the free energy change by

$$\Delta G_a = -RT \ln K_a \quad (5.103)$$

substitution for $\ln K_a$ in Eq. (5.96) leads to

$$\ln k = -\frac{n\Delta G_a}{RT} + \ln C \quad (5.104)$$

This equation shows that a linear relationship should exist between $\ln k$ for the acid catalyzed reaction and ΔG_a for dissociation of the acid. This is an example of a linear free energy relationship.

When two similar acids are considered, the rate constants for reactions in which they are catalysts will be given by k_1 and k_2 , while the dissociation constants will be given by K_{a1} and K_{a2} . Then, subtracting the equation relating k and K_a for the second acid from that for the first acid yields the equation

$$\ln k_1 - \ln k_2 = n(\ln K_{a1} - \ln K_{a2}) \quad (5.105)$$

This equation can be rearranged to give

$$\ln \frac{k_1}{k_2} = n \ln \frac{K_{a1}}{K_{a2}} = nm \quad (5.106)$$

where m is a constant that is equal to the logarithm of the ratio of the dissociation constants for the two acids. As we shall see, when common logarithms are used and the constants on the right-hand side of the equation are represented as ρ and σ , the relationship is known as the *Hammett equation*,

$$\log \frac{k}{k_o} = \rho\sigma \quad (5.107)$$

where k_o is the rate constant for the reaction in the presence of the reference acid. Numerous special cases of this type of equation exist where closely similar reactions are compared to a reference reaction. For example, the rates of hydrolysis of alkyl halides have been correlated in this way.

The Hammett LFER relates the dissociation constants of substituted benzoic acids to that of benzoic acid itself. Described in 1937, the original relationship was developed to explain the electronic effects of substituents on the strengths of *m*- and *p*-substituted benzoic acids. Then, the parameter σ was defined for *m*- and *p*-substituted acids as

$$\sigma_m = \log \frac{K_{mx}}{K_o} \quad (5.108)$$

$$\sigma_p = \log \frac{K_{px}}{K_o} \quad (5.109)$$

where K_o is the dissociation of benzoic acid (the reference) and K_{mx} and K_{px} are the dissociation constants of the *m*- and *p*-XC₆H₄COOH acids that have a group X in the *m* and *p* positions. If the group X is electron withdrawing, the acidity of the COOH group is increased and σ is positive. Conversely, the σ values are negative for electron releasing groups. When the dissociation constants for the acids XC₆H₄COOH were studied, a linear relationship between $\log(K'_x/K'_o)$ (where K'_o is the dissociation constant for the reference acid, C₆H₅CH₂COOH) and the σ values was obtained. Unlike the equations given earlier where the slope is unity, the constant slope was represented as ρ so that

$$\log \frac{K'_x}{K'_o} = \rho\sigma \quad (5.110)$$

When a series of reactions is studied in which the strength of the acid is a rate-determining factor, the rates will be proportional to $[H^+]$, but this is in turn proportional to K_a . Therefore, the rate constants will be related by the equation

$$\log \frac{k_x}{k_o} = \rho\sigma \quad (5.111)$$

When other series of aromatic compounds are considered, the constants K_o and k_o refer to the reference unsubstituted acid. Equation (5.111) shows that if $\rho > 1$, the rate or dissociation constant is enhanced by the electronic effects of substituent X to a greater extent than they are for the benzoic

acids. On the other hand, if $\rho < 0$, the group X is electron releasing and the rate (or dissociation) constant is increased by the presence of group X. Finally, if $1 > \rho > 0$, the rate (or dissociation) constant is increased, but to a lesser extent than the benzoic acid is affected by the same substituent. While the major use of the Hammett relationship is in organic chemistry, a number of interesting correlations have been found for some inorganic reactions involving complexes as well.

The relationship

$$\log \frac{K_x}{K_o} = \rho\sigma \quad (5.112)$$

can be written as

$$\log K_x - \log K_o = \rho\sigma \quad (5.113)$$

and because

$$\Delta G = -RT \ln K = -2.303 RT \log K \quad (5.114)$$

we find that

$$\log K = -\frac{\Delta G}{2.303RT} \quad (5.115)$$

Therefore, for a reference acid that has a dissociation constant K_o and another acid that has a dissociation constant K_x ,

$$\log K_x - \log K_o = \rho\sigma \quad (5.116)$$

and by substitution, we obtain

$$-\frac{\Delta G_x}{2.303RT} + \frac{\Delta G_o}{2.303RT} = \rho\sigma \quad (5.117)$$

which can be simplified to give

$$\Delta G_x = \Delta G_o - 2.303 RT \rho\sigma = \Delta G_o - (\text{constant}) \rho\sigma \quad (5.118)$$

This equation shows the *linear* relationship between the change in free energy and the product of $\rho\sigma$.

The LFER of Hammett is satisfactory only when the reactive site is sufficiently removed from the substituent so that steric factors do not enter into the rate-determining step of the reaction. Also, if the reaction involves a series of substituents that greatly alter the way in which either the reactant or the transition state is solvated, the relationship may be less than satisfactory. It is perhaps wise to remember that the relationships are empirical in origin. This does not detract from their usefulness, neither is it any different

for empirically determined rate laws. While the original Hammett LFER was applied to aromatic compounds, other studies have extended it to other types of compounds (e.g., aliphatic).

The approach taken by R. W. Taft is similar to that of Hammett, and the equation used can be written as

$$\log \frac{k}{k_o} = \rho^* \sigma^* + \delta E_s \quad (5.119)$$

where σ^* is a constant related to polar substituent effects and ρ^* , as was the case for ρ , is a reactant constant, and δE_s is a steric energy term. When a given series of reactants is considered, δE_s is frequently considered to be zero since for any pair of similar species subtraction of two equations having the form of (5.119) would cause the term δE_s to cancel. Frequently, the *Taft equation* is written simply as

$$\log \frac{k}{k_o} = \rho^* \sigma^* \quad (5.120)$$

The Taft equation is essentially similar to the Hammett relationship but has constants that are also appropriate to aliphatic and restricted aromatic materials.

5.9 THE COMPENSATION EFFECT

When a series of reactions involving similar reactants (e.g., a series of substituted molecules having different substituents in a particular position) is studied, it is possible to find that ΔG^\ddagger may show little variation for the series. This may be indicative of there being a relationship of the Hammett or Taft type. However, another explanation that is appropriate in some cases is the so-called *compensation effect*.

We can see how this situation might arise in a very simple way. As an extreme example, consider the solvation of the ions that are present in reactions as the transition states TS_1 and TS_2 . Suppose one has a charge of $+TS_1$ and the other has a charge that is $+TS_2$, where $TS_2 > TS_1$. In a polar solvent, TS_2 will be more strongly solvated than TS_1 , so ΔH_2^\ddagger will be more negative than ΔH_1^\ddagger . However, because this is true, the solvent in the vicinity of TS_2 will be more ordered than it is near TS_1 , and ΔS_2^\ddagger will be more negative than ΔS_1^\ddagger . The free energy of activation, ΔG^\ddagger , is given by

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (5.121)$$

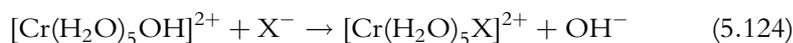
Therefore, if ΔH_2^\ddagger is more negative than ΔH_1^\ddagger and ΔS_2^\ddagger is more negative than ΔS_1^\ddagger , it is possible that ΔG^\ddagger may be approximately constant for the two cases. For a series of reactions, we might find that

$$\Delta H_1^\ddagger - T\Delta S_1^\ddagger = C \quad (5.122)$$

where C is a constant. Therefore, we can write

$$\Delta H_1^\ddagger = T\Delta S_1^\ddagger + C \quad (5.123)$$

and we should expect that a plot of ΔH^\ddagger versus ΔS^\ddagger should be linear with a slope of T . This temperature is sometimes called the *isokinetic temperature* in this *isokinetic relationship*. Figure 5.5 shows such a relationship for the reaction



where $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{SCN}^-$, etc. In this case, a reasonably good linear relationship results when the graph is made in spite of the fact that widely different entering ligands were used. The mechanism of these substitution reactions involves the initial loss of OH^- followed by the entry of X^- into the coordination sphere.

Although we have interpreted the compensation effect in terms of transition states having different charges, there is no reason that transition states having different polarities could not behave similarly when the solvent is polar. Also, if a reduction in charge separation occurs as the transition state forms and the solvent is nonpolar, more favorable solvation

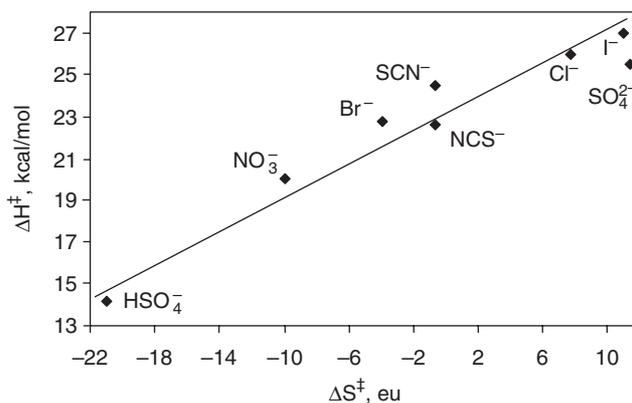


FIGURE 5.5 An isokinetic plot for the formation of $[\text{Cr}(\text{H}_2\text{O})_5\text{X}]^{2+}$ by replacement of OH^- . (Constructed from the data given in D. Thusius, *Inorg. Chem.*, 1971, 10, 1106.)

of the transition state would be expected on the basis of the hard-soft interaction principle. A compensation effect could result in this situation also. When a linear isokinetic relationship is obtained, it is usually taken as evidence for a common mechanism for the series of reactions.

5.10 SOME CORRELATIONS OF RATES WITH SOLUBILITY PARAMETER

The importance of solvent cohesion energy, as reflected by the solubility parameter, and its usefulness for interpreting the effect of the solvent were described briefly in Section 5.5. Because the solubility parameter is such an important (and underutilized) tool for explaining solvent effects on rates, we will describe here more of the details of a few studies. In a general way, solvents having large solubility parameters assist the formation of transition states in which there is high polarity or charge separation (high cohesion energy in the transition state). Conversely, solvents that have large, nonpolar structures hinder the formation of transition states that have large, nonpolar structures.

A reaction that is widely cited as one in which solvent *polarity* plays a major role is the formation of quaternary ammonium salts as shown in the equation



However, the effect of a series of solvents can also be interpreted in terms of the solubility parameters of the solvents. The transition state in this reaction is generally regarded as resembling the product (meaning that it has considerable charge separation and high cohesion energy). Accordingly, it would be logical to expect that the rate of the reaction would be enhanced by using solvents having large solubility parameters. One such reaction of this type that has been studied by Kondo, et al. (1972) in a variety of solvents is



For this reaction, it was found that the rate increases when solvents having large solubility parameters are used. Moreover, the volume of activation for the reaction is negative in all of the solvents, but it is more negative in solvents having smaller solubility parameters.

The free energy of activation for a reaction having a compact, polar (or ionic) transition state will be decreased by solvents having large solubility

parameters. The equilibrium constant for the formation of the transition state is

$$K^\ddagger = \frac{k_1}{k_{-1}} \quad (5.127)$$

where k_1 is the rate constant for the formation of the transition state and k_{-1} is the rate constant for its decomposition. The free energy of activation is related to K^\ddagger by the relationship

$$\Delta G^\ddagger = -RT \ln K^\ddagger \quad (5.128)$$

Because the rate of the reaction will be proportional to the concentration of the transition state, which is in turn related to K^\ddagger , we would expect that a plot of $\ln k$ versus solubility parameter would be linear. We are assuming in this case that the decrease in the free energy of activation is directly proportional to the ability of the solvent to “force” the formation of the transition state. Figure 5.6 shows a test of this relationship using the data given by Kondo, et al. (1972) for the reaction of benzylbromide with pyridine, which is represented by Eq. (5.126). It can be seen that for most of the solvents the relationship is approximately correct.

Furthermore, the ability of the solvent to solvate a transition state that has charge separation is related to the solubility parameter of the solvent. As shown in Figure 5.7, the majority of the solvents give a satisfactory relationship between ΔV^\ddagger and δ in spite of the fact that widely differing solvents were used.

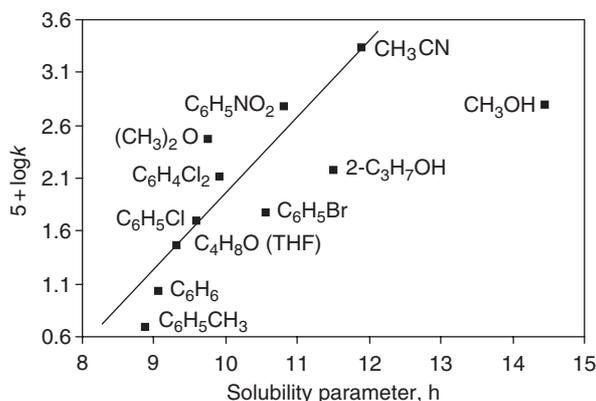


FIGURE 5.6 Relationship between the rate constants for the reaction shown in Eq. (5.126) and the solubility parameter of the solvent. (Constructed using the data of Kondo, et al. (1972).)

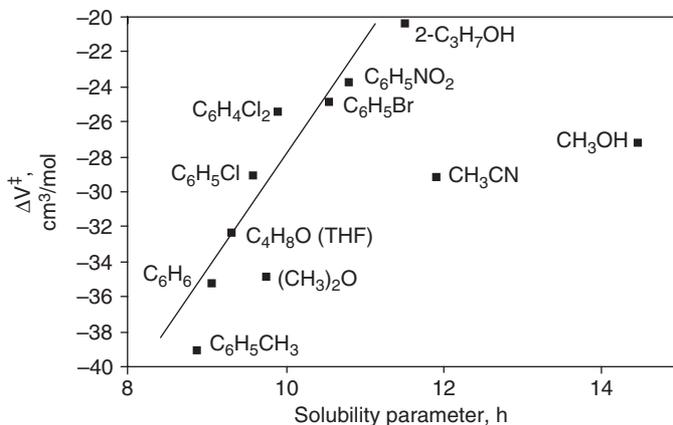


FIGURE 5.7 Relationship between the volume of activation for the reaction shown in Eq. (5.126) and the solubility parameter of the solvent. (Constructed using the data of Kondo, et al. (1972).)

However, two liquids, CH₃CN and CH₃OH, give data that fall far from the line. The solubility parameters for these liquids are larger because of strong dipole-dipole forces (in CH₃CN) and hydrogen bonding (in CH₃OH). The fact that the volume of activation is more negative for solvents with lower cohesion energies is a reflection of the fact that these liquids have more loosely packed structures and that the reactants are much less constricted in these solvents than they are in the transition state. If the transition state is approximately the same in volume when different solvents are used, the *reactants* must occupy a larger effective volume in the solvents of lower solubility parameter. The fact that the solvents CH₃CN and CH₃OH result in an abnormal volume of activation is probably due to the fact that these solvents have much more structure and the reactants already exist in small cavities as a result of electrostriction of the solvent. These solvents are less compressible and have already become tightly bound around the solutes. Consequently, there is a smaller volume change when the transition state forms when the solvent is CH₃OH or CH₃CN.

We can examine the relationship between the solubility parameter of the solvent and the rate of a similar reaction by making use of the data given by Laidler (1965, p. 203) for the reaction



Figure 5.8 shows a plot of $\log k$ versus δ for this reaction carried out at 100°C.

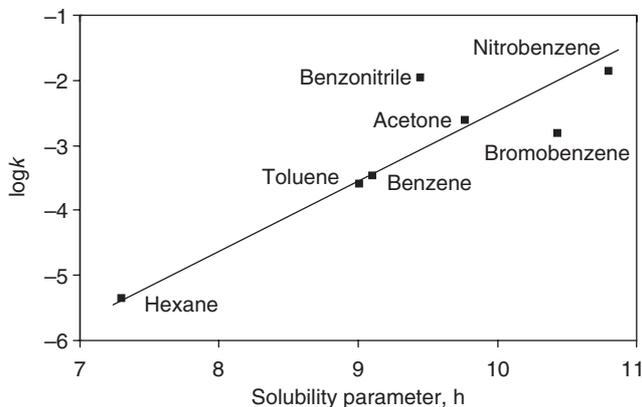


FIGURE 5.8 Relationship between the rate constants for the reaction between ethyl iodide and triethylamine and the solubility parameters of the solvents. (Constructed using the rate constants given by Laidler (1965).)

It is clear that the relationship is approximately linear, and as expected, the rate of the reaction increases with increasing solubility parameter of the solvent. As a general rule, we can conclude that *reactions that pass through transition states that have considerable polarity (or charge separation) induced will have rates that increase with increasing solubility parameter of the solvent.*

We should ask at this point what happens when reactions of a totally different type take place in solvents having different solubility parameters. Reactions in which the transition state is a large, essentially nonpolar species behave in exactly the opposite way to those discussed earlier with respect to the effects of the solvent on the rate of reaction. One case of this type is the esterification that occurs when acetic anhydride reacts with ethanol at 50°C. Using the data given by Laidler (1965, p. 209), Figure 5.9 was constructed showing the relationship between $\log k$ and δ . For this reaction, the rate of the reaction is seen clearly to decrease as the solubility parameter of the solvent increases. The formation of a large transition state having little or no charge separation from two smaller, polar molecules is hampered by solvents having high cohesion energy (or δ). Accordingly, a linear relationship also exists between $\log k$ and δ , but the slope is negative in this case.

Parker and coworkers have investigated solvent effects on a variety of organic reactions. In one massive study on S_N2 reactions (Parker, et al., 1968), data are presented for a large number of substitution reactions carried out in a wide range of solvents. Data for two of the numerous

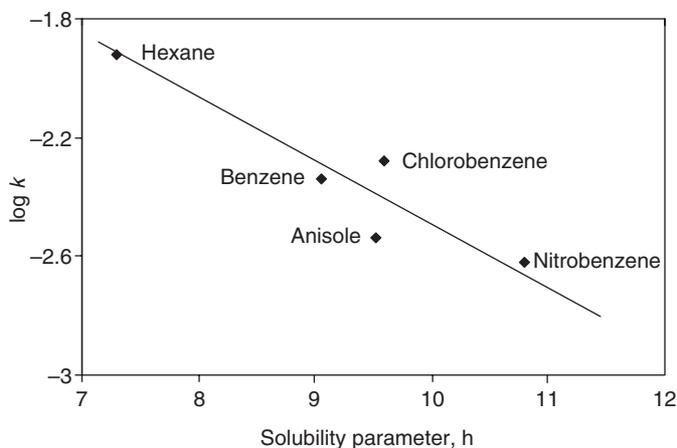


FIGURE 5.9 Dependence of the rate constants for the reaction between acetic anhydride and ethyl alcohol on the solubility parameters of the solvents. (Constructed using rate constants given by Laidler (1965).)

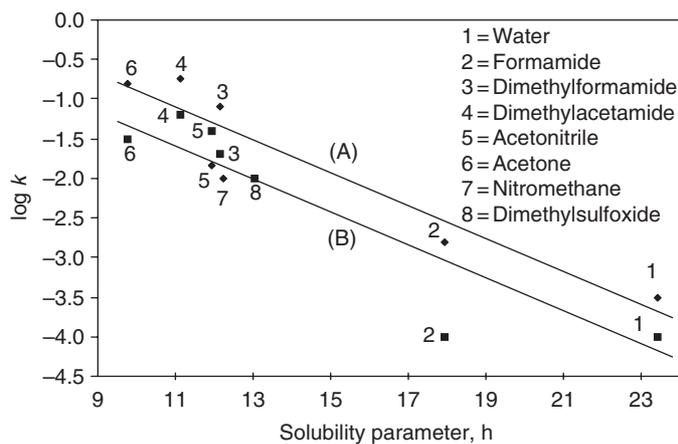
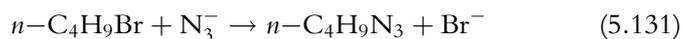
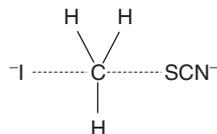


FIGURE 5.10 Relationship between $\log k$ and the solubility parameter of the solvent for nucleophilic substitution. (Constructed using the rate constants from Parker, et al. (1968).)

reactions studied were used to construct Figure 5.10, which shows the variation in $\log k$ as a function of the solubility parameters of the solvents. It is readily apparent that for the reactions



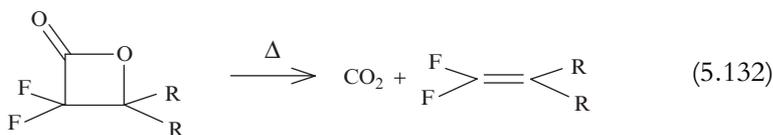
the rate of substitution decreases more or less linearly with increasing solubility parameter of the solvent. In the first of these reactions, SCN^- is more strongly solvated by solvents that contain small, protic molecules (e.g., water or formamide) than is I^- . If a transition state such as



is formed, the charge is dissipated over a large structure so solvents that consist of molecules that are essentially small and hard in character will not solvate the transition state as well as they will the SCN^- . On the other hand, solvents that are essentially soft in character (acetone, acetonitrile, or dimethylacetamide) will solvate the transition state more strongly than they will the reactants. As a result, the rate of the reaction will be greater in softer solvents than it will in solvents that consist of small, polar molecules (having larger δ values). Figure 5.10 shows that these conclusions are borne out by the data for the reaction shown in Eq. (5.130).

Although the rates are lower for the reaction shown in Eq. (5.131) than those for the reaction shown in Eq. (5.130) in each of the solvents tested, the same trend is seen for the reaction of *n*-butyl bromide with azide ion. The azide ion will be rather strongly solvated by solvents that consist of small, polar molecules while the bromide ion will be less well solvated by such solvents. Also, the transition state will have the charge spread over a larger volume so that solvents that are composed of soft molecules will solvate the transition state better than those that consist of small, polar molecules. These conclusions are in accord with the trends shown in Figure 5.10.

Another reaction in which the solvent plays an enormous role is in the decarboxylation of lactones. In one study of this type, Ocampo, Dolbier, Bartberger, and Paredes (1997) investigated the decarboxylation of α,α -difluoro β -lactones in several solvents and in the gas phase. The reaction for the dialkyl compounds can be shown as follows.



When the decarboxylation of the dimethyl compound was studied in the gas phase, the activation energy was found to be 189 kJ/mole. For the reaction

carried out in solutions, the activation energy ranged from 114–137 kJ/mol depending on the solvent. From this and other evidence it was concluded that the reaction follows a different pathway in the two phases. It was concluded that the gas phase reaction takes place by a concerted mechanism that involves a planar, homolytic nonpolar transition state. In polar solvents the reaction probably involves a zwitterion intermediate.

The rate constants for the reaction of the diethyl compound were determined in various solvents at a temperature of 168.1°C. A pathway involving charge separation was postulated for the reaction in solution, and the rate constants were correlated with a solvent parameter known as the E_T value. In view of the success of correlating rates in solution with the solubility parameter of the solvent, the $\log k$ values were plotted against δ to obtain the result shown in Figure 5.11.

The correlation of the rates of decarboxylation of the difluoro diethyl lactone with solubility parameter shows that the rate increases dramatically as the value of δ increases. In fact, there was a factor of almost 500 difference in the rate constants depending on the solvent chosen. This is in agreement with the conclusion that the transition state for the reaction carried out in solution involves a substantial separation of charge. Furthermore, Figure 5.11 shows that the solubility parameter can be a useful index for assessing the role of the solvent in a reaction of a greatly different type than those described earlier in this chapter. The entropy of activation for the reaction was reported

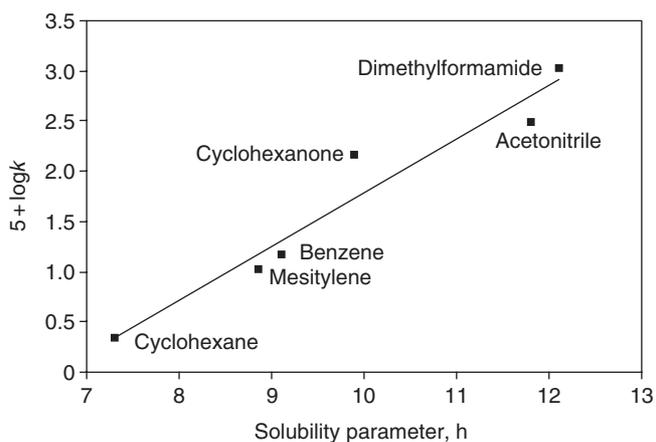


FIGURE 5.11 Correlation of rate constants for decarboxylation of 3,3-difluoro-4,4-diethyloxetan-2-one at 168.1°C with solubility parameters of the solvents. (Rate constants from Ocampo, et al., 1997.)

as -6.7 cal/deg when the solvent was mesitylene and -10.8 cal/deg when the solvent was acetonitrile. This observation is consistent with there being more ordering or electrostriction in the polar solvent. A transition state that involves charge separation is consistent with this behavior.

Historically, solvent effects have been explained primarily in terms of the polarity or other characteristics of the solvent. While these cases illustrate the considerable role that the solubility parameter of the solvent has in influencing the rates of reactions, especially in organic chemistry, space does not permit a full consideration of the vast array of organic reaction types. Undoubtedly, reactions other than the substitution, esterification, and quaternization reactions described earlier are just as strongly influenced by the solvent. One of the best treatments of the broad area of solvent effects in organic chemistry is that given by Leffler and Grunwald (1989), which contains an enormous amount of information. However, that source, as well as most others, does not really do justice to the general application of solubility parameters to explaining rates of reactions. In fact, the solubility parameter is of tremendous importance in predicting solution properties and other facets of liquid state science (Hildebrand and Scott, 1962, 1949).

In this chapter, the basic principles of liquid state and solution behavior have been presented. These ideas form the basis for interpreting and understanding the role of the solvent in affecting the rates of chemical reactions from the standpoint of practical applications. Some additional approaches to describing solvent effects will be presented in Chapter 9.

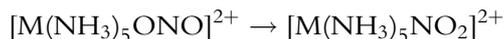
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PROBLEMS

1. For the linkage isomerization reactions of

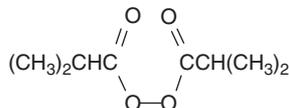


(where M = Co, Rh, or Ir) the activation parameters are as follows (Mares, M., Palmer, D. A., Kelm, H., *Inorg. Chim. Acta* 1978, 27, 153).

	M = Co	M = Rh	M = Ir
ΔH^\ddagger , kJ mol ⁻¹	91.6 ± 0.8	80.2 ± 2.1	95.3 ± 1.3
ΔS^\ddagger , J mol ⁻¹ K ⁻¹	-17 ± 3	-33 ± 7	-11 ± 4

Test these data for an isokinetic relationship. Since the volumes of activation are -6.7 ± 0.4 , -7.4 ± 0.4 , and $-5.9 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$, what mechanism is suggested for these isomerization reactions?

2. The decomposition of diisobutyrylperoxide,



produces C_3H_6 , CO_2 , and $(\text{CH}_3)_2\text{COOH}$. At 40°C , the following data were obtained (Walling, C., Waits, H. P., Milovanovic, J., Pappiaonou, C. G., *J. Amer. Chem. Soc.* 1970, 92, 4927).

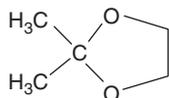
Medium	$10^5 k, \text{ sec}^{-1}$
Gas	1
Cyclohexane	4.70
Nujol	4.63
Benzene	23.8
Acetonitrile	68.1

- (a) In light of these data, speculate on the nature of the transition state for this reaction. From this general knowledge of the transition state, propose a mechanism for the reaction. (b) While the solvent effects were originally explained partially in terms of solvent polarity, determine the relationship between the solubility parameter of the solvent and k .
3. The viscosity of water and hexane vary with temperature as follows:

$t, ^\circ\text{C}$		20	25	40	50
C_6H_{14}	$\eta, \text{ cp}$	0.326	0.294	0.271	0.248
H_2O	$\eta, \text{ cp}$	1.002	0.911	0.653	0.547

Determine the activation energy for viscous flow for these liquids. Explain why they are different.

4. The hydrolysis of 2, 2-dimethyl-1, 3-dioxolane,

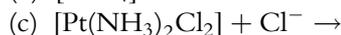
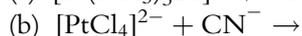


has been studied in mixtures of water and glycerol as the solvent (Schaleger, L. L., Richards, C. N., *J. Amer. Chem. Soc.* 1970, 92, 5565). Activation parameters are as follows.

% Glycerol	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , cal mol ⁻¹ K ⁻¹
0	20.7	7.1
10	19.5	3.5
20	19.7	4.3
30	17.9	-1.6
40	17.6	-2.4

Analyze these data to determine whether a compensation effect is operative. If it is, determine the isokinetic temperature.

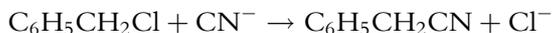
5. How should the following reactions depend on the ionic strength of the reaction medium?



6. The solubility parameter for mixed solvents can be calculated using the equation

$$\delta_M = \sum_{i=1}^n X_i \delta_i$$

where X_i and δ_i are the mole fraction and solubility parameter for component i . The reaction

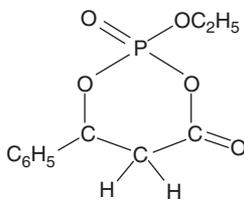


has been studied in mixtures of H₂O and dimethylformamide, DMF. Results obtained were as follows (Jobe, K. I., Westway, K. C., *Can. J. Chem.* 1993, 71, 1353).

Mole % DMF	$10^3 \times k, \mathbf{M}^{-1}\mathbf{s}^{-1}$
2.5	4.40
5.0	3.20
15.0	0.52
20.0	0.57

- (a) Use the data shown in Table 5.2 to determine the solubility parameters of the mixed solvents. (b) Test the relationship between $\ln k$ and δ for the solvents. (c) Discuss the probable mechanism of the reaction in light of the effect of δ on the rate.

7. The hydrolysis of



takes place in solution. The rate varies with pH as follows (Marecek, J. F., Griffith, D. L., *J. Am. Chem. Soc.* 1970, 92, 917):

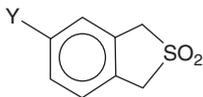
pH	0.5*	1.48	2.01	2.97	4.32	6.03	9.59	10.0	10.8
$10^3 \times k_{\text{obs}}$	13*	6.64	5.90	5.83	5.04	5.05	8.31	11.3	23

*Estimated

Discuss what k_{obs} means in this case and describe a possible mechanism for the hydrolysis.

8. The decomposition of 2, 2-azoisobutane occurs in a 90:10 diphenyl-ether:isoquinoline mixture with $\Delta H^\ddagger = 42.2 \text{ kcal/mol}$ and $\Delta S^\ddagger = 16.2 \text{ cal/mol deg}$. In the gas phase, the values are $42.3 \text{ kcal/mol mol}$ and 17.5 cal/mol deg , respectively. Explain what this signifies in terms of the transition state for the reaction. Speculate how the use of other solvents would likely affect the rate of the equation.

9. The hydrolysis of



has been studied where Y can be one of several different substituents (Zaborsky, O. R., Kaiser, E. T., *J. Am. Chem. Soc.* 1970, 92, 860). The results obtained and the values of the para σ substituent constants (σ_p) are as follows.

Y	$k, \text{M}^{-1} \text{sec}^{-1}$	σ_p
H	37.4	0.00
NH ₂	13.6	-0.66
OCH ₃	21.3	-0.27
CH ₃	24.0	-0.17
Br	95.1	0.23
NO ₂	1430	1.24

Compare the rate constants for the groups to that for hydrogen and test the relationship between $\log(k_{\text{H}}/k_{\text{Y}})$ and σ_p to determine if a linear free energy relationship exists. Provide an explanation for your results.

10. In most polar solvents such as dimethylformamide, the order of reactivity of halide ions in nucleophilic substitution is $\text{Cl}^- > \text{Br}^- > \text{I}^-$. However, in methanol the order of reactivity is reversed. Explain these observations in terms of the properties of the solvents and the nature of the transition state in each case.

