Chapter 4

Background Thermodynamics, Equilibrium Partitioning and Acidity Constants

Whether dealing with partitioning of a given organic pollutant between two phases (e.g., between air and water) or trying to assess abiotic or biological transformation reactions of a chemical in the environment, we are always interested in the situation should it reach *equilibrium*. That is, we want to know what the chemical concentrations will be in the two conditions when no net changes occur anymore. From a practical point of view, we can actually assume that equilibrium is reached, or almost reached, in quite a few instances. For example, equilibrium can always be assumed for proton transfer reactions that are usually much faster than any other process. Furthermore, a partitioning process may be fast compared to a transport process or a chemical reaction in the environment. In such cases, it is appropriate to describe phase interchanges with an equilibrium approach. Furthermore, even for processes that will never reach equilibrium in the time frame considered and where kinetic approaches need to be applied, knowledge of the equilibrium situation is pivotal. For example, one uses equilibrium information to assess the direction of a chemical flux between compartments or to evaluate whether a transformation reaction may occur spontaneously or not. Also, many kinetic models describing phase interchanges assume equilibrium at the interface.

The goal of this chapter is to review some important thermodynamic entities that are relevant to describe partitioning and chemical reaction equilibria, as well as to assess the extent of disequilibria: Gibbs free energy (G), enthalpy (H), entropy (S), chemical potential (μ), fugacity (f), activity (a), and activity coefficient (γ). As for the thermodynamics of chemical reactions, we focus on acid/base equilibria, which we need to take into account when treating phase transfer reactions of acids and bases. We also look at how chemical structure affects the tendency of a given acid or base function to undergo a proton transfer in aqueous solution. A further treatment of more general aspects of reaction thermodynamics will be given in Chapter 21, Section 21.2.

4.1   Important Thermodynamic Functions

Chemical Potential

When considering the relative energy status of the molecules of a particular compound in a given environmental system (e.g., benzene in aqueous solution), we can envision the molecules to embody both *internal and external energies*. *Internal energies* are those associated with the molecule's chemical bonds, bond vibrations, bending, flexing, and rotations. *External energies* include those due to whole-molecule translations, reorientations, and interactions of the molecules with their surroundings. This energy content is dependent on the temperature, pressure, and chemical composition of the system. When we talk about the "energy content" of a given substance, we are usually not concerned with the energy status of a single molecule at any given time, but rather with an average energy status of the entire population of one type of organic molecule (e.g., benzene) in the system. To describe the (average) "energy status" of a compound, *i,* mixed in a milieu of substances, Gibbs (1873, 1876) introduced an entity referred to as *total free energy*, G, of this system, which is composed of enthalpy (H)

and entropy (*TS*) terms (i.e., *G=H-TS*), where *T* is the absolute temperature). *G* can be expressed as the sum of the contributions from all of the different components present:

$$G(p, T, n_1, n_2, \ldots n_i, \ldots n_n) = \sum_{i=1}^{n} n_i \mu_i \qquad (4\text{-}1)$$

where n_i is the amount of compound *i* (in moles) in the system containing N compounds.

The entity μ_i, which is referred to as *chemical potential* of the compound *i*, is given by:

$$\mu_i (\text{J mol}^{-1}) = \left[\frac{\partial G(\text{J})}{\partial n_i (\text{mol})} \right]_{T, p, n_j \neq n_i} \qquad (4\text{-}2)$$

Hence, μ_i expresses the Gibbs free energy (which we denote just as free energy) added to the system at *constant T, p, and composition* with each added increment of compound *i*. Let us now try to evaluate this important function. When adding an *incremental number* of molecules of *i*, but leaving everything else unchanged, free energy is introduced in the form of internal energies of substance *i* as well as by the interaction of *i* with other molecules in the system. As more *i* is added, the composition of the mixture changes and, consequently, μ_i changes as a function of the amount of *i*. The chemical potential μ_i is sometimes also referred to as the *partial molar free energy*, G_i, of a compound. Finally, we note that G_i (J mol^{-1}) is related to the *partial molar enthalpy*, H_i (J mol^{-1}), and *partial molar entropy*, S_i (J mol^{-1} K^{-1}), by:

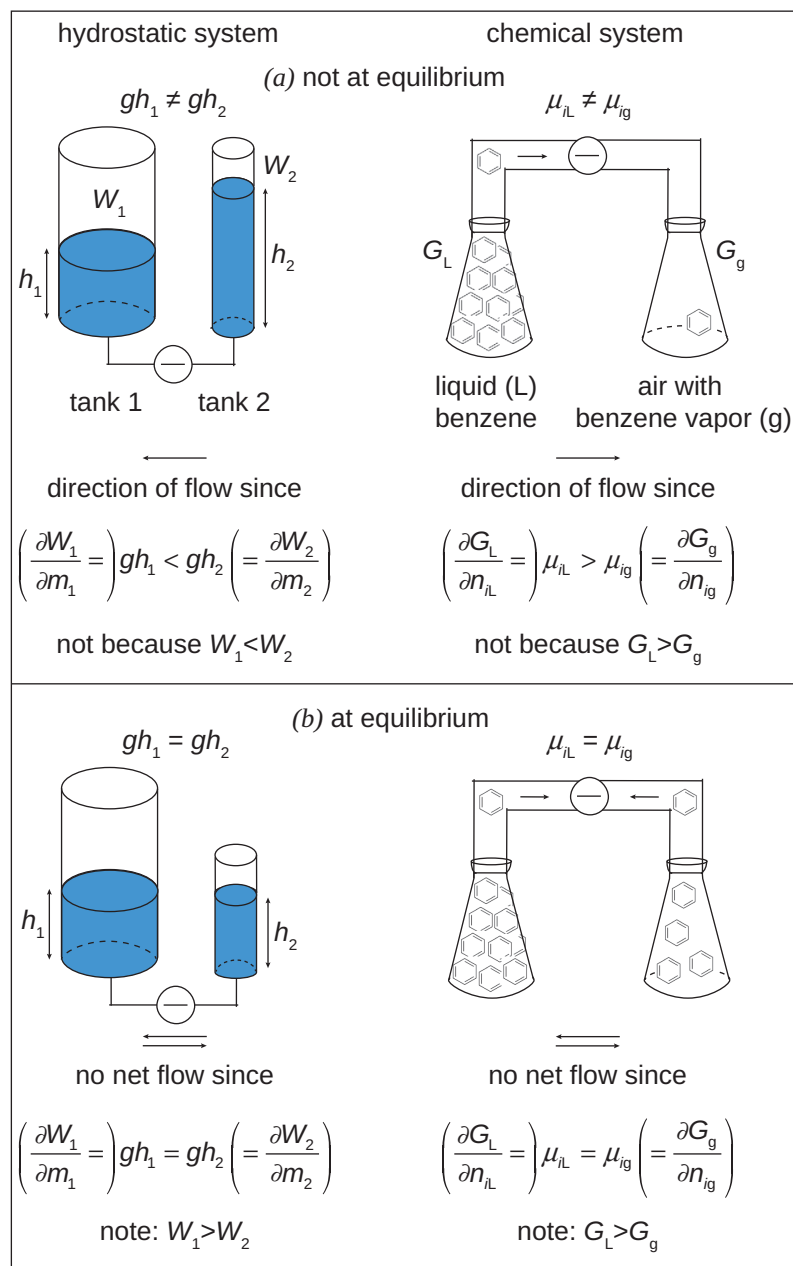$$\mu_i \equiv G_i = H_i - TS_i \qquad (4\text{-}3)$$

Gibbs (1876) recognized that the chemical potential could be used to assess the tendency of component *i* to be transferred from one system to another or to be transformed within a system, which is analogous to the use of hydrostatic head potential for identifying the direction of flow between water reservoirs (Fig. 4.1*a*). We know that equilibrium (no net flow in either direction) is reached when the hydrostatic head potentials of the two reservoirs are equal (Fig. 4.1*b*). Similarly, chemical equilibrium is characterized by equal chemical potentials for each of the constituents. As with hydrostatic head potential, chemical potential is an *intensive* entity, meaning it is independent of the size of the system. This in contrast to the total free energy *G*, which is an *extensive* function that at constant conditions is proportional to the size of the system.

Fugacity

Unfortunately, unlike hydraulic head potentials, we cannot directly observe chemical potentials. Consequently, the concept of *fugacity* was born. Lewis (1901) reasoned that rather than looking into a system and trying to quantify all of the chemical potential energies carried by the various components of interest, it would be more practical to assess a molecule's *urge to escape or flee* that system (hence "fugacity" from Latin *fugere*, to flee). If one could quantify *the relative tendencies* of molecules to flee

various situations, one could simultaneously recognize the *relative* chemical potentials of the compounds of interest in those situations. Based on the differences in their chemical potentials, one could quantify the direction (higher μ_i to lower μ_i) and the extent to which a transfer or transformation process would occur.

Figure 4.1 Conceptualization of the potential functions in a hydrostatic system and in a simple chemical system. (*a*) In the unequilibrated hydrostatic system, water will flow from reservoir 2 of higher hydrostatic potential (=gh_2, where g is the acceleration due to gravity and h_2 is the observable height of water in the tank) to reservoir 1 of lower hydrostatic potential; total water volumes (i.e., total potential energies W_1 and W_2) do not dictate flow. Similarly, benzene molecules move from liquid benzene to the headspace in the unequilibrated chemical system, not because there are more molecules in the flask containing the liquid, but because the molecules initially exhibit a higher chemical potential in the liquid than in the gas. (*b*) At equilibrium, the hydrostatic system is characterized by equal hydrostatic potentials in both reservoirs (not equal water volumes) and the chemical system reflects equal chemical potentials in both flasks (not equal benzene concentrations). In the hydrostatic system, m is the mass, W the weight, and gh is the hydrostatic potential. In the chemical system, n_i is the number of moles of compound i, G is the Gibbs free energy, and μ_i is the chemical potential.

hydrostatic system   *chemical system*

(a) not at equilibrium

$gh_1 \neq gh_2$ $\mu_{iL} \neq \mu_{ig}$

W_2

W_1

G_L G_g

h_1 h_2

tank 1   tank 2   liquid (L) benzene   air with benzene vapor (g)

direction of flow since   direction of flow since

$$\left(\frac{\partial W_1}{\partial m_1} = \right) gh_1 < gh_2 \left(= \frac{\partial W_2}{\partial m_2} \right) \qquad \left(\frac{\partial G_L}{\partial n_{iL}} = \right) \mu_{iL} > \mu_{ig} \left(= \frac{\partial G_g}{\partial n_{ig}} \right)$$

not because $W_1 < W_2$ not because $G_L > G_g$

(b) at equilibrium

$gh_1 = gh_2$ $\mu_{iL} = \mu_{ig}$

h_1 h_2

no net flow since   no net flow since

$$\left(\frac{\partial W_1}{\partial m_1} = \right) gh_1 = gh_2 \left(= \frac{\partial W_2}{\partial m_2} \right) \qquad \left(\frac{\partial G_L}{\partial n_{iL}} = \right) \mu_{iL} = \mu_{ig} \left(= \frac{\partial G_g}{\partial n_{ig}} \right)$$

note: $W_1 > W_2$ note: $G_L > G_g$

Pressure and Fugacities of a Compound in the Gas State

Let us first quantify the "fleeing tendency" or fugacity of molecules in a gas since the gas phase is one of the simplest molecular systems. Imagine a certain number of moles (n_i) of a pure gaseous compound i confined to a volume, V, say in a closed beaker, at

a specific temperature, T. The molecules of the gaseous compound exert a pressure p_i on the walls of the beaker (a quantity we can feel and measure) as they press upon it seeking to pass (Fig. 4.1a). It is not difficult to imagine that if the gas molecules wish to escape more "insistently" (i.e., a higher chemical potential as a result, for example, of the addition of more i molecules to the gas phase in the beaker), their impact on the walls will increase. Consequently, we measure a higher gas pressure. For an *ideal* gas (i.e., one in which the molecules do not interact with each other), the pressure is perfectly proportional to the amount of gaseous compound present. Stating this quantitatively, we see that *at constant T*, the incremental change in chemical potential of the gaseous compound i may be related to a corresponding change in pressure (deduced from the Gibbs-Duhem equation, e.g., Prausnitz, 1969):

$$(d\mu_{ig})_T = \frac{V}{n_{ig}} dp_i \qquad (4\text{-}4)$$

In this case, we can substitute V/n_{ig} with RT/p_i:

$$(d\mu_{ig})_T = \frac{RT}{p_i} dp_i \qquad (4\text{-}5)$$

Now we understand the reason why we cannot give an absolute value of the chemical potential. The integral of the differential expression Eq. 4-5 is only determined up to an arbitrary integration constant or, what is mathematically the same, to the (arbitrary) choice of a lower integration limit. We call this limit the "reference pressure", p_i^0, or the "reference state." In fact, every variable that is a potential, like height, potential energy, or electric potential, only involves relative values, that is, differences between different states. In order to define absolute values, a reference state is also needed for the chemical potential:

$$\int_{\mu_{ig}^0}^{\mu_{ig}} (d\mu_{ig})_T = RT \int_{p_i^0}^{p_i} \frac{1}{p_i} dp_i \qquad (4\text{-}6)$$

Integration of Eq. 4-6 yields:

$$\mu_{ig} = \mu_{ig}^0 + RT \ln\frac{p_i}{p_i^0} \qquad (4\text{-}7)$$

Let us now look at the situation in which we deal with *real* gases, that is, with a situation in which intermolecular forces between the molecules cannot be neglected, as is even more the case for liquids and solids. These forces influence the (partial) pressure of the gas molecules, but not the amount of the gaseous compounds. This real pressure is called fugacity.

In contrast to the pressure of an ideal gas, the fugacity is not only a function of the amount of substance and temperature, but also of the composition (types and amounts of gaseous compounds present) of the gaseous system and total pressure. The fugacity

of a gaseous compound is, however, closely related to its partial pressure. To account for the nonideality of the gas (due to molecule-molecule interactions), one can relate these terms by using a fugacity coefficient, θ_{ig}:

$$f_{ig} = \theta_{ig} p_i \tag{4-8}$$

We use this result in Eq. 4-7 to obtain the correct expression for the chemical potential of a gaseous compound i so it is not based on pressure, but on fugacity:

$$\mu_{ig} = \mu_{ig}^0 + RT \ln \frac{f_i}{p_i^0} \tag{4-9}$$

Note that for the standard state, one defines ideal gas behavior as $f_i^0 = p_i^0$ (commonly 1 bar).

Under typical environmental conditions with atmospheric pressure, gas densities are very low (molecule-molecule interactions are essentially negligible) so that we set $\theta_{ig} = 1$. In other words, in all our following discussions, we assume that any compound exhibits ideal gas behavior (i.e., we use Eq. 4-7 instead of Eq. 4-9).

In a mixture of gaseous compounds having a total pressure p, p_i is the portion of that total pressure contributed by compound i, and it is called the *partial pressure*, which may be expressed as:

$$p_i = x_{ig} p \tag{4-10}$$

where x_{ig} is the mole fraction of i:

$$x_{ig} = \frac{n_{ig}}{\sum_j n_{jg}} \tag{4-11}$$

and $\sum_j n_{jg}$ is the total number of moles present in the gas, and p is the total pressure. Thus, the fugacity of a gas i in a mixture is given by:

$$f_{ig} = \theta_{ig} x_{ig} p \approx p_i \tag{4-12}$$

when the total pressure is near 1 bar.

Reference States and Standard States

Before we discuss the fugacities of compounds in liquid and solid phases, we should remember that the chemical potential, like other potentials such as potential energy or hydrostatic potential, are only defined relative to some reference condition. However, with the choice of an appropriate *reference state*, we can define an absolute value for the chemical potential that can then be related to other characteristics of the system such as pressure and temperature.

When we consider a change in the "energy status" of a compound of interest (e.g., the transfer of organic molecules from the pure liquid phase to the overlying gas phase or a reaction in which bonds are broken), we try to do our energy-change bookkeeping in such a way that we concern ourselves with only those energetic properties of the molecules that undergo change. During the vaporization of liquid benzene, for example, we do not worry about the internal energy content of the benzene molecules themselves, since these molecules maintain the same bonds, and practically the same bond motions, in both the gaseous and liquid states. Rather, we focus on the energy change associated with having benzene molecules in new surroundings. Benzene molecules in gas or liquid phases feel different attractions to their neighboring molecules and contain different translational, rotational, and conformational energies because in a liquid the molecules are packed fairly tightly together, whereas in the gas they are almost isolated. This focus on only the changing aspects is the guiding consideration in our choice of *reference states*. For each chemical species of interest, we want to pick a form (a reference state of the material) that is closely related to the situation at hand. For instance, it would be impractical, although feasible, to consider the energy status of elemental carbon and hydrogen of which the benzene molecule is composed as the reference point with which evaporating benzene should be compared. Instead, we are clever and, in this case, choose the "energy status" of pure liquid benzene as a reference state because liquid benzene includes all of the internal bonding energies common to the compound's gaseous and liquid forms. Similarly, when dealing with simple reactions in aqueous solution such as proton transfer reactions, it would be silly to choose the pure liquid of the organic acid and base as the reference state. Rather, their "energy status" at infinite dilution in water is a better reference.

Therefore, in the field of environmental organic chemistry, the most common *reference states* used include: (i) the *pure liquid state*, when we are concerned with phase transfer processes; (ii) the *infinite dilution state*, when we are dealing with reactions of organic chemicals in (aqueous) solution, and (iii) the elements in their naturally occurring forms (e.g., $C(s)$, H_2, O_2, N_2, Cl_2, Br_2), when we are interested in reactions in which many bonds are broken or formed. Certainly, other reference states may be chosen as convenience dictates, the guiding principle being that one can clearly see how the chemical species considered in a given system is related to the reference state. Once we have chosen an appropriate reference state, we also must specify the conditions of our reference state, that is, the pressure, temperature, and concentration. These conditions are referred to as *standard conditions* and, together with the reference state, form the *standard state* of a chemical species. We then refer to μ_i^0 in Eqs. 4-7 and 4-9 as the *standard chemical potential*, a value that quantifies the "energy status" under these specific conditions. Since we are most often concerned with the behavior of chemicals in the earth's near-surface ecosystems, 1 bar (10^5 Pa or 0.987 atm) is usually chosen as standard pressure. Furthermore, we have to indicate the temperature at which we consider the chemical potential. If not otherwise indicated, we will commonly assume a temperature of 298 K (25°C). In summary, as long as we are unambiguous in our choice of reference state and standard conditions, hopefully chosen so that both the starting and final states of a molecular change may be clearly related to these choices, our energy bookkeeping should be fairly straightforward to understand.

4.2   Using Thermodynamic Functions to Quantify Equilibrium Partitioning

Fugacities of Liquids and Solids

Let us now continue with our discussion of how to relate the chemical potential to measurable quantities and how to apply the results to assess equilibrium partitioning of a given chemical i between different phases. We have already seen that the chemical potential of a gaseous compound can be related to pressure. Since substances in both the liquid and solid phases also exert vapor pressures, Lewis reasoned that these pressures likewise reflected the escaping tendencies of these materials from their condensed phases (Fig. 4.2). He thereby extended this logic by defining the fugacities of pure liquids (including subcooled and superheated liquids, hence the subscript "L") and solids (subscript "s") as a function of their vapor pressures, p_{iL}^* and p_{is}^* (see also Chapter 8):

$$f_{iL} = \gamma_{iL} p_{iL}^*$$
$$f_{is} = \gamma_{is} p_{is}^*$$

(4-13)

pure organic liquid i (•)

(a) ideal gas

(b) (reference state)

measured fugacity: p_i

measured fugacity: p_{iL}^*

$f_{ig} = p_i$

$f_{iL} = f_{ig} = p_{iL}^*$

ideal liquid solution

nonideal liquid solution

(c) of i (•) in j (○)

(d) of i (•) in e.g., water (∧)

measured fugacity: $x_{i\ell} p_{iL}^*$

measured fugacity: $\gamma_{i\ell} x_{i\ell} p_{iL}^*$

$f_{i\ell} = f_{ig} = x_{i\ell} \, p_{iL}^*$

$f_{i\ell} = f_{ig} = \gamma_{i\ell} x_{i\ell} \, p_{iL}^*$
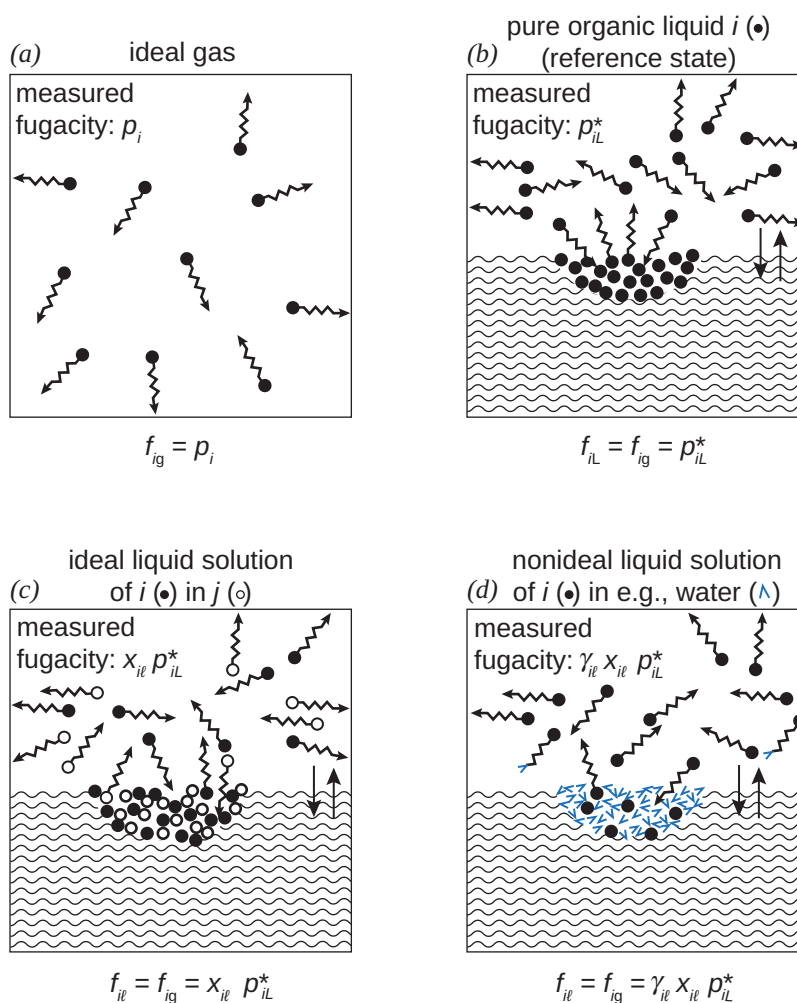
Figure 4.2 Conceptualization of the fugacity of a compound i (*a*) in an *ideal gas*; (*b*) in a *pure* liquid compound i; (*c*) in an *ideal* liquid mixture; and (*d*) in a *nonideal* liquid mixture (e.g., in aqueous solution). In (*b*), (*c*), and (*d*), the gas and liquid phases are in equilibrium with one another.

where the activity coefficient, γ_i, accounts for nonideal behavior resulting from molecule–molecule interactions. These activity coefficients are commonly set equal to 1 when we decide to take as the reference state the pure compound in the phase it naturally assumes under the conditions of interest. Thus, the molecules are viewed as "dissolved" in like molecules. This condition is defined to have "ideal" mixing behavior.

If we consider, for example, compound i in a liquid mixture, such as in an organic or aqueous solution (subscript "ℓ", see Fig. 4.2d), we can now relate its fugacity in the mixture to the fugacity of the pure liquid compound by:

$$f_{i\ell} = \gamma_{i\ell} x_{i\ell} f_{iL}^* = \gamma_{i\ell} x_{i\ell} p_{iL}^* \tag{4-14}$$

where $x_{i\ell}$ is the mole fraction of i (Eq. 4-11) in the mixture or solution. For convenience, we chose the *pure liquid compound* (superscript *) as our *reference state*. If the compounds form an *ideal* mixture (Fig. 4.2c), implying that no nonideal behavior results from interactions among unlike molecules, $\gamma_{i\ell}$ is equal to 1 and Eq. 4-14 represents the well-known *Raoult's Law*.

Activity Coefficient and Chemical Potential

Using the concept of fugacity we can now, in analogy to the gas phase (Eq. 4-9), express the chemical potential of a compound i in a liquid solution by:

$$\mu_{i\ell} = \mu_{iL}^* + RT \ln \frac{f_{i\ell}}{p_{iL}^*} \tag{4-15}$$

where we have chosen the pure liquid compound as the reference state. The chemical potential of the pure liquid, μ_{iL}^*, is nearly equal to the standard free energy of formation, $\Delta_f G_i^o(L)$, of the pure liquid compound, which is commonly defined at 1 bar and not at p_{iL}^*. Hence $\mu_{iL}^* \cong \mu_{iL}^0$. Substitution of Eq. 4-14 into Eq. 4-15 then yields:

$$\mu_{i\ell} = \mu_{iL}^* + RT \ln \gamma_{i\ell} x_{i\ell} \tag{4-16}$$

Generally, the expression $f_i/f_{ref} = \gamma_i x_i = a_i$ is referred to as the *activity* of the compound. That is, a_i is a measure of how active a compound is in a given state (e.g., in aqueous solution) compared to its reference state where activity $\equiv 1$ (e.g., the pure organic liquid at the same T and p). Since γ_i relates a_i, the "apparent concentration" of i, to the real concentration x_i, it is only logical that one refers to γ_i as the *activity coefficient*. We emphasize here *that the activity of a given compound in a given phase is a relative measure and is, therefore, dependent on the reference state*. The numerical value of γ_i will depend on the choice of the reference state, since molecules of i in different reference states (e.g., liquid solutions) interact differently with their surroundings.

Excess Free Energy, Excess Enthalpy, and Excess Entropy

Before we apply Eq. 4-16 to describe the partitioning of a compound i between two phases, a few comments are necessary on the terms included in Eq. 4-16. First, we

rewrite Eq. 4-16 by splitting the second term so that the first part reflects the difference in partial molar free energy of a compound i between its current solution and its situation in its reference state due to entropic differences. The second part captures any extra or "excess" differences associated with i's actual situation in a given solution:

$$\mu_{i\ell} = \mu_{iL}^* + RT \ln x_{i\ell} + RT \ln \gamma_{i\ell}$$
$$\underbrace{\phantom{RT \ln x_{i\ell}}}_{TS_{imix}^{ideal}} \quad \underbrace{\phantom{RT \ln \gamma_{i\ell}}}_{G_{i\ell}^{E}}$$

$$(4\text{-}17)$$

As already pointed out, $\gamma_{i\ell}$ is equal to 1 if a compound forms an ideal solution (i.e., one in which i's interactions with its new molecular neighbors are the same as those when i was dissolved in a liquid of itself). In this rather rare case, the term $RT\ln\gamma_{i\ell}$, which we denote as *partial molar excess free energy* of compound i in solution ℓ, $G_{i\ell}^{E}$, is 0. This means that the difference between the chemical potential of the compound in solution and its chemical potential in the reference state is only due to the different concentrations of the compound i in the two states. The term $R\ln x_{i\ell} = S_{imix}^{ideal}$ expresses the partial molar entropy of *ideal* mixing (a purely statistical term) when diluting the compound from its pure liquid ($x_{i\ell} = 1$) into a solvent that consists of otherwise like molecules.

Let us now have a closer look at the term excess free energy. For simplicity in the following sections and throughout the book, we drop the term "partial molar" and talk about the excess free energy of a given compound in a given molecular environment. To evaluate the excess free energy term, it is useful to first make some general comments on the various enthalpic and entropic contributions (Eq. 4-3) to the free energy of a given compound in a specific molecular environment. We do this in a somewhat simplistic way. In brief, the *enthalpy* term represents all attractions or attachments of a compound's atoms to their surroundings. These include bonds (*intra*molecular forces, e.g., bond energies) as well as *inter*molecular interactions (see Chapter 2). Thus, the enthalpic contributions may be thought of as the "glue" holding the parts of a molecule to their surroundings. When we are only interested in the partitioning of organic compounds, we choose a reference state in a way that we only have to deal with changes in *inter*molecular interactions when comparing the energy of a compound in various molecular environments.

The *entropy* term is best imagined as involving the "freedom" or latitude of orientation, configuration, and translation of the molecules involved. When molecules are forced to be organized or confined, work must be done. As a consequence, energy must be spent in the process. Conversely, the more ways the molecule can twist and turn, the more freedom the bonding electrons have in moving around in the molecular structure, the more "randomness" exists. As a result, the entropy terms are larger. This leads to a more negative free energy term (see Eq. 4-3). By analogy to Eq. 4-3, we can express the excess free energy term in Eq. 4-17 as:

$$RT \ln\gamma_{i\ell} = G_{i\ell}^{E} = H_{i\ell}^{E} - TS_{i\ell}^{E} \qquad (4\text{-}18)$$

where $H_{i\ell}^{E}$ and $S_{i\ell}^{E}$ are the (partial molar) excess enthalpy and excess entropy, respectively, of the compound i in phase ℓ. Let us now inspect the enthalpic and entropic

Table 4.1 Excess Free Energies, Enthalpies and Entropies of Hexane (apolar), Benzene (monopolar), Diethylether (monopolar) and Ethanol (bipolar) in the Ideal Gas Phase, in Hexadecane, and in Water at Infinite Dilution at 25°C [a,b]

Phase Compound (i)	$G_{i\,\text{phase}}^{E}$ (kJ mol^{-1})	=	$H_{i\,\text{phase}}^{E}$ (kJ mol^{-1})	−	$TS_{i\,\text{phase}}^{E}$ (kJ mol^{-1})	$S_{i\,\text{phase}}^{E}$ (J mol^{-1} K^{-1})
Gas Phase						
Hexane	4.0	=	31.6	−	27.6	92.6
Benzene	5.3	=	33.9	−	28.6	96.0
Diethylether	0.8	=	27.1	−	26.3	88.2
Ethanol	6.3	=	42.6	−	36.3	122.0
Hexadecane						
Hexane	−0.2	=	0.6	−	0.8	2.7
Benzene	0.4	=	3.5	−	3.1	9.7
Diethylether	0.0	=	1.9	−	1.9	6.4
Ethanol	8.8	=	26.3	−	17.5	58.7
Water						
Hexane	32.3	=	−0.4	+	32.7	−109.7
Benzene	19.4	=	2.2	+	17.2	−58.4
Diethylether	12.0	=	−19.7	+	31.7	−106.3
Ethanol	3.2	=	−10.0	+	13.2	−44.3

[a] Data from Abraham et al. (1990) and Lide (1995).
[b] Reference state if the pure liquid organic compound.
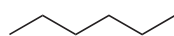
n-hexane

benzene
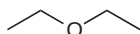
diethylether

ethanol

contributions to $G_{i\ell}^{E}$ for four simple compounds in hexadecane and in water (Table 4.1). Also shown in Table 4.1 are the corresponding values for the ideal gas phase (i.e., G_{ig}^{E}, H_{ig}^{E}, S_{ig}^{E}), which are identical with the free energy, enthalpy, and entropy of vaporization of pure liquid compounds, respectively, which we will discuss in detail in Chapter 8. Here, we note from the examples given in Table 4.1 that when considering a compound in the ideal gas state relative to the pure liquid, both enthalpy costs as well as entropy gains are important in determining the overall excess free energy. The rather high excess enthalpy and excess entropy values observed for ethanol can be fully rationalized by the ability of this compound to undergo quite strong hydrogen bonding (H-bonding, see Chapter 2) within the pure liquid (which is not the case for the other compounds). This results in a stronger "glue" among the molecules and, therefore, in a higher (positive) H_{ig}^{E}. For the same reasons, the ethanol molecules have less freedom to move around in their own liquid phase, which leads to a larger entropy gain when transferred to the (ideal) gas phase, where freedom is maximal.

A very different picture is seen when compounds move from a pure liquid into hexadecane. Here, the compounds that do not hydrogen bond with each other show almost ideal behavior (i.e., $G_{i\ell}^{E} \approx 0$) because in their own liquids, as well as in hexadecane, they only have van der Waals interactions (see discussion of molecular interactions in Chapters 2 and 7). In the case of ethanol, again, a significant enthalpy cost and entropy gain is found, which can be explained with the same arguments used for the

gas phase. The absolute $H_{i\ell}^{\mathrm{E}}$ and $TS_{i\ell}^{\mathrm{E}}$ values are, however, smaller as compared to the gas phase, because ethanol undergoes vdW interactions with the hexadecane solvent molecules, and because the freedom to move around in hexadecane is smaller than in the gas phase.

Finally, the most interesting, and maybe somewhat puzzling, case is the aqueous phase. We might not have guessed that the excess enthalpies in water are close to zero or even negative for all four compounds, even for hexane that cannot form H-bonds (see Chapter 2, Box 2.2). The very high fugacity of hexane in water is, therefore, not due to enthalpic reasons but caused by a very large negative entropy contribution. This effect is also significant for the other three compounds (see Table 4.1). This significant loss in entropy when transferring an organic molecule from one liquid phase (the pure compound) to another liquid phase (water) is, at first glance, rather surprising (compare water with hexadecane). Hence, solutions in water represent a special case, which we need to unravel if we want to understand the environmental partitioning of organic compounds. We learn more about these secrets in Chapter 9. Our next step is to demonstrate how partition constants between two different phases are linked to the corresponding excess free energy terms.

Equilibrium Partition Constants and Standard Free Energy of Transfer

Let us consider a system in which two bulk phases, 1 and 2 (e.g., air and water), are in contact with each other at a given temperature and pressure. We assume that the two phases are in equilibrium with each other with respect to the amounts of all chemical species present in each. We now introduce a very small amount of a given organic compound i into phase 2 (i.e., the properties of both bulk phases are not significantly influenced by the introduction of the compound). After a short time, some molecules of compound i will have been transferred from phase 2 (reactant) to phase 1 (product) as portrayed in Eq. 4-19:

$$i \text{ in phase } 2 \rightleftharpoons i \text{ in phase } 1$$
$$\text{``reactant''} \qquad \text{``product''}$$

(4-19)
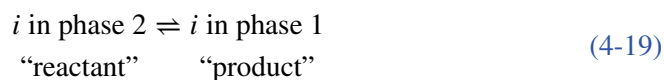
The equilibrium situation can thus be described by an equilibrium partition constant, K_{i12}, which we define as:

$$K_{i12} = \frac{\text{concentration of } i \text{ in phase } 1}{\text{concentration of } i \text{ in phase } 2}$$

(4-20)

Because we have chosen i in phase ℓ as the "product," the abundance of i in phase 1 is in the numerator of Eq. 4-20. Furthermore, for practical purposes, we define a constant expressed as a ratio of concentrations rather than activities. Finally, we consider only situations in which the compound is present as a solute, that is, at low concentrations such that it does not significantly affect the properties of the bulk phase.

At this point, we write the chemical potentials of i in the two phases according to Eq. 4-17:

$$\mu_{i1} = \mu_{iL}^* + RT \ln x_{i1} + RT \ln \gamma_{i1}$$
$$\mu_{i2} = \mu_{iL}^* + RT \ln x_{i2} + RT \ln \gamma_{i2} \tag{4-21}$$

The difference between the two chemical potentials (which corresponds to the free energy of a reaction discussed in Section 4.3 and in Chapter 21) is then given as:

$$\mu_{i1} - \mu_{i2} = RT \ln \frac{x_{i1}}{x_{i2}} + RT \ln \frac{\gamma_{i1}}{\gamma_{i2}} \tag{4-22}$$

One can easily see that at the very beginning of our experiment, μ_{i1} is smaller than μ_{i2} ($x_{i1} \ll x_{i2}$) and thus the difference will be negative, even if the activity coefficients of the compound in the two phases are quite different. Consequently, a net transfer of compound i from phase 2 to phase 1 will occur until equilibrium (i.e., $\mu_{i1} = \mu_{i2}$) is reached. Then, at equilibrium, we obtain after some rearrangement:

$$\ln K'_{i12} \equiv \ln \frac{x_{i1}}{x_{i2}} = -\frac{(RT \ln \gamma_{i1} - RT \ln \gamma_{i2})}{RT} \tag{4-23}$$

which is equivalent to

$$K'_{i12} \equiv \frac{x_{i1}}{x_{i2}} = e^{-(RT \ln \gamma_{i1} - RT \ln \gamma_{i2})/RT} = e^{-\Delta_{12} G_i/RT} \tag{4-24}$$

where K'_{i12} is the partition constant on a *mole fraction* basis. We distinguish this mole fraction basis from the partition constant expressed in molar concentrations by using a prime superscript. We can see now that the free energy of transfer, $\Delta_{12} G$, equals the difference between the (partial molar) excess free energies of i in the two phases under specified conditions:

$$\Delta_{12} G = G_{i1}^E - G_{i2}^E \tag{4-25}$$

We now address the problem of expressing the abundance of compounds in a bulk phase. In environmental chemistry, the most common way to express concentrations is not by mole fraction, but by the number of molecules per unit volume, for example, as moles per liter of solution (mol L^{-1}, M). This molar concentration scale is sometimes not optimal. For example, volumes are dependent on T and p, whereas masses are not. Hence, the use of concentration data normalized per kilogram of seawater is often seen in the oceanographic literature. However, the molar scale is widely used. We can convert mole fractions to molar concentrations by:

$$C_{i\ell} = \frac{x_{i\ell}(\text{mol } i \text{ (total mol)}^{-1})}{\bar{V}_\ell(\text{L(total mol)}^{-1})} \tag{4-26}$$

where $C_{i\ell}$ is the concentration (moles per liter) of i in phase ℓ and $\bar{V}_\ell$ is the molar volume of the mixture or solution. When we deal with a mixture of several components (e.g., organic solvent/water mixtures in Chapter 10), we generally apply Amagat's Law as a first approximation. That is, we assume that the components of the liquid phase mix with no change in volume due to intermolecular interactions:

$$\bar{V}_\ell = \sum_j x_j \bar{V}_j \tag{4-27}$$

where x_j and $\bar{V}_j$ are the mole fractions and molar volumes of the pure components, j. For aqueous solutions of moderately or only sparingly soluble compounds, we can usually neglect the contribution of the organic solute to the molar volume of the mixture. This means that we set $\bar{V}_\ell$ equal to $\bar{V}_w$, the molar volume of water ($\bar{V}_w = 0.0181$ L mol^{-1} at 25°C).

Substitution of x_i by $C_{i\ell} \bar{V}_\ell$ in Eq. 4-23 then yields the partition constant, K_{i12}, expressed in molar concentrations (we now omit the prime superscript):

$$\ln K_{i12} \equiv \ln \frac{C_{i1}}{C_{i2}} = -RT \ln \frac{\bar{V}_1}{\bar{V}_2} - \frac{(RT \ln\gamma_{i1} - RT \ln\gamma_{i2})}{RT} \tag{4-28}$$

which is equivalent to:

$$K_{i12} \equiv \frac{C_{i1}}{C_{i2}} = \frac{\bar{V}_2}{\bar{V}_1} e^{-(RT \ln\gamma_{i1} - RT \ln\gamma_{i2})/RT} = \frac{\bar{V}_2}{\bar{V}_1} e^{-\Delta_{12}G_i/RT} \tag{4-29}$$

Using the excess free energy, enthalpy, and entropy values given for our four model compounds in Table 4.1, we can now calculate how these compounds partition between the various phases (i.e., between air and hexadecane, air and water, and hexadecane and water respectively) at equilibrium (Table 4.2). These results reflect, of course, what we have previously discussed when inspecting the excess energy terms of the compounds in various phases. In Chapters 7 to 10, we address in detail the partitioning of organic compounds between air and liquids (including water), and organic phases and water. Here, we note again the important entropy contributions to the overall excess free energy of transfer of a compound i, if water is one of the phases involved.

Effect of Temperature on Equilibrium Partitioning

So far, we have considered the equilibrium partitioning of an organic compound at a given temperature and pressure. Since partition constants are commonly reported for only one particular temperature (e.g., 25°C), we need to be able to extrapolate these values to other conditions of temperature. In most cases in environmental organic chemistry, we can neglect the effect of pressure changes on equilibrium partitioning. Exceptions might include cases of very high pressure, as for example, in the deep sea (>200 bar), deep groundwater, or in reactors operated at supercritical conditions. For these particular applications, we refer to the corresponding literature (e.g., Prausnitz, 1969; Atkins, 2014). Here, we confine our discussion to the temperature dependence

Table 4.2 Air–Hexadecane, Air–Water, and Hexadecane–Water Equilibrium Partitioning of Hexane, Benzene, Diethylether, and Ethanol: Free Energies, Enthalpies and Entropies of Transfer, as well as Partition Constants Expressed on a Molar Base (i.e., mol L_{phase1}^{-1}/mol L_{phase2}^{-1}) [a]

Phase 1/Phase 2 Compound (i)	$\Delta_{12}G_i$ (kJ mol^{-1})	=	$\Delta_{12}H_i$ (kJ mol^{-1})	−	$T\Delta_{12}S_i$ (kJ mol^{-1})	$\Delta_{12}S_i$ (J mol^{-1} K^{-1})	K_{i12}^a
Air/Hexadecane							
Hexane	4.2	=	31.0	−	26.8	89.9	2.2×10^{-3}
Benzene	4.9	=	30.4	−	25.5	85.6	1.7×10^{-3}
Diethylether	0.8	=	25.2	−	24.4	81.9	8.7×10^{-3}
Ethanol	−2.5	=	16.3	−	18.8	73.3	3.3×10^{-2}
Air/Water							
Hexane	−28.3	=	32.0	−	60.3	202.3	6.5×10^1
Benzene	−14.1	=	29.7	−	43.8	147.0	2.1×10^{-1}
Diethylether	−11.2	=	46.8	−	58.8	194.6	6.6×10^{-2}
Ethanol	3.1	=	52.6	−	49.5	166.3	2.0×10^{-4}
Hexadecane/Water							
Hexane	−32.5	=	1.0	−	33.5	112.4	3.0×10^4
Benzene	−19.0	=	1.3	−	20.3	68.1	1.3×10^2
Diethylether	−12.0	=	21.6	−	33.6	112.8	7.7×10^0
Ethanol	5.6	=	36.3	−	30.7	103.0	6.4×10^{-3}

[a]Eq. 4-29: molar volumes at 25°C and 1 bar: $\bar{V}_{ideal\ gas} = 24.73$ L mol^{-1}, $\bar{V}_{hexadecane} = 0.293$ L mol^{-1}, $\bar{V}_{water} = 0.0181$ L mol^{-1}.

of partitioning. As a starting point, we consider the differentiation of ln K_{i12} (Eq. 4-29) with respect to temperature:

$$\frac{d \ln K_{i12}}{dT} = \frac{d \ln \text{constant}}{dT} - \frac{1}{R}\frac{d(\Delta_{12}G_i/T)}{dT} \tag{4-30}$$

Let us first look at the temperature dependence of the constant. Using the mole fraction basis, i.e., $K_{i12} = K'_{i12}$, this constant is equal to 1 and, therefore, temperature independent if mole fractions or partial pressures are used to express the abundance of *i* in a given liquid or in the gas phase. In contrast, when using molar concentrations, the constant is given by the ratio of the molar volumes of the two phases. These are, of course, influenced by temperature. However, as a first approximation, we may neglect this relatively small effect (<10% in the temperature range between 0°C and 30°C), and rewrite Eq. 4-30 as:

$$\frac{d \ln K_{i12}}{dT} = -\frac{1}{R}\frac{d(\Delta_{12}G_i/T)}{dT} \tag{4-31}$$

Since $\Delta_{12}G_i = \Delta_{12}H_i - T\Delta_{12}S_i$ and assuming that $\Delta_{12}S_i$ does not change with temperature, we may express the right-hand term of Eq. 4-31 as:

$$-\frac{1}{R}\frac{d(\Delta_{12}G_i/T)}{dT} = \frac{1}{R}\frac{\Delta_{12}H_i}{T^2} \tag{4-32}$$

which leads to the well-known van't Hoff equation:

$$\frac{d \ln K_{i12}}{dT} = \frac{\Delta_{12}H_i}{RT^2} \tag{4-33}$$

Equation 4-33 is a very general expression and also applies to describing temperature dependencies of reaction equilibrium constants (of course, with the appropriate reaction enthalpy terms).

If we assume that $\Delta_{12}H_i$ is constant over a small temperature range (say between T_1 and T_2), Eq. 4-33 can be integrated, resulting in:

$$\ln \frac{K_{i12}(T_2)}{K_{i12}(T_1)} = -\frac{\Delta_{12}H_i}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

or
$$\tag{4-34}$$

$$K_{i12}(T_2) = K_{i12}(T_1) \cdot e^{-\frac{\Delta_{12}H_i}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]}$$

By measuring K_{i12} values at various temperatures, $\Delta_{12}H_i$ can be obtained from a linear regression (i.e., a least square fit) of $\ln K_{i12}$ versus 1/T:

$$\ln K_{i12} = -\frac{A}{T} + B \tag{4-35}$$

Since the slope $-A$ (in K) of the regression line is given by $A = \Delta_{12}H_i/R$, the $\Delta_{12}H_i$ value can be obtained by:

$$\Delta_{12}H_i = R \cdot A \tag{4-36}$$

Table 4.3 Effect of Temperature on Equilibrium Partition Constants as a Function of $\Delta_{12}H_i$

$\Delta_{12}H_i$ (kJ mol^{-1})	Factor[a]
−20	0.8
−10	0.9
0	1.0
10	1.2
20	1.3
30	1.5
40	1.8
50	2.0
60	2.4
70	2.8
80	3.1
90	3.6
100	4.1
110	4.7
120	5.4

[a] Average "increase" (factor) of K_{i12} per 10°C increase in temperature.

If one of the phases considered is the gas phase, and if K_{i12} is expressed in molar concentrations (including the gas phase with $n/V = p/RT$), $\Delta_{12}H_i$ in Eqs. 4-34 and 4-36 would have to be replaced by $\Delta_{12}H_i + RT_{av}$, where T_{av} is the average temperature (in Kelvin) of the temperature range considered (Atkinson and Curthoys, 1978). However, from a practical point of view, since RT_{av} is only in the order of 2 to 3 kJ mol^{-1}, we usually neglect it. Finally, we should note that the temperature dependence of K_{i12} over large temperature ranges can be approximated by a function of the type:

$$\ln K_{i12} = a_1 + \frac{a_2}{T} + a_3 \ln T + a_4 \tag{4-37}$$

The parameters a_1, a_2, a_3, and a_4 are obtained similarly as A and B in Eq. 4-35 by fitting experimental K_{i12} data obtained at different temperatures.

Table 4.3 gives the average change in K_{i12} per 10°C increase/decrease in temperature for various $\Delta_{12}H_i$ values. Using the numbers given in Table 4.3, we can now inspect Table 4.2 in order to get some feeling of the temperature dependency of partition constants. Except for the hexadecane–water partitioning of hexane and benzene, we see a significant effect of temperature on the partition constants, particularly if one of the

phases is the gas phase. For example, the air–water partition constant of diethylether is about four times larger at 25°C as compared to 5°C ($\Delta_{12}H_i = 48.8$ kJ mol^{-1}). As we will see later in other chapters (e.g., in Chapter 19), in cases in which equilibrium is not established, temperature may have an important effect on the direction of fluxes of compounds between environmental compartments.

4.3 Organic Acids and Bases I: Acidity Constant and Speciation in Natural Waters

As we discussed in Chapter 3, some important environmental organic chemicals exhibit acid or base functional groups. These may undergo proton transfer reactions resulting in the formation of *charged* species (i.e., anions or cations). These charged species also have *very different properties and reactivities as compared to their neutral counterparts*. Therefore, it is important to know to what extent the molecules of an organic compound may form ions in a given environmental system.

A proton transfer can occur only if an *acid* (HA), a proton *donor* (Brønsted and Pedersen, 1924), reacts with a *base* (B), a *proton acceptor*, as isolated protons are quite unstable species:

$$
\begin{aligned}
HA &\rightleftharpoons A^- + H^+ \\
H^+ + B &\rightleftharpoons BH^+ \\
\hline
HA + B &\rightleftharpoons BH^+ + A^-
\end{aligned}
\tag{4-38}
$$
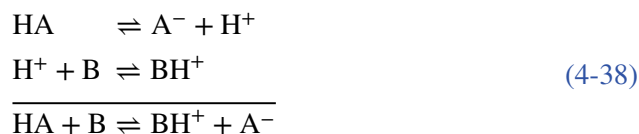
Note that A$^-$ is called the *conjugate* base of HA and BH$^+$ the conjugate acid of B. Proton transfer reactions are usually *very fast* and *reversible*. It makes sense then that we treat such reactions as *equilibrium processes*, and that we are interested in the equilibrium distribution of the species involved in the reaction. In this section, we confine our discussion to proton transfer reactions in *aqueous solution,* although in some cases, such reactions may also be important in nonaqueous media. Our major concern is the speciation of an organic acid or base (neutral versus ionic species) in water under given conditions. In order to do so, we need to recall some basic thermodynamic aspects used to describe acid–base reactions in aqueous solution.

Thermodynamic Considerations of Acid/Base Equilibrium

Organic Acids. Let us first consider the reaction of an organic acid (HA) with water playing the role of the base:

$$
HA + H_2O \rightleftharpoons H_3O^+ + A^-
\tag{4-39}
$$
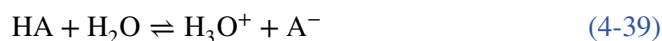
So far, we have used the pure liquid compound as the reference state for describing the thermodynamics of transfer processes between different media. When treating reactions of several different chemical species in one medium (e.g., water), it is much more convenient to use the infinite dilution state in that medium as the reference state for

the solutes. With infinite dilution we refer to a state in which the dissolved molecules do not "feel" each other, meaning they behave as they would be infinitely diluted. For acid–base reactions in aqueous solutions, we express the chemical potential of the solute i as:

$$\mu_i = \mu_i^{0\prime} + RT \ln \frac{\gamma_i'[i]}{(\gamma_i^{0\prime} = 1)[i]^0} \tag{4-40}$$

where the product, $\gamma_i'[i]$ is the activity of i in the solution at its real concentration and $\gamma^{0\prime}[i]^0$ is the activity at the compound's reference concentration. In this case, the standard chemical potential corresponds to the standard free energy of formation of the species i in *aqueous solution*:

$$\mu_i^{0\prime} \equiv \Delta_f G_i^0(aq) \tag{4-41}$$

at given p and T (e.g., 1 bar, 25°C), γ_i' is the activity coefficient, $[i]$ is the actual concentration of the species i, and $[i]^0$ is its concentration in the *standard* state. For our treatment of acid–base reactions we will set $[i]^0 = 1$ M. For the activity coefficient, we use the prime superscript to denote the infinite dilution reference state (in distinction to the pure liquid state), and we omit any subscript to indicate that we are dealing with aqueous solutions. Also, because we have chosen the 1 M aqueous solution as standard state, in many cases γ_i' will not be substantially different from 1. Exceptions are the charged species at high ionic strength, as for example, encountered in seawater.

Before we go on to define the acidity constant of a given organic acid in water, we need to introduce a thermodynamic convention for scaling such constants. We do this relative to H_3O^+ in that we define the dissociation of H_3O^+ in water to have a standard free energy change $\Delta_r G^0 = 0$, which means that the equilibrium constant of this reaction is equal to 1 (see Eq. 4-49):

$$H_3O^+ \rightleftharpoons H_2O + H^+ \; ; \; \Delta_r G^0 = 0 \text{ kJ mol}^{-1} \text{ or } K = 1 \tag{4-42}$$
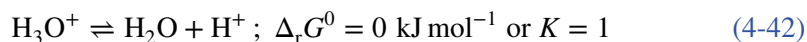
This is equivalent to the definition that the free energy of formation of the proton in aqueous solution is equal to zero, i.e., $\Delta_f G_{H^+}^0(aq) = 0$ at any temperature (Stumm and Morgan, 1996). Hence, we can rewrite Eq. 4-39 as:

$$HA \rightleftharpoons H^+ + A^- \tag{4-43}$$

By setting $[i]^0 = 1$ M and $\mu_{H^+}^{0\prime} \equiv \Delta_f G_{H^+}^0(aq) = 0$ J mol^{-1}, we can now express the chemical potentials of the three species in reaction Eq. 4-43 by:

$$\begin{aligned}
\mu_{HA} &= \mu_{HA}^{0\prime} + RT \ln\gamma_{HA}'[HA] \\
\mu_{H^+} &= \qquad\quad RT \ln\gamma_{H^+}'[H^+] \\
\mu_{A^-} &= \mu_{A^-}^{0\prime} + RT \ln\gamma_{A^-}'[A^-]
\end{aligned} \tag{4-44}$$

Let us first consider the situation in which equilibrium of reaction Eq. 4-43 is not yet reached. From Eqs. 4-1 and 4-2, one may deduce that if the reaction proceeds by the increment, dn_r, the change in the total free energy of the system considered is given by:

$$dG = -\mu_{HA}dn_r + \mu_{H^+}dn_r + \mu_{A^-}dn_r \tag{4-45}$$

The quantity dG/dn_r is referred to as the *free energy of reaction*, and is usually denoted as $\Delta_r G$. Thus, we may write:

$$\Delta_r G = -\mu_{HA} + \mu_{H^+} + \mu_{A^-} \tag{4-46}$$

We discuss this quantity in more detail in Chapter 21 (Section 21.2), when we introduce reactions for which we may not assume are in equilibrium. Here, we are interested only in the equilibrium situation; that is, the situation in which $\Delta_r G = 0$. By inserting Eq. 4-44 into Eq. 4-46 and by setting $\Delta_r G = 0$, we obtain:

$$0 = -\mu_{HA}^{0'} + \mu_{A^-}^{0'} + RT \ln \frac{(\gamma'_{H^+}[H^+])(\gamma'_{A^-}[A^-])}{(\gamma'_{HA}[HA])} \tag{4-47}$$

The algebraic sum of the *standard chemical potentials* is called the standard free energy of reaction and is denoted as $\Delta_r G^0$. In our case:

$$\Delta_r G^0 = -\mu_{HA}^{0'} + \mu_{A^-}^{0'} = -\Delta_f G_{HA}^0(aq) + \Delta_f G_{A^-}^0(aq) \tag{4-48}$$

Hence, the equilibrium constant, K_{ia}, which is commonly referred to as *acidity constant* or *acid dissociation constant* of the acid $i = $ HA is given by:

$$K_{ia} = \frac{(\gamma'_{H^+}[H^+])(\gamma'_{A^-}[A^-])}{(\gamma'_{HA}[HA])} = e^{-\Delta_r G^0/RT} \tag{4-49}$$

In logarithmic form, this is the same as:

$$\log K_{ia} = -\Delta_r G^0/2.303RT \tag{4-50}$$

When determining K_{ia} values of organic acids, one generally uses techniques by which the hydrogen ion activity [pH = $-\log(\gamma'_{H^+}[H^+])$] is measured, while HA and A$^-$ are determined as molar concentrations. Thus, many acidity constants reported in the literature are so-called "mixed acidity constants," which are operationally defined for a given aqueous medium (e.g., $0.05 - 0.1$ M salt solutions):

$$K_{ia}^* \equiv (\gamma'_{H^+}[H^+]) \frac{[A^-]}{[HA]} = K_{ia} \frac{\gamma'_{HA}}{\gamma'_{A^-}} \tag{4-51}$$

In some cases, the "true" thermodynamic K_{ia} values are extrapolated by measurements of K_{ia}^* values at different ionic strengths, and by estimating the activity coefficients, particularly, γ'_{A^-}, using approaches like the Davies equation to quantify the excess free energy of such ions (Stumm and Morgan, 1996). Considering the uncertainties in the measurements, it is reasonable to assume that at the moderate to low ionic strengths at which K_{ia}^* values are typically determined, we can set $K_{ia}^* \cong K_{ia}$. For following discussions, we also assume that γ'_{HA} and γ'_{A^-} are approximately 1. When dealing with saline waters (e.g., seawater), the K_{ia}^* values may differ more substantially from K_{ia} (e.g., a factor of 2 has been found for some phenols (Demianov et al., 1995)).

When assuming that $\gamma'_{HA} = \gamma'_{A^-} = 1$, and by using the common chemical shorthand of $pX = -\log X$, we can rewrite Eq. 4-51 as:

$$\log\frac{[A^-]}{[HA]} = \log K_{ia} - \log\left(\gamma'_{H^+}[H^+]\right) = pH - pK_{ia} \qquad (4\text{-}52)$$

Equation 4-52 allows us to visualize the meaning of the *acidity constant* for a given organic compound. We can see that the pK_{ia} is a measure of the *strength of an organic acid* relative to the acid–base pair H_3O^+/H_2O. For example, it tells us at which hydrogen ion activity (expressed by the pH) our organic acid is present in equal parts in the dissociated (A^-) and nondissociated (HA) forms:

$$[A^-] = [HA] \quad \text{at} \quad pH = pK_{ia} \qquad (4\text{-}53)$$
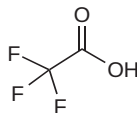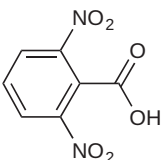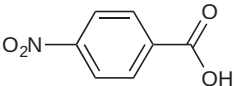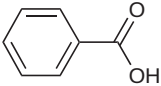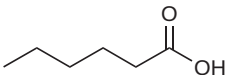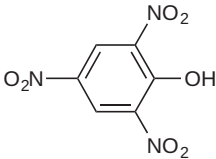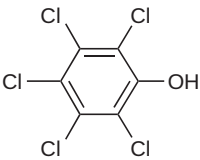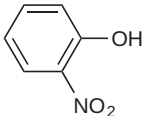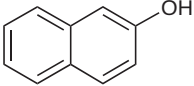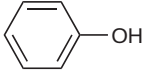
The pK_{ia} values of organic acids of environmental concern cover a broad range (Table 4.4). If the pK_{ia} of an organic acid is very low, (i.e., $pK_{ia} < 3$), we speak of a strong organic acid. A strong acid has a high tendency to deprotonate even in an aqueous solution of high H^+ activity (low pH). Examples of strong organic acids are trifluoroacetic acid, 2,4-dinitrobenzoic acid, and 2,4,6-trinitrophenol (see Table 4.4). At ambient pH values (i.e., pH = 4 to 9), such acids will be present in natural waters predominantly in their dissociated anionic form. In contrast, very weak acids (i.e., $pK_{ia} \geq 10$) will be present in natural waters primarily in their nondissociated form. However, many important organic acids have pK_{ia} values between 4 and 10. In these cases, exact knowledge of the pK_{ia} is necessary, since the environmental behavior of the dissociated form of the molecule is very different from that of the nondissociated form.

Organic Bases. Analogous to acids, we can define a basicity constant for the reaction of an organic base ($i = B$) with water:

$$B + H_2O \rightleftharpoons OH^- + BH^+$$
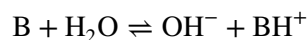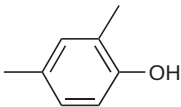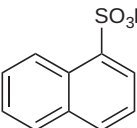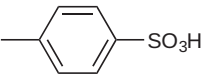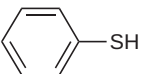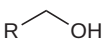
$$K_{ib} = \frac{(\gamma'_{OH^-}[OH^-])(\gamma'_{BH^+}[BH^+])}{(\gamma'_B[B])} \qquad (4\text{-}54)$$

Table 4.4 Examples of Organic Acids

Name	Structure	pK_{ia} (25°C) [a]	α_{ia} [b] (pH 7)
Carboxylic Acids $(R-COOH \leftrightharpoons R-COO^- + H^+)$			
Trifluoroacetic acid (TFA)		0.40	< 0.001
2,6-Dinitrobenzoic acid		1.14	< 0.001
4-Nitrobenzoic acid		3.44	< 0.001
Benzoic acid		4.19	0.002
Acetic acid		4.75	0.006
Hexanoic acid		4.89	0.008
Phenolic Groups $(Ar-OH \leftrightharpoons Ar-O^- + H^+)$			
2,4,6-Trinitrophenol		0.38	< 0.001
Pentachlorophenol		4.75	0.006
2-Nitrophenol		7.20	0.613
2-Naphthol		9.51	0.997
Phenol		9.90	0.998

(*continued*)

Table 4.4 (*Continued*)

Name	Structure	pK_{ia} (25°C) [a]	α_{ia} [b] (pH 7)
2,4,6-Trimethylphenol		10.90	> 0.999
Miscellaneous Groups ($AH \rightleftharpoons A^- + H^+$)			
1-Naphthalene-sulfonic acid		0.57	< 0.001
p-Toluenesulfonic acid		0.70	< 0.001
Thioacetic acid		3.33	< 0.001
Thiophenol		6.50	0.240
Ethanethiol		10.61	>0.999
Aliphatic alcohols		>14	>> 0.999

[a] Data from Dean (1985) and Lide (1995).
[b] Fraction in neutral (acidic) form at pH 7 (Eq. 4-59).

Here, the reaction of a neutral base with water results in the formation of a cation. Some examples of important organic bases are shown in Table 4.5. To compare acids and bases on a uniform scale, it is convenient to use the acidity constant of the conjugate acid ($i = BH^+$) as a measure of the base strength:

$$BH^+ \rightleftharpoons H^+ + B$$
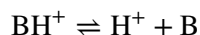
$$K_{ia} = \frac{(\gamma'_{H^+}[H^+])(\gamma'_B[B])}{(\gamma'_{BH^+}[BH^+])} \tag{4-55}$$

K_{ib} and K_{ia} are quantitatively related by the *ionization constant of water* (*ion product of water*), K_w, which, at 25°C is:

$$K_w = K_{ia}K_{ib} = (\gamma'_{H^+}[H^+])(\gamma'_{OH^-}[OH^-]) = 1.01 \times 10^{-14} \tag{4-56}$$

K_w is strongly temperature dependent (see Table 4.6 and Appendix D). Using our pX nomenclature:

$$pK_w = pK_{ia} - pK_{ib} \tag{4-57}$$

Table 4.5 Examples of Organic Bases

Name	Structure	pK_{ia} (25°C) ^{a} (= pK_{iBH+})	$1-\alpha_{ia}$ ^{b} (pH 7)
	Aliphatic and Aromatic Aminogroups $(Ar-$ or $R-\overset{\mid}{N^+}-H \rightleftharpoons Ar-$ or $R-\overset{\mid}{N}:+H^+)$		
4-Nitroaniline		1.01	< 0.999
1-Naphthylamine		3.92	0.999
4-Chloroaniline		3.99	0.999
Aniline		4.63	0.996
N,N-Dimethylaniline		5.12	0.987
Trimethylamine		9.81	0.002
n-Hexylamine		10.64	< 0.001
Piperidine		11.12	< 0.001
	Heterocyclic Nitrogen $(\overset{+}{N}-H \rightleftharpoons N:+H^+)$		
4-Nitropyridine		1.23	> 0.999
4-Chloropyridine		3.83	> 0.999
Pyridine		5.25	0.983
Isoquinoline		5.40	0.975
Benzimidazole		5.53	0.967
Imidazole		7.00	0.500
Benzotriazole		8.50	0.031

^{a} Data from Dean (1985) and Lide (1995).
^{b} Fraction in neutral (base) form at pH 7 (Eq. 4-59).

Table 4.6 Acidity Constants (pK_{ia}) of Some Organic Acids and of H_2O at Different Temperatures

Acid (i) (HA, BH$^+$) [a]	0°C	10°C	pK_{ia} [b] 20°C	30°C	40°C
4-Nitrobenzoic acid		3.45	3.44	3.44	3.45
Acetic acid	4.78	4.76	4.76	4.76	4.77
2-Nitrophenol	7.45	7.35	7.24	7.15	
Imidazole	7.58	7.33	7.10	6.89	6.78
4-Aminopyridine	9.87	9.55	9.25	8.98	8.72
Piperidine	11.96	11.61	11.28	10.97	10.67
H_2O	14.94	14.53	14.16	13.84	13.54

[a] For structures see Tables 4.4 and 4.5.
[b] Data from Dean (1985) and Schwarzenbach et al. (1988).

From Eq. 4-57, it follows that the stronger an acid is (low pK_{ia}), the weaker the basicity of its conjugate base (high pK_{ib}), while the stronger the base (low pK_{ib}), the weaker its conjugate acid (high pK_{ia}). Thus, a neutral base with a pK_{ib} value < 3 (i.e., the pK_{ia} of the conjugate acid > 11 at 25°C) will be present in water predominantly as a cation at ambient pH values.

Effect of Temperature on Acidity Constants

In analogy to the temperature dependence of partition constants (Eq. 4-34), the effect of temperature on K_{ia} over a small temperature range can be described by:

$$K_{ia}(T_2) = K_{ia}(T_1) \cdot e^{-\frac{\Delta_r H^0}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]} \tag{4-58}$$

where $\Delta_r H^0$ is the *standard enthalpy of reaction* of the reactions in Eqs. 4-43 and 4-55. In general, $\Delta_r H^0$ is very small for strong acids and increases with increasing pK_{ia} value. Therefore, for stronger acids we may neglect the effect of temperature on K_{ia}, whereas for very weak acids this effect is substantial. For example, the ionization constants of piperidine and water (K_w) change by about one order of magnitude between 0 and 30°C, whereas for 4-nitrobenzoic acid or acetic acid, almost no temperature dependence is observed (Table 4.6).

A Few Comments on Experimental Data

Acidity has long been recognized as a very important property of some organic compounds. Experimental methods for determining acidity constants are well established, and one can find quite large databases of pK_{ia} values of organic acids and bases (e.g., Kortüm et al., 1961; Perrin, 1972; Serjeant and Dempsey, 1979; Dean, 1985; Lide, 1995). The most common procedures discussed by Kortüm et al. (1961) include titration, determination of the concentration ratio of acid–base pairs at various pH values using conductance methods, electrometric methods, and spectrophotometric methods. The pK_{ia} values reported in the literature are often "mixed acidity constants," commonly measured at 20 or 25°C, and at a given ionic strength (e.g., 0.05 – 0.1 M salt

solution). Depending on the type of measurement and the conditions chosen, reported pK_{ia} values might vary by as much as 0.3 pK_a units. Also, primarily depending on the strength of an acid or base, the effect of temperature may be more or less pronounced (Table 4.6).

Speciation in Natural Waters

Given the pK_{ia} of an organic acid or base, we can now ask to what extent this compound is ionized in natural waters. The pH of natural water is primarily determined by various *inorganic* acids and bases (e.g., H_2CO_3, HCO_3^-, CO_3^{2-} which are usually present at much higher concentrations than organic compounds of interest (see Chapter 5). These acids and bases act as hydrogen ion buffers (pH buffers), meaning that the addition of a very small quantity of an organic acid or base will not cause significant change in pH. We can easily visualize this buffering effect by the following simple example. Let us assume that of a hypothetical acid–base pair with $pK_{ia} = 7.00$, its undissociated and its dissociated forms are present at equal concentrations in one liter of water, say, 10^{-3} mol L^{-1}. According to Eq. 4-52, the pH of this aqueous solution will be:

$$pH = 7.00 + \log \frac{10^{-3} \text{ mol L}^{-1}}{10^{-3} \text{ mol L}^{-1}} = 7.00$$

If we now add 10^{-5} moles of a *strong* organic acid, (i.e., effectively, we add 10^{-5} moles H^+ and A^- each), the pH would change by less than 0.01 units:

$$pH = 7.00 + \log \frac{0.99 \times 10^{-3} \text{ mol L}^{-1}}{1.01 \times 10^{-3} \text{ mol L}^{-1}} = 6.991$$

As a first approximation, we may assume that adding a "trace" organic acid or base (where trace < 0.1 mM) to natural water will, in most cases, not substantially affect the pH of the water.

For a given pH, we may now express the fraction of our organic acid (denoted as HA, the same holds for BH^+) present in the acid form in the water, α_{ia}, by:

$$\alpha_{ia} = \frac{[HA]}{[HA] + [A^-]} = \frac{1}{1 + \frac{[A^-]}{[HA]}} = \frac{1}{1 + \frac{K_{ia}}{\{H^+\}}} = \frac{1}{1 + 10^{(pH-pK_{ia})}} \quad (4\text{-}59)$$

Now, α_{ia} or $(1-\alpha_{ia})$ values for various acids and bases in water at pH 7 can be readily calculated (Tables 4.4 and 4.5). One can also readily picture the fraction of the acid (or base) form of a given acid (or base) as a function of pH (Fig. 4.3). We re-emphasize that the neutral and ionic "forms" of a given neutral acid (base) behave very differently in the environment. Depending on the process considered, either the neutral or ionic species may be the dominant chemical species participating in the compound's partitioning or reactivity, even if the relative amount of that species is very low.

Figure 4.3 Fraction in acid form as function of pH. At pH = pK_{ia}, the acid and base forms are present at equal concentrations, i.e., [HA] = [A^-]; [BH^+] = [B].

4.4   ## Organic Acids and Bases II: Chemical Structure and Acidity Constant

Overview of Acid and Base Functional Groups

Since environmental systems typically have pH values between 4 and 9 (Fig. 5.10), we are primarily interested in compounds having pK_{ia} values in the range of 2 to 11. Therefore, the most important functional groups we have to consider include aliphatic and aromatic carboxyl groups, aromatic hydroxyl groups (e.g., phenolic compounds), aliphatic and aromatic amino groups, nitrogen atoms incorporated in aromatic compounds, and aliphatic or aromatic thiols and sulfonic acids (Tables 4.4 and 4.5). The range in pK_{ia} values for a given functional group may vary by many units because of the structural characteristics of the rest of the molecule. Depending on the type and number of substituent groups on the aromatic ring, for example, the pK_{ia} values for substituted phenols may differ by almost 10 units (Table 4.4).

Therefore, it is necessary that we make an effort to understand the effects of various structural entities on the acid or base properties of a given functional group. To this end, we recall that the standard free energy, $\Delta_r G^0$, for the proton dissociation reaction is given by the difference in the standard free energies of formation of the acid and conjugate base in aqueous solution (Eq. 4-48). Therefore, when comparing acidity constants of compounds exhibiting a specific acid or base functional group, the question is simply how much the rest of the molecule favors (decreases the free energy of formation) or disfavors (increases the free energy of formation) the ionic versus the neutral form of the compound in aqueous solution. Hence, we have to evaluate electronic and steric effects of substituents on the relative stability of the acid–conjugate base couple considered.

Inductive Effects

Let us first consider a simple example, the influence of a chloro-substituent on the pK_{ia} of butyric acid:

$i =$	CH$_3$CH$_2$CH$_2$COOH	CH$_2$CH$_2$CH$_2$COOH$\;$$\underset{Cl}{|}$	CH$_3$CHCH$_2$COOH$\;$$\underset{Cl}{|}$	CH$_3$CH$_2$CHCOOH$\;$$\underset{Cl}{|}$
pK_{ia}	4.81	4.52	4.05	2.86

In this example, we see that if we substitute a hydrogen atom by chlorine, which is much more electronegative than hydrogen (see Chapter 2, Table 2.5), the pK_a of the carboxyl group decreases. Furthermore, the closer the electron-withdrawing chlorine substituent is to the carboxyl group, the stronger its effect in decreasing the pK_{ia}. We can intuitively explain these findings by realizing that any group that will have an electron-withdrawing effect on the carboxyl group (or any other acid function) will help to accommodate a negative charge and increase the stability of the ionized form. In the case of an organic base, an electron-withdrawing substituent will, of course, destabilize the acidic form (the cation) and also lower the pK_{ia}. This effect is called a *negative inductive effect* (–I). Most functional groups with which we are concerned

Table 4.7 Inductive and Resonance Effects of Some Common Substituents[a]

Effect [b]	Substituents
Inductive	
+ I	O^-, NH^-, alkyl
− I	SO_2R, NH_3^+, NO_2, CN, F, Cl, Br, COOR, I, COR, OH, OR, SR, phenyl, NR_2
Resonance	
+ R	F, Cl, Br, I, OH, OR, NH_2, NR_2, NHCOR, O^-, NH^-
− R	NO_2, CN, CO_2R, $CONH_2$, phenyl, COR, SO_2R

[a] Data from Clark and Perrin (1964).
[b] A plus sign means that the effect increases the pK_{ia}; a minus sign means that the effect decreases the pK_{ia}.

have inductive electron-withdrawing (–I) effects (Table 4.7), but only a few such as alkyl groups have electron-donating (+I) effects:

$i =$	CH_3COOH	CH_3CH_2COOH
pK_{ia}	4.75	4.87

As illustrated by the chlorobutyric acids, in *saturated* molecules, inductive effects usually fall off quite rapidly with distance.

Resonance Effects

In unsaturated chemicals, such as aromatic or olefinic compounds (i.e., compounds with "mobile" π-electrons; see Chapter 2), the inductive effect of a substituent may be felt over larger distances (i.e., more bonds). In such systems, however, another effect, the *delocalization of electrons*, may be of even greater importance. In Chapter 2, we learned that the delocalization of electrons (i.e., the "smearing" of π-electrons over several bonds) may significantly increase the stability of an organic species. In the case of a deprotonated organic acid, delocalization of the negative charge may lead to a considerable decrease in the pK_a of a given functional group, as one can see from comparing the pK_a of an aliphatic alcohol with that of phenol (Fig. 4.4).

Figure 4.4 Effect of delocalization on the pK_{ia} of an –OH group.

Figure 4.5 Influence of the position of a nitro substituent on the pK_{ia} of a phenolic hydrogen.

In the next step, we introduce a substituent on the aromatic ring, which through the aromatic π-electron system, may develop shared electrons (i.e., through "resonance" or "conjugation") with the acid or base function (e.g., the –OH or –NH$_2$ group). For example, the much lower pK_{ia} value of *para*-nitrophenol as compared with *meta*-nitrophenol may be attributed to additional resonance stabilization of the anionic species by the *para*-positioned nitro group (Fig. 4.5). In the *meta* position, only the electron-withdrawing negative inductive effect of the nitro group is felt by the –OH group. Other substituents that increase acidity (i.e., that lower the pK_{ia} through a resonance or "–R" effect) are listed in Table 4.7. All of these substituents can help to accommodate electrons. In contrast, substituents with heteroatoms having nonbinding electrons that may be in resonance with the π-electron system, have an *electron-donating resonance effect* (+R, Table 4.7), and, therefore, decrease acidity (i.e., increase pK_a). Many groups that have a negative inductive effect (–I) have a positive resonance effect (+R) at the same time. The overall impact of such substituents depends critically on their location in the molecule. In monoaromatic molecules, for example, resonance in the *meta* position is negligible, but will be significant in both the *ortho* and *para* positions.

Figure 4.6 Example of a proximity effects on the acidity constant: hydrogen bonding.

Proximity Effects

Another important group of effects are *proximity effects.* These effects arise from the influence of substituents that are physically close to the acid or base function under consideration. Here, two *intra*molecular (within the same molecule) interactions are important: *hydrogen bonding and steric effects.* An illustration of the effect of intramolecular hydrogen bonding can be seen by comparing *para-* and *ortho*-hydroxybenzoic acids (Fig. 4.6). The stabilization of the carboxylate anion by the hydroxyl hydrogen in *ortho*-hydroxy-benzoic acid (salicylic acid) leads to a much lower pK_{a1} value and to a much higher pK_{a2} value as compared with *para*-hydroxobenzoic acid in which no intramolelcular hydrogen bonding is possible.

In some cases, steric effects may have a measurable impact on the pK_{ia} of a given acid or base. Such effects include steric constraints that inhibit optimum solvation of the ionic species by the water molecules (and thus increase the pK_{ia}). Also, steric juxtaposition of moieties may cause groups to twist with respect to one another and thereby hinder co-planarity needed to enable resonance of the electrons of a acid or base group with other parts of the molecule. This can impact pK_{ia}.

In summary, the most important factors influencing the pK_{ia} of a given acid or base function are inductive, resonance, and, sometimes, proximity effects. The impact of a substituent on the pK_{ia} depends critically on where the substituent is located in the molecule relative to the acid or base group. In one location, a given substituent may have only one of the mentioned effects, while in another location, all effects may play a role. Therefore, it is quite difficult to establish simple general rules for quantifying the effects of structural entities on the pK_{ia} of an acid or base function. Nevertheless, in certain cases, a quantification of the effects of substituents on the pK_{ia} value is possible. In the following section, we discuss one example of such an approach, the *Hammett correlation* for substituted aromatic compounds.

Estimation of Acidity Constants: The Hammett Relationship

A long time ago, Hammett (1940) recognized that for *substituted benzoic acids* (see Fig. 4.7) the effect of substituents in either the *meta* or *para* position on the standard free energy change of the carboxyl group's dissociation could be expressed as the sum

Figure 4.7 Effects of ring substituents on the pK_a of benzoic acid, phenyl acetic acid, and phenol.

of the free energy change of the dissociation of the unsubstituted compound, $\Delta_r G_H^0$, and the contributions of various substituents; $\Delta_r G_j^0$:

$$\Delta_r G^0 = \Delta_r G_H^0 + \sum_j \Delta_r G_j^0 \qquad (4\text{-}60)$$

To express the effect of substituent j on the pK_a, Hammett introduced a constant σ_j, which is defined as:

$$\sigma_j = \frac{-\Delta_r G_j^0}{2.303RT} \qquad (4\text{-}61)$$

Since *meta* and *para* substitutions result in different combinations of inductive and resonance effects, there are two sets of σ_j values, σ_{jmeta} and σ_{jpara}. *Ortho* substitution is excluded because as previously discussed, proximity effects, which are difficult to separate from electronic factors, may play an important role. Since $\Delta_r G^0 = -2.303$

Table 4.8 Hammett Constants for Some Common Substituents [a]

Substituent j	σ_{jmeta}	σ_{jpara}	Substituent j	σ_{jmeta}	σ_{jpara}	σ^-_{jpara}
– H	0.00	0.00	– OH	0.10	−0.36	
– CH$_3$	−0.06	−0.16	– OCH$_3$	0.11	−0.24	−0.12
– CH$_2$CH$_3$	−0.06	−0.15	– OCOCH$_3$	0.36	0.31	
– CH$_2$CH$_2$CH$_2$CH$_2$	−0.07	−0.16	– CHO	0.36	0.22	1.03
– C(CH$_3$)$_3$	−0.10	−0.20	– COCH$_3$	0.38	0.50	0.82
– CH = CH$_2$	0.08	−0.08	– COOCH$_3$	0.33	0.45	0.66
– C$_6$H$_5$ (phenyl)	0.06	0.01	– CN	0.62	0.67	0.89
– CH$_2$OH	0.07	0.08	– NH$_2$	−0.16	−0.66	
–– CH$_2$Cl	0.12	0.18	– NHCH$_3$	−0.25	−0.84	
– CCl$_3$	0.40	0.46	– N(CH$_3$)$_2$	−0.15	−0.83	
– CF$_3$	0.44	0.57	– NO$_2$	0.73	0.78	1.25
– F	0.34	0.05	– SH	0.25	0.15	
– Cl	0.37	0.22	– SCH$_3$	0.13	0.01	
– Br	0.40	0.23	– SOCH$_3$	0.50	0.49	
– I	0.35	0.18	– SO$_2$CH	0.68	0.72	
			– SO$_3^-$	0.05	0.09	

[a]Data from Dean (1985) and Shorter (1994 and 1997).

$RT \log K_a$ (Eq. 4-50), we may write Eq. 4-60 in terms of acidity constants, omitting subscript i to denote the acid function:

$$\log \frac{K_a}{K_{aH}} = \sum_j \sigma_j \quad \text{or} \quad pK_a = pK_{aH} - \sum_j \sigma_j \tag{4-62}$$

Table 4.8 lists σ_{jmeta} and σ_{jpara} values for some common substituent groups. These σ values are a quantitative measurement of a given substituent's effect on the pK_a of *benzoic acid*. As we would expect from our previous discussion, the sign of the σ_j value reflects the net electron-withdrawing (positive sign) or electron-donating (positive sign) character of a given substituent in either the *meta* or *para* position. For example, we see that –NO$_2$ and –CN are strongly electron-withdrawing in both positions, whereas the electron-providing groups, –NH$_2$ or –N(CH$_3$)$_2$, are strongly electron-donating in the *para* position, but show a much weaker effect in the *meta* position. The differences between σ_{jmeta} and σ_{jpara} of a given substituent are due to the difference in importance between the inductive and resonance effects which, as we mentioned earlier, may have opposite signs (see Table 4.7).

Let us now examine the effects of the *same* substituents on the pK_{ia} of another group of acids, the substituted phenyl acetic acids (Fig. 4.7). As we might have anticipated, the various substituents exert the same relative effect as in their benzoic counterparts. However, in the case of phenyl acetic acid, the greater separation between substituent and reaction site makes the impact less pronounced than in the benzoic acid. Plotting $pK_{aH}-pK_a$ values for *meta*- and *para*-substituted phenyl acetic acids versus $\sum \sigma_j$ values results in a straight line with a slope, ρ, of less than 1 (Fig. 4.8). In this case, introduction of a substituent on the aromatic ring has only about half the effect on
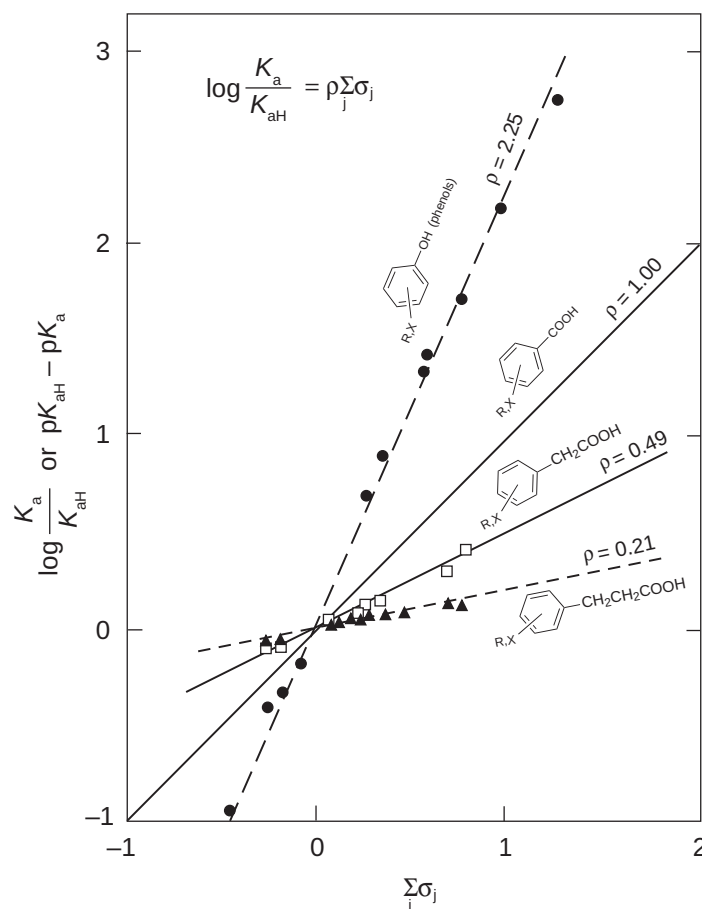
$$\log \frac{K_a}{K_{aH}} = \rho \sum_j \sigma_j$$

Figure 4.8 Hammett plots for *meta-* and *para-*substituted phenols, phenylacetic acids, and 3-phenylpropionic acids; data from Serjeant and Dempsey (1979).

the pK_a as compared with the effect of the same substituent on the pK_a of benzoic acid. Thus, ρ is a measure of how sensitive the dissociation reaction is to substitution as compared with substituted benzoic acid. It is commonly referred to as the *susceptibility factor* that relates one set of reactions to another. If we consider another group of acids, the substituted β-phenyl propionic acids, where the substituents are located at even greater distances from the carboxyl group, even smaller ρ values are found ($\rho = 0.21$, Fig. 4.8).

If we express these findings in energetic terms, we obtain the classical form of the *Hammett Equation*:

$$\Delta_r G^0 = \Delta_r G_H^0 - \rho(2.303RT) \sum_j \sigma_j \tag{4-63}$$
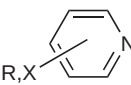
Expressed in terms of equilibrium constants (i.e., acidity constants):

$$\log K_a = \log K_{aH} + \rho \sum_j \sigma_j$$

or $\tag{4-64}$

$$pK_a = pK_{aH} - \rho \sum_j \sigma_j$$

Table 4.9 Hammett Relationships for Quantification of Aromatic Substituent Effects on the Acidity of Various Acids [a]

Acid	pK_{aH} (pK_a of unsubstituted compound)	ρ
R,X—⟨benzene⟩—CH_2-CH_2-COOH	4.55	0.21
R,X—⟨benzene⟩—$O-CH_2-COOH$	3.17	0.30
R,X—⟨benzene⟩—CH_2-COOH	4.30	0.49
R,X—⟨benzene⟩—$COOH$	4.19	1.00 (by definition)
R,X—⟨benzene⟩—OH	9.90	2.25 [b]
R,X—⟨benzene⟩—NH_3^+	4.63	2.90 [b]
R,X—⟨pyridine⟩—NH^+	5.25	5.90 [b]

[a] Eq. 4-64; data from Williams (1984). [b] Use σ_{jpara}^- instead of σ_{jpara} for substituents that are in direct resonance will the acid function (Table 4.8).

pK_{aH} and ρ values have been found for a variety of aromatic substituents on various types of aromatic acids (Table 4.9). For compound classes such as phenols, anilines, and pyridines where the acid (base) function is in resonance with the aromatic ring, the ρ values obtained are significantly greater than 1; that is, the electronic effect of the substituents is greater than in the case of benzoic acid.

A simple case where the general σ constants in Table 4.8 do not succeed in correlating acidity constants occurs when the acid or base function is in *direct resonance* with the substituent. This may happen in cases such as substituted phenols, anilines, and pyridines. For example, owing to resonance (see Fig. 4.5), a *para* nitro group decreases the pK_a of phenol much more than would be predicted from the σ_{jpara} constant obtained from the dissociation of *p*-nitrobenzoic acid (another example would be the anilines). In such "direct resonance" cases, a special set of σ values (denoted as σ_{jpara}^-) has been derived (Table 4.8) to try to account for both inductive and direct resonance effects. If these values are employed, good correlations are obtained, as shown for *meta*- and *para*-substituted phenols in Fig. 4.8.

We stated earlier that because of differential proximity effects on various acid functions, a single set of σ values for *ortho* substitution cannot be found for all aromatic

Table 4.10 Examples of Apparent Hammett Constants for *ortho*-Substitution in Phenols and in Anilines [a]

Substituent j	$\sigma_{jortho}^{phenols}$	$\sigma_{jortho}^{anilines}$	Substituent j	$\sigma_{jortho}^{phenols}$	$\sigma_{jortho}^{anilines}$
$- CH_3$	−0.13	0.10	$- OH$		−0.09
$- CH_2CH_2CH_2CH_3$	−0.18		$- OCH_3$	0.00	0.02
$- CH_2OH$	0.04		$- CHO$	0.75	
$- F$	0.54	0.47	$- NH_2$		0.00
$- Cl$	0.68	0.67	$- NO_2$	1.24	1.72
$- Br$	0.70	0.71			
$- I$	0.63	0.70			

[a]Data from Clark and Perrin (1964) and Barlin and Perrin (1966).

acids. Nevertheless, one can determine a set of σ_{jortho} values for a specific type of reaction, as for example (called "apparent" σ constants). For example, for the dissociation of substituted phenols one can find a set of σ_{jortho} values that work for other phenols (Table 4.10). Such apparent σ_{jortho} constants are used for estimating pK_a values of substituted phenols and anilines. Of course, in cases of multiple substitutions, substituents may interact with one another, thereby resulting in larger deviations of experimental from predicted pK_{ia} values.

In our discussion of the Hammett correlation, we confine ourselves mostly to benzene derivatives. Of course, a similar approach can be taken for other aromatic and aliphatic systems, such as for the derivatives of polycyclic aromatic hydrocarbons, heterocyclic aromatic compounds, and aliphatic acids. For a discussion of such applications, we refer to papers by Clark and Perrin (1964), Barlin and Perrin (1966), and Perrin (1980). Using the Hammett equation as a starting point, a variety of refinements using more sophisticated sets of constants have also been suggested. The interested reader can find a treatment of these approaches in various textbooks, as well as compilations of substituent constants (e.g., Taft, 1956; Hine, 1975; Lowry and Schueller-Richardson, 1981; Williams, 1984; Exner, 1988) and in data collections (e.g., Harris and Hayes, 1982; Dean, 1985; Hansch et al., 1991; Hansch et al., 1995a and b).

Finally, our discussion on the Hamlett correlation is not only important for understanding the effect of structural entities on the pK_{ia} of acids and bases, but will also be very useful for evaluating what such effects have on the reactivity of organic compounds where electronic and steric effects play an important role (see Chapter 22). Furthermore, it is an example of a so-called *linear free energy relationship* (LFER). Such approaches for correlation are called extra-thermodynamic or outside thermodynamics. They rely on the understanding of how a portion of a molecule's structure influences properties through incremental changes in intermolecular interactions or reactivities through inductive, resonance, and steric effects. Such extra-thermodynamic methods will allow us to link chemical structures to their properties. We will encounter more of these LFERs throughout the book (e.g., in Chapter 7).

| 4.5 | ## Questions and Problems |

Special note: Problem solutions are available on the book's website. Solutions to problems marked with an asterisk are available for everyone. Unmarked problems have solutions only available to teachers, practitioners, and others with special permission.

Questions

Q 4.1

Give at least three reasons why, in environmental organic chemistry, it is so important to understand the *equilibrium* partitioning behavior of a given organic compound between gaseous, liquid, and solid phases.

Q 4.2

One of your friends has difficulty understanding what the *chemical potential* of a given compound in a given system expresses. Try to explain it in words to him or her. What do the quantities *fugacity* and *activity* describe? How are they related to the *activity coefficient*?

Q 4.3

What are the advantages and disadvantages of choosing the pure liquid compound as reference state? When would you use a different reference state? Which one?

Q 4.4

What is meant by excess free energy, excess enthalpy, and excess entropy? How are they related to each other?

Q 4.5

Which thermodynamic function needs to be known for assessing the temperature dependence of equilibrium partitioning? How can this function be derived from experimental data? What caution is advised when extrapolating partition constants from one temperature to another temperature?

Q 4.6

Name at least four different acid or base functional groups present in environmental organic chemicals. Which factors determine the pK_a of a given acid or base function? Indicate the pK_a ranges of the various functions.

Q 4.7

Explain the terms *inductive effect* and *resonance effect* of substituents. What makes a substituent exhibit a *negative* resonance effect? Which types of substituents have a positive resonance effect? Can a given substituent exhibit a negative inductive and a positive resonance effect at the same time? If yes, give some examples of such substituents.
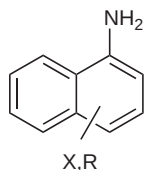
Q 4.8

How are the Hammet σ_{jmeta} and σ_{jpara} substituent constants defined? Are there cases in which the σ_{jpara} values are not applicable? If yes, give some examples.
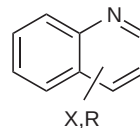
Q 4.9

For –OH and –OCH$_3$, the σ_{jmeta} values are positive, whereas σ_{jpara} is negative (Table 4.8). Explain these findings.

Q 4.10

As indicated, 1-naphthylamine and quinoline exhibit very different susceptibility factors ρ (2.81 versus 4.90) in the corresponding Hammett equations (Dean, 1985). Explain this fact.

1-naphthylamine

quinoline

$$pK_a = 3.84 - 2.81 \sum_j \sigma_j \quad pK_a = 4.88 - 4.90 \sum_j \sigma_j$$

Q 4.11

The two isomers 2,4,6-trichlorophenol and 3,4,5-trichlorophenol have quite different pK_{ia} values. What are the reasons for this big difference?

i = 2,4,6-trichlorophenol
(pK_{ia} = 6.15)

i = 3,4,5-trichlorophenol
(pK_{ia} = 7.73)

Q 4.12

The pK_{ia} of the herbicide sulcotrion is 3.13 (Tomlin, 1994). Would you have expected that this compound is such a strong acid? Write down the structure of the conjugate base of sulcotrion and try to explain the rather strong acidity of this herbicide.
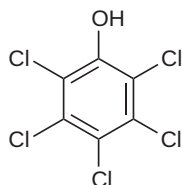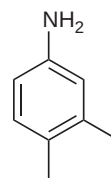

i = sulcotrion

Problems

P 4.1[*] *Assessing the Speciation of Organic Acids and Bases in Natural Waters*

Calculate the fraction of (a) pentachlorophenol (PCP), (b) 3,4-dimethylaniline (DMA) present at 24°C as neutral species in a raindrop (pH = 4.0) and in lake water (pH = 8.0).

*i* = pentachlorophenol
(PCP)
pK_{ia} = 4.75

i = 3,4-dimethylaniline
(DMA)
pK_{ia} = 5.28

P 4.2[*] *Estimating Acidity Constants of Aromatic Acids and Bases Using the Hammett Equation*
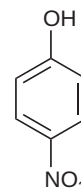
Estimate the pK_{ia} values at 25°C of (a) pentachlorophenol (PCP), (b) 4-nitrophenol (4-NP), (c) 3,4-dimethylaniline (3,4-DMA, pK_{ia} of conjugate acid), and (d) 2,4,5-trichlorophenoxy acetic acid (2,4,5-T), Use the Hammett relationship Eq. 4-62:

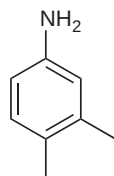$$pK_{ia} = pK_{aH} - \rho \sum_j \sigma_j$$
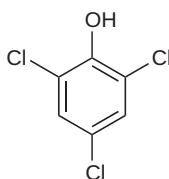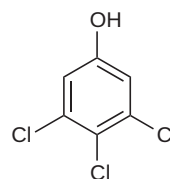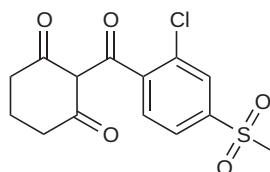
to estimate the pK_{ia} values of compounds (a) – (d). Get the necessary σ, pK_{aH}, and ρ values from Tables 4.8, 4.9, and 4.10.
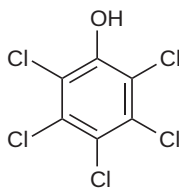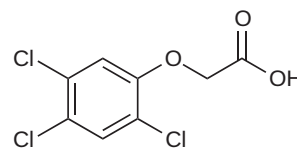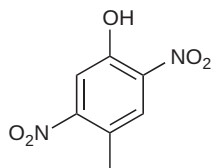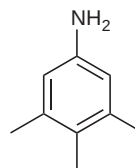

i = PCP

i = 4-NP

i = 3,4-DMA

i = 2,4,5-T

P 4.3 *Estimation of Acidity Constants and Speciation in Water of Aromatic Organic Acids and Bases*

Represent graphically (as shown in Fig. 4.3) the speciation of (a) 4-methyl-2,4-dinitrophenol, and (b) 3,4,5-trimethylaniline as a function of pH (pH range 2-12) at 25°C. Estimate, the pK_{ia} values of the compounds.

i = 4-methyl-2,5-dinitro-phenol

i = 3,4,5-trimethyl-aniline

4.6   Bibliography

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