ENVIRONMENTAL ORGANIC CHEMISTRY

Second Edition

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Chapter 3

PARTITIONING: MOLECULAR INTERACTIONS AND THERMODYNAMICS

3.1 Introduction

The goal of this chapter is to summarize the concepts needed in the following chapters for a qualitative and quantitative treatment of environmental equilibrium partitioning processes. We start by developing some general understanding of the intermolecular forces that govern the partitioning of organic compounds between different phases. This is done by visualizing the interactions between molecules using examples that will be treated in more detail in later chapters. Then, in Sections 3.3 and 3.4 we discuss how molecular interactions are characterized via thermodynamic functions that enable us to quantitatively describe the distribution of molecules participating in a specific partitioning process. Here, we will focus on those thermodynamic entities that are relevant to our problem: Gibbs free energy (G), enthalpy (H), entropy (S), chemical potential (μ), fugacity (f), activity (a), and activity coefficient (γ). In Section 3.4 we also discuss some common "extrathermodynamic" approaches with which we may estimate data for new chemicals of interest from experience with old ones. Finally, in Section 3.5 we address the issue of how we may generally calculate the fraction of a substance's occurrence in any environmental phase of interest at equilibrium with other environmental media.

3.2 Molecular Interactions Determining the Partitioning of Organic Compounds Between Different Phases

Partitioning "Reactions"

The partitioning of an organic compound, i, between two phases, 1 and 2, may be thought of like a chemical reaction in which "bonds" are broken and formed. In this case, however, the "bonds" involve intermolecular attraction energies, which are, however, much weaker than covalent bonds. For example, if the process of interest involves moving i from within phase 1 (i.e., *desorption* from phase 1) to within a different phase 2 (i.e., *absorption* into phase 2), or vice versa, we may write the partitioning "reaction":

$$1{:}i{:}1 + 2{:}2 \rightleftharpoons 1{:}1 + 2{:}i{:}2 \tag{3-1}$$

where the colons indicate intermolecular "attractions" which are broken and formed during the exchange. Here we show the compound, i, to be inside phase 1 ($1{:}i{:}1$) and phase 2 ($2{:}i{:}2$) by putting it between two numbers.

We distinguish this *absorptive* exchange (Eq. 3-1) from one in which i partitions to an interface. In this new case, the process should be viewed as an *adsorption* of i to the surface of phase 2:

$$1{:}i{:}1 + 1{:}2 \rightleftharpoons 1{:}1 + 1{:}i{:}2 \tag{3-2}$$

Here, the reaction shown as Eq. 3-2 indicates the presence of an interface between phases 1 and 2. Unlike the case of *absorption* where attractions between 2 and 2 had to be broken and ones between 1 and 1 were made, now in this *adsorption* case the intermolecular bonds between 1 and 2 must be broken as such bonds between 1 and 1 are made.

This "reaction" point of view enables us to organize our thinking about partitioning. First, we must identify the combinations of materials that are juxtaposed before and after the partitioning process. Second, we must ascertain what kinds of chemical structure elements (e.g., $-CH_2-$, $-OH$) are present in the partitioning molecules (i.e., in *i*) and the material of which each participating phase is made (i.e., 1 or 2 above). This allows us to identify the kinds of intermolecular interactions that control the strengths of the "bonds" that are broken and formed. Finally, we need to consider the numbers of interactions, or areas of contact, which are changed in the process.

To understand the extent of such partitioning processes, we have to evaluate how various parts of *i* are attracted to structures of phases 1 and 2. It will be the summation of all these attractions that are broken and formed that will dictate the relative affinity of *i* for the two competing phases with which it could associate. Since these attractive forces stem from uneven electron distributions, we need to discuss where in the structures of organic chemicals and in condensed phases there are electron enrichments and deficiencies. Subsequently, we can examine the importance of these uneven electron distributions with respect to attracting molecules to other materials.

Origins of Intermolecular Attractions

The attractive forces between *uncharged molecules* generally result from the electron-deficient regions in a molecule attracting electron-rich counterparts in neighboring molecules or the atoms making up surfaces. The total affinity of molecules for one another comes from the summation of all attractions. The resulting interactions (Fig. 3.1) can be divided into two categories:

(1) "*Nonspecific*" interactions that exist between any kinds of molecules, no matter what chemical structure these molecules may have. These nonspecific interactions are generally referred to as *van der Waals (vdW)* interactions. They are a superposition of the following components:

(i) Attractions between *time-varying, uneven electron distributions* in adjacent molecules are the origin of *London dispersive energies*. The intensity of such unevenness in a particular molecule or material is related to its polarizability. As a result, the strength of intermolecular attraction energies arising from these time-varying dipoles is proportional to the product of the polarizabilities of each of the interacting sets of atoms.

(ii) Dipole-induced dipole interactions are the source of *Debye energies*. Dipoles exist within chemical structures because of the juxtaposition of atoms with different electronegativities (e.g., an oxygen bonded to a carbon atom). When such a permanent dipole moment in one chemical is juxtaposed to material with a time-averaged even electron distribution, then the first molecule causes an uneven electron distribution to form in the second material. The strength of the resultant intermolecular attraction is proportional to the product of the dipole moment of the first molecule and the

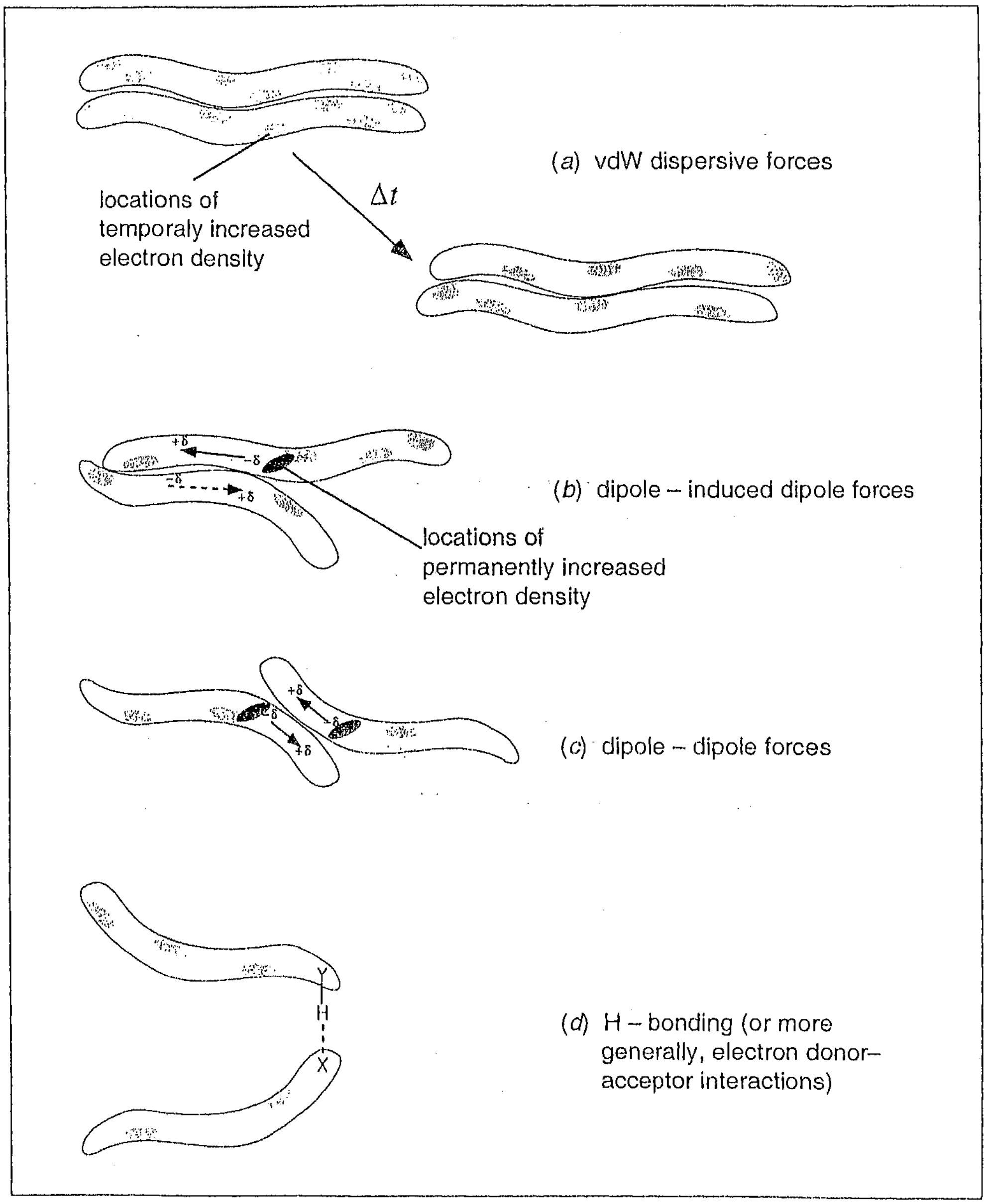

Figure 3.1 Illustration of the various molecular interactions arising from uneven electron distributions: (*a*) dispersive forces, (*b*) dipole–induced dipole forces, (*c*) dipole–dipole forces, (*d*) electron acceptor–electron donor forces.

polarizability of the second molecule.

(iii) Dipole–dipole interactions are the cause of *Keesom energies*. In this case, permanent dipoles in each substance cause the molecules to orient so that the two dipoles face each other in a head-to-tail fashion. The strengths of these attractions are proportional to the product of the dipole moments of the two interacting molecules and depend on the orientation of the interacting partners.

(2) *Specific* interactions (Fig. 3.1*d*) that result from particular molecular structures that enable relatively strong local attractions between permanently electron-poor parts of a chemical structure (e.g., the hydrogen attached to an oxygen) and corresponding permanently electron-rich sites of another molecule (e.g., the nonbonded electrons

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Box 3.1 Classification of Organic Compounds According to Their Ability to Undergo Particular Molecular Interactions

Compounds that undergo only vdW interactions (London plus Debye plus Keesom interactions) are commonly referred to as *apolar*. Examples include alkanes, chlorinated benzenes, and PCBs.

If a chemical exhibits a functionality that has either donor or acceptor character but not both, we call such a compound *monopolar*. Examples include structures with an ether function, –C–O–C– (an electron donor or H-acceptor), a keto group, >C=O (an electron donor or H-acceptor), or an aromatic ring carrying electron withdrawing substituents (an electron acceptor).

Some molecules contain moieties like amino ($-NH_2$), hydroxyl (–OH), and carboxyl groups (–COOH) that exhibit both donor and acceptor properties. We refer to these compounds as *bipolar*.

For large, complex compounds, it is often not obvious how the whole compound should be classified. Such compounds may exhibit functional groups that participate in locally strong polar interactions. However, due to the large size of the molecule, the overall behavior of the compound is dominated by vdW-interactions. It has, therefore, become common practice to divide the world of chemicals into only two categories, namely, *polar* and *nonpolar* compounds. The nonpolar chemicals include all those chemicals whose molecular interactions are dominated by vdW forces.

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of atoms like oxygen and nitrogen). These specific interactions, which we will refer to as *polar* interactions are, of course, only possible between molecules that exhibit complementary structural moieties, that is, if one moiety acts as an *electron acceptor* (often also referred to as *H-donor*) and the other one as an *electron donor* (or *H-acceptor*). Hence, polar interactions can be classified as *electron donor–acceptor* (EDA) or *hydrogen donor–acceptor* (HDA) interactions. Note that both terms are widely used in the literature.

As indicated in Box 3.1, the ability (or inability) of a given compound to undergo specific interactions can be used to divide organic chemicals into different categories. This classification will ultimately be useful when we want to determine whether we should include various factors for quantifying the contributions of these forces in our estimates of the energies controlling specific absorption or adsorption associations in which we are interested.

In the absence of electron donor-acceptor interactions, the London dispersive energy is the dominant contributor to the overall attractions of many molecules to their surroundings. Hence, understanding this type of intermolecular interaction and its dependency on chemical structure allows us to establish a baseline for chemical attractions. If molecules exhibit stronger attractions than expected from these interactions, then this implies the importance of other intermolecular forces. To see the superposition of these additional interactions and their effect on various partitioning phenomena below, we have to examine the role of dispersive forces in more detail, because these forces generally dominate the vdW interactions (Fowkes, 1991; Good and Chaudhury, 1991). The goal of the following discussion is to derive a quantitative measure for these forces. In Chapters 4 and 5 we will then address approaches to quantify polar interactions.

Relative Strengths of Dispersive Energies Between Partitioning Partners

As noted above, London dispersive interactions occur even between molecules of apolar compounds like alkanes, that *on average over time* exhibit a rather smooth distribution of electrons throughout the whole molecular structure. This interaction occurs in all chemicals because there are momentary (order of femtosecond timescales) displacements of the electrons within the structure such that short-lived electron-rich and electron-poor regions temporarily develop. This continuous movement of electrons implies the continuous presence of short-lived dipoles in the structure. This fleeting dipole is felt by neighboring molecules whose electrons respond in a complementary fashion. Consequently, there is an intermolecular attraction between these molecular regions. In the next moment, these attractive interactions shift elsewhere in the molecule.

To think about the strength of dispersive attractions, we consider a situation in which a molecule, i, is moved from a gas phase and mixed into (i.e., absorbed by) a liquid made of the substance, 1:

$$i(\mathrm{g}) + 1{:}1 \rightarrow 1{:}i{:}1 \tag{3-3}$$

where the parenthetic g indicates that i is coming from a gas phase. In this particular partitioning process, we assume ideal behavior in the gas phase, that is, we ignore intermolecular attractions in this phase. Hence, we can focus on the forming interactions between the molecules of i and the liquid 1 medium. Even if the structure of i does not give rise to permanently uneven electron distributions, there will at least be a dispersive interaction energy with 1.

Considering one molecule of i next to one molecule of 1, we have a dispersive attraction energy, $\Delta_{\mathrm{disp}}g$, given by (Israelachvili, 1992):

$$\Delta_{\mathrm{disp}}g\ /\mathrm{J\ per\ interaction} = -\left(3/2\right)\left(I / \sigma^{6}\right)\left(\alpha_i\,\alpha_1\right) / \left(4\pi\varepsilon_{o}\right)^{2} \tag{3-4}$$

where I is equal to $(I_i\ I_1/I_i{+}I_1)$ and I_i and I_1 are the first ionization energies of chemicals i and 1, respectively,

σ is the distance of separation between the temporary dipoles,
α_i is the polarizability of i,
α_1 is the polarizability of 1, and
ε_o is the permittivity of vacuum.

Generally, molecules exhibit I values between 8 and 12 eV (i.e., 1.3 and 2×10^{-18} J), and the separations between molecules must be related to the molecular sizes. The polarizability, α, of a molecule is related to its ability to develop uneven electron distributions in response to imposed electric fields on femtosecond timescales. Since visible light corresponds to electromagnetic radiation with frequencies around

10^{15} Hz, a material's ability to respond to light, as indicated by a property like the refractive indices, n_{Di}, is related to the material's polarizability. This relationship is known as the Lorenz-Lorentz equation (Israelachvili, 1992):

$$\alpha_i / (4\pi\varepsilon_0) = [(n_{Di}^2 - 1)/(n_{Di}^2 + 2)](3M_i / 4\pi\,\rho N_A) \tag{3-5}$$

where M_i is the molar mass,
ρ is the density, and
N_A is Avogadro constant.

It is instructive to look at the refractive indices for a variety of chemical structures (Table 3.1.) What one quickly sees is that polar compounds *are not the same as polarizable* compounds. Indeed, polarizability is more related to chemical structure features like overall size (higher homologs within a compound family have greater polarizabilities), and presence of conjugated electron systems (benzene is more polarizable than hexane; polarizability increases in the order: benzene < naphthalene < pyrene). Finally, molecules with large atoms containing nonbonded electrons far from the nucleus (e.g., bromine, iodine) are generally more polarizable. After this brief diversion, now we continue to use refractive indices to estimate polarizabilities.

We may modify the Lorenz-Lorentz expression, if we note that $M_i / \rho N_A$ is an estimate of an individual molecule's volume. Assuming the molecule is spherical, we may deduce that:

$$M_i / \rho N_A = (4\pi/3)(\sigma/2)^3 \tag{3-6}$$

Note that here we assume that the distance separating the temporary dipoles in adjacent molecules is, on average, the same as the sum of the radii of those molecules. Therefore, we find:

$$(3M_i / 4\pi\rho N_A) = (\sigma)^3 / 8 \tag{3-7}$$

Substituting this result into the Lorenz-Lorentz equation, and then using that result in Eq. 3-4, we find:

$$\Delta_{\text{disp}} g \,/\, \text{J per interaction} = -(3I/256)\left[\frac{n_{Di}^2 - 1}{n_{Di}^2 + 2}\right]\left[\frac{n_{D1}^2 - 1}{n_{D1}^2 + 2}\right] \tag{3-8}$$

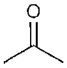
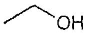
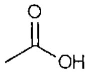
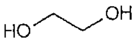
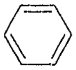
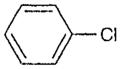
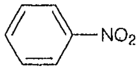
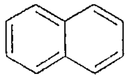
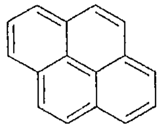
Finally, the molecule i does not interact with one solvent molecule, 1, but rather is surrounded by a number of molecules. This "stoichiometry" (i.e., ratio of i to 1) is given by the ratio of the total surface area, TSA_i (m^2), of i and the contact area, CA (m^2), of i with each solvent molecule. Hence, the integrated intermolecular interaction may be:

$$\Delta_{\text{disp}} G / \text{J}\cdot\text{mol}^{-1} = N_A (\text{TSA}_i / \text{CA}) \Delta_{\text{disp}} g$$

$$= -N_A (\text{TSA}_i / \text{CA})(3I/256)\left[\frac{n_{Di}^2 - 1}{n_{Di}^2 + 2}\right]\left[\frac{n_{D1}^2 - 1}{n_{D1}^2 + 2}\right] \tag{3-9}$$

Since parameters like the solvent contact area, the first ionization potential, and the

Table 3.1 Some Examples of Refractive Indices, n_{Di}, of Organic Compounds. Note that Larger Values of n_{Di} Imply Greater Molecular Polarizability and Dispersive Interactions with a Molecule's Surroundings[a]

Compound	Structure	Refractive Index[a]
Methanol	CH_3-OH	1.326
Acetone		1.342
Ethanol		1.359
Acetic acid		1.370
Hexane		1.372
Octanol		1.427
Ethylene glycol		1.429
Trichloromethane	$CHCl_3$	1.444
Benzene		1.498
Chlorobenzene		1.523
Nitrobenzene		1.550
Naphthalene		1.590
Tribromomethane	$CHBr_3$	1.601
Pyrene		1.770

[a] Data from Lide (1995).

distance of separation between neighboring molecules are fairly invariant, one may expect the dispersive energies to vary between various molecules as:

$$\Delta_{\text{disp}}G \,/\, \text{J mol}^{-1} \approx -\text{constant}\ (\text{TSA}_i)\left[\frac{n_{Di}^2-1}{n_{Di}^2+2}\right]\left[\frac{n_{D1}^2-1}{n_{D1}^2+2}\right] \qquad (3\text{-}10)$$

This result suggests that we can look at the partitioning of various compounds (i.e., vary i) from the gas phase and expect that their relative tendencies to go into or onto differing media (i.e., vary the chemical nature of medium 1) will depend, at least in part, on predictable dispersive force attractions. Partitioning that is in excess of what we expect from this baseline attractive energy for any chemical must indicate the presence of functional groups in that chemical's structure and/or in the interacting medium that allows additional attractive intermolecular forces [Debye, Keesom, or EDA (HDA) interactions]. Hence, in the next section, we examine partitioning of various chemicals into and onto different defined media to see the roles of chemical structure.

A First Glance at Equilibrium Partition Constants

To explore how molecular structures give rise to intermolecular attractions, and these in turn dictate phase partitioning of those molecules, we need to introduce a parameter that quantifies the relative abundance of the molecules of a given organic compound i in each phase *at equilibrium*. First, we note that we consider the reversible partitioning of a compound i between a phase 1 and a phase 2. As we have done before, but now only mentioning the chemical which is partitioning, we can write this process as a "reaction" by arbitrarily choosing phase 2 as "reactant" and phase 1 as product:

$$\underset{\text{“reactant”}}{i \text{ in phase } 2} \rightleftharpoons \underset{\text{“product”}}{i \text{ in phase } 1} \tag{3-11}$$

The equilibrium situation can thus be described by an *equilibrium partition constant*, K_{i12}, which we define as:

$$K_{i12} = \frac{\text{concentration of } i \text{ in phase 1}}{\text{concentration of } i \text{ in phase 2}} \tag{3-12}$$

Note that we have chosen i in phase 2 as the "reactant" in order to have the abundance of i in phase 1 in the numerator of Eq. 3-12. Furthermore, for practical purposes, we define a constant expressed as a ratio of concentrations rather than activities (see Section 3.4). Finally, we consider only situations in which the compound is present as a solute, that is, at low concentrations at which it does not significantly affect the properties of the bulk phase.

K_{i12} is related to a (Gibbs) free energy term, $\Delta_{12}G_i$ by a Boltzmann-type expression (e.g., Atkins, 1998):

$$K_{i12} = \text{constant} \cdot e^{-\Delta_{12}G_i / RT}$$

$$\ln K_{i12} = -\frac{\Delta_{12}G_i}{RT} + \ln \text{ (constant)} \tag{3-13}$$

where we will refer to $\Delta_{12}G_i$ as the *free energy of transfer* of i from phase 2 to phase 1, R is the universal gas constant ($8.31 \text{ J} \cdot \text{mol}^{-1}\text{K}^{-1}$), and T is the absolute temperature in Kelvin. The constant in Eq. 3-13 depends on how we express the abundance of the compounds in the two phases (e.g., as partial pressure, mole fraction, or molar concentration). We will address this issue as well as the derivation of $\Delta_{12}G_i$ in Sections 3.3 and 3.4 when we discuss some important thermodynamic functions. At this point, we note that $\Delta_{12}G_i$ expresses the free energy change (per mole i) for the process of taking molecules of the compound i out of phase 2 and putting them into phase 1 under standard conditions. Hence, $\Delta_{12}G_i$ sums both the *enthalpic* and *entropic* effects (see Section 3.3) that result from the changes occurring in the intermolecular interactions in both phases when removing or adding molecules of compound i. These changes are caused by differences in the interactions of i with the molecules forming the bulk phases between which the compound is partitioned (e.g., $i{:}1$ interactions), and also by changes in the interactions among the bulk phase molecules themselves (e.g., 1:1 interactions). As we will soon see, these latter contributions to $\Delta_{12}G_i$ are particularly important for partitioning processes involving aqueous phases (i.e., $1 = H_2O$) . If the overall $\Delta_{12}G_i$ is negative, the compound prefers to be in phase 1 as compared to phase 2. Thus, at equilibrium, its abundance will be higher in phase 1 (and vice versa, if $\Delta_{12}G_i$ is positive). By examining the relative sizes of $\ln K_{i12}$ as a function of chemical structure, we will be able to see when particular types of intermolecular interactions become important.

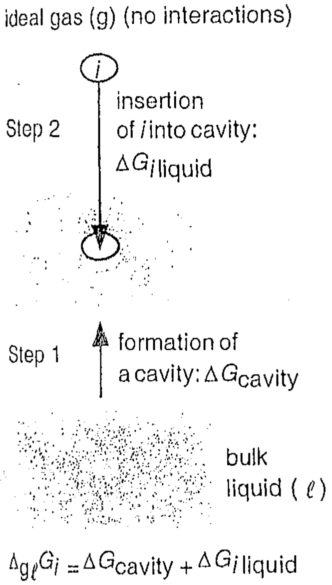


Figure 3.2 Absorption of a compound i from an ideal gas phase *into* a bulk liquid.

Examples of Absorption from the Gas Phase

Let us now look at some partitioning data. We will discuss the two general cases: (i) the partitioning of organic compounds between the (ideal) gas phase and a bulk liquid (*absorption*, Fig. 3.2), and (ii) the partitioning between the gas phase and a solid surface (*adsorption*, Fig. 3.3). In order to emphasize the influence of single pairs of molecule:molecule interactions, we confine our discussion to the partitioning of neutral organic compounds from an *ideal gas phase* (e.g., air). This is another way of saying that there are no intermolecular attractions to break when i leaves the gas phase. First, we consider partitioning "reactions" of the form:

$$i(g) + 1{:}1 \rightleftharpoons 1{:}i{:}1 \qquad (3\text{-}14)$$

As is illustrated in Fig. 3.2, when considering the *ab*sorption of a gaseous molecule into a bulk liquid, the free energy term can be broken up into a term describing the energy that has to be spent to create a cavity in the liquid (ΔG_{cavity} = breaking 1:1 interactions in Eq. 3-3) and a term describing the free energy change caused upon insertion of the compound into the cavity ($\Delta G_{i\text{liquid}}$ = making $i{:}1$ interactions in Eq. 3-3). The former energy involves disruption of solvent:solvent interactions as we discussed earlier. The latter free energy involves the formation of solute:solvent attractions. It is easy to conceive that the overall free energy of transfer, and thus the partition constant of a compound i (see Eq 3-12), will depend strongly on the type of compound as well as on the type of bulk liquid considered. Therefore, in our following examples, we will inspect gas-liquid equilibrium partition constants of members of a variety of different compound classes for bulk liquids exhibiting very different properties: (1) the pure organic liquid compound itself, (2) one apolar organic liquid, hexadecane, and (3) one polar solvent, water.

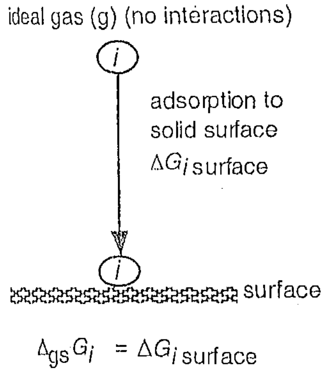


Figure 3.3 Adsorption of a compound i from an ideal gas phase *to* a surface.

Example 1: Vapor Pressure and Molecular Interactions in the Pure Liquid Compound

We start out by evaluating the intermolecular interactions among the molecules of a given compound in its own pure liquid state by considering the equilibrium partitioning with the gas phase:

$$i(\mathrm{g}) + i{:}i \rightleftharpoons i{:}i{:}i \tag{3-15}$$

In this case, the free energy of transfer of i from the pure liquid to an ideal gas phase (i.e., air) $\Delta_{\mathrm{aL}}G_i$, and thus the corresponding gas (air)–liquid equilibrium partition constant, $K_{i\mathrm{aL}}$ (see Eq. 3-16 below), are direct measures of the attractive forces between like molecules in the liquid (recall we assume no interactions among gas phase molecules). Note that for the following discussion we use a subscript "a" (air) to denote the ideal gas phase. Furthermore a capital "L" is used to describe the pure liquid in order to distinguish from other liquid phases (subscript ℓ). Finally, the superscript * indicates that we are dealing with a property of a pure compound.

Commonly, gas-liquid partitioning is expressed by the saturated liquid vapor pressure, $p_{i\mathrm{L}}^*$, of the compound i. This important chemical property will be discussed in detail in Chapter 4. Briefly, $p_{i\mathrm{L}}^*$ is the pressure exerted by the compound's molecules in the gas phase above the pure liquid at equilibrium. Since this pressure generally involves only part of the total pressure, we often refer to it as a partial pressure due to the chemical of interest. In this case, when there is no more build up of vapor molecules in a closed system, we say that the gas phase is "saturated" with the compound. Note that because $p_{i\mathrm{L}}^*$ is strongly temperature dependent, when comparing vapor pressures of different compounds to see the influence of chemical structure, we have to use $p_{i\mathrm{L}}^*$ values measured at the same temperature (which also holds for all other equilibrium constants discussed later; see Section 3.4).

For comparison of chemical's partition constants between air and different bulk liquids, it is useful to express $p_{i\mathrm{L}}^*$ as a constant, $K_{i\mathrm{aL}}$, that describes the relative amount of the compound in the two phases in molar concentrations (i.e., $\mathrm{mol \cdot L^{-1}}$):

$$K_{i\mathrm{aL}} = \frac{C_{i\mathrm{a}}^{\mathrm{sat}}}{C_{i\mathrm{L}}}\left(\frac{\mathrm{mol\cdot L^{-1}\ air}}{\mathrm{mol\cdot L^{-1}\ pure\ liquid\ compound}}\right) \tag{3-16}$$

Using the ideal gas law ($pV = nRT$), the saturation concentration in the air, $C_{i\mathrm{a}}^{\mathrm{sat}} (= n / V)$, can be calculated from $p_{i\mathrm{L}}^*$ by:

$$C_{i\mathrm{a}}^{\mathrm{sat}} = \frac{p_{i\mathrm{L}}^*}{RT} \tag{3-17}$$

$C_{i\mathrm{L}}$ can be derived from the density, $\rho_{i\mathrm{L}}$, of the liquid compound and from its molar mass, M_i:

$$C_{i\mathrm{L}} = \frac{\rho_{i\mathrm{L}}}{M_i}\left(\frac{\mathrm{g\cdot L^{-1}}}{\mathrm{g\cdot mol^{-1}}}\right) \tag{3-18}$$

Note that $C_{i\mathrm{L}}$ is the inverse of the molar volume of the liquid compound, which we denote as $\overline{V}_{i\mathrm{L}}$. Substitution of Eqs. 3-17 and 3-18 into Eq. 3-16 yields:

$$K_{i\mathrm{aL}} = \frac{M_i}{\rho_{i\mathrm{L}} \cdot RT}\, p_{i\mathrm{L}}^* \tag{3-19}$$

Armed with such partition constants, we can calculate the free energies involved in exchanging substances between a gas and their own pure liquids.

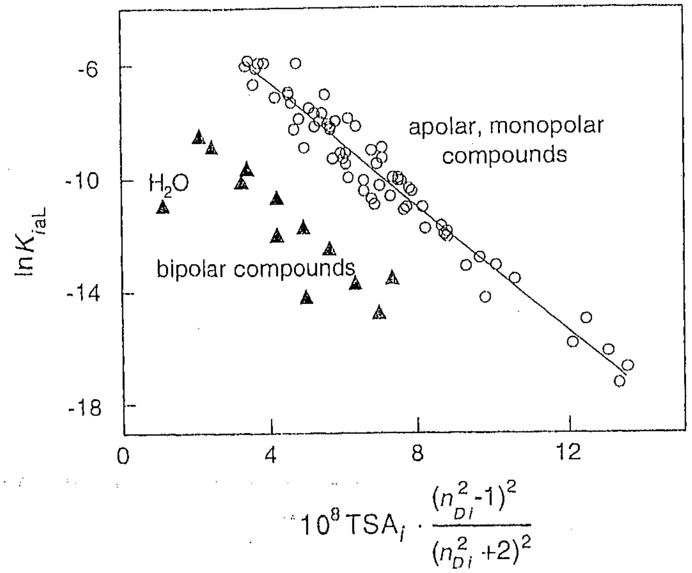
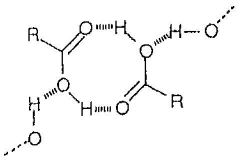


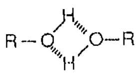
Figure 3.4 Plot of ln K_{iaL} (25°C) (Eq. 3-19) versus the dispersive vdW-parameter defined by Eq. 3-10 with 1 = i. Note that TSA_i is in $\mathrm{cm}^2\ \mathrm{mol}^{-1}$.

Now we are prepared to observe how chemical structures control this particular case of partitioning: the distribution of molecules between their own pure liquid phase and an equilibrated gas phase. To indicate the importance of the dispersion forces among the molecules in their pure liquid phase, we examine K_{iaL} values determined for a wide variety of liquid compounds as a function of their $\Delta_{\mathrm{disp}}G$ defined above by Eq. 3-10 (Fig. 3.4). The compounds chosen are composed of less than 10 carbon atoms and exhibit no more than one functional group. Hence, the functional group can be considered to contribute significantly to the overall capability of the molecules to interact with neighboring molecules. Compound classes are *n*-alkanes, alkylated benzenes, polychlorinated methanes and ethanes (include permanent dipoles), aliphatic ketones (include permanent dipoles and can act as electron donors), aldehydes (include permanent dipoles and can act as electron donors), carboxylic acid esters (include permanent dipoles and can act as electron donors), alcohols (include permanent dipoles, can act as electron acceptors and donors), and carboxylic acids (include permanent dipoles and can act as electron acceptors and donors). Note that these functional groups are discussed in Section 2.3 (Figs. 2-15 and 2-17).

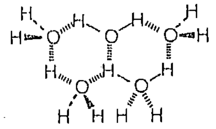
As demonstrated for all *apolar* and *monopolar* compounds (see Box 3.1 for definitions), which cannot undergo electron donor-acceptor interactions with like molecules in their pure liquid, a good inverse linear correlation is found between ln K_{iaL} and our metric of $\Delta_{\mathrm{disp}}G$. Some of the variation in ln K_{iaL} is due to the polarizability contribution (ranges over about a factor of 1.6), while some is also due to changes in TSA_i (factor of about 7). This factor of about 10 in $\Delta_{\mathrm{disp}}G$ is consistent with the ln K_{iaL} changing by about 10 ln units (Fig. 3.4.) Note that some of the scatter is due to the compounds classified as "monopolar" having additional dipole–induced dipole, dipole–dipole interactions, and possibly also having some weak bipolar character (e.g., the ketones, aldehydes, esters). Furthermore, the TSA_i value used is only a very crude approximation of the actual contact area among the molecules. Nevertheless, Fig. 3.4 nicely shows the dominating role of dispersive vdW interactions in determining the air/pure liquid partitioning (i.e., the vapor pressure) of apolar and monopolar organic compounds.



carboxylic acids



alcohols



water

Figure 3.5 H-bonding in various pure liquids.

The truly bipolar compounds that may form rather strong hydrogen bonds in their pure liquids (Fig. 3.5) have, however, distinctly lower K_{iaL} values than expected solely from their vdW interactions. The most extreme case is water, which has a K_{iaL} value that is almost four orders of magnitude smaller than the value one would expect for a nonpolar compound with similar size and dispersive vdW interactions. From this finding, we see the great importance of superimposing hydrogen-bonding interactions on the dispersive interactions of molecules like water.

Example 2: Air–Solvent Partitioning

In our next example we compare the partitioning of the same set of compounds between air (gas phase) and two very different solvents, hexadecane and water. These two liquids are chosen to represent two extreme cases, both with respect to the free energy costs of changing solvent:solvent interactions as well as with respect to the type of interactions the solvent molecules may have with the organic solute. In the case of hexadecane, all compounds, irrespective of their polarity, can undergo only vdW interactions with these hydrocarbon solvent molecules. Furthermore, the free energy cost for cavity formation reflects breaking only vdW interactions among the hexadecane molecules. Thus, as is nicely illustrated by Fig. 3.6*a*, for *all compounds* (apolar, monopolar, and bipolar), an inverse relationship is found between $\ln K_{iah}$ and the dispersive vdW parameter of the compound expressed as product of the solute's total surface area and refractive index estimator of polarizability (Eq. 3-10).

The situation is completely different in the air/water partitioning system (Fig. 3.6*b*). As is evident, very large differences in K_{iaw} are observed between members of different compound classes. For example, the air/water partition constants of the *n*-alkanes are more than two orders of magnitude larger than those of the corresponding ethers, and even five orders of magnitude larger than those of the alcohols exhibiting a similar dispersive vdW parameter. These differences reflect the different abilities of the compound molecules to undergo polar interactions with the water molecules, interactions that help to counterbalance the rather large free energy costs for creating a cavity in the bulk water. Thus, in contrast to the partitioning from air to a solvent like hexadecane, apolar compounds such as the *n*-alkanes are "expelled" from the bulk water phase. This is not because they do not have attractive vdW interactions with the water molecules, but rather because of the high costs of cavity formation (breaking H_2O:H_2O interactions). This effect is also seen within each series of compounds that differ only by entities that add vdW interactions (i.e., CH_2-groups). K_{iaw} increases with increasing size of the molecule (Fig. 3.6*b*), which is in contrast to the situation found in the air/hexadecane system (Fig. 3.6*a*).

Examples of Adsorption from the Gas Phase

Now we shift to cases which allow us to gain insights into the intermolecular forces between organic molecules and a given surface (Fig. 3.3). By inspecting gas/solid adsorption constants of a variety of compounds interacting with two surfaces exhibiting very different properties (i.e., quartz versus teflon), we will learn a few somewhat surprising facts. For instance, we will see that in this case, a nonpolar hydrocarbon interacts more strongly with a polar surface than with a nonpolar surface. Intuitively, this might not have been expected.

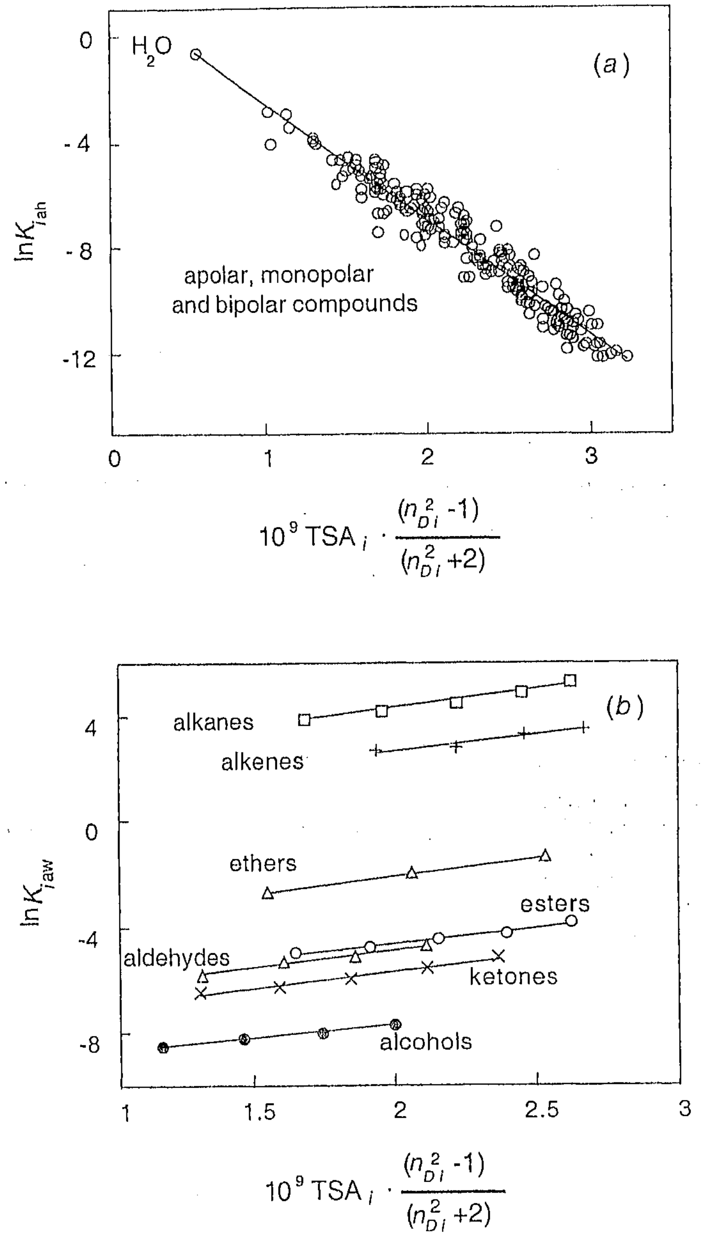


Figure 3.6 Plot of the natural logarithms of the partition constants at 25°C of a series of apolar, monopolar, and bipolar organic compounds between air and (*a*) *n*-hexadecane (*n*-$C_{16}H_{34}$) and (*b*) water versus the dispersive vdW-parameter of the compounds defined by Eq. 3-10. Note that from Eq. 3-10 only the compound part is used because the solvent part (1) is the same for all compounds, and that TSA_i is in cm^2 mol^{-1}.

Example 3: Air–Solid Surface Partitioning

In our final example, we consider the partitioning of a small set of organic compounds between air and two different solid surfaces, teflon and quartz (Fig. 3.7). The two surfaces differ distinctly in their properties in that the teflon surface is made up of atoms that cannot participate in EDA interactions, while the quartz surface (which exhibits OH-groups), has a strongly bipolar character (much like a water surface). In the case of air/surface partitioning, the partition constants reflect the interactions of a given organic compound with the aggregate of atoms making up the surface. In contrast to air/bulk liquid partitioning, for these surface interactions no cavity as in the solvent has to be formed. Hence, in this case (Fig. 3.3), the free energy change on

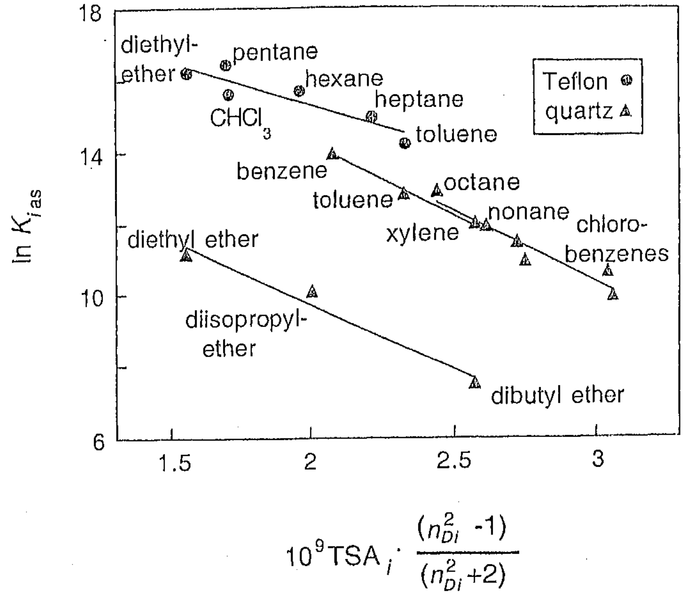


Figure 3.7 Plots of the natural logarithms of the air/surface partition constants, K_{ias}, of a series of apolar and monopolar compounds for two different surfaces (i.e., teflon and quartz) versus the dispersive vdW-parameter of the compounds defined by Eq. 3-10. Note that from Eq. 3-10 only the compound part is used because the solvent part (1) is the same for all compounds, and that TSA_i is in cm^2 mol^{-1}. (Data at 25°C from Goss and Schwarzenbach, 1998.)

exchange does not include a term like ΔG_{cavity}. Had the solid been immersed in a liquid so that there were liquid molecules:solid surface interactions, insertion of our partitioning substance i at the surface would have required us to consider the free energy of making room for the adsorbate (e.g., breaking 1:2 interactions in partitioning "reaction" shown in Eq. 3-2).

In the case of the teflon surface where only vdW interactions are possible for any adsorbing molecule, a plot of lnK_{ias} versus the sorbate's dispersive vdW parameter yields a straight line for apolar and polar compounds (Fig. 3.7). In contrast, for the bipolar quartz surface, apolar and monopolar compounds are separated into several groups according to their ability (or inability) to undergo polar interactions. One interesting additional detail that can be seen from Fig. 3.7 is that nonpolar or weakly monopolar compounds such as alkanes and alkylbenzenes are slightly more attracted to the polar quartz surface as compared to the nonpolar teflon surface. This finding may be somewhat surprising. Intuitively, we still might have the idea that nonpolar compounds are attracted more strongly by nonpolar counterparts as compared to polar counterparts. This expectation is not generally true. The reason in this particular case is that the ability of a quartz surface to undergo vdW interactions is larger than that of a teflon surface (see Section 11.2). In this context it is important to realize that compounds which we denote as being *hydrophobic* (i.e., disliking water) are actually attracted to water *surfaces*. One example illustrating this point is the thin gasoline films that all of us have seen on the surface of polluted lakes or rivers. Obviously, in this case, the attractive (vdW) forces between the *hydrophobic* hydrocarbons and the water molecules at the water surface overcome the (vdW) forces among the hydrocarbon molecules themselves that would favor the formation of oil droplets. Hence, the term *hydrophobicity* of a compound should only be used in connection with a compound's tendency to be *dissolved in a bulk water phase*. In such cases, the balance between the free energy costs for cavity formation *and* the free energy gains due to the interactions of the compound with the water molecules is important. Moreover, as has become evident from our above discussion, the hydrophobicity of organic compounds will increase with increasing size of the molecules. For a given size, hydrophobicity will be maximal for compounds that can only undergo vdW interactions with water. We will come back to this point in Chapter 5, when discussing water solubilities and aqueous activity coefficients of organic compounds.

With these first insights into the molecular interactions that govern the partitioning of organic compounds between different phases in the environment, we are now prepared to tackle some thermodynamic formalisms. We will need these parameters and their interrelationships for quantitative treatments of the various phase transfer processes discussed in the following chapters.

3.3 Using Thermodynamic Functions to Quantify Molecular Energies

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 different forms of energies. Some energies are those associated with the molecule's chemical bonds and bond vibrations, flexations, and rotations. Other energies include those due to whole-molecule translations, reorientations, and interactions of the molecules with their surroundings. The whole energy content is the *internal* energy and 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 could be expressed as the sum of the contributions from all of the different components present:

$$G(p,T,n_1,n_2,....n_i,...n_N) = \sum_{i=1}^{N} n_i \mu_i \tag{3-20}$$

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 then given by:

$$\mu_i(\mathrm{J\cdot mol^{-1}}) \equiv \left[\frac{\partial G(\mathrm{J})}{\partial n_i(\mathrm{mol})}\right]_{T,p,nj\neq i} \tag{3-21}$$

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 μ_i. When adding an *incremental number* of molecules of i, 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. We should note that μ_i is sometimes also referred to as the *partial molar free energy*, G_i, of a compound. Finally, we recall that G_i ($\mathrm{J\cdot mol^{-1}}$) is related to the *partial molar enthalpy*, H_i ($\mathrm{J\cdot mol^{-1}}$), and

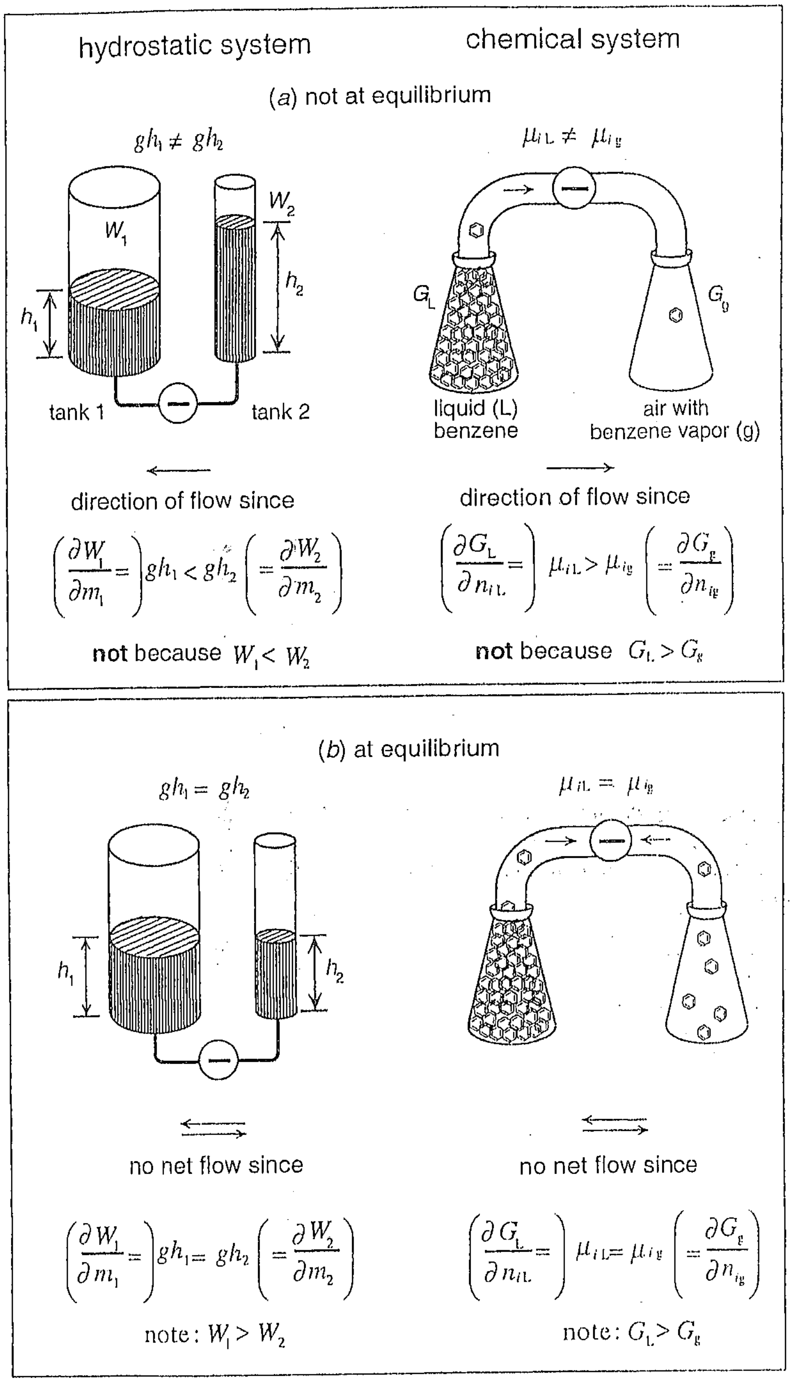


Figure 3.8 Conceptualization of the potential functions in a hydrostatic system and in a simple chemical system. (*a*) In the unequilibrated hydrostatic system, water will flow from reservoir 2 of higher hydrostatic potential ($=gh_2$, where g is the acceleration due to gravity and h_2 is the observable 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 head space in the nonequilibrated 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).

partial molar entropy, S_i (J.mol^{-1} K^{-1}), by the well-known general relationship:

$$\mu_i \equiv G_i = H_i - T \cdot S_i \tag{3-22}$$

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. This is analogous to the use of hydrostatic head potential for identifying the direction of flow between water reservoirs (Fig. 3.8*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. 3.8*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 (in contrast to the total free energy G, which is an *extensive* function).

Fugacity

Unfortunately, unlike hydraulic head potentials, there is no way of directly observing chemical potentials. Consequently, the concept of *fugacity* was born. Lewis (1901) reasoned that rather than look into a system and try 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 extent to which a transfer process would occur.

Pressure and Fugacities of a Compound in the Gas State

Let us quantify first the "fleeing tendency" or fugacity of molecules in a gas (just about the simplest molecular system) in a way we can observe or measure. 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. 3.9*a*). 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 will measure a higher gas pressure. For an *ideal* gas, the pressure is perfectly proportional to the amount of gaseous compound. 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; see, e.g., Prausnitz, 1969, p. 17):

$$(d\mu_{ig})_T = \frac{V}{n_{ig}}dp_i \qquad (3\text{-}23)$$

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

$$(d\mu_{ig})_T = \frac{RT}{p_i}dp_i \qquad (3\text{-}24)$$

As mentioned above, the absolute value of the chemical potential cannot be measured but we can measure the absolute value of pressure or the amount of substance in the gas phase. Hence, we may define a standard value of the chemical potential of the gaseous compound i, μ_{ig}^0, by defining a standard amount and standard pressure in the form of one variable, the standard pressure $p_i = p_i^0$ (commonly 1 bar). We do this by integration of Eq. 3-24:

$$\int_{\mu_{ig}^0}^{\mu_{ig}} (d\mu_{ig})_T = RT \int_{p_i^0}^{p_i} \frac{1}{p_i}\, dp_i \qquad (3\text{-}25)$$

which yields:

$$\mu_{ig} = \mu_{ig}^0 + RT \ln\left[\frac{p_i}{p_i^0}\right] \qquad (3\text{-}26)$$

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 will be even more the case for liquids and solids, see below). These forces influence the (partial) pressure of the gas molecules, but not the amount of the gaseous compound(s). 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 of the total pressure. The fugacitiy of a gaseous compound is, however, closely related to its partial pressure. To account for the nonideality of the gas, one can relate these terms by using a fugacity coefficient, θ_{ig}:

$$f_{ig} = \theta_{ig} p_i \qquad (3\text{-}27)$$

It is now easy to see that the correct expression for the chemical potential of a gaseous compound i is not based on pressure but on fugacity:

$$\mu_{ig} = \mu_{ig}^0 + RT \ln\left[\frac{f_i}{p_i^0}\right] \qquad (3\text{-}28)$$

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

Under typical environmental conditions with atmospheric pressure, gas densities are very low so that we set $\theta_i = 1$. In other words, for all our following discussion, we will assume that any compound will exhibit ideal gas behavior (i.e., we will use Eq. 3-26 instead of Eq. 3-28).

In a mixture of gaseous compounds having a total pressure p, p_i is the partial pressure of compound i, which may be expressed as:

$$p_i = x_{ig} p \qquad (3\text{-}29)$$

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

$$x_{ig} = \frac{n_{ig}}{\sum_j n_{jg}} \qquad (3\text{-}30)$$

and $\Sigma_j n_{jg}$ 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:

$$\begin{aligned} f_{ig} &= \theta_{ig} x_{ig} p \\ &\cong p_i \end{aligned} \tag{3-31}$$

Reference States and Standard States

Before we discuss the fugacities of compounds in liquid and solid phases, a few remarks on the choice of reference states are necessary. As we have seen in the development of Eq. 3-26, we face one obvious difficulty. Since we cannot compute an absolute value for the chemical potential, we must be content with computing *changes* in the chemical potential as caused by changes in the independent variables of temperature, pressure, and composition. This difficulty, however, is apparent rather than fundamental; it is really no more than an inconvenience. It results because the relationships between the chemical potential and the physically measurable quantities are in the form of differential equations, which upon integration yield only differences. With the choice of an appropriate reference state, it is usually possible to express the energetics of a given process in rather simple terms. This is similar to concepts used in everyday life, where we choose reference states to express the magnitude of entities, for example, the altitude of a mountain relative to sea level.

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 (vaporization), as discussed in Section 3.2], 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 will 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 will focus on the energy change associated with having benzene molecules in new surroundings. Benzene molecules in gas or liquid phases will, therefore, feel different attractions to their neighboring molecules and will contain different orientational and translational energies since in a liquid the molecules are packed fairly tightly together, while 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 silly (though 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 shall be clever and, in this case, choose the "energy status" of pure liquid benzene as a reference state, since liquid benzene includes all of the internal bonding energies common to both the gaseous and liquid forms of the compound.

In the field of environmental organic chemistry, the most common *reference states* used include: (1) the *pure liquid state*, when we are concerned with phase transfer processes; (2) the *infinite dilution state*, when we are dealing with reactions of organic chemicals in solution (e.g., proton transfer reactions in water, see Chapter 8); and (3) the elements in their naturally occurring forms (e.g., C, H_2, O_2, N_2, and Cl_2), when we are interested in reactions in which many bonds are broken and/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 this state. Once we have chosen an appropriate reference state, we also must specify the conditions of our reference state; that is, the pressure and the 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. 3-26 and 3-27 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, standard conditions, and temperatures, 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.

Fugacities of Liquids and Solids

Let us now continue with our discussion of how to relate the chemical potential to measurable quantities. 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. 3.9). 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}^*:

$$\begin{aligned} f_{iL} &= \gamma_{iL} \cdot p_{iL}^* \\ f_{is} &= \gamma_{is} \cdot p_{is}^* \end{aligned} \tag{3-32}$$

where γ_i now 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. The molecules are viewed, therefore, as "dissolved" in like molecules, and this condition is defined to have "ideal" mixing behavior.

If we consider, for example, compound i in a liquid mixture, e.g., in organic or in aqueous solution; (subscript "ℓ" see Fig. 3.9*d*), we can now relate its fugacity in the mixture to the fugacity of the pure liquid compound by [note that for convenience, we have chosen the *pure liquid compound* (superscript *) as our *reference state*]:

$$\begin{aligned} f_{i\ell} &= \gamma_{i\ell} \cdot x_{i\ell} \cdot f_{iL}^* \\ &= \gamma_{i\ell} \cdot x_{i\ell} \cdot p_{iL}^* \end{aligned} \tag{3-33}$$

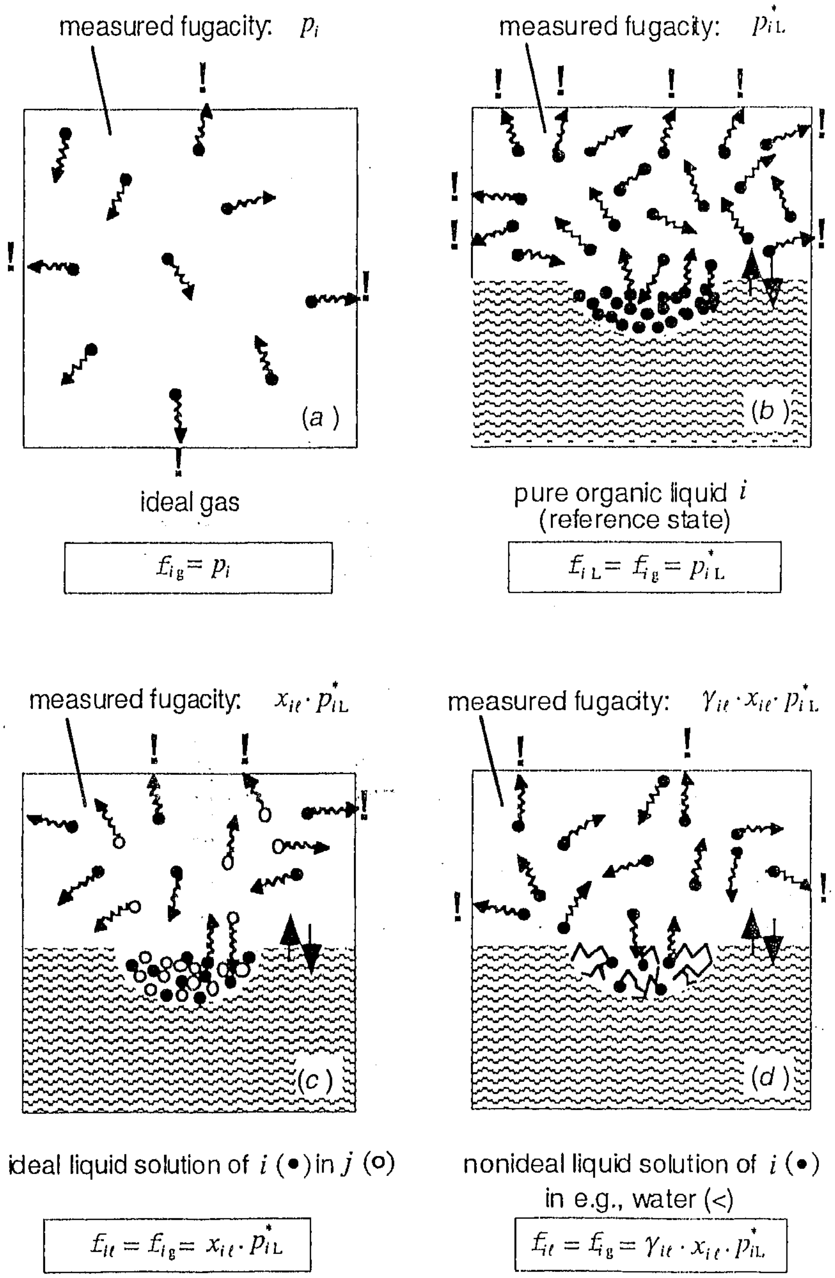


Figure 3.9 Conceptualization of the fugacity of a compound i (*a*) in an *ideal gas*; (*b*) in a *pure* liquid compound i; (*c*) in an *ideal* liquid mixture; and (*d*) in a *nonideal* liquid mixture (e.g., in aqueous solution). Note that in (*b*), (*c*), and (*d*), the gas and liquid phases are in equilibrium with one another.

where $x_{i\ell}$ is the mole fraction of i (Eq. 3-30) in the mixture (or solution). If the compounds form an *ideal* mixture (Fig. 3.9*c*), implying that no nonideal behavior results from interactions among unlike molecules, $\gamma_{i\ell}$ is equal to 1 and Eq. 3-33 represents the well-known *Raoult's Law.*

Activity Coefficient and Chemical Potential

Using the concept of fugacity we can now, in analogy to the gaseous phase (Eq. 3-28), express the chemical potential of a compound i in a liquid solution by:

$$\mu_{i\ell} = \mu_{i\mathrm{L}}^{*} + RT\ln\left[\frac{f_{i\ell}}{p_{i\mathrm{L}}^{*}}\right] \tag{3-34}$$

where we have chosen the pure liquid compound as reference state. Note that $\mu_{i\mathrm{L}}^{*}$ is nearly equal to the standard free energy of formation $\Delta_f G_i^{\circ}(\mathrm{L})$ of the pure liquid compound, which is commonly defined at 1 bar and not at $p_{i\mathrm{L}}^{*}$. Hence $\mu_{i\mathrm{L}}^{*} \cong \mu_{i\mathrm{L}}^{0}$. Substitution of Eq. 3-33 into Eq. 3-34 then yields:

$$\mu_{i\ell} = \mu_{i\mathrm{L}}^{*} + RT\ln \gamma_{i\ell} \cdot x_{i\ell} \tag{3-35}$$

Generally, the expression $f_i/f_{\mathrm{ref}} = \gamma_i \cdot x_i = a_i$ 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 standard state (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.* It must be emphasized here *that the activity of a given compound in a given phase is a relative measure and is, therefore keyed to the reference state.* The numerical value of γ_i will therefore depend on the choice of reference state, since, as we have seen in Section 3.2, molecules of i in different reference states (i.e., liquid solutions) interact differently with their surroundings.

It is instructive to examine the activity coefficients of a few organic compounds in different solvents using the pure organic liquid compound as the reference state (Table 3.2). These $\gamma_{i\ell}$ values express the escaping tendency of a given compound from the respective solution *relative to the compound's escaping tendency from its own pure liquid.* Note that with this choice, for each compound i, we define a different molecular environment as reference state. At first glance, this might seem to be somewhat strange. It would, of course, also be feasible and, if the necessary data were available, even meaningful, to choose the same reference state for all compounds (e.g., infinitely dilute in hexadecane). By doing so, activity coefficients for other molecular environments (e.g., water) could be more easily compared, because they would all be related to a situation where all compounds exhibit solely vdW interactions. Another option would be to use the ideal gas phase as the reference state where no interactions occur at all. Nevertheless, as we will see in the following chapters, the choice of the pure liquid as reference state has significant practical advantages, in that the pertinent properties of the pure liquid are known or can be estimated for many organic compounds.

But let us now inspect the $\gamma_{i\ell}$ values for the various chemicals given in Table 3.2. As we would probably have expected intuitively from our discussions in Section 3.2, $\gamma_{i\ell}$ values close to 1 are found in those cases in which molecular interactions in the solution are nearly the same as in the pure liquid compound. For example, when the intermolecular interactions in a pure liquid are dominated by vdW interactions, and when solutions also exhibit only vdW interactions between the solute and solvent and between the solvent molecules themselves, we have $\gamma_{i\ell}$ values close to 1. Examples include solutions of nonpolar and monopolar compounds in an apolar solvent (e.g., *n*-hexane, benzene, and diethylether in hexadecane), as well as solutions of nonpolar solutes in monopolar solvents (e.g., *n*-hexane in chloroform). In contrast, if we consider situations in which strong polar interactions are involved between the solute

Table 3.2 Activity Coefficients[a], $\gamma_{i\ell}$, of Hexane (apolar), Benzene (monopolar), Diethylether (monopolar), and Ethanol (bipolar) in Different Solvents at Infinite Dilution at 25°C. Reference: Pure Liquid Organic Compound.

Solvent (*Polarity*)	Solute Hexane (*apolar*)	 Benzene (*monopolar, H-acceptor*)	 Diethylether (*monopolar, H-acceptor*)	 Ethanol (*bipolar*)
n-Hexadecane (n-$C_{16}H_{34}$) (*apolar*)	~ 1	~ 1	~ 1	35
Trichloromethane ($CHCl_3$) (*monopolar, H-donor*)	1.8	0.8	0.3	4.5
Ethanol (C_2H_5OH) (*bipolar*)	12	5.4	n.a.[b]	1
Water (*bipolar*)	460000	2500	130	3.6

[a]Data from Gmehling et al. (1994). [b]n.a. = not available.

molecules in their pure liquid and/or among the solvent molecules, but not in the solute:solvent interactions, activity coefficients of much greater than 1 may be found. For example, the activity coefficient of ethanol in hexadecane is 35 (Table 3.2). This significant deviation from 1 is due to the polar interactions of the ethanol molecules in their pure liquid, which cannot be counterbalanced by the vdW interactions in solution. The most striking example in Table 3.2 is, however, the solution of *n*-hexane in water ($\gamma_{iw} = 460000$). As pointed out in Section 3.2, this extremely high escaping tendency of nonpolar organic compounds from bulk water is not due to a lack of attractive interactions between the organic molecules and the water molecules, but to the very high free energy costs for cavity formation.

Finally, inspection of Table 3.2 shows also that there are cases in which $\gamma_{i\ell}$ can be even smaller than 1. An example is a solution of diethylether in chloroform. Here, the solute is an electron donor (H-acceptor), while the chloroform solvent is an electron acceptor (H-donor). In this case, the solute and solvent both acquire additional intermolecular interactions that were unavailable to them in their pure liquid forms. The monopolar diethylether (only vdW interactions in its pure liquid) can add polar interactions to its vdW attractions with the molecules of the monopolar chloroform solvent exhibiting a complementary electron acceptor property.

Excess Free Energy, Excess Enthalpy, and Excess Entropy

Before we go on and apply Eq. 3-35 to describe the partitioning of a compound *i* between two phases, a few comments are necessary on the various partial molar free energy terms included in Eq. 3-35. First, we rewrite Eq. 3-35 by splitting the term that expresses the difference in partial molar free energy of a compound *i* between its actual situation in a given solution and its situation in the reference state:

$$\mu_{i\ell} = \mu_{iL}^{*} \quad + \quad \underbrace{RT \ln x_{i\ell}}_{T \cdot S_{\text{imix}}^{\text{ideal}}} \quad + \quad \underbrace{RT \ln \gamma_{i\ell}}_{\text{partial molar } \textit{excess} \text{ free energy "} G_{i\ell}^{\mathrm{E}} \text{"}} \tag{3-36}$$

As already pointed out, $\gamma_{i\ell}$ is 1 if a compound forms an ideal solution. 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, $G_{i\ell}^{\mathrm{E}}$, 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 concentration of the compound i in the two states. The term $R \ln x_{i\ell} = S_{\text{imix}}^{\text{ideal}}$ expresses the partial molar entropy of *ideal* mixing (a purely statistical term) when diluting the compound from its pure liquid ($x_{iL} = 1$) into a solvent that consists of otherwise like molecules.

Let us now have a closer look at this excess free energy term. Note that, for simplicity, in the following and throughout the book we will drop the term "partial molar" and just 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. 3-22) to the free energy of a given compound in a specific molecular environment. We will do this in a somewhat simplistic way. In brief, the *enthalpy* term represents all attractions or attachments of a compound's molecule to its surroundings. These include *inter*-molecular interactions as discussed in Section 3.2 as well as the internal attraction or bonds (*intra*molecular forces, e.g., bond energies, see Section 2.2). Thus, the enthalpic contributions may be thought of as the "glue" holding the parts of a molecule to its surroundings. As we have already pointed out several times, when we are only interested in the partitioning of organic compounds we choose a reference state in a way that we have only 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, then the more "randomness" exists. As a result, the entropy terms are larger. This leads to a more negative free energy term (see Eq. 3-22). By analogy to Eq. 3-22, we can express the excess free energy term in Eq. 3-36 as:

$$G_{i\ell}^{\mathrm{E}} = RT \ln \gamma_{i\ell} = H_{i\ell}^{\mathrm{E}} - T \cdot S_{i\ell}^{\mathrm{E}} \tag{3-37}$$

where $H_{i\ell}^{\mathrm{E}}$ and $S_{i\ell}^{\mathrm{E}}$ 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 contributions to $G_{i\ell}^{\mathrm{E}}$ for four simple compounds in hexadecane and in water (Table 3.3). Also shown in Table 3.3 are the corresponding values for the ideal gas phase (i.e., $G_{ig}^{\mathrm{E}}, H_{ig}^{\mathrm{E}}, S_{ig}^{\mathrm{E}}$), which are, of course, identical with the free energy, the enthalpy, and the entropy of vaporization of the pure liquid compounds, respectively,

Table 3.3 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.[a] All Data at 25°C. Reference: Pure Liquid Organic Compound.

Phase Compound (i)	$G^E_{i\,\text{phase}}$ (kJ · mol^{-1})	=	$H^E_{i\,\text{phase}}$ (kJ · mol^{-1})	−	$T\ S^E_{i\,\text{phase}}$ (kJ · mol^{-1})	$S^E_{i\,\text{phase}}$ (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).

which we will discuss in detail in Chapter 4. Here, we just note from the examples given in Table 3.3 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 bipolar compound to undergo quite strong polar interactions 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^E_{ig}. 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 found for the compounds in hexadecane. Here, the apolar and monopolar compounds show almost ideal behavior (i.e., $G^E_{i\ell} \approx 0$) because in their own liquids, as well as in hexadecane, they can undergo only vdW interactions. In the case of ethanol, again, a significant enthalpy cost and entropy gain is found, which can be explained with the same arguments used above for the gas phase. The absolute $H^E_{i\ell}$ and $T \cdot S^E_{i\ell}$ 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 perhaps not have guessed that the excess enthalpies in water are close to zero or even negative for all four compounds, even for the apolar hexane. The very high fugacity of hexane in water (as compared to its pure liquid) is therefore not due to enthalpic reasons. Rather this is caused by a very large negative entropy contribution. This effect is also significant for the other three compounds (see Table 3.3). 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 involve some special intermolecular interactions which we need to unravel when we want to understand the environmental partitioning of organic compounds. We will learn more about these secrets in Chapter 5. Our next step here is to demonstrate how partition constants between two different phases are linked to the corresponding excess free energy terms.

3.4 Using Thermodynamic Functions to Quantify Equilibrium Partitioning

The next task in our general discussion of equilibrium partitioning of organic compounds between two different phases is to visualize how equilibrium partition constants as defined by Eq. 3-12 are related to the various energy terms discussed in Section 3.3. Then, we will be interested in the free energy term $\Delta_{12}G_i$ introduced in Eq. 3-13, and we will briefly address the effect of *temperature* on equilibrium partitioning. Finally, we will make a few comments on some simple *linear free energy relationships (LFERs)*, which, when applied with appropriate caution, are extremely powerful extrathermodynamic tools (i.e., empirical approaches that cannot be derived strictly from thermodynamic theory) used to predict and/or evaluate partition constants of organic compounds in different two-phase systems.

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, an organic phase 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. 3-11. At this point we write down the chemical potentials of i in the two phases according to Eq. 3-36:

$$\begin{aligned} \mu_{i1} &= \mu_{iL}^{*} + RT\ln x_{i1} + RT\ln \gamma_{i1} \\ \mu_{i2} &= \mu_{iL}^{*} + RT\ln x_{i2} + RT\ln \gamma_{i2} \end{aligned} \tag{3-38}$$

The difference between the two chemical potentials (which corresponds to the free energy of a reaction, see Chapter 12), is then given as:

$$\mu_{i1} - \mu_{i2} = RT \ln \frac{x_{i1}}{x_{i2}} + RT \ln \frac{\gamma_{i1}}{\gamma_{i2}} \qquad (3\text{-}39)$$

It is easy to see that at the very beginning of our experiment, μ_{i1} will be smaller than μ_{i2} ($x_{i1} < x_{i2}$) and, hence, the difference will be negative. 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:

$$\ln K'_{i12} = \ln \frac{x_{i1}}{x_{i2}} = -\frac{(RT \ln \gamma_{i1} - RT \ln \gamma_{i2})}{RT} \qquad (3\text{-}40)$$

which is equivalent to:

$$K'_{i12} = e^{-(RT \ln \gamma_{i1} - RT \ln \gamma_{i2}) / RT}$$

or:

$$K'_{i12} = e^{-\Delta_{12}G_i / RT} \qquad (3\text{-}41)$$

where K'_{i12} is the partition constant on a mole fraction basis. We distinguish this mole fraction basis by using a superscript prime. Comparison of Eq. 3-41 with Eq. 3-13 reveals that, when expressing the abundance of the compound i in mole fractions, the constant in Eq. 3-13 is equal to 1. Furthermore, and more importantly, we can see now that the free energy of transfer $\Delta_{12}G_i$ equals the difference between the (partial molar) excess free energies of i in the two phases under specified conditions:

$$\Delta_{12}G_i = G^E_{i1} - G^E_{i2} \qquad (3\text{-}42)$$

At this point let us address the problem of expressing 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 ($\text{mol} \cdot \text{L}^{-1}$, M). This *molar* concentration scale is sometimes not optimal (volumes are, for example, 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:

$$C_{i\ell} = \frac{x_{i\ell}\,(\text{mol (total mol)}^{-1})}{\overline{V}_\ell(\text{L (total mol)}^{-1})} \qquad (3\text{-}43)$$

where $C_{i\ell}$ is the concentration (moles per liter) of i in phase ℓ and $\overline{V}_\ell$ 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 5) we will 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:

$$\overline{V}_\ell = \sum_j x_j \overline{V}_j \qquad (3\text{-}44)$$

where x_j and $\overline{V}_j$ are the mole fractions and molar volumes, respectively, of the pure component 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 $\overline{V}_\ell$ equal to $\overline{V}_w$, the molar volume of water ($\overline{V}_w = 0.018\ \mathrm{L \cdot mol^{-1}}$ at 25°C).

Substitution of x_i by $C_{i\ell} \cdot \overline{V}_\ell$ in Eq. 3-40 then yields the partition constant, K_{i12}, expressed in molar concentrations (note that we now omit the prime superscript):

$$\ln K_{i12} = \ln \frac{C_{i1}}{C_{i2}} = -\ln \frac{\overline{V}_1}{\overline{V}_2} - \frac{(RT \ln \gamma_{i1} - RT \ln \gamma_{i2})}{RT} \tag{3-45}$$

This is equivalent to:

$$K_{i12} = \frac{\overline{V}_2}{\overline{V}_1} \cdot e^{-(RT \ln \gamma_{i1} - RT \ln \gamma_{i2}) / RT}$$

or: (3-46)

$$K_{i12} = \frac{\overline{V}_2}{\overline{V}_1} \cdot e^{-\Delta_{12}G_i / RT}$$

Comparison of Eq. 3-46 with Eq. 3-13 shows that, when expressing the abundance of the compound i in molar concentrations, the constant in Eq. 3-13 corresponds to ($\overline{V}_2 / \overline{V}_1$). Note again that this is strictly true only when we consider infinitely dilute solutions of i in the two phases. Note also that one could debate whether this constant term should be incorporated into the $\Delta_{12}G_i$ term, that is, $\Delta_{12}G_i^c = \Delta_{12}G_i + RT \ln(\overline{V}_1 / \overline{V}_2)$, where $\Delta_{12}G_i^c$ is the free energy of transfer expressed on a molar concentration base (Vitha and Carr, 2000). In our following discussions we will, however, use Eq. 3-46 for relating partition constants with free energies of transfer.

Using the excess free energy, enthalpy, and entropy values given for our four model compounds in Table 3.3, we can now easily 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 3.4 summarizes the results of these calculations. These results reflect, of course, what we have already discussed above when inspecting the excess energy terms of the compounds in the various phases. In Chapters 6 and 7 we will address in detail the partitioning of organic compounds between air and liquids (including water), and organic phases and water, respectively. Here we just note again the very 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, as is the case for the data summarized in Appendix C), we need to be able to extrapolate these values to other conditions of temperature.

We should note that in most cases in environmental organic chemistry, we can neglect the effect of pressure changes on equilibrium partitioning. Exceptions might

Table 3.4 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 $\cdot$L^{-1}phase 1/mol $\cdot$ L^{-1}phase 2)

Phase 1/Phase 2 Compound (i)	$\Delta_{12}G_i$ (kJ$\cdot$mol^{-1})		$\Delta_{12}H_i$ (kJ$\cdot$mol^{-1})		$T\Delta_{12}S_i$ (kJ$\cdot$mol^{-1})	$\Delta_{12}S_i$ (kJ$\cdot$mol^{-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. 3-13 with const. = $\overline{V}_1 / \overline{V}_2$; molar volumes at 25°C and 1 bar: $\overline{V}_{\text{ideal gas}} = 24.73$ L$\cdot$mol^{-1}, $\overline{V}_{\text{hexadecane}} = 0.293$ L$\cdot$mol^{-1}, $\overline{V}_{\text{water}} = 0.018$ L$\cdot$mol^{-1}

include cases of very high pressure, as for example, in the deep sea (>200 bar) or in deep groundwater. For these particular applications we refer to the corresponding literature (e.g., Prausnitz, 1969; Atkins, 1998).

Here, we confine our discussion to the *temperature dependence* of partitioning. As a starting point we consider the differentiation of $\ln K_{i12}$ (Eq. 3-46) with respect to temperature:

$$\frac{d\ln K_{i12}}{dT} = \frac{d\ln \text{constant}}{dT} - \frac{1}{R} \cdot \frac{d\left(\Delta_{12}G_i / T\right)}{dT} \tag{3-47}$$

Let us first look at the temperature dependence of the constant. Using the mole fraction basis, this constant is equal to 1 and therefore temperature independent if mole fractions or partial pressures, respectively, are used to express the abundance of i in a given liquid or in the gas phase, respectively. 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. 3-47 as:

$$\frac{d\ln K_{i12}}{dT} = -\frac{1}{R} \cdot \frac{d\left(\Delta_{12}G_i / T\right)}{dT} \tag{3-48}$$

Applying the well-known *Gibbs-Helmholtz equation* (Atkins, 1998), we may express the right-hand term of Eq. 3-48 as:

$$-\frac{1}{R}\cdot\frac{d\left(\Delta_{12}G_i\,/\,T\right)}{dT}=\frac{1}{R}\cdot\frac{\Delta_{12}H_i}{T^2} \tag{3-49}$$

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

$$\frac{d\ln K_{i12}}{dT}=\frac{\Delta_{12}H_i}{RT^2} \tag{3-50}$$

Note that Eqs. 3-49 and 3-50 are very general equations which also apply, for example, to describing temperature dependencies of reaction equilibrium constants, as will be discussed in Chapters 8 and 12 (of course, with the appropriate reaction free energy and 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. 3-50 can be integrated. The result of this integration is:

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

or: (3-51)

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

Note that 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 $1/T$:

$$\ln K_{i12}=-\frac{A}{T}+B \tag{3-52}$$

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:

$$\Delta_{12}H_i=R\cdot\text{slope }A \tag{3-53}$$

It should be pointed out that if one of the phases considered is the gas phase, and if K_{i12} is expressed in molar concentrations (including the gas phase), $\Delta_{12}H_i$ in Eqs. 3-51 and 3-53 has to be replaced by $\Delta_{12}H_i+RT_{\text{av}}$, where T_{av} is the average temperature (in K) of the temperature range considered (for details see Atkinson and Curthoys, 1978). Finally, we should note that the temperature dependence of K_{i12} (and other equilibrium constants) over *large* temperature ranges can be approximated by a function of the type:

$$\ln K_{i12}=a_1+\frac{a_2}{T}+a_3\ln T+a_4\mathrm{T} \tag{3-54}$$

The parameters a_1, a_2, a_3, and a_4 are obtained similarly as A and B in Eq. 3-53 by fitting experimental K_{i12} data obtained at different temperatures.

Table 3.5 Effect of Temperature on Equilibrium Partition Constants as a function of $\Delta_{12}H_i$

$\Delta_{12}H_i$ ($\text{kJ} \cdot \text{mol}^{-1}$)	Factor[a]
–20	0.75
–10	0.86
0	1.00
10	1.16
20	1.33
30	1.53
40	1.77
50	2.04
60	2.36
70	2.72

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

Table 3.5 gives the average change in K_{i12} per 10°C increase/decrease in temperature for various $\Delta_{12}H_i$ values. A much more comprehensive table which is extremely useful for assessing the temperature dependence of equilibrium constants as well as of reaction rate constants is Table D1 in Appendix D.

Using the numbers given in Table 3.5 we can now inspect Table 3.4 in order to get some feeling of the temperature dependency of partition constants. Except for the hexadecane/water partitioning of hexane and benzene, there is 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 4 times larger at 25°C as compared to 5°C ($\Delta_{12}H_i = 46.8\ \text{kJ} \cdot \text{mol}^{-1}$). As we will see later in various other chapters, in cases in which equilibrium is not established, temperature may have an important effect on the direction of fluxes of compounds between environmental compartments.

Using Linear Free Energy Relationships (LFERs) to Predict and/or to Evaluate Partition Constants and/or Partition Coefficients

We conclude this section by a few general remarks about *extrathermodynamic* approaches. These quantitative methods involve empirical approaches that cannot be derived strictly from thermodynamic theory. They are widely used to predict and/or to evaluate partition constants and/or partition coefficients (see Box 3.2 for nomenclature) of organic compounds. There are many situations in which some of the data required to assess the partitioning behavior of a compound in the environment are not available, and, therefore, have to be estimated. For example, we may need to know the water solubility of a given compound, its partition coefficient between natural organic matter and water, or its adsorption constant from air to a natural surface. In all these, and in many more cases, we have to find means to predict these unknown entities from one or several known quantities.

The basic idea behind the most common approaches used for predicting partition constants (including vapor pressure and water solubility or partition coefficients) is to express the (unknown) free energy of transfer, $\Delta_{12}G_i$, of a given compound in the two-phase system of interest by one or several other (known) free energy terms chosen in a way that these terms can be linearly related to $\Delta_{12}G_i$. We will encounter and discuss such *linear free energy relationships (LFERs)* in various other chapters of this book. Here we will confine ourselves to some general remarks sketching the basic idea. It should be pointed out that, in practice, such LFERs are sometimes used without the necessary caution. Our considerations of molecular interactions and our discussion on the excess energy terms of organic compounds in various phases will help us throughout the book to develop a more critical attitude toward such LFERs, which is necessary for a proper application of these powerful tools.

To illustrate, we first consider a simple one-parameter LFER approach that is very widely used and, unfortunately, often also abused in environmental organic chemistry. In this approach, a linear relationship is assumed between the free energies of transfer of a series of compounds in two different two-phase systems:

$$\Delta_{12}G_i = a \cdot \Delta_{34}G_i + \text{constant} \tag{3-55}$$

Box. 3.2 Partition Constants, Partition Coefficients, and Distribution Ratios, A Few Comments on Nomenclature

In the literature there is sometimes a certain confusion about the proper use of the terms "partition constant," "partition coefficient," and "distribution ratio." Throughout this book, we will use these terms in the following way. We will talk of a partition constant or a partition coefficient when we consider only *one chemical species* in each phase. Thereby, we will reserve the term partition *constant* for those cases where we deal with the equilibrium partitioning between two *well-defined* phases, where we can be sure that the proportionality factor between the concentrations in the two phases is actually a concentration-independent constant at given conditions. Examples include the air–pure surface partition constant (Chapter 4), the air–pure water partition constant (Chapter 6), and the *n*-octanol–water partition constant (Chapter 7). In all other cases where this proportionality factor may vary somewhat with different related phases, we will talk about a partition *coefficient*. A prominent example is the natural organic matter–water partition coefficient that we will discuss in Chapter 9. Furthermore, we will use the very general term "distribution *ratio*" when we deal with situations where we just want to express the ratio of total concentrations of a given chemical in two phases. Examples include the equilibrium distribution ratio of organic acids or bases in air-water, organic solvent–water, or natural organic matter–water systems (where these compounds may be present both as neutral and charged species (Chapters 8 and 9), and the natural solid-water distribution ratio of a chemical where *various* different sorption mechanisms may be responsible for the presence of the compound in the solid phase (Chapter 11). Finally, we should note that several other terms including "distribution constants," "distribution coefficients," and "accumulation factors" are often used in the literature to describe partitioning. We will generally not use these terms except for our discussion on bioaccumulation, where we will adopt the commonly used "bioaccumulation factor" (Chapter 10).

where very often one of the phases is the same in the two systems (e.g., 2 = 4). In terms of partition constants/coefficients, Eq. 3-55 can be written as (see Eq. 3-46; note that decadic instead of natural logarithms are commonly used):

$$\log K_{i12} = a \cdot \log K_{i34} + \text{constant}' \tag{3-56}$$

Table 3.6 gives some prominent examples of such LFERs. Note that in all cases indicated in Table 3.6, the two systems related by the LFER have one phase in common (i.e., air, water). As should be evident from our basic considerations of molecular interactions, such LFERs can work properly only if various criteria are fulfilled. Important aspects that have to be taken into account include the type of molecular interactions that the compounds considered may undergo in the various phases, as well as the factors that determine the free energy costs of cavity formation, if bulk liquid phases are involved. Hence, for example, it should not come as a big surprise that very poor correlations are generally found when trying to relate partition constants/coefficients of a series of compounds of different polarities between two systems that contain phases exhibiting very different properties (e.g., air/hexadecane and air/water partitioning). On the other hand, rather good correlations can be expected when considering two similar systems (e.g., two organic phase/water systems), particularly when choosing groups of compounds that undergo the same type

Table 3.6 Examples of Simple One-Parameter Linear Free Energy Relationships (LFERs) for Relating Partition Constants and/or Partition Coefficients in Different Two-Phase Systems (Including the Pure Compound as Phase)

Partition Constants/Coefficients Correlated	LFER	Discussed in Chapter
Octanol–water partition constant and aqueous solubility of the pure liquid compound	$\log K_{iow} = -a \cdot \log C_{iw}^{sat} + b$	7
Natural organic carbon–water partition coefficient and octanol–water partition constant	$\log K_{ioc} = a \cdot \log K_{iow} + b$	9
Lipid–water partition coefficient and octanol–water partition constant	$\log K_{ilipw} = a \cdot \log K_{iow} + b$	10
Air–solid surface partition constant and vapor pressure of the pure liquid compound	$\log K_{ias} = a \cdot \log p_{iL}^{*} + b$	11
Air–particle partition coefficient and air–octanol partition constant	$\log K_{iap} = a \cdot \log K_{iao} + b$	11

of interactions in a given phase. In these cases, an LFER established from a set of compounds with known partition constants /coefficients in both systems (from which the slope a and the constant term in Eq. 3-56 can be determined by a linear regression analysis) can be used with good success to predict partition constants/coefficients of compounds for which the partition constants/coefficients are known only in one of the systems considered (e.g., prediction of natural organic matter–water partition coefficients from octanol–water partition constants, see Chapter 9).

However, LFERs of the type of Eq. 3-56 may not only be used as predictive tools; they may also serve other purposes. For example, they may be very helpful to check reported experimental data for consistency (i.e., to detect experimental errors). They may also enable us to discover unexpected partitioning behavior of a given compound, for example, if a compound is an outlier, but, based on its structure, is expected to fit the LFER. Finally, as will be discussed in various other chapters, if for a given set of model compounds such LFERs have been established for various two-phase systems, where one of the phases is not very well characterized (e.g., various natural organic matter–water systems, different atmospheric particle–air systems), the slopes a of the respective LFERs may yield some important information on the nature of the phases considered (e.g., to detect differences or similarities among the phases).

A second, very different general approach to predict the partition constant of a compound in a given two-phase system assumes that the free energy of transfer term for the whole molecule can be expressed by a linear combination of terms that describe the free energy of transfer of parts of the molecules (at the extreme of the atoms of which the molecule is made up):

$$\Delta_{12}G_i = \sum_{\text{parts}} \Delta_{12}G_{\text{part of } i} + \text{special interaction terms} \tag{3-57}$$

Stated in terms of partition constants, this becomes:

$$\log K_{i12} = \sum_{\text{parts}} \Delta \log K_{\text{part of } i12} + \text{special interaction terms} \tag{3-58}$$

The special interaction terms are necessary to describe *intra*molecular interactions between different parts of the molecule that cannot be accounted for when considering the transfer of the isolated parts. Obviously, this type of approach has a big advantage in that it allows one to estimate a partition constant based solely on the compound's structure. Good results can be anticipated particularly in those cases where the partition constant of a structurally closely related compound is known, and thus only the contributions of the parts that are different between the two compounds have to be added and/or subtracted, respectively. The most advanced and most widely used method that is based on this concept is the structural group contribution method for estimating octanol–water partition constants. We will discuss this method in Chapter 7.

Finally, we should note that there are a series of more sophisticated methods available that may be used for estimating partition constants. We will discuss the most promising approaches that are based on a direct quantification of molecular interactions later in the following chapters.

Concluding Remarks

The goal of this chapter was to take a first glimpse at the molecular interactions that govern the partitioning behavior of organic compounds between gaseous, liquid, and solid phases, and to recall how simple thermodynamic concepts, in particular, chemical potential, can be used to quantify equilibrium partitioning. In the following chapters, we will discuss important measurable quantities that we need to know when assessing environmental partitioning of organic chemicals. We will continue our effort to visualize the molecule:molecule interactions as well as the freedom of motion of the molecules in a given phase, in order to understand the enthalpic and entropic contributions to the free energy status of the molecules of a given compound in a given molecular environment relative to the pure liquid compound (which we have chosen to be our reference state). By doing so we will hopefully improve our ability to rationalize how pertinent compound properties are related to the compound's structure. It is very important to realize that developing some skills in structure-property considerations is essential for a critical evaluation of experimental data, and, particularly, for a proper use of predictive tools (e.g., LFERs) used to estimate such properties when experimental data are not available.

3.5 Using Partition Constants/Coefficients to Assess the Equilibrium Distribution of Neutral Organic Compounds in Multiphase Systems

Our final task in this chapter is to demonstrate how partition constants/coefficients can be used to calculate the equilibrium distribution of a compound i in a given multiphase system. As already pointed out earlier, for simplicity, we consider only neutral species. As we will see in Chapter 8, the equilibrium partitioning of ionogenic compounds (i.e., compounds that are or may also be present as charged species, as, for example, acids or bases) is somewhat more complicated to describe. However, the general approach discussed here is the same.

We start out by considering a very simple example, the partitioning of a compound i between two bulk phases 1 and 2 exhibiting the volumes V_1 and V_2. As discussed in the previous section, at equilibrium the molar concentrations C_{i1} and C_{i2} of i in the two phases are related by the corresponding equilibrium partition constant/coefficients:

$$K_{i12} = \frac{C_{i1}}{C_{i2}} \tag{3-59}$$

It is now easy to see that we may calculate the fraction of the total amount of i present at equilibrium in phase 1, f_{i1}, simply by:

$$f_{i1} = \frac{\text{mass of } i \text{ in phase 1}}{\text{total mass of } i} = \frac{C_{i1} \cdot V_1}{C_{i1} \cdot V_1 + C_{i2} \cdot V_2} \tag{3-60}$$

Dividing the numerator and denominator of the right-hand side of Eq. 3-60 by $(C_{i1} \cdot V_1)$ yields:

$$f_{i1} = \frac{1}{1 + \dfrac{C_{i2}}{C_{i1}} \cdot \dfrac{V_2}{V_1}} \tag{3-61}$$

By substituting Eq. 3-59 into Eq. 3-61 and by defining the (volume) ratio of the two phases $r_{12} = V_1/V_2$, one obtains:

$$f_{i1} = \frac{1}{1 + \dfrac{1}{K_{i12} \cdot r_{12}}} \tag{3-62}$$

and analogously for the fraction of i in phase 2:

$$f_{i2} = \frac{1}{1 + K_{i12} \cdot r_{12}} \tag{3-63}$$

Of course, in a two-phase system, $f_{i1} + f_{i2}$ must be equal to 1 (which can be easily checked). Note that Eqs. 3-62 and 3-63 are also valid if one of the phases is a solid (e.g., solid–water partitioning in a lake or in an aquifer, or solid–air partitioning in the atmosphere). In such cases, K_{i12} is often expressed by the ratio of mole of i per mass of solid concentration and mole of i per volume concentration, and therefore, r_{12} is then given by the ratio of the mass of solid and the volume of the bulk liquid or gas phase present in the system considered.

The equations derived for calculating the fractions of total i present in each phase at equilibrium in a two-phase system (Eqs. 3-62 and 3-63) can be easily extended to a multiphase system containing n phases (e.g., to a "unit world"). If we pick one phase (denoted as phase 1) as the reference phase and if we use the partition constants of i between this phase and all other phases present in the system:

$$K_{i1\mathrm{n}(\mathrm{n}\neq 1)} = \frac{C_{i1}}{C_{i\mathrm{n}(\mathrm{n}\neq 1)}} \tag{3-64}$$

then, the fraction of i in phase 1 is given by:

$$f_{i1} = \frac{1}{1+\sum\limits_{\mathrm{n}=2}^{\mathrm{n}} \dfrac{1}{K_{i1\mathrm{n}}} \cdot \dfrac{1}{r_{1\mathrm{n}}}} \tag{3-65}$$

Note that the partition constant/coefficient of i for any other two phases in the system can be calculated from the $K_{i1\mathrm{n}(\mathrm{n}\neq 1)}$ values. Thus, for example, K_{i23} is given by:

$$K_{i23} = \frac{C_{i2}}{C_{i3}} = \frac{C_{i1}\ /\ C_{i3}}{C_{i1}\ /\ C_{i2}} = \frac{K_{i13}}{K_{i12}} \tag{3-66}$$

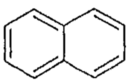
Obviously, as is demonstrated by Illustrative Example 3.1, since any of the phases can be chosen as phase 1, Eq. 3-65 can be used to calculate the fraction of total i at equilibrium in each of the phases present in the system.

Illustrative Example 3.1

The "Soup Bowl" Problem

Problem

A covered soup bowl contains 1 L of a very diluted, cold soup (25 °C), 1 L of air, and a floating blob of fat of a volume of 1 mL. The system also contains 1 mg of naphthalene. Estimate the amount of naphthalene you would ingest if you were to eat only the fat blob. Assume that equilibrium is established.



i=naphthalene

$K_{i\mathrm{aw}} = 10^{-1.76}$

$K_{i\mathrm{fw}} \approx K_{i\mathrm{ow}} = 10^{3.36}$

$r_{\mathrm{fw}} = 10^{-3}$

$r_{\mathrm{fa}} = 10^{-3}$

In the Appendix C you find the air–water partition constant ($K_{i\mathrm{aw}}$) of naphthalene and its octanol–water partition coefficient ($K_{i\mathrm{ow}}$) that you use as surrogate for the fat–water partition coefficient, $K_{i\mathrm{fw}}$). Note that these entities are given as ratios of molar concentrations. Use the fat (octanol) as phase 1 and calculate the fat–air (octanol–air) partition constant, $K_{i\mathrm{fa}}$:

$$K_{i\mathrm{fa}} = \frac{K_{i\mathrm{fw}}}{K_{i\mathrm{aw}}} = \frac{10^{3.36}}{10^{-1.76}} = 10^{5.12}$$

Insertion of $K_{i\mathrm{fw}}$, $K_{i\mathrm{fa}}$, r_{fw}, r_{fa} into Eq. 3-65 yields the fraction in the fat blob:

$$f_{i\mathrm{f}} = \frac{1}{1+\dfrac{1}{10^{3.36}}\cdot\dfrac{1}{10^{-3}}+\dfrac{1}{10^{5.12}}\cdot\dfrac{1}{10^{-3}}} \cong 0.7$$

Hence, you would take up *0.7* mg of the 1mg total naphthalene if only eating the fat blob, or you would take up only *0.3* mg when leaving the fat blob, and just eating the soup (the part in the air can more or less be neglected).

3.6 Questions and Problems

Questions

Q 3.1

Give at least 3 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 3.2

How is the equilibrium partition constant defined? To which thermodynamic function(s) is the partition constant related, and which molecular factors determine its magnitude, in the case of

(a) Partitioning between the gas phase and a bulk liquid?
(b) Partitioning between the gas phase and the surface of a condensed phase?
(c) Partitioning between two bulk liquid phases?
(d) Partitioning between a bulk liquid and a solid surface?

Q 3.3

Give at least three examples of environmentally relevant classes of (a) apolar, (b) monopolar, and (c) bipolar compounds. In the case of the monopolar compounds, indicate whether they are electron donors (H-acceptors) or electron acceptors (H-donors).

Q 3.4

Fig. 3.4 shows that when plotting the air–pure liquid compound partition constants of a large number of chemicals versus their dispersive vdW parameters, the apolar and monopolar compounds fall more or less on one line, while the bipolar compounds do not show this behavior. Explain these findings. For which kind of bulk liquids (give examples) would you expect that in a similar plot, *all* compounds (including the bipolar ones) should fit one line?

Q 3.5

The apolar compound *n*-hexane is considered to be quite *hydrophobic* ("water-hating"). Does this mean that there are repulsive forces between hexane and water molecules?

Q 3.6

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*?

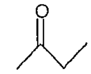
Q 3.7

Somebody claims that the activity coefficient of *n*-hexane in water is close to 1. Table 3.2 indicates, however, that this is not at all true, but that γ_{iw} of hexane is 460000! Why could this person also be right?

Q 3.8

What are the advantages and disadvantages of choosing the pure liquid compound as reference state?

Q 3.9

2-butanone () is an important chemical intermediate. When using the pure liquid compound as reference state, in which solvents (give examples) would you expect that this compound has an activity coefficient of (a) close to 1, (b) smaller than one, and (c) larger than one? (Table 3.2 might be helpful.)

Q 3.10

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 3.11

Explain in words the basic idea behind simple one-parameter LFERs for evaluation and/or prediction of equilibrium partition constants. What are the most common approaches? What are the dangers when using such LFERs?

Q 3.12

In Table 3.6 some simple LFERs relating partition constants/coefficients are given. These include vapor pressure and water solubility. Why are these properties, in principle, also partition constants? What is the difference to other partition constants?

Problems

P 3.1 *How Much of the Benzene Initially Present in a Water Sample Has Partitioned into the Headspace of the Sampling Flask?*

You are the boss of a commercial analytical laboratory and your job is to check all results before they are sent to the customers. One day you look at the numbers from the analysis of benzene in BTEX (see Chapter 2) contaminated groundwater samples. For a given sample, your laboratory reports a benzene concentration in water of 100 $\mu g \cdot L^{-1}$.

Knowing the problems associated with the analysis of volatile organic compounds, you inquire about the handling of the samples. Here we go! The samples (100 mL) were put into 1 L flasks, which were then sealed and stored at 5°C for several days. Then, in the cooling room, an aliquot of the water was withdrawn and analyzed for benzene. What was the original concentration of benzene in the water sample? Assume that equilibrium is established between the gas phase and the water and neglect adsorption of benzene to the glass walls of the bottle. The data required to answer this question can be found in Table 3.4.

Chapter 4

VAPOR PRESSURE

4.1 **Introduction**

4.2 **Theoretical Background**

Aggregate State and Phase Diagram: Normal Melting Point (T_m), Normal Boiling Point (T_b), and Critical Points (T_c, p_{ic}^*)

Thermodynamic Description of the Vapor Pressure–Temperature Relationship

Illustrative Example 4.1: *Basic Vapor Pressure Calculations*

4.3 **Molecular Interactions Governing Vapor Pressure**

Enthalpy and Entropy Contributions to the Free Energy of Vaporization

Trouton's Rule of Constant Entropy of Vaporization at the Boiling Point

Quantifications of van der Waals and of Polar Interactions Determining Vapor Pressure of Pure Liquids

4.4 **Availability of Experimental Vapor Pressure Data and Estimation Methods**

Experimental Data

Vapor Pressure Estimation Methods for Liquids

Entropy of Fusion and the Vapor Pressure of Solids

Box 4.1: *Parameters Used to Estimate Entropies of Phase Change Processes*

4.5 **Questions and Problems**

4.1 Introduction

Transport and transformation processes in the atmosphere are among the key processes that govern the distribution and fate of organic chemicals in the environment. In addition, other gaseous phases, such as air pockets in unsaturated soils or bubbles in biological water treatment facilities, may significantly influence the behavior of organic compounds in natural or engineered systems. Hence, one important aspect in our treatment of the partitioning of organic compounds in the environment is the quantitative description of how much a compound likes or dislikes being in the gas phase as compared to other relevant (condensed) phases. In this chapter, we will focus primarily on the equilibrium partitioning of an organic compound between the gas phase and the pure compound itself. That is, we will treat the (*saturation*) *vapor pressure* of organic compounds.

The vapor pressure of a compound is not only a measure of the maximum possible concentration of a compound in the gas phase at a given temperature, but it also provides important quantitative information on the attractive forces among the compound's molecules in the condensed phase. As we will see below, vapor pressure data may also be very useful for predicting equilibrium constants for the partitioning of organic compounds between the gas phase and other liquid or solid phases. Finally, we should note that knowledge of the vapor pressure is required not only to describe equilibrium partitioning between the gas phase and a condensed phase, but also for quantification of the *rate of evaporation* of a compound from its pure phase or when present in a mixture.

In the following sections, we will first look at some thermodynamic aspects concerning the vapor pressure of organic compounds (Section 4.2). This theoretical background will not only enable us to assess vapor pressure data at any given temperature, it will also allow us to deepen our insights into the molecular interactions between organic compounds that we started to discuss in Chapter 3. Note that in Section 4.3, we will introduce a simple model for quantification of molecular interactions that we will continue to use in the following chapters.

4.2 Theoretical Background

To begin, it is instructive to visualize what the molecules of a substance do to establish an equilibrium vapor pressure. We can do this by using a kinetic-molecular description, where we consider the case in which the rate of evaporation balances the rate of condensation. Let us consider a condensed pure compound (either liquid or solid) in equilibrium with its vapor phase (see Fig. 3.9*b*). At a given temperature, a certain number of molecules thermally jostling about in the condensed phase will continuously acquire sufficient energy to overcome the forces of attraction to their neighboring molecules and escape from the condensed phase. Meanwhile in the vapor phase, there will be continuous collisions of some vapor molecules with the surface of the condensed phase. A fraction of the colliding molecules will have so little kinetic energy, or will dissipate their energy upon collision with the condensed surface, that rather than bounce back into the vapor phase, they will be combined into the condensed phase. At a given temperature, these opposing processes of evaporation and condensation reach an equilibrium state that is controlled primarily by molecule–molecule attractions in the condensed phase and is characterized by the amount of molecules in the vapor above the condensed phase. This gas phase amount is expressed as the equilibrium vapor pressure, p_i^*, of the compound i. Recall that we use the superscript * to denote that we look at the (partial) pressure exerted by the compound's molecules at saturation. Furthermore, note that when we speak of the gas phase, for simplicity, we are assuming that all compounds behave like an *ideal gas*. This means that we do not consider the composition of the gas phase. Thus, it does not matter in the following whether the gas is air (mostly N_2 and O_2), an inert gas such as helium or argon, or the saturated vapor of the compound itself. In all these cases, we assume that the various species present in the gas phase do not "feel" each other. This is not appropriate for situations under "high pressure" (>10 bar), as would be seen for gas phases in the ocean or deep groundwater (e.g., greater than 100 m below the water surface) or in pressurized reactors. In such cases, the deviations from ideality begin to exceed about 5% and molecule:molecule interactions must be considered (see Prausnitz, 1969).

From daily life, we know that at ambient conditions of temperature (e.g., 25°C) and pressure (e.g., 1 bar), some organic chemicals are gases, some are liquids, and others are solids when present in their *pure form*. It may perhaps be somewhat trivial, but we should recall that when we talk about a pure chemical, we mean that only molecules of that particular compound are present in the phase considered. Hence, in a pure gas, the partial pressure of the compound is equal to the total pressure. As already addressed to a certain extent in Chapter 3, a pure compound will be a liquid or a solid at ambient conditions, if the forces between the molecules in the condensed phase are strong enough to overcome the tendency of the molecules to fly apart. In other words, if the enthalpy terms (which reflect the "glue" among the molecules in the liquid) outweigh the entropy terms (which is a measure of "freedom" gained when going from the liquid phase to the gas phase), then one has a positive free energy term and the material will exist as a liquid or solid. Conversely, if this free energy term is negative, then the compound is a gas at given conditions (e.g., 25°C and 1 bar). This is illustrated by the series of *n*-alkanes, where the C_1–C_4 compounds are gases, the C_5–C_{17} compounds are liquids, and the compounds with more than 18 carbon atoms are solids at 25°C and 1 bar total pressure (Fig. 4.1.) This family of hydrocarbons exhibits a vapor pressure range of more than 15 orders of magnitude ranging from 40.7 bar or 4.07×10^6 Pa (C_2H_6) down to about 10^{-14} bar or 10^{-9} Pa (n–$C_{30}H_{62}$). Note that there is no vapor pressure defined for methane at 25°C because methane cannot exist in a defined condensed form at this temperature, even at a very high pressure (see below). In the following, we will use these *n*-alkanes to illustrate some important general points.

Aggregate State and Phase Diagram: Normal Melting Point (T_m), Normal Boiling Point (T_b), and Critical Points (T_c, p_{ic}^*)

According to the Gibbs phase rule (number of degrees of freedom = number of components – number of phases + 2; see Atkins, 1998), for a system containing a single chemical distributed between two phases at equilibrium, there is only one

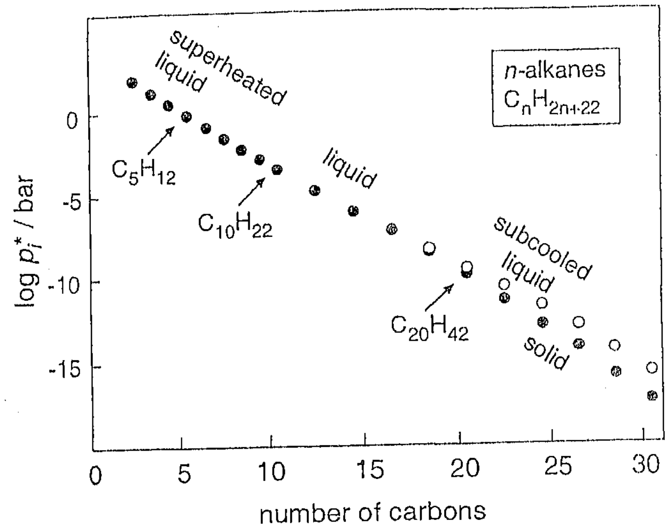


Figure 4.1 Vapor pressure at 25°C of *n*-alkanes as a function of chain length. The subcooled liquid vapor pressures have been calculated by extrapolation of p_{iL}^* values determined above the melting point (Eq. 4-8). Data from Daubert (1997) and Lide (1995).

degree of freedom. Therefore, by choosing a temperature of interest (i.e., using the one degree of freedom), everything else is fixed. Here, the vapor pressure of the compound in the gas phase is fixed. This dependence of vapor pressure on temperature can be conveniently diagramed in a pressure–temperature plot (Fig. 4.2). Such a "phase diagram" also identifies some important single temperature/pressure points. The diagram also allows us to assess the aggregate state (i.e., solid, liquid, gas, supercritical fluid) of the compound under various conditions of temperature and pressure. Let us look at this phase diagram more closely by using four *n*-alkanes (Table 4.1) as illustrative examples.

First we inspect the *normal melting points* (T_m) of the compounds. Note that because T_m, T_b and T_c already have a subscript denoting that they are compound specific parameters, we omit the subscript *i*. T_m is the temperature at which the solid and the liquid phase are in equilibrium at 1.013 bar (= 1 atm) total external pressure. At 1 bar total pressure, we would refer to T_m as *standard* melting point. As a first approximation, we assume that small changes in pressure do not have a significant impact on the melting point. Extending this, we also assume that T_m is equal to the *triple point temperature* (T_t). This triple point temperature occurs at only one set of pressure/temperature conditions under which the solid, liquid, and gas phase of a pure substance all simultaneously coexist in equilibrium.

Among our model compounds (Table 4.1), only *n*-eicosane has a T_m value that is above 25°C; that is, it is the only alkane in this group that is a solid at room temperature. The three other compounds have much lower melting points, which means that, in these cases, we would have to lower the temperature at least to −29.7, −138.4, and −182.5°C in order to "freeze" *n*-decane, *n*-butane, and methane, respectively.

Let us now perform a little experiment with *n*-eicosane. We place pure (solid) *n*-eicosane at 25°C in an open vessel (vessel 1, Fig. 4.3*a*) and in a closed vessel (vessel 2, Fig. 4.3*b*). In the open vessel we have an ambient total pressure of 1 atm or

Table 4.1 Normal Melting Points (T_m), Normal Boiling Points (T_b), and Critical Points (T_c, p^*_{ic}) of some *n*-Alkanes. Note that temperatures are given in °C and not in K[a]

Compound	T_m (°C)	T_b (°C)	T_c (°C)	p^*_{ic} (bar)	Location of Ambient Temperature (i.e., 25°C in Fig. 4.2 ($T_1 \ldots T_4$)	Aggregate State at 25°C
Methane (CH_4)	−182.5	−164.0	−82.6	46.04	T_4	gas
n-Butane (C_4H_{10})	−138.4	−0.5	152.0	37.84	T_3	gas
n-Decane ($C_{10}H_{22}$)	−29.7	174.1	344.5	21.04	T_2	liquid
n-Eicosane ($C_{20}H_{42}$)	36.8	343.0	496.0	11.60	T_1	solid

[a] All data from Lide (1995).

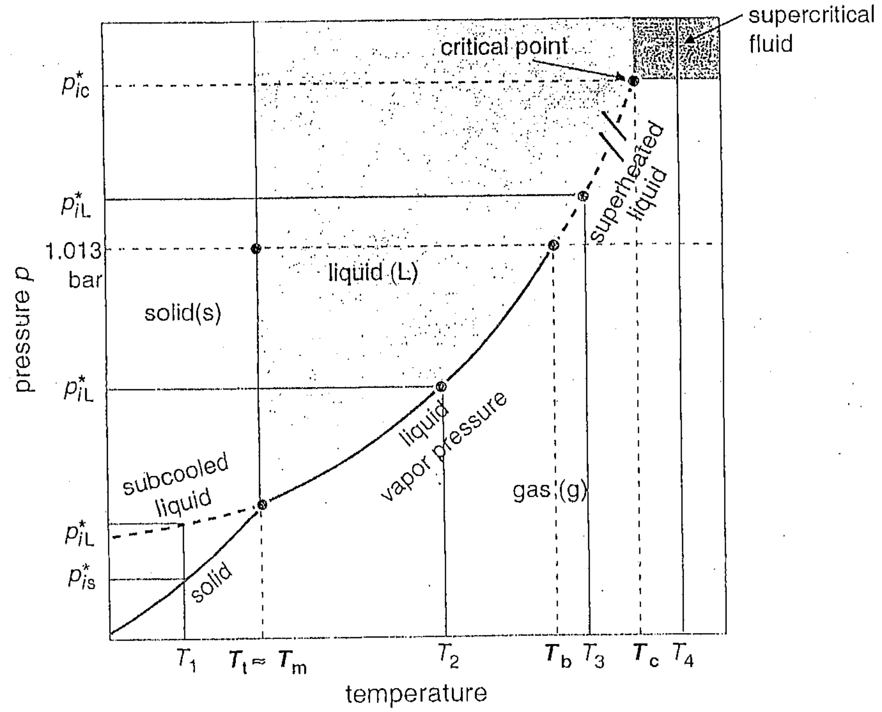


Figure 4.2 Simplified phase diagram of a pure organic chemical. Note that the boundary between the solid and liquid phase has been drawn assuming the chemical's melting point (T_m) equals its triple point (T_t), the temperature–pressure condition where all three phases coexist.) In reality, T_m is a little higher than T_t for some compounds and a little lower for others.

1.013 bar (exerted mostly by the nitrogen and oxygen molecules in the air). In contrast, in the closed vessel, we start out with a vacuum, that is, we allow no molecules other than eicosane in this vessel. Now we wait until equilibrium between the solid and vapor phase is reached, and then we measure the partial pressure of *n*-eicosane in the gas phase in each vessel. In the closed vessel, the total pressure will be equal to the vapor pressure, p^*_{is}, of solid eicosane. At 25°C this is 10^{-8} bar or 10^{-3} Pa. In our phase diagram in Fig. 4.2, this pressure/temperature point is represented by the point on the bold line at T_1. Now the question is: What is the partial pressure of eicosane in the gas phase in equilibrium with the solid phase in the open vessel 1? Is it also equal to p^*_{is}? The answer is yes because, particularly in the case of a solid compound, for pressures less than about 10 bar the total system pressure has a small influence on p^*_{is}. In general, at pressures near 1 bar we can assume that the difference in the partial pressures between the situations depicted by Figs. 4.3*a* and *b* will be less than 0.5% for most organic compounds (Atkins, 1998).

Note, however, that in the open vessel the compound would vanish because molecules could continuously leave the vessel and thus would have to be replenished from the condensed phase to keep a constant saturation vapor pressure.

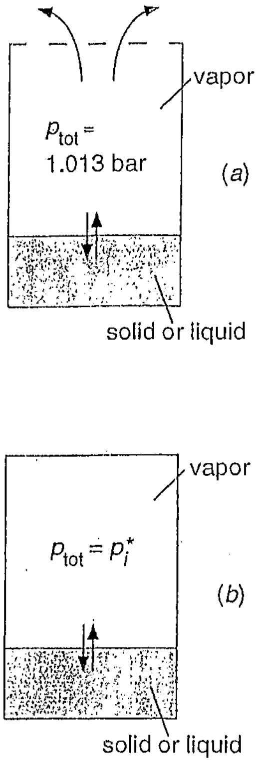


Figure 4.3 Open (*a*) and closed (*b*) vessel containing a pure condensed phase and a vapor phase. In case (*a*) the total pressure (1 bar) is exerted by the compound molecules, and by other gaseous species (e.g., O_2, N_2) that do not significantly alter the composition of the condensed phase. In case (*b*) the total pressure is equal to the partial pressure of the compound molecules; that is, there are no other gaseous species present.

Returning to our experiment, if we now increase the temperature, then we observe that p^*_{is} of *n*-eicosane increases. In our phase diagram, we move on the solid line from T_1 toward T_m. At T_m, the compound melts and becomes a liquid. Above T_m, a further increase of temperature leads, of course, to a further increase of the vapor pressure which we now denote as p^*_{iL}, indicating that we are now dealing with the vapor pressure of a *liquid* (L) compound (e.g., pressure/temperature point at T_2 in Fig. 4.2). We continue to raise the temperature until p^*_{iL} reaches 1 atm (1.013 bar), which equals the total external pressure in vessel 1. Now we have a very different situation in vessel 1 as compared to vessel 2. In the open vessel 1, the compound *boils*, while in vessel 2, boiling cannot occur (there is no escape for the molecules). The temperature, T_b, at which p^*_{iL} is 1 atm is referred to as the *normal boiling point* temperature (or *standard* boiling point temperature, if p^*_{iL} is 1 bar). Note that, historically, the standard pressure has been taken to be 1 atm (1.013 bar) and that, therefore, most T_b values are still reported as *normal* boiling points, which are somewhat higher than the *standard* boiling points. However, for practical purposes, we will neglect these small differences and just refer to *the* boiling point, T_b. The boiling point of *n*-eicosane is 343°C (Table 4.1). We should recall that boiling means that in an open system, vaporization can occur throughout the bulk of the liquid and the vapor can expand freely into the surroundings. Hence, in contrast to the melting point, the boiling point of a compound depends strongly on the external pressure. A well-known example illustrating this fact is the boiling point of pure water. This is 100°C at 1.013 bar; but at lower pressures such as would apply on the summit of Mt. Everest (0.357 bar external pressure), pure water boils at lower temperatures (about 73°C on Mt. Everest, which renders cooking rather tedious!).

At temperatures above the boiling point (e.g., T_3), at a given external pressure (e.g., 1.013 bar) a compound exists only in the gas phase. For ambient temperatures, this is the case only for a limited number of organic chemicals. Examples are *n*-butane and methane, which have boiling points of –0.5 and –164°C, respectively (Table 4.1). Other examples include some of the halogenated methanes such as the pesticide methyl bromide (CH_3Br), or some of the freons (e.g., CCl_2F_2, $CClF_3$; see Appendix C).

In contrast to the open system, in our closed system (Fig. 4.3*b*) we can increase the temperature above the boiling point and create a situation where we have a vapor pressure, p^*_{iL}, of greater than 1.013 bar. We take advantage of this fact, for example, in pressure cookers or autoclaves, which allow us to cook food or kill bacteria at elevated water temperatures. In such a case, we still have both a liquid and a gas phase (e.g., pressure/temperature point on bold broken line and T_3 in Fig. 4.2). We then commonly refer to the liquid phase as being a *superheated* liquid. For gases at ambient temperature, this means that, in order to be able to store them as liquids (for example, in a pressure bottle) we have to increase their partial pressure in the gas phase until we reach the vapor pressure of the superheated liquid. For *n*-butane (which we use, for example, as fuel for barbeque) this pressure is 2.5 bar and for CCl_2F_2 (a freon that has been widely used as a propellant and foaming agent) the corresponding p^*_{iL} value is 5.6 bar at 25°C (see Appendix C). In the case of methane, however, we would encounter some serious difficulties if we tried to condense this compound to a liquid at 25°C. Before we try to understand this problem with methane, we first continue our experiment with *n*-eicosane in the closed vessel. If we continue to raise the temperature, we build up more and more molecules in the gas phase (increasing the gas density) at the same time as we continuously decrease the density of the liquid. Finally, we reach a point where the density of the vapor is equal to that of the remaining liquid, meaning that we do not have two distinguishable phases anymore. This pressure/temperature point is called the critical point of the compound (T_c, p^*_{ic}, see Fig. 4.2). For *n*-eicosane, the corresponding T_c and p^*_{ic} values are 496°C and 11.6 bar, respectively. Above these values the compound exists only as one phase, which is commonly referred to as *supercritical fluid.* Methane has a critical temperature of −82.6°C (Table 4.1). Hence, liquid methane will exist only below this temperature. In our phase diagram this means that methane belongs to those rather few chemicals for which the ambient temperature is above T_c (e.g., T_4 in Fig. 4.2). Other prominent examples of such chemicals are O_2 ($T_c = -118.6°C$) and N_2 ($T_c = -147°C$.)

Before we turn to a quantitative description of the vapor pressure–temperature boundaries, we need to define one important additional vapor pressure value: the *subcooled liquid vapor pressure* of a compound. Imagine what is happening if we cool liquid eicosane from an elevated temperature (e.g., T_2 in Fig. 4.2) to a temperature below its melting (or freezing) point (e.g., T_1 in Fig. 4.2). Above the melting point ($T_m = 36.8°C$) we observe a decrease in p^*_{iL} according to the solid line describing the liquid–gas boundary. Below the melting point we follow another solid line now describing the solid–gas boundary until we reach $p^*_{is}(T_1)$. We note that, below the melting point, the decrease in vapor pressure with decreasing temperature is steeper than in the region above the melting point, where the compound is a liquid. This finding can be rationalized by recognizing that the energy required to transfer molecules from the solid to the gas phase is higher than transferring them from the corresponding liquid to the gas phase. Hence, below the melting point, if we continued to move along the liquid–gas boundary (dashed line in Fig. 4.2) at T_1, we would have reached another vapor pressure value, p^*_{iL}, which is larger than the corresponding p^*_{is} of the solid compound (examples in Fig. 4.1). This p^*_{iL} value, which is referred to as the vapor pressure of the *subcooled liquid*, is an important entity, because it tells us something about the molecular interactions of the compound in its pure liquid at a temperature where the compound is actually a solid! At this point it might be somewhat unclear why this is so important to know. Knowledge of the properties of the subcooled liquid compound are necessary for understanding and quantifying the molecular situations in environments in which molecules exist in a liquid state (e.g., dissolved in water), although they would be solids if pure. This is a major reason why we have chosen the pure liquid compound as reference state for describing partitioning processes.

Thermodynamic Description of the Vapor Pressure–Temperature Relationship

Liquid–Vapor Equilibrium. In order to quantify the vapor pressure–temperature relationship (bold line in Fig. 4.2) we start out by considering the *liquid–vapor* *equilibrium*. To this end, we first write down the chemical potentials of a given compound i in the gas phase and in its pure liquid, respectively (see Eq. 3-36; note that $x_{ig} = p_i / p^0$):

$$\mu_{ig} = \mu_{iL}^* + RT \ln (p_i / p^0) + RT \ln \gamma_{ig} \tag{4-1}$$

$$\mu_{iL} = \mu_{iL}^* + RT \ln x_{iL} + RT \ln \gamma_{iL} \tag{4-2}$$

where p^0 is the standard pressure (1 bar), and $RT \ln \gamma_{ig}$ is the excess free energy of the compound, G_{ig}^{E}, in the gas phase (see Chapter 3).

Note that for the pure liquid (Eq. 4-2) we explicitely show both the ideal mixing entropy term ($RT \ln x_{iL}$) and the excess free energy term ($RT \ln \gamma_{iL}$), although these two terms are both equal to zero, when we choose the pure liquid to be our reference state. We do this to show that we are dealing here with a partitioning process, and we must consider both forms of the chemical of interest relative to the same reference. The amount of the compound in the gas phase is described by its partial pressure, p_i. Note also that, without writing it down explicitly, we always have to divide any concentration terms by the corresponding standard concentration in the reference state. For the gas phase, we have chosen a standard pressure, p_i^0, of 1 bar since that is close to the pressure we usually have on the surface of the earth. At *liquid–vapor equilibrium* (i.e., $\mu_{ig} = \mu_{iL}$), at a given temperature we then obtain:

$$\ln \frac{p_i / p^0}{x_{iL}} = -\frac{\left(RT \ln \gamma_{ig} - RT \ln \gamma_{iL}\right)}{RT} \tag{4-3}$$

Substituting p_i/x_{iL} by p_{iL}^* (the saturation vapor pressure of the pure liquid compound, since x_{iL}=1) and by realizing that in this case, $\Delta_{12}G_i$ (see Eq. 3-46) is simply given by G_{ig}^{E} (the excess free energy of the compound in the gas phase; see examples given in Table 3.2) we may rewrite Eq. 4-3 as:

$$G_{ig}^{E} = -RT \ln(p_{iL}^* / p^0) \tag{4-4}$$

By denoting G_{ig}^{E} as $\Delta_{\text{vap}}G_i$, the free energy of vaporization of the liquid compound, and by omitting to write down every time that we have to divide p_{iL}^* by p^0 (which is commonly 1 bar), we get:

$$\Delta_{\text{vap}}G_i = -RT \ln p_{iL}^* \tag{4-5}$$

From Eq. 4-5 we can see that $\Delta_{\text{vap}}G_i$ will be positive at temperatures at which the vapor pressure is smaller than the standard pressure (i.e., 1 bar), which is, of course, the case at temperatures below the boiling point. At T_b, $p_{iL}^* = p^0$, and therefore:

$$-RT \ln 1 = 0 = \Delta_{\text{vap}}G_i(T_b) = \Delta_{\text{vap}}H_i(T_b) - T_b \cdot \Delta_{\text{vap}}S_i(T_b)$$

or:

$$T_b \cdot \Delta_{\text{vap}}S_i(T_b) = \Delta_{\text{vap}}H_i(T_b) \tag{4-6}$$

Hence, at the boiling point, the compound molecules in the liquid state can "fly apart" because their gain in entropy on vaporizing now matches the enthalpic attractions that are trying to hold them together. Above the boiling point, $\Delta_{\text{vap}}G_i$ will be negative (because $T\Delta_{\text{vap}}S_i > \Delta_{\text{vap}}H_i$). That is, we have to apply compound partial pressures greater than 1 bar to be able to keep a liquid phase present.

We have also seen that we can treat the vapor pressure like an equilibrium constant K_{i12}. Hence, the temperature dependence of p^*_{iL} can be described by the *van't Hoff* equation (Eq. 3-50):

$$\frac{d \ln p^*_{iL}}{dT} = \frac{\Delta_{\text{vap}}H_i(T)}{RT^2} \tag{4-7}$$

In this case, this equation is commonly referred to as *Clausius-Clapeyron* equation (e.g., Atkins, 1998). We can integrate Eq. 4-7 if we assume that $\Delta_{\text{vap}}H_i$ is *constant* over a given temperature range. We note that $\Delta_{\text{vap}}H_i$ is zero at the critical point, T_c, it rises rapidly at temperatures approaching the boiling point, and then it rises more slowly at lower temperatures (Reid et al., 1977). Hence, over a narrow temperature range (e.g., the ambient temperature range from 0°C to 30°C) we can express the temperature dependence of p^*_{iL} by (see Eq. 3-51):

$$\ln p^*_{iL} = -\frac{A}{T} + B \tag{4-8}$$

where $A = \Delta_{\text{vap}}H_i / R$.

For liquids, plotting the observed $\log p^*_{iL}$ ($= \ln p^*_{iL} / 2.303$) versus inverse T(K) over the ambient temperature range (Fig. 4.4) yields practically linear relations, as expected from Eq. 4-8. Therefore, over narrow temperature ranges in which there are some vapor pressure data available, Eq. 4-8 can be used to calculate vapor pressures at any other temperature *provided that the aggregate state of the compound does not change within the temperature range considered, i.e., that the compound does not become a solid.* If the temperature range is enlarged, the fit of experimental data may be improved by modifying Eq. 4-8 to reflect the temperature dependence of ΔH_{vap}. This is done by the introduction of a third parameter C:

$$\ln p^*_{iL} = -\frac{A}{T + C} + B \tag{4-9}$$

Eq. 4-9 is known as the Antoine equation. It has been widely used to regress experimental data. Values for A, B, and C can be found for many compounds in the literature (e.g., Lide, 1995, Daubert, 1997). Note, however, that when using Eqs. 4-8 and 4-9 to extrapolate vapor pressure data below the melting point, one gets an estimate of the vapor pressure of the subcooled liquid compound at that temperature (e.g., naphthalene in Fig. 4.4).

Solid–Vapor Equilibrium. In a very similar way as for the liquid–vapor equilibrium, we can derive a relationship for the temperature dependence of the vapor pressure of the solid compound. By analogy to Eq. 4-5, we write:

$$\ln p^*_{is} = -\frac{\Delta_{\text{sub}}G_i}{RT} \tag{4-10}$$

where we have replaced the free energy of vaporization by the free energy of

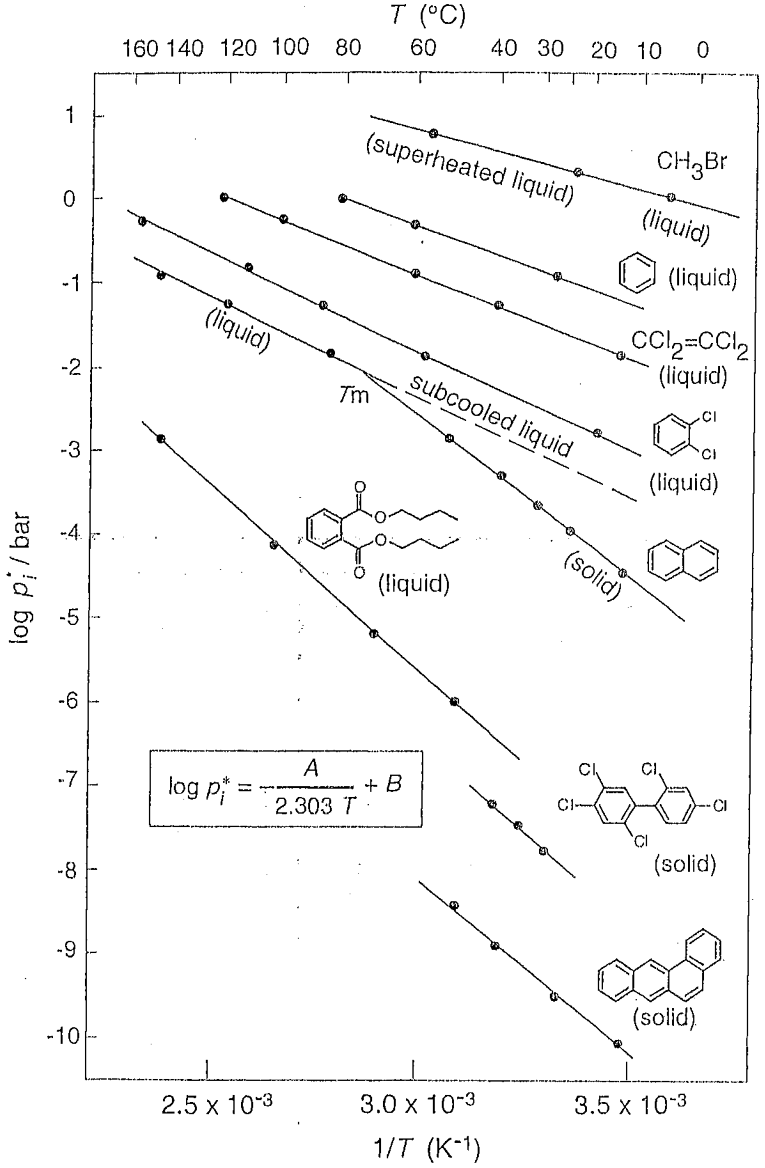


Figure 4.4 Temperature dependence of vapor pressure for some representative compounds. Note that the decadic logarithm is used ($\ln p_i^* = 2.303 \log p_i^*$).

sublimation (transfer from a solid to the gas phase), $\Delta_{\text{sub}}G_i$. Note that $\Delta_{\text{sub}}G_i$ is given by the difference between the excess free energy of the compound in the gas phase, $G^{\text{E}}_{i\text{g}}$, and its excess free energy in the solid phase, $G^{\text{E}}_{i\text{s}}$. Because the excess free energy in the solid phase is negative (the fugacity in the solid phase is smaller than in the liquid phase due to lattice formation), $\Delta_{\text{sub}}G_i$ is larger than $\Delta_{\text{vap}}G_i$ of the subcooled liquid compound by a term that is commonly referred to as the *free energy of fusion*, $\Delta_{\text{fus}}G_i$ ($= \Delta_{\text{fus}}H_i - T\Delta_{\text{fus}}S_i$):

$$\Delta_{\text{sub}}G_i = \Delta_{\text{fus}}G_i + \Delta_{\text{vap}}G_i \qquad (4\text{-}11)$$

In terms of enthalpy and entropy, this means:

$$\Delta_{\text{sub}}H_i = \Delta_{\text{fus}}H_i + \Delta_{\text{vap}}H_i \qquad (4\text{-}12)$$

and:

$$\Delta_{\text{sub}}S_i = \Delta_{\text{fus}}S_i + \Delta_{\text{vap}}S_i \tag{4-13}$$

The first thermodynamic expression above states that the intermolecular attraction forces we must overcome to sublime the molecules of a substance are equal to the sum of the forces required to first melt it and then vaporize it. Likewise, the increased randomness obtained as molecules sublime is the same as the sum of entropies associated with the sequence of melting and vaporizing. Consequently, if we can predict such thermodynamic terms for vaporization or melting, we already know the corresponding parameters for sublimation.

Now, $\Delta_{\text{fus}}G_i$ is equal to the negative excess free energy of the compound in the solid state G_{is}^{E}, since we have chosen the liquid state as our reference state. This free energy change is given by:

$$\Delta_{\text{fus}}G_i = \Delta_{\text{sub}}G_i - \Delta_{\text{vap}}G_i = RT \ln \frac{p_{i\text{L}}^*}{p_{is}^*} \tag{4-14}$$

or:

$$p_{i\text{L}}^* = p_{is}^* \cdot e^{+\Delta_{\text{fus}}G_i/RT} \tag{4-15}$$

In other words, $\Delta_{\text{fus}}G_i$ is the free energy required to convert the compound's molecules from the pure solid state to the pure liquid state. Knowledge of $\Delta_{\text{fus}}G_i$ at a given temperature is extremely important for estimating other properties of the subcooled liquid compound. As can be qualitatively seen from Fig. 4.2, $\Delta_{\text{fus}}G_i$ decreases with increasing temperature (the solid and broken bold vapor pressure lines approach each other when moving toward the melting point). At the melting point, T_{m}, $\Delta_{\text{fus}}G_i$ becomes zero, and, by analogy to the situation at the boiling point (Eq. 4-6), we can write:

$$T_{\text{m}} \cdot \Delta_{\text{fus}}S_{\text{i}}(T_{\text{m}}) = \Delta_{\text{fus}}H_{\text{i}}(T_{\text{m}}) \tag{4-16}$$

Also by analogy to the case for the liquid compound, we can describe the temperature dependence of p_{is}^* by (see Eq. 4-8):

$$\ln p_{is}^* = -\frac{A}{T} + B \tag{4-17}$$

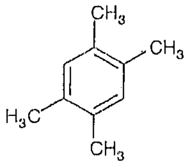
where $A = \Delta_{\text{sub}}H_i/R$. One may also add a third parameter (like C in Eq. 4-9) to correct for the temperature dependence of $\Delta_{\text{sub}}H_i$. Illustrative Example 4.1 shows how to derive and apply Eqs. 4-8 and 4-17. It also demonstrates how to extract free energies, enthalpies, and entropies of vaporization and fusion from experimental vapor pressure data.

Illustrative Example 4.1 Basic Vapor Pressure Calculations

Consider the chemical 1,2,4,5-tetramethylbenzene (abbreviated TeMB and also called durene). In an old *CRC Handbook of Chemistry and Physics* you find vapor pressure data that are given in mm Hg (torr; see left margin).

Problem

Estimate the vapor pressure p_i^*, of TeMB (*in bar and Pa*) at 20°C and 150°C using the experimental vapor pressure data given in the margin. Also express the result in *molar concentration* $(\text{mol} \cdot \text{L}^{-1})$ and in *mass concentration* $(\text{g} \cdot \text{L}^{-1})$ of TeMB in the gas phase.



1,2,4,5-tetramethylbenzene (TeMB)

$M_i = 134.2 \text{ g mol}^{-1}$
$T_m = 79.5°\text{C}$
$T_b = 195.9°\text{C}$

T (°C)	p_i^* (mm Hg)
45.0 s[a]	1
74.6 s[a]	10
104.2	40
128.1	100
172.1	400
195.9	760

[a] Means that TeMB is a solid at these temperatures

Answer

Convert temperatures in °C to K (add 273.2) and calculate $1/T$ values. Also, take the natural logarithms of the p_i^* values. Note that at 45.0 and 74.6°C, TeMB is a solid. Hence, group the data according to the aggregate state of the compound:

Solid Compound ($T < T_m$)

$1/T$ (K^{-1})	0.003143	0.002875
$\ln p_{is}^* / \text{mm Hg}$	0	2.303

Liquid Compound ($T > T_m$)

$1/T$ (K^{-1})	0.002650	0.002492	0.002246	0.002132
$\ln p_{iL}^* / \text{mm Hg}$	3.689	4.605	5.991	6.633

Perform least squares fits of $\ln p_i^*$ versus $1/T$ (see Fig. 1). The results are:

Solid compound: $$\ln p_{is}^* / \text{mm Hg} = -\frac{8609 \text{ K}}{T} + 27.1 \qquad (1)$$

Liquid compound: $$\ln p_{iL}^* / \text{mm Hg} = -\frac{5676 \text{ K}}{T} + 18.7 \qquad (2)$$

Note that if we had converted mm Hg to bar (1 mm Hg = 0.00133 bar), the intercepts of Eqs. 1 and 2 would be 20.5 and 12.1, respectively.

Insert $T = 293.2$ K (= 20°C) into Eq. 1, calculate $\ln p_{is}^*$, and get p_{is}^*:

$$p_{is}^* \text{ (20°C)} = 0.10 \text{ mm Hg} = 0.000133 \text{ bar} = \mathit{13.3} \text{ Pa}$$

For calculating p_{iL}^* at 150°C, set $T = 423.2$ K in Eq. 2. The resulting p_{iL}^* value is:

$$p_{iL}^* \text{ (150°C)} = 198 \text{ mm Hg} = 0.264 \text{ bar} = \mathit{26400} \text{ Pa}$$

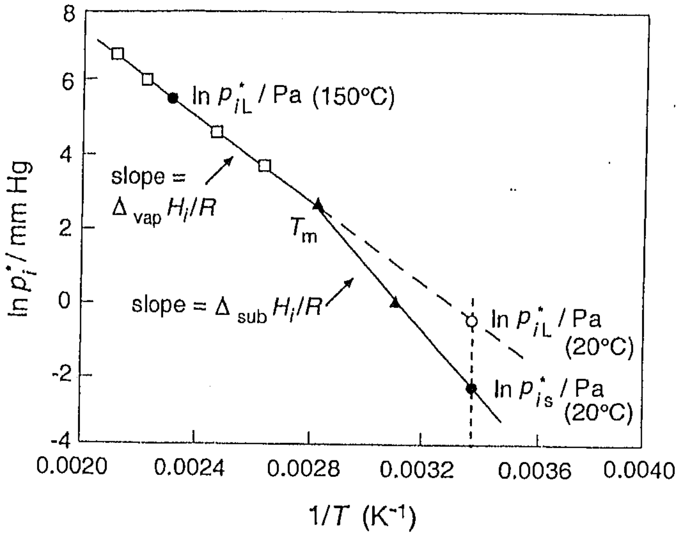


Figure 1 Temperature dependence of the vapor pressure of TeMB: plot of $\ln p_i^* / \text{mm Hg}$ versus $1/T$.

Hence, the vapor pressure of TeMB is more than three orders of magnitude greater at 150°C as compared to 20°C, which illustrates the strong temperature dependence of this compound property.

For calculating the molar and mass concentrations in the gas phase, assume that TeMB behaves like an ideal gas ($pV = nRT$). Then the gas phase concentration, C_{ig}, is given by:

$$C_{ig} = \frac{n_{ig}}{V_g} = \frac{p_i^*}{RT}$$

With $R = 0.0831$ L·bar·mol^{-1}·K^{-1} and $T = 293.2$ K or 423.2 K, respectively, the calculated concentrations are (note that 1 mol TeMB corresponds to 134.2 g):

$$C_{ig}\,(20\,°\text{C}) = \frac{(0.000133)}{(0.0831)\,(293.2)} = 5.5 \times 10^{-6}\ \text{mol} \cdot \text{L}^{-1} = 7.3 \times 10^{-4}\ \text{g} \cdot \text{L}^{-1}$$

and

$$C_{ig}\,(150\,°\text{C}) = \frac{(0.264)}{(0.0831)\,(423.2)} = 7.5 \times 10^{-3}\ \text{mol} \cdot \text{L}^{-1} = 1.01\ \text{g} \cdot \text{L}^{-1}$$

Problem

Estimate the free energy ($\Delta_{\text{fus}} G_i$, in kJ·mol^{-1}), the enthalpy ($\Delta_{\text{fus}} H_i$, kJ·mol^{-1}), and the entropy ($\Delta_{\text{fus}} S_i$, kJ·mol^{-1}K^{-1}) of fusion of TeMB at 20°C using the vapor pressure data given above.

Answer

Insert $T = 293.2$ K into Eq. 2 to estimate the vapor pressure of subcooled TeMB at 20°C:

$$p_{iL}^*\ (20°\text{C}) = 0.52\ \text{mm Hg} = 0.00069\ \text{bar} = 69\ \text{Pa}$$

Hence, at 20°C, p^*_{iL} is about five times larger as compared to p^*_{is}. Note, however, that you have extrapolated this value over quite a large temperature range. Use Eq. 4-14 to calculate $\Delta_{\text{fus}}G_i$:

$$\Delta_{\text{fus}}G_i\ (20\ ^\circ\text{C}) = RT \ln \frac{p^*_{iL}}{p^*_{is}} = (2.44\ \text{kJ} \cdot \text{mol}^{-1}) \ln \frac{(0.00069)}{(0.000133)} = \mathit{4.0}\ \text{kJ} \cdot \text{mol}^{-1}$$

Estimate $\Delta_{\text{fus}}H_i$ from the average $\Delta_{\text{vap}}H_i$ and $\Delta_{\text{sub}}H_i$ that you can derive from the slopes of the regression lines Eqs. 1 and 2:

$$\begin{aligned}\Delta_{\text{fus}}H_i &= \Delta_{\text{sub}}H_i - \Delta_{\text{vap}}H_i = \text{R} \cdot \text{slope 1} - \text{R} \cdot \text{slope 2} \\ &= (8.3145\ \text{J} \cdot \text{mol}^{-1}\ \text{K}^{-1})\ (8609\ \text{K}) - (8.3145\ \text{J} \cdot \text{mol}^{-1}\ \text{K}^{-1})\ (5676\ \text{K}) \\ &= 71.6\ \text{kJ} \cdot \text{mol}^{-1} - 47.2\ \text{kJ} \cdot \text{mol}^{-1} = \mathit{24.4}\ \text{kJ} \cdot \text{mol}^{-1}\end{aligned}$$

Since $\Delta_{\text{fus}}S_i = (\Delta_{\text{fus}}H_i - \Delta_{\text{fus}}G_i)\ /\ T$, you get:

$$\Delta_{\text{fus}}S_i = (24.4\ \text{kJ} \cdot \text{mol}^{-1} - 4.0\ \text{kJ} \cdot \text{mol}^{-1})\ /\ 293.2\ \text{K} = \mathit{69.6}\ \text{J} \cdot \text{mol}^{-1}\ \text{K}^{-1}$$

Note again that in these calculations, all $\Delta_{12}H_i$ values have been assumed to be constant over the temperature range considered. Therefore, all changes in $\Delta_{\text{fus}}G_i$ (which is zero at T_m) are attributed to a change in $\Delta_{\text{fus}}S_i$ with changing temperature. This is, of course, not exactly correct.

4.3 Molecular Interactions Governing Vapor Pressure

Enthalpy and Entropy Contributions to the Free Energy of Vaporization

Now we can see how a chemical's structure causes it to have a particular vapo pressure. This is possible because, as a first approximation, the free energy o vaporization, $\Delta_{\text{vap}}G_i$, mostly differs from compound to compound due to difference in those substances' enthalpies of vaporization, $\Delta_{\text{vap}}H_i$. These enthalpies reflect th sum of intermolecular attractions that act to hold those liquid molecules togethe Thus, we can expect that substances that exhibit high vapor pressures hav structures that do not enable the molecules to have strong intermolecular attractions Conversely, molecules with low vapor pressures must have structures that cause th molecules to be substantially attracted to one another.

Moreover, this relation between chemical structure and vapor pressure also hold because enthalpies and entropies of vaporization are directly related, in general Recall that the entropy of vaporization reflects the difference of a molecule' freedom in the gas phase versus the liquid phase ($\Delta_{\text{vap}}S_i = S_{ig} - S_{iL}$). At ambien pressures, we may assume that differences in $\Delta_{\text{vap}}S_i$ between different compound are primarily due to differences in molecular freedom in the liquid phase. (Th freedom of the molecules in the gas phase is not that different between compounds) Hence, not surprisingly, molecules that exhibit stronger intermolecular attraction

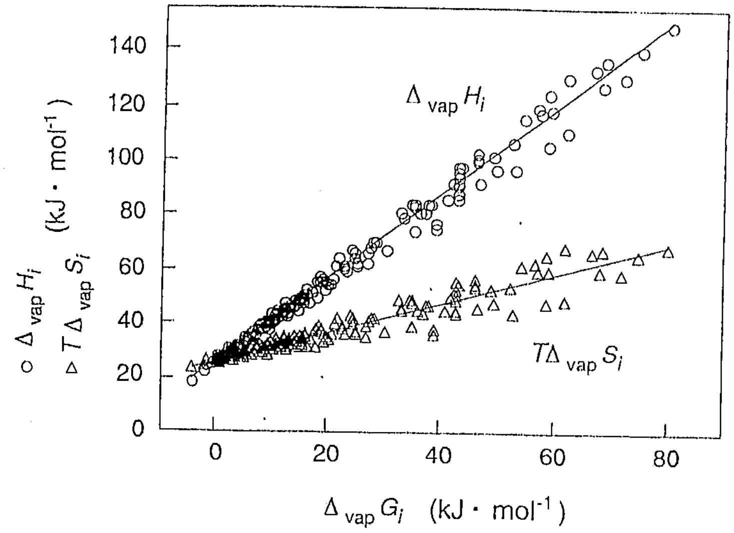


Figure 4.5: Plot of $\Delta_{\text{vap}}H_i$ and $T\Delta_{\text{vap}}S_i$ versus $\Delta_{\text{vap}}G_i$ for a wide variety of organic compounds at 25°C. At the intercept (i.e., for $\Delta_{\text{vap}}G_i = 0$) the value for $\Delta_{\text{vap}}H_i$ ($= T\Delta_{\text{vap}}S_i$) obtained from a linear regression analysis is 25.8 kJ·mol^{-1}.

(and hence greater $\Delta_{\text{vap}}H_i$ values) have lower values of S_{iL}, causing higher values of $\Delta_{\text{vap}}S_i$. Since the total free energy of vaporization is given by:

$$\Delta_{\text{vap}}G_i(T) = \Delta_{\text{vap}}H_i(T) - T\Delta_{\text{vap}}S_i(T) \tag{4-18}$$

correlated differences from compound to compound in $\Delta_{\text{vap}}H_i$ and $\Delta_{\text{vap}}S_i$ result in changes in $\Delta_{\text{vap}}G_i$ which are proportional to either $\Delta_{\text{vap}}H_i$ or $\Delta_{\text{vap}}S_i$! We can see this quantitatively if we look at the enthalpic and entropic contributions to the total free energy of vaporization for a large number of compounds (Fig. 4.5).

In general, we see that the enthalpic contribution is larger than the entropic one, but also that these contributions co-vary. This is true for a very diverse group of compounds at a given temperature (25°C), including apolar, monopolar, and bipolar compounds. Hence, if we view the forces between the molecules (the "glue") to be reflected primarily in the enthalpy term, then p^*_{iL} is a direct measure of these forces in the pure liquid.

Trouton's Rule of Constant Entropy of Vaporization at the Boiling Point

An interesting point in Fig. 4.5 is the $\Delta_{\text{vap}}H_i$ intercept where $\Delta_{\text{vap}}G_i = 0$. At this point, $\Delta_{\text{vap}}H_i$ is 25.8 kJ · mol^{-1}. This point represents a compound with a boiling point of 25°C. Hence, for this compound the entropy of vaporization at T_b can be calculated by (Eq. 4-6):

$$\Delta_{\text{vap}}S_i(T_b) = \frac{\Delta_{\text{vap}}H_i(T_b)}{T_b} = \frac{25.8 \text{ kJ mol}^{-1}}{298 \text{ K}} = 86.6 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$$

This $\Delta_{\text{vap}}S_i(T_b)$ value is typical for many other organic compounds that boil at very different temperatures (Table 4.2). In fact, long ago, Trouton (1884) recognized that the entropy of vaporization at the boiling point for many apolar and monopolar substances is more or less constant: between *85 and 90* J · mol^{-1} K^{-1}. Note that the "constancy" of $\Delta_{\text{vap}}S_i(T_b)$ implies that there must be a close relationship between $\Delta_{\text{vap}}H_i(T_b)$ and T_b.

Table 4.2 Variations in Normal Boiling Points, Liquid Vapor Pressure at 25°C, Observed Enthalpies and Entropies, and Predicted Entropies of Vaporization at the Boiling Point of Substituted Benzenes and Some Other Compounds [a]

Compound	Substituent(s) or Formula	T_b (°C)	$\log p^*_{iL}$/Pa at 25 °C	Observed $\Delta_{vap}H_i(T_b)$ (kJ · mol^{-1})	Observed $\Delta_{vap}S_i(T_b)$ (J · mol^{-1} K^{-1})	Predicted $\Delta_{vap}S_i(T_b)$ Eq. 4-20 (J · mol^{-1} K^{-1})	Predicted $\Delta_{vap}S_i(T_b)$ Eq. 4-21 (J · mol^{-1} K^{-1})
Substituted Benzenes							
Benzene	$-H$	80.1	4.10	30.7	86.9	85.3	86.0
Methylbenzene (Toluene)	$-CH_3$	110.6	3.57	33.2	86.5	86.0	86.0
Ethylbenzene	$-CH_2CH_3$	136.2	3.09	35.6	87.0	86.6	86.0
n-Propylbenzene	$-(CH_2)_2CH_2$	159.2	2.65	38.2	88.4	87.0	86.4
n-Butylbenzene	$-(CH_2)_3CH_2$	183.3	2.15	39.9	87.4	87.5	86.8
Fluorobenzene	$-F$	84.7	4.00	31.2	87.2	85.5	86.0
Chlorobenzene	$-Cl$	131.7	3.20	35.2	86.9	86.5	86.0
1,2-Dichlorobenzene	2x–Cl	180.0	2.26	39.7	87.6	87.4	86.0
1,4-Dichlorobenzene	2x–Cl	174.0	2.37	38.8	86.8	87.3	86.0
Nitrobenzene	$-NO_2$	210.8	1.48	40.8	84.3	88.0	86.0
Aminobenzene (Aniline)	$-NH_2$	169.1	1.95	42.4	95.9	96.0	91.0
Hydroxybenzene (Phenol)	$-OH$	181.8	1.74	45.7	100.5!	100.6	101.0
Benzylalcohol	$-CH_2OH$	205.3	1.18	50.5	105.6!	114.2	101.0
Other Compounds							
n-Hexane	$CH_3(CH_2)_4CH_3$	68.7	4.30	28.9	84.6	85.1	87.2
n-Decane	$CH_3(CH_2)_8CH_3$	174.1	2.24	38.8	86.8	87.3	88.8
n-Hexadecane	$CH_3(CH_2)_{14}CH_3$	287.0	−0.73	53.9	96.2	89.2	91.2
Ethanol	CH_3CH_2OH	78.3	3.90	38.6	115.8!	110.9	116.9
Naphthalene	see Fig. 2.13	218.0	1.75	43.7	89.0	88.1	86.0
Anthracene	see Fig. 2.13	341.0	−1.15	54.8	89.0	90.0	86.0
Phenanthrene	see Fig. 2.13	339.0	−1.14	53.0	86.6	90.0	86.0

[a] Data from Lide (1995), and Delle Site (1997).

Kistiakowsky (1923) utilized the Clapeyron equation and the ideal gas law to derive an expression to estimate each individual compound's $\Delta_{\text{vap}}S_i(T_b)$ in which the chemical's boiling temperature is used:

$$\Delta_{\text{vap}}S_i(T_b) = (36.6 + 8.31 \ln T_b) \quad \text{J} \cdot \text{mol}^{-1}\,\text{K}^{-1} \tag{4-19}$$

This expression reflects a weak relationship between the apolar or monopolar compound boiling temperature and entropy of vaporization, but substantially verifies Trouton's empirical observation.

Examination of the $\Delta_{\text{vap}}S_i\,(T_b)$ for various apolar and monopolar compounds reveals some small differences which are understandable in the light of intermolecular forces operating in the liquid phase. For example, elongate molecules such as *n*-hexadecane show higher $\Delta_{\text{vap}}S_i\,(T_b)$ than their corresponding shorter-chain homologues (e.g., *n*-hexane, see Table 4.2). This makes sense since the longer molecules have more contact area for each molecule and thus have a greater tendency to organize in parallel, maximizing the vdW attractions. This decrease in $S_{i\text{L}}$ translates into a larger $\Delta_{\text{vap}}S_i$ $(= S_{ig} - S_{i\text{L}})$.

For bipolar organic liquids, especially for hydrogen-bonding liquids such as alcohols and amines, the tendency to orient in the liquid phase, due to these highly directional intermolecular attractions, is greatly increased by this intermolecular interaction. We can see the effect of this in the significantly larger entropies of vaporization of bipolar chemicals, like aniline, phenol, benzyl alcohol, or ethanol (Table 4.2).

Fishtine (1963) provided a set of empirical factors, K_F, which correct the Kistiakowsky estimation of $\Delta_{\text{vap}}S_i(T_b)$ for such polar interactions:

$$\Delta_{\text{vap}}S_i(T_b) = K_F\,(36.6 + 8.31 \ln T_b) \quad \text{J} \cdot \text{mol}^{-1}\,\text{K}^{-1} \tag{4-20}$$

K_F values are equal to 1.0 for apolar and many monopolar compounds. For compounds exhibiting weakly bipolar character (e.g., esters, ketones, nitriles), a modest correction with a K_F of about 1.04 can be made. Significant corrections are necessary for primary amines (K_F = 1.10), phenols (K_F = 1.15), and aliphatic alcohols (K_F = 1.30). For a more comprehensive compilation of K_F values, we refer to the literature (e.g., Grain, 1982a).

By considering the important structural features of molecules, Myrdal et al. (1996) have developed an alternative way for estimating $\Delta_{\text{vap}}S_i(T_b)$. In their approach, which is also based on Trouton's rule, both the flexibility of the molecule (i.e., the presence of single-bonded atoms in long chains) and the inclusion of moieties able to participate in polar interactions are taken into account:

$$\Delta_{\text{vap}}S_i(T_b) = (86.0 + 0.4\,\tau + 1421\,\text{HBN}) \qquad \text{J} \cdot \text{mol}^{-1}\,\text{K}^{-1} \tag{4-21}$$

where

$\tau = \Sigma\,(\text{SP3} + 0.5\ \text{SP2} + 0.5\ \text{RING}) - 1$ is the effective number of torsional bonds, SP3 is the number of nonring, nonterminal atoms bound to four other atoms (where the nonbonded electron pairs in NH, N, O, and S should be counted as a "bond"),

SP2 is the number of nonring, nonterminal atoms singly bound to two other atoms and doubly bound to a third partner atom,

RING indicates the number of independent ring systems in the compound, and

τ is set equal to zero if its value is negative (for more explanations of parameter τ see Box 4.1).

HBN is the hydrogen bond number and is defined by the following equation:

$$\mathrm{HBN} = \frac{\sqrt{\mathrm{OH} + \mathrm{COOH}} + 0.33\sqrt{\mathrm{NH}_2}}{M_i} \tag{4-22}$$

where OH, COOH, and NH_2 represent the number of hydroxy, carboxylic acid, and amino groups, respectively, and M_i is the molar mass of the compound.

As is indicated by the examples given in Table 4.2, both methods (Eqs. 4-20 and 4-21) provide reasonable estimates of $\Delta_{\mathrm{vap}}S_i(T_\mathrm{b})$. Such equations, along with the generally applicable integrated Clapeyron expression, establish a highly flexible means of estimating compound vapor pressures as a function of temperature (see Section 4.4 for examples).

Quantifications of Van der Waals and of Polar Interactions Determining Vapor Pressure of Pure Liquids

By looking at vapor pressures as a function of chemical structures, we can conclude that the vapor pressure of a liquid or a subcooled liquid depends on the size of the molecule, on its specific ability to undergo vdW interactions, and on its specific ability to be engaged in polar interactions. For example, each addition of a $-CH_2-$ group in the series of the *n*-alkanes (Fig. 4.1) or in the series of the *n*-alkyl-benzenes (Table 4.2) leads to a *decrease* in $p^*_{i\mathrm{L}}$ at 25°C by about a factor of 3 (or an *increase* in T_b by between 20 and 25 degrees). Similarly, when increasing the number of rings in aromatic hydrocarbons (e.g., benzene → naphthalene → anthracene, phenanthrene), T_b increases and $p^*_{i\mathrm{L}}$ decreases significantly (Table 4.2).

The very significant effect of the presence of a bipolar group on T_b and $p^*_{i\mathrm{L}}$ can be nicely seen when comparing hydroxybenzene (phenol) and toluene (Table 4.2). In this case, the difference in T_b (~ 70°C) and in $p^*_{i\mathrm{L}}$ (factor of 40 at 25°C) can be attributed primarily to the polar interactions among the phenol molecules because both compounds have similar sizes and a similar specific ability to be engaged in vdW interactions.

Let us now try to derive a model that allows us to express quantitatively the molecular interactions that govern the liquid vapor pressure. We do this, not primarily with the goal of developing a predictive tool for estimating $p^*_{i\mathrm{L}}$, but to introduce a conceptual approach that we will extend and apply later when discussing other partitioning processes.

The basic idea is that we assume that we can *separate the free energy contributions of the vdW and polar interactions and that these contributions are additive:*

$$\Delta_{\text{vap}}G_i = \Delta_{\text{vap}}G_i^{\text{vdW}} + \Delta_{\text{vap}}G_i^{\text{polar}} \tag{4-23}$$

Note that $\Delta_{\text{vap}}G_i^{\text{vdW}}$ encompasses dispersive (i.e., London), dipole-induced dipole (i.e., Debye), and dipole–dipole (i.e., Keesom) contributions (Section 3.2). However, in most organic liquids, dipole interactions are generally of secondary importance. Hence, as a first approximation, we consider only the dispersive interactions. Then we can use the approach described in Section 3.2 to quantify the vdW term (Eq. 3-10, Fig. 3.4). Since $\ln p_{i\text{L}}^* = -\Delta_{\text{vap}}G_i / RT$, we may express Eq. 4-23 as:

$$\ln p_{i\text{L}}^* = a(\text{TSA}_i)\left(\frac{n_{Di}^2 - 1}{n_{Di}^2 + 2}\right)^2 + b(\text{HD}_i)(\text{HA}_i) + c \tag{4-24}$$

where we have also introduced a compound-specific H-donor (HD_i) and a compound-specific H-acceptor (HA_i) descriptor for quantification of $\Delta_{\text{vap}}G_i^{\text{polar}}$. Note that a, b, and c are proportionality and scaling coefficients that also contain the term $(RT)^{-1}$.

There are a variety of methods for estimating the total surface area, TSA_i, of a given compound on a molar base; here we use a simple one; that is, we estimate TSA_i from the molar volume, $\overline{V}_i$, and by assuming that the molecules are perfect spheres:

$$\text{TSA}_i \cong 4\pi N_{\text{A}}\left(\overline{V}_{i\text{L}}\frac{3}{4\pi N_{\text{A}}}\right)^{2/3} \tag{4-25}$$

where N_{A} is the Avogadro's number, and the molar volume of a pure liquid compound can be calculated from its molar mass and its density $\overline{V}_{i\text{L}} = M_i / \rho_i$.

The *H-bond descriptors,* HD_i (donor property) and HA_i (acceptor property), of a compound depend on the type and number of functional groups in a molecule. Using spectroscopic and chromatographic measurements on a larger number of chemicals, Abraham and coworkers (Abraham et al., 1994a and b) have derived an empirical parameter set of α_i and β_i values that can be used as a quantitative measure of the H-donor and H-acceptor properties of a compound on a molar base (Table 4.3). The functional groups exhibiting the strongest *bipolar* character are alcohols and carboxyl acids; that is, these compound classes have values of α_i and β_i which are well above zero. Interestingly, most of the *monopolar* compounds exhibit predominantly H-acceptor characteristics. Furthermore, there are significant differences in the α_i- and β_i-values between different polyhalogenated alkanes. These compounds also possess H-donor characteristics, due to the electron-withdrawing nature of the halogens. Finally, water has a strong tendency to undergo interactions with both H-acceptors and H-donors. When considering the small size of the water molecules, this is what makes water such a special solvent.

Table 4.3 α_i- and β_i-Values for Some Selected Compounds[a]

Compound (Class), Functional Group		α_i (H-Donor)	β_i (H-Acceptor)
Alkanes	(C_nH_{2n+2})	0	0
1-Alkenes	(1-C_nH_{2n})	0	0.07
Aliphatic ethers	(ROR')	0	0.45
Aliphatic aldehydes	(RCHO)	0[b]	0.45
Carboxylic acid esters	(RCOOR')	0[b]	0.45
Aliphatic ketones	(RCOR')	0[b]	0.51
Aliphatic amines	(R–NH_2)	0.16	0.61
Aliphatic alcohols	(R–OH)	0.37	0.48
Carboxylic acids	(R–COOH)	0.60	0.45
Benzene		0	0.14
Methylbenzene		0	0.14
Ethylbenzene		0	0.15
Dimethylbenzene		0	0.16
Trimethylbenzene		0	0.19
Chlorobenzene		0	0.07
1,2-Dichlorobenzene		0	0.04
1,3-Dichlorobenzene		0	0.02
Chlorobenzene	(Cl_n, $n > 2$)	0	0
Aniline		0.26	0.41
Benzaldehyde		0	0.39
Phenol		0.60	0.31
Pyridine		0	0.52
Naphthalene		0	0.20
Indane		0	0.17
Acenaphthene		0	0.20
Fluorene		0	0.20
Phenanthrene		0	0.26
Anthracene		0	0.26
Fluoranthene		0	0.20
Benzo(a)fluorene		0	0.20
Pyrene		0	0.29
Benzo(a)anthracene		0	0.33
Chrysene		0	0.33
Perylene		0	0.40
Benzo(a)pyrene		0	0.44
Benzo(ghi)perylene		0	0.46
Dichloromethane		0.10	0.05
Trichloromethane		0.15	0.02
Tetrachloromethane		0	0
1,1,1-Trichloroethane		0	0.09
1,1,2,2-Tetrachloroethane		0.16	0.12
Trichloroethene		0.08	0.03
Tetrachloroethene		0	0
Water		0.82	0.35

[a] Data from Abraham et al. (1994a and b). [b] Some other sources (Reichardt, 1988; Fowkes et al., 1990) indicate that aldehydes, esters, and ketones also exhibit a weak H-donor property.

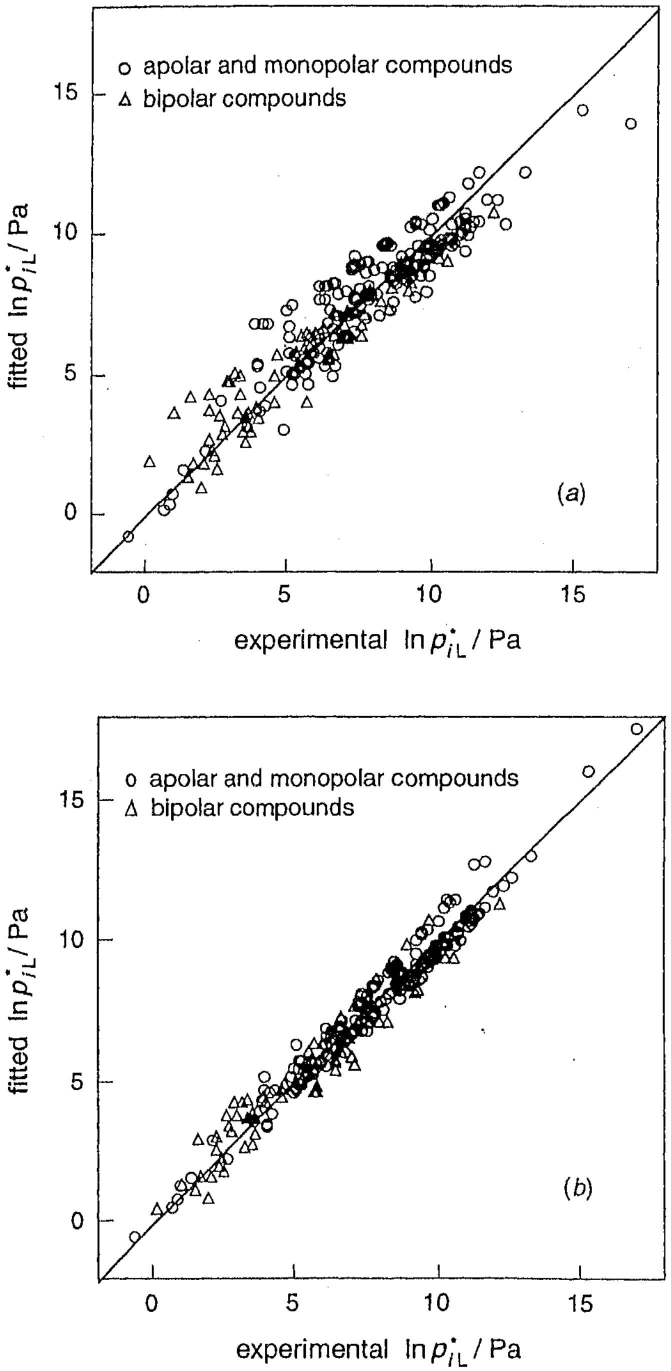


Figure 4.6 Fitted versus experimental liquid vapor pressures of a series of organic compounds, including apolar and monopolar (o) as well as bipolar (Δ) representatives. The set of compounds is the same as in Figs. 3.4 and 3.6*a*. (*a*) Data fitted by using Eq. 4.27. (*b*) Data fitted by the equation $\ln p^*_{i\mathrm{L}} = 1.02 \ln K_{iah} - 13.8\ (\alpha_i)\ (\beta_i) + 15.8$, where K_{iah} is the air-*n*-hexadecane partition constant.

Substitution of α_i and β_i and of TSA_i from Eq. 4-25 into Eq. 4-24 yields:

$$\ln p^*_{i\mathrm{L}} = a\left[\left(\overline{V}_{i\mathrm{L}}\right)^{2/3}\left(\frac{n_{Di}^2-1}{n_{Di}^2+2}\right)^2\right]+b\,(\alpha_i)\,(\beta_i)+c \qquad (4\text{-}26)$$

Note that the constant term $4\pi N_A\,(3/4\pi N_A)^{2/3}$ has been included into the coefficient *a*. Considering the same set of compounds included in Fig. 3.4, we see that adding the hydrogen-bonding interaction term allows us to reasonably predict the vapor pressures of apolar, monopolar, *and* bipolar compounds (Fig. 4.6*a*). Using a multiple regression analysis of Eq. 4-26 against the experimental $p_{i\mathrm{L}}^{*}$ values at 25°C of the compounds of the model set yields:

$$\ln p_{i\mathrm{L}}^{*}/\mathrm{Pa} = -4.49\left[\left(\overline{V}_{i\mathrm{L}}\right)^{2/3}\left(\frac{n_{Di}^{2}-1}{n_{Di}^{2}+2}\right)^{2}\right] - 15.1\,(\alpha_i)\,(\beta_i) + 14.5 \qquad (4\text{-}27)$$

where $\overline{V}_{i\mathrm{L}}$ is in cm^{3}mol^{-1}.

The rather large scatter in the data points shown in Fig. 4.6*a* could be reduced by using a more refined approach for quantifying the nonspecific interaction parameter. For example, by using the air–hexadecane partition constant $K_{i\mathrm{ah}}$ (see Section 3.2) as a more appropriate measure of the vdW interactions, the predicted vapor pressures are even closer to their corresponding observed values. Furthermore, in the literature (Abraham et al., 1994a), an additional polarity/polarizability parameter (π_i) is commonly included in this type of models. This parameter improves the quantitative prediction of the aqueous activity coefficients (see Section 5.3). That is, it seems to be of some importance when polar water molecules surround an organic compound. In the case of vapor pressure, however, introduction of this additional parameter does not significantly improve the result.

4.4 Availability of Experimental Vapor Pressure Data and Estimation Methods

Experimental Data

Many organic chemicals of environmental concern have rather low vapor pressures at ambient temperatures (Appendix C). Since simple measurements of vapor pressures by *manometric methods* or by determining *boiling points at reduced pressures* are restricted to relatively volatile compounds ($p_i^* > 1$ to 10 Pa), more sophisticated methods have to be applied for compounds of low volatility ($p_i^* < 1$ Pa). The methods most widely used are *gas saturation* and *effusion* [see Delle Site (1997) for a review of these and other methods]. In the case of *gas saturation*, a saturated vapor phase is produced by passing an inert gas, air, nitrogen, or oxygen (when a combustion procedure is used for analysis) through a thermostated column packed with the powdered compound or with an analyte-coated inert support. The saturation pressure of the substance is represented by its partial vapor pressure. Usually, the vapor is collected on liquid or solid traps and the substance is determined by suitable means. The *effusion methods* determine the vapor pressure at constant temperature from the measurement of the weight loss through a small orifice into a vacuum.

An attractive alternative to the direct measurement of vapor pressure is the use of *gas chromatographic retention* to estimate p_i^* (e.g., Hinckley et al., 1990). This method is based on the evaluation of the partitioning behavior of a given compound between the gas phase (i.e., the mobile phase) and a bulk organic phase (i.e., the stationary phase) at different temperatures. The method hinges on the selection of an appropriate reference compound for which accurate vapor pressure data is available, as well as on the choice of an appropriate stationary phase, in which both compound and reference exhibit similar activity coefficients. Note that for solid compounds, since the molecules are *dissolved* in the stationary phase, the gas chromatographic method yields the vapor pressure of the subcooled liquid (p^*_{iL}).

Inspection of the literature shows that vapor pressure data are readily available for many high-to-medium-volatility compounds (i.e., compounds with $T_b < 400°C$). These data can be found in data compilations (e.g., Daubert, 1997; Mackay et al., 1992–1997; Lide, 1995). For compounds exhibiting very low vapor pressures, the data are more scattered throughout the literature with the exception of agrochemicals (e.g., Montgomery, 1997). Furthermore, for such compounds, p^*_i values obtained by different methods and/or different laboratories may vary by as much as a factor of 2 to 3, in some cases, by more than an order of magnitude. In addition, in many cases, vapor pressure data have been determined at elevated temperatures, and ambient values must be extrapolated. Such data should, therefore, be treated with the necessary caution. One way of deciding which vapor pressure should be selected is to compare the experimental data with values predicted using other compound properties (see below).

Finally, very often vapor pressures are reported only for one particular temperature (e.g., 20°C or 25°C, as in Appendix C). Since vapor pressure is strongly dependent on temperature, it is necessary to be able to extrapolate such values over the ambient temperature range. Hence, it is necessary to know the enthalpy of vaporization or sublimation at ambient temperature. As we have seen in Section 4.3, for *liquid* compounds, a proportionality between $\Delta_{\text{vap}}H_i$ and $T\Delta_{\text{vap}}S_i$ is observed (Fig. 4.5). This means that $\Delta_{\text{vap}}G_i$ is proportional to $\Delta_{\text{vap}}H_i$. This can be used to derive an extremely useful empirical relationship between $\Delta_{\text{vap}}H_i$ and ln p^*_{iL} (or log p^*_{iL}) *for a given temperature* T_1 (Goss and Schwarzenbach, 1999a):

$$\Delta_{\text{vap}}H_i(T_1) = -\text{a} \log p^*_{iL}(T_1) + \text{b} \qquad (4\text{-}28)$$

At 25°C (298 K), the linear regression derived for the data set shown in Fig. 4.7 is:

$$\Delta_{\text{vap}}H_i(298\,\text{K})/(\text{kJ}\cdot\text{mol}^{-1}) = -8.80(\pm 0.07)\log p^*_{iL}(298\,\text{K})/\text{Pa} + 70.0(\pm 0.2) \qquad (4\text{-}29)$$

Note that in contrast to Fig. 4.7, we use the decadic logarithm in Eq. 4-29 and that this relationship holds over a very large vapor pressure range (> 15 orders of magnitude).

Assuming that this $\Delta_{\text{vap}}H_i$ value is constant over the ambient temperature range, it can be used to estimate p^*_{iL} at other temperatures (see also Eq. 3-51):

$$p^*_{iL}(T) = p^*_{iL}(298\,\text{K})\cdot e^{-\frac{\Delta_{\text{vap}}H_i(298\,\text{K})}{R}\left[\frac{1}{T}-\frac{1}{298\,\text{K}}\right]} \qquad (4\text{-}30)$$

It should be pointed out again that Eq. 4-29 applies to the vapor pressure of the *liquid* compound. For solids, the difference between p^*_{is} and p^*_{iL} can be estimated using the melting point temperature of the compound, see below (Eq. 4-40).

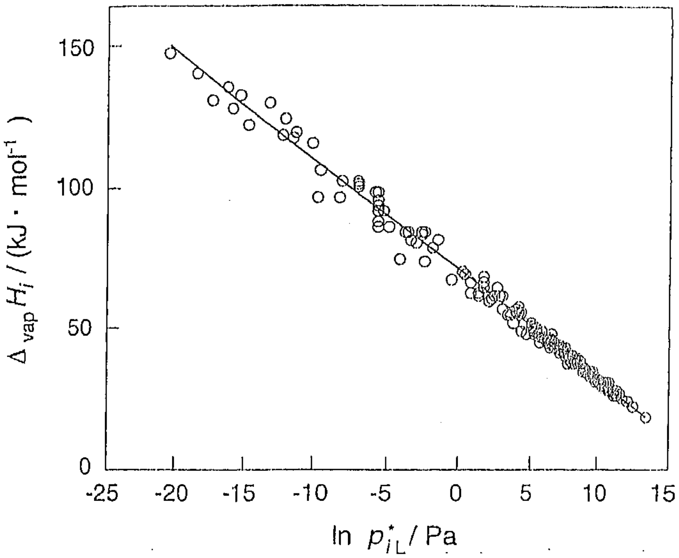


Figure 4.7 Plot of $\Delta_{\text{vap}}H_i$ versus ln p^*_{iL} for a large number of apolar, monopolar, and bipolar compounds. Note that some bipolar outliers are not included. (For details see Goss and Schwarzenbach, 1999a.)

Vapor Pressure Estimation Methods for Liquids

One strategy for estimating the vapor pressure of (subcooled) liquid compounds is to derive multiple parameter regression equations that relate the free energy of vaporization (and thus ln p^*_{iL}) to other properties and/or structural descriptors of the compound. The goal of all these approaches is to express the molecular interactions that determine $\Delta_{\text{vap}}G_i$ by readily accessible entities. Examples of such parameters include constitutional descriptors (e.g., partial charges), shape descriptors (e.g., topological indices), geometrical descriptors (e.g., surface area, molar volume), and quantum-chemical descriptors (e.g., dipole moment, quadrupole moment, polarizability). For an overview of these methods, we refer to the literature (Delle Site, 1997; Liang and Gallagher, 1998).

Here, we confine our discussion to an approach that can be easily handled because it requires only knowledge of the chemical's structure, its normal boiling point, and, if the compound is a solid, its melting point. Note that if T_b and T_m are not available, they can also be estimated (for details see Boethling and Mackay, 2000). Various equations using this approach have been proposed (Delle Site, 1997; Myrdal and Yalkowski, 1997), but they are all based on the same general idea. To predict the *liquid vapor pressure curve* below the boiling point [see solid and broken (below T_m) bold line in Fig. 4.2], we use the Clausius-Clapeyron equation:

$$\frac{d \ln p^*_{iL}}{dT} = -\frac{\Delta_{\text{vap}}H_i(T)}{RT^2} \qquad (4\text{-}7)$$

and properties of the compound at the boiling point, T_b. As we recall (Section 4.2), at the boiling point the enthalpy of vaporization can be related to the entropy of vaporization:

$$\Delta_{\text{vap}}H_i(T_b) = T_b \cdot \Delta_{\text{vap}}S_i(T_b) \qquad (4\text{-}6)$$

This entropy change can be estimated with reasonable accuracy (Section 4.3).

Hence, for temperatures very close to the boiling point, we integrate Eq. 4-7 by assuming that $\Delta_{\text{vap}}H_i(T) = \Delta_{\text{vap}}H_i(T_\text{b})$ = constant (see Section 4.2). However, in most cases, one would like to estimate the vapor pressure at temperatures (e.g., 25°C) that are well below the boiling point of the compound. Therefore, one has to account for the temperature dependence of $\Delta_{\text{vap}}H_i$ below the boiling point. A first approximation is to assume a linear temperature dependence of $\Delta_{\text{vap}}H_i$ over the temperature range considered, that is, to assume a constant heat capacity of vaporization, $\Delta_{\text{vap}}C_{pi}$ (the difference between the vapor and liquid heat capacities). Thus, if the heat capacity of vaporization, $\Delta_{\text{vap}}C_{pi}(T_\text{b})$, at the boiling point is known, $\Delta_{\text{vap}}H_i(T)$ can be expressed by (e.g., Atkins, 1998):

$$\Delta_{\text{vap}}H_i(T) \cong \Delta_{\text{vap}}H_i(T_\text{b}) + \Delta_{\text{vap}}C_{pi}(T_\text{b}) \cdot (T - T_\text{b}) \tag{4-31}$$

Substitution of Eqs. 4-31 and 4-6 into Eq. 4-7 and integration from 1 bar to $p^*_{i\text{L}}$ and from T_b to T then yields:

$$\ln p^*_{i\text{L}}\,/\,\text{bar} \cong -\frac{\Delta_{\text{vap}}S_i(T_\text{b})}{R}\left[\frac{T_\text{b}}{T} - 1\right] + \frac{\Delta_{\text{vap}}C_{pi}(T_\text{b})}{R}\left[\left(\frac{T_\text{b}}{T} - 1\right) - \ln\frac{T_\text{b}}{T}\right] \tag{4-32}$$

In the literature, various suggestions have been made of how to estimate $\Delta_{\text{vap}}S_i\,(T_\text{b})$ and $\Delta_{\text{vap}}C_{pi}\,(T_\text{b})$. One approach that works well primarily for prediction of vapor pressures of relatively low boiling compounds (i.e., $T_\text{b} < \sim 300°\text{C}$) was proposed by Mackay et al. (1982). In this approach, the Kistiakowsky-Fishtine expression (Eq. 4-20) is used to estimate $\Delta_{\text{vap}}S_i\,(T_\text{b})$, and it is assumed that, particularly for smaller molecules, the ratio of $\Delta_{\text{vap}}C_{pi}\,(T_\text{b})\,/\Delta_{\text{vap}}S_i\,(T_\text{b})$ has an average value of 0.8 (± 0.2). Inserting Eq. 4-20 and substituting $\Delta_{\text{vap}}C_{pi}\,(T_\text{b})$ by 0.8 $\Delta_{\text{vap}}S_i\,(T_\text{b})$ into Eq. 4-32 thus yields:

$$\ln p^*_{i\text{L}}\,/\,\text{bar} \cong -K_\text{F}\,(4.4 + \ln T_\text{b})\left[1.8\left(\frac{T_\text{b}}{T} - 1\right) - 0.8\,\ln\frac{T_\text{b}}{T}\right] \tag{4-33}$$

Another approach has been put forward by Myrdal and Yalkowsky (1997), which the authors contend is superior for high boiling compounds. Using Eq. 4-21 to estimate $\Delta_{\text{vap}}S_i(T_\text{b})$ and an additional empirical equation for quantification of $\Delta_{\text{vap}}C_{pi}\,(T_\text{b})$:

$$\Delta_{\text{vap}}C_{pi}(T_\text{b}) \cong -(90 + 2.1\tau) \quad \text{J} \cdot \text{mol}^{-1}\,\text{K}^{-1} \tag{4-34}$$

they propose the following equation for estimating vapor pressures of organic compounds:

$$\ln p^*_{i\text{L}}\,/\,\text{bar} = -(21.2 + 0.3\,\tau + 177\ \text{HBN})\left(\frac{T_\text{b}}{T} - 1\right) + (10.8 + 0.25\,\tau) \cdot \ln\frac{T_\text{b}}{T} \tag{4-35}$$

As discussed in Section 4.3, the two parameters τ and HBN, which describe the overall flexibility and the hydrogen-bonding capacity, respectively, of the molecules, can be easily derived from the structure of the compound.

Table 4.4 shows that these relatively simple approaches work quite well for compounds with boiling points not exceeding 300°C. Larger discrepancies to experimental values up to a factor of 10 have to be expected for very high boiling

Table 4.4 Comparison of Predicted and Experimental Vapor Pressures at 25°C for Selected (Subcooled) Liquid Organic Compounds[a]

Compound	T_b/°C	T_m/°C	K_F	Predicted (Eq. 4-33) p^*_{iL}/Pa	τ	HBN	Predicted (Eq. 4-35) p^*_{iL}/Pa	Experimental p^*_{iL}/Pa
Benzene	80.1	5.5	1.00	1.3×10^4	0	0	1.3×10^4	1.3×10^4
1,2,4,5-Tetramethylbenzene	195.9	79.5	1.00	8.6×10^1	0	0	7.2×10^1	6.9×10^1 [b]
Naphthalene	218.0	80.2	1.00	3.2×10^1	0	0	2.4×10^1	3.0×10^1 [c]
Anthracene	341.0	217.5	1.00	5.6×10^{-2}	0	0	4.3×10^{-2}	1.0×10^{-1} [c]
Pyrene	403.0	156.0	1.00	2.0×10^{-3}	0	0	1.5×10^{-3}	1.3×10^{-2} [c]
Tetrachlorethene	121.4	−22.4	1.01	2.4×10^3	0	0	2.2×10^3	2.5×10^3
Hexane	69.0	−95.0	1.00	2.1×10^4	3	0	1.7×10^4	2.0×10^4
Hexadecane	287.0	18.2	1.00	9.6×10^{-1}	13	0	2.3×10^{-2}	1.9×10^{-1}
Aniline	184.0	−6.3	1.10	1.7×10^2	0	0.0035	7.9×10^1	1.3×10^2
Benzylalcohol	205.3	−15.2	1.30	5.7×10^0	0	0.0092	1.7×10^1	1.5×10^1

[a] Data from Appendix C, if not otherwise indicated. [b] See Illustrative Example 4.1. [c] Average value determined by gas chromatography and estimated from Eq. 4-35 using experimental $\Delta_{fus}S_i(T_m)$ values. Data from Hinckley et al. (1990).

compounds. For such compounds, however, the experimental data are often not very accurate. Note again that any approach using solely boiling point data can predict only the (subcooled) liquid vapor pressure. Hence, for compounds that are solids at the temperature of interest, one has to estimate additionally the contribution of fusion; that is, we have to predict the solid–vapor boundary below the melting point (solid bold line below T_{m} in Fig. 4.2).

Entropy of Fusion and the Vapor Pressure of Solids

In a very similar way as discussed above for estimating $p^*_{i\text{L}}$ from boiling point data, one can treat the vapor pressure curve *below the melting point*. Again we use the Clausius-Clapeyron equation:

$$\frac{d \ln p^*_{is}}{dT} = \frac{\Delta_{\text{sub}} H_i(T)}{RT^2} \tag{4-36}$$

Since we are only interested in the ratio of $p^*_{is}/p^*_{i\text{L}}$ at a given temperature (i.e., in the contribution of melting), we can subtract Eq. 4-7 from Eq. 4-36 to get:

$$\frac{d \ln p^*_{is}/p^*_{i\text{L}}}{dT} = \frac{\Delta_{\text{sub}} H_i(T) - \Delta_{\text{vap}} H_i(T)}{RT^2} = \frac{\Delta_{\text{fus}} H_i(T)}{RT^2} \tag{4-37}$$

If, as a first approximation, we assume that $\Delta_{\text{fus}} H_i$ is constant over the temperature range below the melting point, and if we substitute Eq. 4-16 into Eq. 4-37, we can integrate Eq. 4-37 from 1 ($p^*_{is} = p^*_{i\text{L}}$ at T_{m}!) to $p^*_{is}/p^*_{i\text{L}}$ and from T_{m} to T, respectively. We then obtain for $T \leq T_{\text{m}}$:

$$\ln \frac{p^*_{is}}{p^*_{i\text{L}}} = -\frac{\Delta_{\text{fus}} S_i(T_{\text{m}})}{R} \left[\frac{T_{\text{m}}}{T} - 1 \right] \tag{4-38}$$

Hence, now we are left with the problem of estimating the entropy of fusion at the melting point. Unfortunately, $\Delta_{\text{fus}} S_i(T_{\text{m}})$ (Table 4.5) is much more variable than $\Delta_{\text{vap}} S_i(T_{\text{b}})$ (Table 4.2). This might be expected since $\Delta_{\text{fus}} S_i(T_{\text{m}})$ is equal to $S_{i\text{L}}(\text{T}_{\text{m}}) - S_{is}(\text{T}_{\text{m}})$ and both of these entropies can vary differently with compound structure. One reason is that molecular symmetry is an important determinant of the properties of a solid substance in contrast to a liquid, where the orientation of a molecule is not that important (Dannenfelser et al., 1993). Nevertheless, as demonstrated by Myrdal and Yalkowski (1997), a reasonable estimate of $\Delta_{\text{fus}} S_i(T_{\text{m}})$ can be obtained by the empirical relationship (Table 4.5):

$$\Delta_{\text{fus}} S_i(T_{\text{m}}) \cong (56.5 + 9.2\,\tau - 19.2 \log \sigma) \quad \text{J} \cdot \text{mol}^{-1}\,\text{K}^{-1} \tag{4-39}$$

where

τ is the effective number of torsional bonds (see Box 4.1), and

σ is the rotational symmetry number that describes the indistinguishable orientations in which a compound may be positioned in space (Box 4.1).

Table 4.5 Comparison of Experimental and Predicted (Eq. 4-39) Entropies of Fusion at the Normal Melting Point[a]

	Experimental			Predicted (Eq. 4-39)		
Compound	T_m (°C)	$\Delta_{fus}H_i\ (T_m)$ ($kJ \cdot mol^{-1}$)	$\Delta_{fus}S_i\ (T_m)$ ($J \cdot mol^{-1}\ K^{-1}$)	τ	σ	$\Delta_{fus}S_i\ (T_m)$
Benzene	5.5	10.0	35.7	0	12	35.8
n-Butylbenzene	–88.0	11.2	60.5	2	2	69.1
1,4-Dichlorobenzene	52.7	17.2	52.8	0	4	45.0
Naphthalene	80.2	18.6	52.7	0	4	45.0
Phenanthrene	101.0	18.1	48.6	0	2	50.7
Fluoranthene	107.8	18.9	49.6	0	2	50.7
Pyrene	151.2	17.1	40.3	0	4	45.0
Decane	–29.7	28.8	118.3	7	2	115.1
Eicosane	36.8	69.9	225.6	17	2	207.1
Benzoic acid	122.4	18.1	45.8	0	2	50.7
2,2',4,5,5'-Pentachlorobiphenyl	77.0	18.8	53.6	0	1	56.5
p,p'-DDT	109.0	27.4	71.6	1	1	65.7

[a] Data from Hinckley et al. (1990) and Lide (1995)

Obviously, for compounds exhibiting no rotational symmetry axis, σ is equal to 1 (which is the case for many of the more complex environmental chemicals). For benzene, on the other hand, $\sigma = 12$ (there are six twofold rotational axes), while for 1,4-dichlorobenzene $\sigma = 4$ (only two twofold rotational axes). Some examples of the application of Eq. 4-36 are given in Table 4.5. For a detailed discussion of the symmetry aspects (i.e., the derivation of σ) we refer to the articles by Dannenfelser et al. (1993) and Dannenfelser and Yalkowsky (1996). Finally, we should note that Eq. 4-39 does not work well for small spherical molecules or for polar compounds for which H-bonding has a significant impact on $\Delta_{fus}S_i\ (T_m)$. Hence, there is certainly room for improvement of this empirical relationship.

Substitution of Eq. 4-39 into Eq. 4-38 then gives ($R = 8.31\ J \cdot mol^{-1}\ K^{-1}$):

$$\ln \frac{p^*_{is}}{p^*_{iL}} = -(6.80 + 1.1\tau - 2.3 \log \sigma)\left[\frac{T_m}{T} - 1\right] \tag{4-40}$$

which can be used to estimate p^*_{is} from the subcooled liquid vapor pressure p^*_{iL}, and vice versa. Note that insertion of Eq. 4-40 into Eq. 4-14 yields an estimate of the free energy of fusion:

$$\Delta_{fus}G_i = +(56.5 + 9.2\,\tau - 19.2 \log \sigma)\,[T_m - T] \quad J \cdot mol^{-1} \tag{4-41}$$

an entity that will be important for estimating other properties of the subcooled liquid such as water solubility.

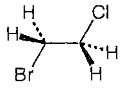
Box 4.1 **Parameters Used to Estimate Entropies of Phase Change Processes**

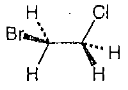
In phase change processes, the overall entropy changes, $\Delta_{12}S_i$, can be understood by considering the degrees of freedom lost when molecules in one condition (e.g., as a liquid) are packed into a less free, new condition (e.g., as a solid). Such transformations have been viewed as involving three contributions to the change in molecular freedom: (1) positional, (2) conformational, and (3) rotational (Yalkowsky, 1979; Dannenfelser and Yalkowsky, 1996):

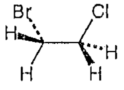
$$\Delta_{12}S_i = \Delta_{12}S_{i\,\text{positional}} + \Delta_{12}S_{i\,\text{conformational}} + \Delta_{12}S_{i\,\text{rotational}}$$

For the process of condensation (i.e., opposite direction to vaporization), the positional freedom loss involves about $-86\ \text{J}\cdot\text{mol}^{-1}\ \text{K}^{-1}$, while for the process of freezing (i.e., opposite direction to fusion), the positional freedom loss involves -50 to $-60\ \text{J}\cdot\text{mol}^{-1}\ \text{K}^{-1}$.

When a substance is packed into a liquid from a gas or into a solid from a liquid, the molecules also have a reduced ability to assume the various conformations. This loss of freedom is reflected in $\Delta_{12}S_{i\,\text{conformational}}$. Different conformations arise from the ability of structures to rotate around single bonds. For example, consider 1-bromo-2-chloro-ethane. Viewing the two carbons and the chlorine substituent as co-existing in a plane, we recognize that the bromine atom can occur in the same plane opposite the chlorine atom, or above the plane or behind the plane:

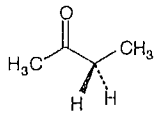


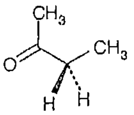




This amounts to rotating around the single bond connecting the two carbons. Every bond capable of such rotations offers three distinguishable orientations. Hence, if we increased the chain length by one $-CH_2$ unit, there would be $3 \times 3 = 9$ distinguishable conformations. Note that three atoms in such a chain do not enable conformation variation since three points always determine a single plane. Hence, $\Delta_{12}S_{i\,\text{conformational}}$ increases as the number of bonds capable of rotation minus two (equivalent to number of nonterminable sp^3 atoms in chain; note hydrogens are not sp^3 atoms).

Atoms in chain that include doubly bonded moieties do not offer as much conformational variety. Consider methyl ethyl ketone; rotation around the bond between the carbonyl carbon and the C_3 allow two (not three) distinguishable conformers:



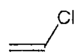


Hence, such atoms need to be discounted in their contribution to $\Delta_{12}S_{i\,\text{conformational}}$ and this is done by applying a factor of 0.5 times the number of such sp^2 members of a chain. This discounting also applies to ring systems. Hence, we can estimate a parameter, τ:

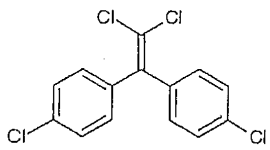
$$\tau = (\text{number of nonterminable } sp^3) + 0.5 \times (\text{number of nonterminate } sp^2) + 0.5 \times (\text{ring systems}) - 1$$

and the number of distinguishable conformers is approximately 3^{τ}. Empirically the observed data for the entropy of fusion at T_m are best fit using 2.85^{τ}. With this estimate, one finds $\Delta_{12}S_{i\,\text{conformational}}$ is approximately R ln (number of distinguishable conformers) $\approx R \ln (2.85^{\tau}) = 9.2\ \tau$ (see Eq. 4-39). For the case of 1-bromo-2-chloro-ethane with τ of 1, $R \ln (2.85^{\tau}) = 9\ \text{J}\cdot\text{mol}^{-1}\ \text{K}^{-1}$. As chains get longer, the magnitude of this contribution grows quickly (see Table 4.5).

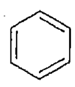
Changes in rotational freedom and $\Delta_{12}S_{i\,\text{rotational}}$ can be understood by considering the "symmetry" of a molecule. This entropy contribution may be quantified by a parameter, σ, quantifying the number of indistinguishable ways a given molecule can exist in space. The more indistinguishable orientations there are, the easier it is to convert the molecules to a more packed phase (hence making the absolute value of $\Delta_{12}S_{i\,\text{rotational}}$ smaller). One may begin by assessing whether a three dimensional view of a given molecule looks the same from above and below (i.e., is there a plane of symmetry in the plane of paper on which a molecule can be drawn?) A molecule like vinyl chloride does not look the same (σ=1), while DDE does (σ=2). Next, one may ask is there a way to rotate a molecule around an axis perpendicular to any plane of symmetry (e.g., perpendicular to the paper on which the molecule is drawn) and have orientations that look the same. In this sense, vinyl chloride and DDE have only one orientation that look the same, but 1,4-dichlorobenzene looks the same from above and below as well as if it is rotated 180° ($\sigma = 2\times2$) and benzene looks the same from above and below and every time it is rotated 60° ($\sigma = 2\times6$). The product of these numbers of indistinguishable orientations yields the symmetry number, σ. The higher a molecule's symmetry number, the less freedom change there is associated with packing or unpacking molecules. In the case of the entropy of fusion, $\Delta_{12}S_{i\,\text{rotational}} = R \ln \sigma = 19.2 \log \sigma$. When σ is 1, $\Delta_{12}S_{i\,\text{rotational}}$ is zero; and when σ is 12, the absolute value is about 20 $\text{J}\cdot\text{mol}^{-1}\ \text{K}^{-1}$. Note that the sign depends on whether one considers unpacking (more freedom so $\Delta_{12}S_{i\,\text{rotational}}$ has positive sign) or the packing (e.g., freezing or condensation) direction of phase change.



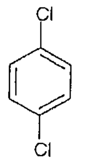
vinyl chloride
(chloroethene)



DDE



benzene



1,4-dichlorobenzene

4.5 Questions and Problems

Questions

Q 4.1

Give at least five examples of environmentally relevant organic chemicals that are (a) solids, (b) liquids, and (c) gases at 25°C.

Q 4.2

Why are certain chemicals gases at ambient conditions?

Q 4.3

Propane ($T_b = -42.1°\text{C}$, $T_c = 101.2°\text{C}$) is a gas at 25°C. How can you "produce" liquid propane (give two options)?

Q 4.4

What is the difference between the *normal* and the *standard* boiling point?

Q 4.5

Explain in words the terms *subcooled liquid*, *superheated liquid*, and *supercritical fluid*.

Q 4.6

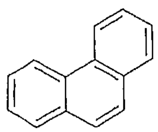
Why is the excess free energy of a solid, G_{is}^{E}, negative? How is G_{is}^{E} related to the free energy of fusion, $\Delta_{\mathrm{fus}}G_i$? How does G_{is}^{E} change with temperature? At which temperature is G_{is}^{E} equal to zero?

Q 4.7

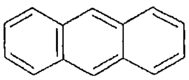
How are the (subcooled) liquid and solid vapor pressures of a given compound at a given temperature related to each other?

Q 4.8

The two isomeric polycyclic aromatic hydrocarbons phenanthrene and anthracene are solids at 25°C. Although these compounds have almost the same boiling point (see below), their vapor pressures at 25°C differ by more than one order of magnitude (see Appendix C). Explain these findings. What differences would you expect for the subcooled liquid vapor pressures of the two compounds at 25°C?



phenanthrene
T_m = 101.0 °C
T_b = 339.0 °C



anthracene
T_m = 217.5 °C
T_b = 341.0 °C

Q 4.9

Which thermodynamic function needs to be known for assessing the temperature dependence of the vapor pressure of a given compound? How can this function be derived from experimental data? What caution is advised when extrapolating vapor pressure data from one temperature to another temperature?

Problems

P 4.1 *A Solvent Spill*

You teach environmental organic chemistry and for a demonstration of partitioning processes of organic compounds you bring a glass bottle containing 10 L of the common solvent tetrachloroethene (perchloroethene, PCE) into your class room. After closing the door you stumble and drop the bottle. The bottle breaks and the solvent is spilled on the floor. Soon you can smell the solvent vapor in the air. (The odor threshold of PCE is between 8 and 30 $\mathrm{mg \cdot m^{-3}}$). Answer the following questions:

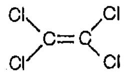
(a) What is the maximum PCE concentration that you can expect in the air in the room (T = 20°C)? How much of the solvent has evaporated if you assume that the air volume is 50 m^3? (Neglect any adsorption of PCE on the walls and on the furniture).

(b) If the same accident happened in your sauna (volume 15 m^3, $T = 80°C$), what maximum PCE concentration would you and your friends be exposed to there?

In the *CRC Handbook of Chemistry and Physics* (Lide, 1995) you find the following vapor pressure data for PCE:

T/°C	25	50	75	100
p_i^*/kPa	2.42	8.27	22.9	54.2

All other necessary data can be found in Appendix C.



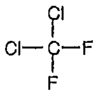
tetrachloroethene
(PCE)

P 4.2 *How Much Freon Is Left in the Old Pressure Bottle?*

In a dump site, you find an old 3-liter pressure bottle with a pressure gauge that indicates a pressure of 2.7 bar. The temperature is 10°C. From the label you can see that the bottle contains Freon 12 (i.e., dichlorodifluoromethane, CCl_2F_2). You wonder how much Freon 12 is still left in bottle. Try to answer this question. In the *CRC Handbook of Chemistry and Physics* (Lide, 1995) you find the following data on CCl_2F_2:

T/°C	–25	0	25	50	75
p_i^*/kPa	123	308	651	1216	2076

Using these data, estimate the free energy ($\Delta_{\text{cond}}G_i$), the enthalpy ($\Delta_{\text{cond}}H_i$), and the entropy ($\Delta_{\text{cond}}S_i$) of condensation of Freon 12 at 25°C. Note that condensation is the opposite of vaporization (watch out for the signs of the three quantities).

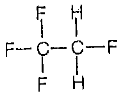


dichlorodifluoromethane
(Freon 12)

P 4.3 *What Are the Differences Between Freon 12 and Its Replacement HFC-134a? (From Roberts, 1995)*

Hydrofluorocarbon 134a (1,1,1,2-tetrafluoroethane) is used as a replacement for Freon 12 (see Problem 4.2) for refrigeration applications. (Why is such a replacement necessary and what is the advantage of HFC-134a from an environmental protection point of view?) Some vapor pressure data for Freon 12 is given in Problem 4.2. The vapor pressure data of HFC-134a have been determined very carefully and are as follows:

T/°C	−40.0	−30.0	−20.0	−10.0	0	+10.0
p_i^*/kPa	51.6	84.7	132.9	200.7	292.9	414.8



1,1,1,2-tetrafluoroethane
(HFC-134a)

(a) Determine the normal boiling points (in°C) of these compounds from the data provided.

(b) At what temperature (in°C) will they have an equal vapor pressure?

(c) Compare the (average) enthalpies ($\Delta_{\text{vap}}H_i$) and entropies ($\Delta_{\text{vap}}S_i$) of vaporization of the two compounds at the temperatures calculated under (b). Can you rationalize any differences you observe between the two compounds?

(d) Automobile air conditioners commonly operate at temperatures between 30 and 50°C. Are the vapor pressures of the two compounds significantly (i.e., greater than 10%) different in this temperature region?

P 4.4 *A Public Toilet Problem*

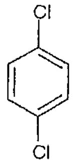
Pure 1,4-dichlorobenzene (1,4-DCB) is still used as a disinfectant and airfreshener in some public toilets. As an employee of the health department of a large city you are asked to evaluate whether the 1,4-DCB present in the air in such toilets may pose a health problem to the toilet personnel who are exposed to this compound for several hours every day. In this context you are interested in the maximum possible 1,4-DCB concentration in the toilet air at 20°C. Calculate this concentration in g per m^3 air assuming that

(a) You go to the library and get the vapor pressure data given below from an old edition of the *CRC Handbook of Chemistry and Physics.*

(b) You have no time to look for vapor pressure data, but you know the boiling point (T_b = 174.0°C) and the melting point (T_m = 53.1°C) of 1,4-DCB.

Compare the two results. What would be the maximum 1,4-DCB concentration in the air of a public toilet located in Death Valley (temperature 60°C)? Any comments?

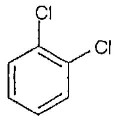
T/°C	29.1s	44.4s	54.8	84.8	108.4	150.2
p_i^*/mm Hg	1	4	10	40	100	400



1,4-dichlorobenzene
(1,4-DCB)

P 4.5 ***True or False?***

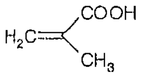
Somebody bets you that at 60°C, the vapor pressure of 1,2-dichlorobenzene (1,2-DCB) is smaller than that of 1,4-dichlorobenzene (1,4-DCB), but that at 20°C, the opposite is true; that is, p_i^* (1,2-DCB, 20°C) > p_i^* (1,4-DCB, 20°C). Is this person right? If yes, at what temperature do both compounds exhibit the same vapor pressure? Try to answer these questions by using only the T_m and T_b values given in Appendix C.



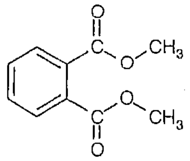
1,2-dichlorobenzene
(1,2-DCB)

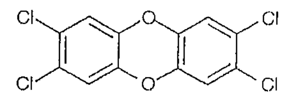
P 4.6 ***Estimating Vapor Pressure Data***

Since you live in a cold area, you are more interested in the vapor pressure of organic compounds at 0°C as compared to 25°C. Estimate the vapor pressures at 0°C from (i) the p_i^* values given in Appendix C for 25°C, and (ii) only using the T_m and T_b values (also given in Appendix C) for the following compounds:

(a) Methacrylate: 

$H_2C{=}C(COOH)CH_3$

(b) Dimethyl phthalate: 

(c) 2,3,7,8-Tetrachlorodibenzo-p-dioxin: 

Compare and discuss the results.

P 4.7 ***Evaluating Experimental Vapor Pressure Data of the Widely Used Pesticide Lindane***

Using the *Knudsen effusion technique* and *highly purified* samples of lindane [(γ-HCH), one of the most widely used and most frequently detected organochlorine pesticides; see Willet et al. (1998)], Boehncke et al. (1996) determined the vapor pressure of this compound in the temperature range between 20 and 50°C. For this temperature range they derived the following relationship (note that the melting point of lindane is 112.5°C; its boiling point is 323.4°C):

$$\ln p_i^* / \text{Pa} = -\frac{11754\text{ K}}{T} + 34.53 \tag{1}$$

Wania et al. (1994) used *commercial* lindane and a *gas saturation method*, and they obtained for the temperature range between −30° and +30°C:

$$\ln p_i^* / \text{Pa} = -\frac{12816\text{ K}}{T} + 39.12 \tag{2}$$

Finally, Hinckley et al. (1990), using the *gas chromatographic technique*, reported:

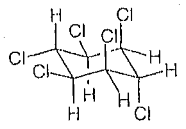
$$\ln p_i^* / \text{Pa} = -\frac{8478\text{ K}}{T} + 25.67 \tag{3}$$

for the temperature range between 40 and 85°C.

(a) Calculate the vapor pressure and the enthalpy of sublimation of lindane at 25°C from each of these three equations, and compare the different values. Why does Eq. 3 yield such a different result as compared to Eqs. 1 and 2? Try to explain the differences between Eq. 1 and Eq. 2. Which equation would you recommend for estimating the vapor pressure of lindane in the ambient temperature range?

(b) Estimate the free energy of fusion ($\Delta_{\text{fus}}G_i$) of lindane at 25°C, (i) from the data given above (Eqs. 1–3), and (ii) using only the normal melting point temperature. Any comments?

(c) Estimate the vapor pressure of lindane at 25°C from its boiling and melting point temperatures given above. Use both equations given in Section 4.4 (Eqs. 4-33 and 4-35) to estimate p_{iL}^*, and Eq. 4-40 to get p_{is}^*. Compare the results with the p_i^* values derived from the experimental data.



1,2,3,4,5,6-Hexachlorocyclohexane
(γ-HCH, Lindane)

Chapter 5

ACTIVITY COEFFICIENT AND SOLUBILITY IN WATER

5.1 Introduction

Whether an organic compound "likes" or "dislikes" being surrounded by liquid water, or alternatively whether water "likes" or "dislikes" to accommodate a given organic solute, is of utmost importance to the environmental behavior and impact of that compound. Due to its small size and hydrogen-bonding characteristics, water is a rather exceptional solvent. Indeed, environmentally relevant compounds have aqueous solubilities ranging over more than ten orders of magnitude — from completely soluble compounds (i.e., miscible) to levels of saturation that are so low that the concentration can be measured only with very sophisticated methods (Appendix C). In this chapter, we will discuss and try to visualize the molecular factors that cause this immense range of results associated with transferring an organic compound from a nonaqueous phase to an aqueous solution (or vice versa).

We will start our discussion by considering a special case, that is, the situation in which the molecules of a pure compound (gas, liquid, or solid) are partitioned so that its concentration reflects equilibrium between the pure material and aqueous solution. In this case, we refer to the equilibrium concentration (or the *saturation* concentration) in the aqueous phase as the *water solubility* or the *aqueous solubility* of the compound. This concentration will be denoted as C_{iw}^{sat}. This compound property, which has been determined experimentally for many compounds, tells us the maximum concentration of a given chemical that can be dissolved in pure water at a given temperature. In Section 5.2, we will discuss how the aqueous activity coefficient *at saturation*, γ_{iw}^{sat}, is related to aqueous solubility. We will also examine when we can use γ_{iw}^{sat} as the activity coefficient of a compound in *diluted* aqueous solution, γ_{iw}^{∞} (which represents a more relevant situation in the environment).

In the next step in Section 5.3, we will explore how chemical structures of the solutes govern their aqueous activity coefficients. This will be done by inspecting how the chemical structures of the solutes correspond to different enthalpic and entropic contributions to the excess free energy of putting those substances in aqueous solution. Using these insights we will extend the molecular interaction model that we introduced and applied in Chapter 4 to quantitatively describe activity coefficients in pure water. In Section 5.4, we will then deal with the effects of temperature and of certain dissolved water constituents that may be present in the environment (i.e., inorganic ions, organic cosolutes and cosolvents) on the solubilities and the aqueous activity coefficients of organic compounds. Finally, in Section 5.5 we will comment on experimental methods and on predictive tools used to estimate aqueous solubilities and aqueous activity coefficients of organic compounds.

5.2 Thermodynamic Considerations

Solubilities and Aqueous Activity Coefficients of Organic Liquids

Let us first imagine an experiment in which we bring a pure, water-immiscible organic *liquid* into contact with pure water at a given temperature and ask what will happen. Intuitively, we know that some organic molecules will leave the organic phase and dissolve into water, while some water molecules will enter the organic liquid. After some time, so many organic molecules will have entered the water that some will begin to return to the organic phase. When the fluxes of molecules into and out of the organic phase are balanced, the system has reached a state of equilibrium. At this point, the amount of organic molecules in the water is the water solubility of that liquid organic compound. Similarly, the amount of water molecules in the organic phase reflects the solubility of water in that organic liquid.

To describe this process thermodynamically, at any instant in time during our experiment, we can express the chemical potentials of the organic compound i in each of the two phases (Chapter 3). For the compound in the *organic liquid phase,* we have:

$$\mu_{iL} = \mu_{iL}^{*} + RT \ln \gamma_{iL} \cdot x_{iL} \tag{5-1}$$

where we use the subscript L to indicate the pure liquid organic phase, although it contains some water molecules. For the compound in the aqueous phase, the corresponding expression of its chemical potential is:

$$\mu_{iw} = \mu_{iL}^{*} + RT \ln \gamma_{iw} \cdot x_{iw} \tag{5-2}$$

where we use the subscript w to refer to parameters of the compound i in the *water.* Note that both expressions relate chemical potential to the same reference potential, μ_{iL}^{*}. Hence at any given time, the difference in chemical potentials of the "product" (solutes in aqueous solution) minus the "reactant" (i in its pure liquid) molecules is given by:

$$\mu_{iw} - \mu_{iL} = RT \ln \gamma_{iw} \cdot x_{iw} - RT \ln \gamma_{iL} \cdot x_{iL} \tag{5-3}$$

In the beginning of our experiment, μ_{iL} is much larger than μ_{iw} (x_{iw} is near zero). Therefore, a net flux of organic molecules from the organic phase (higher chemical potential) to the aqueous phase (lower chemical potential) occurs. This process continues and x_{iw} increases until the chemical potentials (or the fugacities) become equal in both phases. At this point, equilibrium is reached and we may say: $\gamma_{iw}\, x_{iw} = \gamma_{iL}\, x_{iL}$ and $f_{iw} = f_{iL}$! Once at equilibrium, we obtain:

$$\ln \frac{x_{iw}^{\text{sat}}}{x_{iL}} = \frac{RT \ln \gamma_{iL} - RT \ln \gamma_{iw}^{\text{sat}}}{RT} \tag{5-4}$$

where now we use the superscript "sat" to indicate that we are dealing with a saturated aqueous solution of the compound. In Eq. 5-4 we also retain the product of the gas constant and system temperature, RT, to indicate that the ratio of concentrations in the two phases is related to a difference in free energies (i.e., each term, $RT \ln \gamma$, is a free energy term for one mole of molecules in a particular state).

For the majority of the compounds of interest to us, we can now make two important simplifying assumptions. First, in the organic liquid, the mole fraction of water is small compared with the mole fraction of the compound itself; that is, x_{iL} remains nearly 1 (see Table 5.1). Also, we may assume that the compound shows ideal behavior in its water-saturated liquid phase; that is, we set $\gamma_{iL} = 1$. With these assumptions, after some rearrangement, Eq. 5-4 simplifies to:

Table 5.1 Mole Fraction of Some Common Organic Liquids Saturated with Water [a]

Organic Liquid i	x_{iL}	Organic Liquid i	x_{iL}
n-Pentane	0.9995	Chlorobenzene	0.9981
n-Hexane	0.9995	Nitrobenzene	0.9860
n-Heptane	0.9993	Aminobenzene	0.9787
n-Octane	0.9994		
n-Decane	0.9994	Diethylether	0.9501
n-Hexadecane	0.9994	Methoxybenzene	0.9924
		Ethyl acetate	0.8620
Trichloromethane	0.9948	Butyl acetate	0.9000
Tetrachloromethane	0.9993	2-Butanone	0.6580
Trichloroethene	0.9977	2-Pentanone	0.8600
Tetrachloroethene	0.9993	2-Hexanone	0.8930
Benzene	0.9975	1-Butanol	0.4980
Toluene	0.9976	1-Pentanol	0.6580
1,3-Dimethylbenzene	0.9978	1-Hexanol	0.7100
1,3,5-Trimethylbenzene	0.9978	1-Octanol	0.8060
n-Propylbenzene	0.9958		

[a] Data from a compilation presented by Demond and Lindner (1993).

$$\ln x_{iw}^{\text{sat}} = -\frac{RT \ln \gamma_{iw}^{\text{sat}}}{RT} = -\frac{G_{iw}^{\text{E,sat}}}{RT} \qquad (5\text{-}5)$$

where $G_{iw}^{\text{E,sat}}$ is the *excess free energy* of the compound in *saturated* aqueous solution (see Chapter 3).

Now we can see a key result. The aqueous mole fraction solubility of an organic liquid is simply given by the inverse aqueous activity coefficient:

$$x_{iw}^{\text{sat}} = \frac{1}{\gamma_{iw}^{\text{sat}}} \quad \textit{for liquids}$$

or in the more usual molar units (Eq. 3-43): (5-6)

$$C_{iw}^{\text{sat}} = \frac{1}{\overline{V}_{\text{w}} \cdot \gamma_{iw}^{\text{sat}}} \quad \textit{for liquids}$$

where $\overline{V}_{\text{w}}$ is the molar volume of water (0.018 L/mol).

Obviously, we can also say that for a liquid compound, the aqueous activity coefficient at saturation is given by the inverse of its mole fraction solubility:

$$\gamma_{iw}^{\text{sat}} = \frac{1}{x_{iw}^{\text{sat}}}$$

or: (5-7)

$$\gamma_{iw}^{\text{sat}} = \frac{1}{\overline{V}_{\text{w}} \cdot C_{iw}^{\text{sat}}}$$

Solubilities and Aqueous Activity Coefficients of Organic Solids

When considering the solubility of a solid organic compound in water, conceptually we can imagine first converting it to the liquid state and then proceeding as above for a liquid compound. The free energy cost involved in the solid-to-liquid conversion is referred to as the free energy of fusion, $\Delta_{\text{fus}}G_i$ (Chapter 4). This entity can be derived from experimental vapor pressure data (Eq. 4-14):

$$\Delta_{\text{fus}}G_i = RT \ln \frac{p_{iL}^*}{p_{is}^*} \tag{5-8}$$

It can also be estimated from the melting point of the compound (Eq. 4-41).

Now, we can express the difference in chemical potential as:

$$\begin{aligned}\mu_{iw} - \mu_{is} &= \mu_{iw} - (\mu_{iL} - \Delta_{\text{fus}}G_i) \\ &= RT \ln \gamma_{iw} \cdot x_{iw} - (RT \ln \gamma_{iL} \cdot x_{iL} - \Delta_{\text{fus}}G_i)\end{aligned} \tag{5-9}$$

By setting x_{iL} and γ_{iL} equal to 1, and by proceeding as above for liquids, we then obtain at equilibrium ($\mu_{iw} - \mu_{is} = 0$):

$$x_{iw}^{\text{sat}}(\text{s}) = \frac{1}{\gamma_{iw}^{\text{sat}}} \cdot e^{-\Delta_{\text{fus}}G_i/RT} \quad \textit{for solids}$$

or in molar units:

$$C_{iw}^{\text{sat}}(\text{s}) = \frac{1}{\overline{V}_w \cdot \gamma_{iw}^{\text{sat}}} \cdot e^{-\Delta_{\text{fus}}G_i/RT} \quad \textit{for solids} \tag{5-10}$$

Now it is clear that the solubilities of organic solids in water are dependent on both the incompatibility of the chemicals with the water *and* the ease with which the solids are converted to liquids.

One may also see how the aqueous activity coefficient is related to solubility for organic substances that are solids:

$$\gamma_{iw}^{\text{sat}} = \frac{1}{x_{iw}^{\text{sat}}(\text{s})} \cdot e^{-\Delta_{\text{fus}}G_i/RT}$$

or:

$$\gamma_{iw}^{\text{sat}} = \frac{1}{\overline{V}_w \cdot C_{iw}^{\text{sat}}(\text{s})} \cdot e^{-\Delta_{\text{fus}}G_i/RT} \tag{5-11}$$

Recalling the concept of a *subcooled* liquid compound as one that has cooled below its freezing temperature without becoming solid (Chapter 4.2), we may evaluate the solubility of such a hypothetical liquid, $C_{iw}^{\text{sat}}(\text{L})$, from Eq. 5-11 as:

$$\gamma_{iw}^{\text{sat}} = \frac{1}{\overline{V}_w \cdot C_{iw}^{\text{sat}}(\text{L})} \tag{5-12}$$

where the liquid compound solubility is related to the actual experimental solubility of the solid compound by:

$$C_{iw}^{\text{sat}}(\text{L}) = C_{iw}^{\text{sat}}(\text{s}) \cdot e^{+\Delta_{\text{fus}}G_i/RT} \tag{5-13}$$

Solubilities and Aqueous Activity Coefficients of Organic Gases

The aqueous solubility of a gaseous compound is commonly reported for 1 bar (or 1 atm = 1.013 bar) partial pressure of the pure compound. One of the few exceptions is the solubility of O_2 which is generally given for equilibrium with the gas at 0.21 bar, since this value is appropriate for the earth's atmosphere at sea level. As discussed in Chapter 3, the partial pressure of a compound in the gas phase (ideal gas) at equilibrium above a liquid solution is identical to the fugacity of the compound in the solution (see Fig. 3.9*d*). Therefore equating fugacity expressions for a compound in both the gas phase and an equilibrated aqueous solution phase, we have:

$$p_i = \gamma_{iw} \cdot x_{iw} \cdot p_{iL}^* \tag{5-14}$$

Now we can see how to express the mole fraction solubility of a gaseous organic substance as a function of the partial pressure p_i:

$$x_{iw}^{p_i} = \frac{1}{\gamma_{iw}^{p_i}} \cdot \frac{p_i}{p_{iL}^*} \quad \textit{for gases}$$

or in molar units: (5-15)

$$C_{iw}^{p_i} = \frac{1}{\overline{V}_w \cdot \gamma_{iw}^{p_i}} \cdot \frac{p_i}{p_{iL}^*} \quad \textit{for gases}$$

It thus follows that the aqueous activity coefficient of a gaseous pure compound is related to the solubility by:

$$\gamma_{iw}^{p_i} = \frac{1}{x_{iw}^{p_i}} \cdot \frac{p_i}{p_{iL}^*}$$

or: (5-16)

$$\gamma_{iw}^{p_i} = \frac{1}{\overline{V}_w \cdot C_{iw}^{p_i}} \cdot \frac{p_i}{p_{iL}^*}$$

Note that $\gamma_{iw}^{p_i}$ is not necessarily constant with varying p_i. In fact, evaluation of the air–water equilibrium distribution ratio as a function of p_i is one of the methods that can be used to assess the concentration dependence of γ_{iw} of an organic compound, regardless whether the compound is a gas, liquid, or solid at the temperature considered (see below).

If, for sparingly soluble gases, we assume that $\gamma_{iw}^{p_i}$ is independent of concentration (even at saturation, i.e., at $p_i = p_{iL}^*$, where the compound is also present as a liquid), then we can calculate the solubility of the *superheated liquid compound*, $C_{iw}^{\text{sat}}(\text{L})$, from the actual solubility determined at p_i (e.g., at 1 bar) by:

$$C_{iw}^{\text{sat}}(\text{L}) = C_{iw}^{p_i} \cdot \frac{p_{iL}^*}{p_i} \tag{5-17}$$

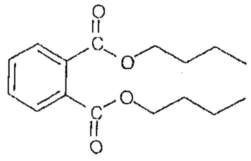
Some example calculations demonstrating how to derive γ_{iw} and G_{iw}^{E} values from experimental solubility data are given in Illustrative Example 5.1.

Illustrative Example 5.1

Deriving Liquid Aqueous Solubilities, Aqueous Activity Coefficients, and Excess Free Energies in Aqueous Solution from Experimental Solubility Data

Problem

Calculate the $C_{iw}^{sat}(L)$, γ_{iw}^{sat} and G_{iw}^{E} of (a) di-*n*-butyl phthalate, (b) γ-1,2,3,4,5,6-hexachlorocyclohexane (γ-HCH, lindane), and (c) chloroethene (vinyl chloride) at 25°C using the data provided in Appendix C.



di-*n*-butyl phthalate

C_{iw}^{sat} (25°C) = 3.4×10^{-5} mol·L^{-1}
$T_m < 25$°C

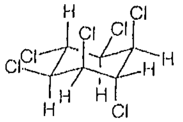
Answer (a)

Di-*n*-butylphthalate is a liquid at 25°C. Hence, $C_{iw}^{sat} = C_{iw}^{sat}(L) = 3.4 \times 10^{-5}$ mol·L^{-1}, and (Eq. 5-7):

$$\gamma_{iw}^{sat} \cong \frac{1}{(0.018\ \mathrm{L \cdot mol^{-1}})(3.4 \times 10^{-5}\ \mathrm{mol \cdot L^{-1}})} = 1.6 \times 10^{6}$$

which yields an excess free energy of:

$$G_{iw}^{E,sat} = RT \ln \gamma_{iw}^{sat} = (8.314\ \mathrm{J \cdot mol^{-1}\ K^{-1}})\ (298.1\ \mathrm{K})\ (14.3) = 35.4\ \mathrm{kJ \cdot mol^{-1}}$$



1,2,3,4,5,6-hexachlorocyclohexane
(γ-HCH)

C_{iw}^{sat} (25°C) = 2.5×10^{-5} mol·L^{-1}
$T_m = 113$°C

Answer (b)

γ-HCH is a solid at 25°C. To calculate the solubility of liquid γ-HCH, estimate first the free energy of fusion from the normal melting point temperature (Eq. 4-41, see also Problem 4.7):

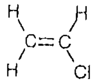
$$\Delta_{fus}G_i \cong (56.5)\ [386 - 298] \cong 5.0\ \mathrm{kJ \cdot mol^{-1}}$$

Insert the values for C_{iw}^{sat} and $\Delta_{fus}G_i$ into Eq. 5-13 to get $C_{iw}^{sat}(L)$:

$$C_{iw}^{sat}(L) = (2.5 \times 10^{-5}) \cdot e^{+(5.0/2.48)} = 1.9 \times 10^{-4}\ \mathrm{mol \cdot L^{-1}}$$

Insertion of $C_{iw}^{sat}(L)$ into Eq. 5-12 yields:

$$\gamma_{iw}^{sat} \cong 2.9 \times 10^{5}, \text{ and } G_{iw}^{E} = 31.2\ \mathrm{kJ \cdot mol^{-1}}$$



Chloroethene (vinyl chloride)

C_{iw}^{1bar} (25°C) = 4.4×10^{-2} mol·L^{-1}
p_{iL}^{*} (25°C) = 3.55 bar

Answer (c)

Chloroethene (Vinylchloride) is a gas at 25°C. Calculate first the solubility of superheated liquid vinylchloride (Eq. 5-17):

$$C_{iw}^{sat}(L) = (4.4 \times 10^{-2})\left(\frac{3.55}{1}\right) = 1.6 \times 10^{-1}\ \mathrm{mol \cdot L^{-1}}$$

This yields

$$\gamma_{iw}^{sat} \cong 3.5 \times 10^{2}, \text{ and } G_{iw}^{E} = 14.5\ \mathrm{kJ \cdot mol^{-1}}$$

Table 5.2 Comparison of Activity Coefficients and Corresponding Excess Free Energies of a Series of Organic Compounds in Dilute and Saturated Aqueous Solution at 25°C (recall that $G_{iw}^{\mathrm{E}} = RT \ln \gamma_{iw}$)

Compound	$\gamma_{iw}^{\mathrm{sat}}$	$G_{iw}^{\mathrm{E,sat}}$ [a] (kJ·mol^{-1})	γ_{iw}^{∞}	$G_{iw}^{\mathrm{E},\infty}$ [b] (kJ·mol^{-1})
Methanol	miscible	miscible	1.6	1.2
Ethanol	miscible	miscible	3.7	3.2
Acetone	miscible	miscible	7.0	4.8
1-Butanol	7.0×10^1	10.5	5.0×10^1	9.7
Phenol	6.3×10^1	10.3	5.7×10^1	10.0
Aniline	1.4×10^2	12.3	1.3×10^2	12.1
3-Methylphenol	2.5×10^2	13.7	2.3×10^1	13.5
1-Hexanol	9.0×10^2	16.9	8.0×10^2	16.5
Trichloromethane	7.9×10^2	16.5	8.2×10^2	16.6
Benzene	2.5×10^3	19.4	2.5×10^3	19.4
Chlorobenzene	1.4×10^4	23.7	1.3×10^4	23.5
Tetrachloroethene	7.5×10^4	27.8	5.0×10^4	26.8
Naphthalene	6.7×10^4	27.5	6.9×10^4	27.6
1,2-Dichlorobenzene	6.2×10^4	27.3	6.8×10^4	27.6
1,3,5-Trimethylbenzene	1.3×10^5	29.2	1.2×10^5	29.0
Phenanthrene	2.0×10^6	35.9	1.7×10^6	35.5
Anthracene	2.5×10^6	36.5	2.7×10^6	36.7
Hexachlorobenzene	4.3×10^7	43.6	3.5×10^7	43.0
2,4,4'-Trichlorobiphenyl	5.6×10^7	44.2	4.7×10^7	43.8
2,2',5,5'-Tetrachlorobiphenyl	7.0×10^8	46.5	7.5×10^7	44.9
Benzo(a)pyrene	3.2×10^8	48.5	2.7×10^8	48.1

[a] Data from Appendix C using enthalpy and entropy of fusion values given by Hinckley et al. (1990), and Lide (1995). [b] Data from Sherman et al. (1996), Staudinger and Roberts (1996), Mitchell and Jurs (1998).

Concentration Dependence of the Aqueous Activity Coefficient

From an environmental point of view, it is often of most interest to know the activity coefficient of an organic compound in *dilute* aqueous solution. This activity coefficient is commonly denoted as γ_{iw}^{∞}, and is referred to as *limiting* activity coefficient or *infinite dilution* activity coefficient.

As we have shown above, activity coefficients can be deduced from the aqueous solubilities (together with vapor pressure or melting data, as necessary). In this case, the activity coefficient reflects the compatibility of the organic solute with water solutions that may have been significantly modified by the presence of the solute itself. It is important to know when such values of $\gamma_{iw}^{\mathrm{sat}}$ will be the same as the corresponding γ_{iw}^{∞} values. Table 5.2 shows a comparison of $\gamma_{iw}^{\mathrm{sat}}$ values obtained from solubility measurements (Eqs. 5-6 and 5-10) with γ_{iw}^{∞} values determined by various methods (that will be addressed in Section 5.5) for a series of compounds covering a very large range in activity coefficients. As is evident, even for compounds exhibiting a substantial aqueous solubility (e.g., 1-butanol, phenol), the differences between the activity coefficients in dilute solution and in saturated solution are not larger than about 30%. In fact, particularly for the more sparingly soluble compounds, the differences are well within the range of error of the experimental data. Hence, for compounds exhibiting activity coefficients larger than about 100 (which represents the majority of the chemicals of interest to us), we will assume that γ_{iw} is independent of the concentration of the compound (and, therefore, we will typically omit any superscript). By making this assumption, we imply that the organic solutes do not "feel" each other in the aqueous solution even under saturation conditions. Or to put it more scientifically, we assume that the solvation of a given organic molecule by water molecules is not influenced by the other organic molecules present. But, as we will see in the following, this assumption is not always true!

5.3 Molecular Interpretation of the Excess Free Energy of Organic Compounds in Aqueous Solutions

Enthalpic and Entropic Contributions to the Excess Free Energy

Water is a very unique solvent that has two outstanding characteristics: (1) the small size of its molecules, and (2) the strong hydrogen bonding between these molecules. Hence, when we consider the molecular factors that govern the free energy of the transfer of an organic compound from its pure liquid into a pure aqueous phase, we have to be aware that it takes quite a number of water molecules to surround each organic molecule. Also, the water molecules adjacent to the organic solute are in a special situation with respect to forming hydrogen bonds as compared to the other bulk water molecules.

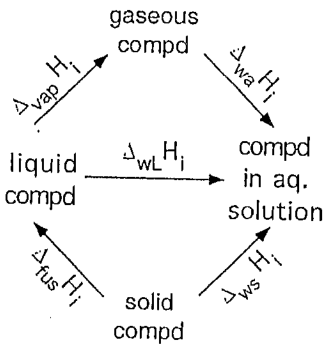


Figure 5.1 Enthalpies of the various phase transfers that can be used to derive the excess enthalpy, H_{iw}^{E}, of an organic compound in saturated and in dilute aqueous solution.

Before we deal with these molecular aspects in detail, it is instructive to inspect the enthalpic (H_{iw}^{E}) and entropic ($-T \cdot S_{iw}^{E}$) contributions to the excess free energies of various organic compounds in aqueous solution (Table 5.3). Values representative of *saturated* aqueous solutions of the compounds have been derived from measurements of the enthalpies of dissolution of the liquids (i.e., $H_{iw}^{E} = \Delta_{wL}H_i$, Fig. 5.1) or solids ($H_{iw}^{E} = \Delta_{ws}H_i - \Delta_{fus}H_i$, Fig. 5.1). Data suited to *dilute* conditions have been obtained from enthalpies of air–water partitioning (i.e., $H_{iw}^{E} = \Delta_{vap}H_i + \Delta_{wa}H_i$, Fig. 5.1). Since in both the saturated and dilute solution, the excess free energies are indistinguishable [data in Table 5.2 gives G_{iw}^{E} (dilute) = 0.989 $G_{iw}^{E,sat}$ (saturated) – 0.038, $R^2 = 0.99$], the entropy contributions have been calculated using one (average) G_{iw}^{E} value. Note that the experimental data reported in the literature show considerable scatter, particularly when comparing H_{iw}^{E} values determined for saturated conditions with those determined for dilute solutions. Therefore, the numbers given in Table 5.3 should be treated with some caution. Nevertheless, these data allow us to draw some important general conclusions.

The first and most important feature that can be seen from the data (Table 5.3) is that the excess enthalpies of the smaller-sized compounds are close to zero (i.e., between –10 and +10 kJ · mol^{-1}). This is even true for apolar compounds such as tetrachloroethene or hexane. Hence in these cases, the intermolecular interactions that must be disrupted to remove a small organic molecule from its pure liquid (i.e., the enthalpy

Table 5.3 Enthalpic (H_{iw}^{E}) and Entropic (S_{iw}^{E}) Contributions to the Excess Free Energy of a Series of Organic Compounds in Saturated ("Sat") and Dilute ("Dil") Aqueous Solution at 20 to 25°C. The Compounds are Ordered by Increasing Size Expressed by Their Molar Volume

Compound	Molar Volume[a] ($cm^3 \cdot mol^{-1}$)	G_{iw}^{E} ($kJ \cdot mol^{-1}$)	H_{iw}^{E} ($kJ \cdot mol^{-1}$) Sat[b]/Dil[c,d]	$T \cdot S_{iw}^{E}$ ($kJ \cdot mol^{-1}$) Sat/Dil
Trichloromethane	81	17	–2/3	–19/–20
Benzene	89	19	2/4	–21/–23
2-Butanone	90	8	–7/–5	–15/–13
Trichloroethene	90	22	–4/2	–26/–20
Phenol	90	10	1/8	–9/–2
Aniline	91	12	2	–10
Tetrachloromethane	97	23	–4/–2	–27/–25
Tetrachloroethene	102	27	–5/3	–32/–24
Benzaldehyde	102	19	4/10	–15/–9
4-Methylphenol	103	13	2/11	–11/–2
Diethylether	104	18	–20/–14	–31/–25
Benzylalcohol	104	12	–7	–19
Methylbenzene	106	23	2/6	–21/–17
2-Pentanone	106	11	–7	–19
Diethylsulfide	108	18	–1/–1	–19/–19
1-Pentanol	109	13	–8	–21
n-Pentane	116	29	–2	–31
1,4-Dimethylbenzene	123	26	3/9	–23/–16
Naphthalene	130	28	9/12	–19/–16
n-Hexane	132	32	~0	–32
1,3,5-Trimethylbenzene	139	29	8	–21
n-Propylbenzene	139	29	2	–27
1-Octanol	158	23	–3	–26
n-Octane	164	40	6	–34
Hexachlorobenzene	167	43	11/27	–32/–16
Phenanthrene	171	36	17/46	–19/+10!
Anthracene	171	37	20/43	–17/+6!
Benzo(a)pyrene	223	48	25/61	–23/+13!

[a] Calculated from density and molar mass. [b] Data from Whitehouse (1984), Abraham et al. (1990), and Shiu et al. (1997). [c] Data from Dewulf et al. (1995), Dohnal and Fenclová (1995), Staudinger and Roberts (1996), and Alaee et al. (1996). [d] Enthalpies of vaporization from Hinckley et al. (1990), and Lide (1995).

of vaporization) are more or less replaced by intermolecular interactions of equal strength in the water.

Only for larger apolar and weakly monopolar compounds (e.g., PAHs, PCBs) are significantly more positive H_{iw}^{E} values found. Indeed, if we examine the H_{iw}^{E} values within single compound classes, we can see that this parameter becomes more positive as the sizes of the structures increase (e.g., benzene, naphthalene, anthracene, benzo(a)pyrene).

Thus, for small organic compounds (molar volumes < 150 $cm^3 mol^{-1}$), it is the unfavorable entropy term that dominates the excess free energy of solution. Since these chemicals were historically studied first, this is probably the origin of the "sense" that entropic effects determine the "hydrophobicity" of organic compounds. However, since larger organic compounds have increasingly disfavorable enthalpic contributions, when we are interested in these substances both enthalpy and entropy must be considered. At this point it should be noted that for these compounds (e.g., hexachlorobenzene, phenanthrene, anthracene) the H_{iw}^{E} values derived for saturated and dilute conditions show considerable differences (Table 5.3). In all these cases the H_{iw}^{E} values are significantly larger for dilute conditions. This difference in excess enthalpy is obviously compensated by an increase in excess entropy, since G_{iw}^{E} is more or less independent of concentration (see above). To date, however, there are not enough experimental data available to assess whether this is a real phenomenon, or whether these findings are due to experimental artifacts.

Molecular Picture of the Dissolution Process

Let us now try to visualize the various molecular changes that determine the enthalpies and entropies of transfering an organic molecule from its pure liquid into water. As already pointed out, one of the key concerns in this process is how the water molecules surrounding the organic compound arrange themselves to optimize their own interactions from an energetic point of view. Since water is an "associated" liquid, meaning that its molecules are hydrogen-bonded so extensively that they act as "packets" of several H_2O molecules tied together, one must also consider the organic solute's influence on water molecules that are not in direct contact with the organic solute.

In the classical model view, it is thought that the water molecules form an ice-like structure around the organic molecule (Frank and Evans, 1945; Shinoda, 1977). This results from the need of water molecules to maximize their hydrogen bonding. Since the apolar portions of organic solutes cannot participate in this type of intermolecular interaction, the water molecules lining the "solute cavity" were believed to orient so as to maximize their hydrogen bonding to the waters away from the solute. Such orientation would limit the directions these cavity-lining water molecules could face, thereby having the effect of "freezing" them in space. This freezing effect would give rise to an enthalpy gain and an entropy loss, which would be in accordance with the experimental solubility data.

However, the results from numerous, more recent experimental and theoretical studies support an alternative picture (Blokzijl and Engberts, 1993; Meng and Kollman, 1996). In this scenario, the water surrounding a nonpolar solute maintains, but does not enhance, its H-bonding network. One can imagine that, at ambient temperatures, the packets of water molecules adjacent to an apolar organic molecule lose only a very small proportion of their total hydrogen bonds (i.e., the packet:packet interactions). By doing so, they are able to host an apolar solute of limited size without losing a significant number of their H-bonds (Blokzijl and Engberts, 1993). Hence, the introduction of a relatively small apolar or weakly polar organic solute that undergoes primarily vdW interactions should not provoke a significant loss in enthalpy due to the breaking of H-bonds among the water molecules. For such solutes it is, therefore, not surprising that the enthalpy that has to be spent to isolate the compounds from their pure liquid (i.e., the enthalpy of vaporization) is about equal to the enthalpy gained from the vdW interactions of the organic molecules with the water molecules in the aqueous solution. Examples of such compounds include benzene, tetrachloromethane, tetrachloroethene, methylbenzene (toluene), *n*-pentane, 1,4-dimethylbenzene, and *n*-hexane (Table 5.3).

The factors that determine the large unfavorable entropy terms for these compounds are somewhat more difficult to rationalize. First, there is a diminishing effect of the favorable entropy of dissolving (or mixing) a (large) organic compound in a solvent consisting of very small molecules, which is, of course, particularly true for water. This excess entropy term can be as big as -8 kJ·mol^{-1}, depending on the size of the organic compound. Note that a difference of about 6 kJ·mol^{-1} (i.e., $RT \ln 10$) means a factor of 10 difference in the activity coefficient. However, as can be seen from Table 5.3, the actual negative entropy contributions found for the apolar compounds mentioned above are much larger (i.e., 20 – 30 kJ·mol^{-1}). Hence, there must be other factors that contribute significantly to this large negative entropy. It is conceivable that the water molecules forming the hydration shell lose some of their freedom of motion as compared to the bulk water molecules when accommodating an (apolar) organic compound. Alternatively, the organic compound itself could experience such a loss of freedom when being transferred from its pure liquid into an environment that is more "rigid," because it is now surrounded by many solvent molecules that are interconnected by hydrogen bonds. Moving from a liquid to a more solid-like environment (thus losing translational, rotational, and flexing freedom) could explain the quite substantial differences in excess entropy found between rigid aromatic (e.g., benzene, methylbenzene, naphthalene) and aliphatic compounds (e.g., pentane, hexane) of similar size (Table 5.3). Indeed, we have already noticed these differences when discussing entropies of fusion in Section 4.4 (Table 4.5) and the involved magnitudes are similar.

Let us now examine what happens to the enthalpy and entropy of solution in water if we introduce a polar group on a small nonpolar organic structure. Generally, the presence of a monopolar or bipolar group leads to a decrease in the enthalpy term and an increase in the entropy term. For example, we can see such changes if we contrast data for 2-pentanone with that for pentane (Table 5.3). Both of these thermodynamic parameters imply that the polar moiety promotes the new compound's solubility over the unsubstituted structure. Note that in the case of bipolar compounds (e.g., alcohols), the effect might not seem as dramatic as may be expected (e.g., compare pentane, 2-pentanone, and 1-pentanol in Table 5.3). But one has to keep in mind that for bipolar compounds (in contrast to the monopolar compounds), polar attractions in the pure organic liquid have to be overcome as part of the total energy of transferring the compound to water.

To rationalize the effect of polar groups on $H^{\mathrm{E}}_{i\mathrm{w}}$ and $S^{\mathrm{E}}_{i\mathrm{w}}$, we can imagine that polar interactions with the water molecules around the solute cavity replace some of the hydrogen bonds between the water molecules. As indicated by the experimental data, this loss of water:water interaction enthalpy seems to be compensated by the enthalpy gained from the organic solute:water polar interactions. At this point it should also be mentioned that additional polarization effects could enhance the interaction between the organic solute and the water molecules in the hydration shell

(Blokzijl and Engberts, 1993). To explain the entropy gain, we can imagine that a (partial) "loosening up" of the waters surrounding an organic solute will increase the freedom of motion of both the water molecules and the organic solute involved.

So far, we have considered rather small-sized organic molecules. Larger molecules such as the PAHs or the PCBs exhibit large positive excess enthalpies (Table 5.3). Apparently, with increasing apolar solute size, water is not able to maintain a maximum of hydrogen bonds among the water molecules involved. Hence, for these types of compounds the excess enthalpy term may become dominant (Table 5.3).

In summary, we can conclude that the excess free energy of an organic compound in aqueous solution, and thus its activity coefficient, depends especially on (1) the size and the shape of the molecule, and (2) its H-donor and/or H-acceptor properties.

Model for Description of the Aqueous Activity Coefficient

Let us now extend our molecular descriptor model introduced in Chapter 4 (Eqs. 4-26 and 4-27) to the aqueous activity coefficient. We should point out it is not our principal goal to derive an optimized tool for prediction of γ_{iw}, but to develop further our understanding of how certain structural features determine a compound's partitioning behavior between aqueous and nonaqueous phases. Therefore, we will try to keep our model as simple as possible. For a more comprehensive treatment of this topic [i.e., of so-called linear solvation energy relationships (LSERs)] we refer to the literature (e.g., Kamlet et al., 1983; Abraham et al., 1990; Abraham, 1993; Abraham et al., 1994a and b; Sherman et al., 1996).

First, we consider how a compound's size may influence its activity coefficient, which is related to its liquid aqueous solubilities (Section 5.2). Generally, within any one compound class, we have already seen that the excess free energy of solution in water becomes more positive as we consider larger and larger members of each compound class. In each case, we are increasing the size of the molecules in the compound class by adding apolar portions to the overall structure (e.g., $-CH_2-$ groups). Consequently, the integral interactions with the solvent water molecules become increasingly unfavorable.

In light of such empirical trends, and as is illustrated by Fig. 5.2, we should not be surprised to see that relationships of the following forms can be found for individual compound classes:

$$\ln \gamma_{iw} = a \cdot (size_i) + b$$

or:

$$\ln C_{iw}^{\mathrm{sat}}(\mathrm{L}) = -c \cdot (size_i) + d \qquad (5\text{-}18)$$

The size parameter in such correlations can come from molecular weights, molar volumes, or other related parameters. One such parameter is the estimate of compound size based on the incremental contributions of the atoms involved. Such an approach is the basis for methods like those of McGowan (see Box 5.1 below).

Having means to estimate relative solute sizes, we recognize that we can now estimate a new compound's aqueous activity coefficient and/or liquid solubility from

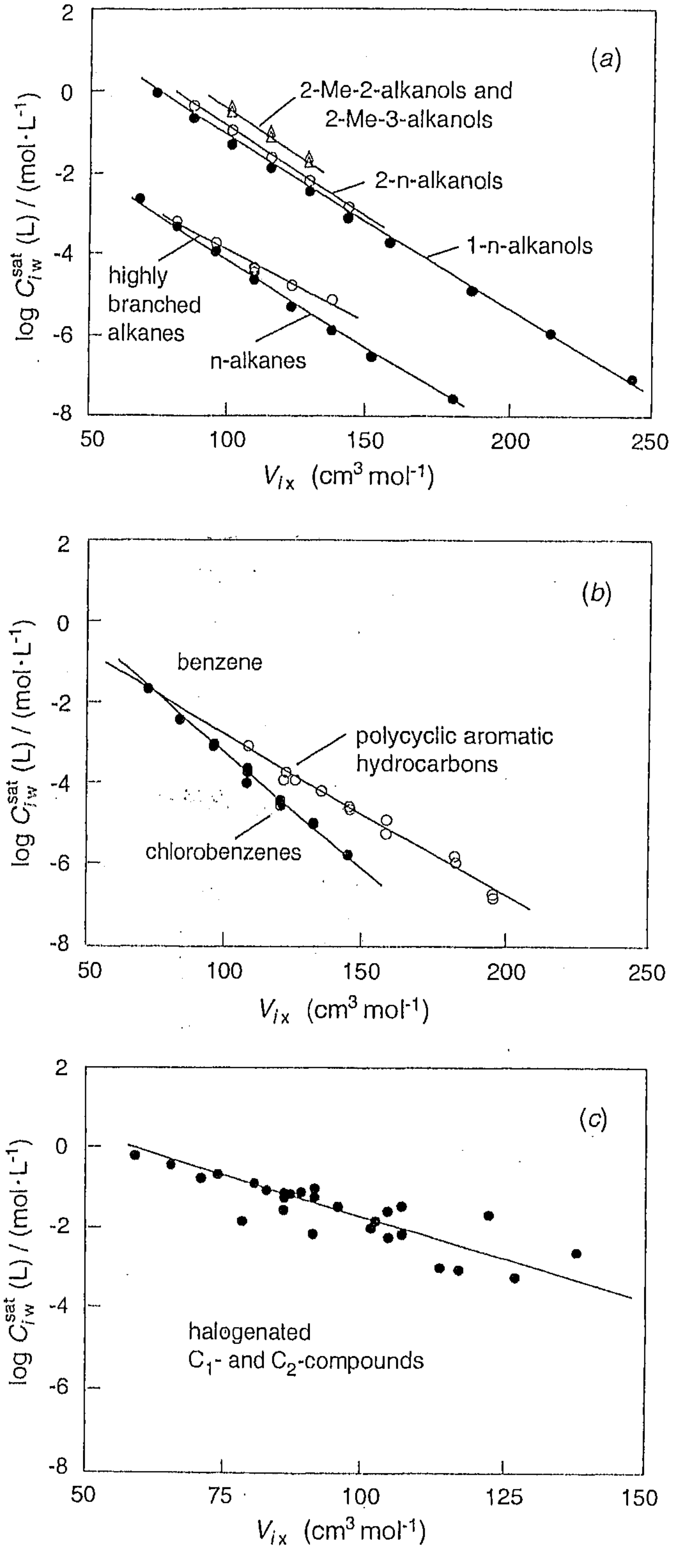


Figure 5.2 Aqueous solubility of the (subcooled) liquid compound at 25°C as a function of the estimated molar volume (V_{ix}, see Box 5.1) of the molecule for various compound classes. The linear regression equations and correlation coefficients (R^2) for the various sets of compounds are given in Table 5.4. Note that for practical reasons, decadic instead of natural logarithms are used.
(a) *n*-alkanes (C_4–C_{16}), highly branched alkanes (C_5–C_9), 1-3-methyl-3-alkanols (C_6–C_8); *(b)* chlorobenzenes (Cl_1–Cl_6), polycyclic aromatic hydrocarbons (benzene-benzo(a)pyrene); *(c)* polyhalogenated methanes, ethanes, and ethenes. Data from Appendix C and from data compilations reported by Ruelle and Kesselring (1997a and b).

Table 5.4 Linear Relationships Between log C_{iw}^{sat}(L) and V_{ix} [a] for the Various Sets of Compounds Shown in Fig. 5.2 (all data for 25°C).

		log C_{iw}^{sat}(L) /(mol·L^{-1}) $= -c \cdot V_{ix} + d$ [b]		
Set of Compounds	n [c]	c	d	R^2
n-Alkanes	8	0.0442	0.34	0.99
Branched alkanes	7	0.0349	–0.38	0.97
Primary alkanols	10	0.0416	3.01	0.99
Secondary alkanols	5	0.0435	3.52	0.99
Tertiary alkanols	6	0.0438	4.01	0.99
Chlorinated benzenes	13	0.0556	2.27	0.99
Polycyclic aromatic hydrocarbons	13	0.0399	1.90	0.99
Polyhalogenated C_1- and C_2-compounds	27	0.0404	1.85	0.86

[a] Molar volume in cm^3·mol^{-1} estimated by the method discussed in Box. 5.1. [b] Eq. 5-18; note that decadic instead of natural logarithms are used. [c] Number of compounds.

knowledge of the liquid solubilities of other chemicals in its compound class (see examples given in Table 5.4).

While the relations of chemical size and solubility are gratifying to recognize, we still notice that each compound class exhibits its own behavior (Fig. 5.2). Hence, we may wonder if there is any means to account for variations from compound class to compound class. Based on our visualizations of organic solute intermolecular interactions, it is not surprising to learn that parameters that quantify the importance of interactions like hydrogen bonding can be used to adjust for differences between compound classes.

Thinking in analogy to our discussions of the influence of molecular structure on vapor pressures (Eqs. 4-24 to 4-27), we can try to express lnγ_{iw} by a series of terms describing the various molecular interactions and freedoms of motions when transferring a compound from its pure liquid to water. Unlike the cases discussed in Chapter 4, where one of the phases was the gas phase, now we need to account for both the molecular interactions between the compound and the water and the interactions in the pure liquid. This latter group of interactions, however, can simply be characterized by using the vapor pressure of the compound as a quantitative measure of the intermolecular interactions in the pure liquid. Our problem then reduces to describing the transfer of an organic compound from the gas phase to water:

$$\ln \gamma_{iw} = -\ln p_{iL}^{*} + \text{terms describing the gas–water transfer} \qquad (5\text{-}19)$$

It is easy to see that for describing the solvation of an organic solute in water we need to account not only for the size of the molecule (or of the cavity that needs to be formed), but also for the vdW and hydrogen-bonding interactions of the solute with the water molecules. By assuming that the average vdW, H-donor, and H-acceptor properties of the water forming the hydration shell do not vary much with the type of organic solute that they surround, we can include these properties in a correlation equation with appropriate scaling coefficients:

$$\ln \gamma_{iw} = -\ln p^{*}_{iL} + s\left[(V_i)^{2/3}\left(\frac{n_{Di}^2-1}{n_{Di}^2+2}\right)\right] + a(\alpha_i) + b(\beta_i) + vV_i + \text{constant} \qquad (5\text{-}20)$$

vdW (dispersive) H-donor H-acceptor size

Note that our *multiparameter LFER* Eq. 5-20 includes two terms that contain a volume term (a quantitative measure of the volume of one mole molecules) as a size parameter ("vdW," "size"-terms). This V_i value can be the molar volume, $\overline{V}_i$, of the compound (derived from the molar mass and the density of the compound, see Chapters 3 and 4), or it can be an estimated entity (see Box 5.1). Therefore, we denote this term as V_i and not $\overline{V}_i$. We will, however, use the term "molar volume" even if we refer to estimated V_i values.

A question that one might ask is whether it is necessary to include two volume terms in Eq. 5-20, because one could imagine that these two terms are strongly correlated

Box 5.1 Estimating Molar Volumes from Structure

A very common way of expressing the bulk size of the molecules of a given compound (or more precisely of 1 mole of the compound) is to use the "molar volume," V_i, of the compound. As we have already discussed in Chapters 3 and 4, we can derive V_i from the molar mass and from the liquid density (i.e., $V_i = \overline{V}_i = M_i / \rho_{iL}$ a given temperature. This way of defining V_i has, however, certain disadvantages when we want to express the bulk size of a given compound molecule in equations such as Eq. 5-20. First, because ρ_{iL} is a bulk property, for polar compounds (e.g., alcohols) that have a network-like hydrogen-bond structure, the calculated V_i value represents a molar volume that reflects not only the *intrinsic molecular volume* but also the bulk structure. Second, adjustments have to be made when dealing with compounds that are solids. Therefore, various methods for estimating V_i values from the structure of the compound have been developed (for an overview see Chapter 18 and Yalkowski and Banerjee, 1992; Mackay et al., 1992–1997). Although each of these methods yields different absolute V_i values, the various data sets correlate reasonably well with each other (Mackay et al., 1992–1997). A simple method that seems to work almost as well as the more sophisticated approaches has been proposed by McGowan and coworkers (McGowan and Mellors, 1986; Abraham and McGowan, 1987). In this method, each element is assigned a characteristic atomic volume (see table below) and the total volume, which is denoted as V_{ix}, is calculated by just summing up all atomic volumes and by subtracting 6.56 $\text{cm}^3\,\text{mol}^{-1}$ for each bond, no matter whether single, double, or triple. Thus, V_{ix} for benzene is calculated as $V_{ix} = (6)(16.35) + (6)(8.71) - (12)(6.56) = 71.6\ \text{cm}^3\,\text{mol}^{-1}$, an example that illustrates how trivial the calculation is. Of course, by this method, identical V_{ix} values will be obtained for structural isomers, which is, however, a reasonable first approximation for many applications. Note again that for each bond between two atoms, 6.56 $\text{cm}^3\,\text{mol}^{-1}$ is to be subtracted. Some example calculations are included in some of the illustrative examples.

Characteristic Atomic Volumes in $\text{cm}^3\,\text{mol}^{-1}$ (From Abraham and McGowan, 1987)

C	16.35	H	8.71	O	12.43	N	14.39	P	24.87	F	10.48	Cl	20.95
Br	26.21	I	34.53	S	22.91	Si	26.83						

to each other. In fact, when applying Eq. 5-20 to nonpolar organic solvents (see Chapter 6), it is sufficient to use only the vdW term (which decreases γ_{iw} because s is negative; see below). We can, however, easily see that in the special case of water as a solvent, we need to include an additional size term in order to address the large entropy costs when inserting an organic solute into the bulk water. Figure 5.3*a* shows that with this equation, the aqueous activity coefficients of over 250 compounds covering a wide variety of compound classes can be collapsed onto one line reasonably well.

This result is accomplished without considering the dipolarity/polarizability characteristics that one can expect to play a role in a polar solvent such as water. Consequently, it can be expected that the still-large scatter observed in the data shown in Fig. 5.3*a* can be further reduced, if one adds another parameter that takes into account these aspects. One widely used additional parameter (in addition to α_i and β_i) that is thought to express the dipolarity/polarizability of an organic compound is a parameter commonly denoted as π_i. Note that several sets of π_i values have been derived that may be somewhat different in absolute numbers (e.g., π_i values reported by Li et al., 1993). Table 5.5 summarizes π_i values for some representative compounds. Inspection of Table 5.5 shows that π_i ranges between 0 for the apolar alkanes up to almost 2 for aromatic compounds exhibiting several polar groups (e.g., 4-nitrophenol). For more details, particularly with respect to the derivation of this not-so-easy-to-interpret parameter, we refer to the literature (e.g., Abraham et al., 1991 and 1994a, and references cited therein). Inclusion of π_i into Eq. 5-20 then yields:

$$\ln \gamma_{iw} = -\ln p^*_{iL} + \underset{\text{vdW (dispersive)}}{s\left[(V_i)^{2/3}\left(\frac{n_{Di}^2-1}{n_{Di}^2+2}\right)\right]} + \underset{\text{dipolarity/ polarizability}}{p(\pi_i)} + \underset{\text{H-donor}}{a(\alpha_i)} + \underset{\text{H-acceptor}}{b(\beta_i)} + \underset{\text{size}}{vV_i} + \text{constant} \qquad (5\text{-}21)$$

As is illustrated by Fig. 5.3*b*, with this extended equation, the fit of the experimental data can be improved significantly. The best fit equation obtained from the experimental data set is:

$$\ln \gamma_{iw} = -\ln p^*_{iL} / \text{bar} - 0.572\left[(V_{ix})^{2/3}\left(\frac{n_{Di}^2-1}{n_{Di}^2+2}\right)\right] - 5.78\,(\pi_i) - 8.77\,(\alpha_i) - 11.1\,(\beta_i) + 0.0472\,V_{ix} + 9.49 \qquad (5\text{-}22)$$

Note that for the derivation of Eq. 5-22 we have adopted a very simple characteristic atomic volume contribution method estimating V_i (see Box 5.1), which we denote as V_{ix}. Since the various methods commonly used to assess "molar volumes" yield quite different absolute values (see e.g., Mackay et al., 1992–1997), V_{ix} values in $\text{cm}^3\,\text{mol}^{-1}$ calculated by this method should be used when applying Eq. 5-22. Hence, if, in addition to V_{ix}, p^*_{iL}, n_{Di}, p_i, a_i, and b_i are known or can be estimated for a given

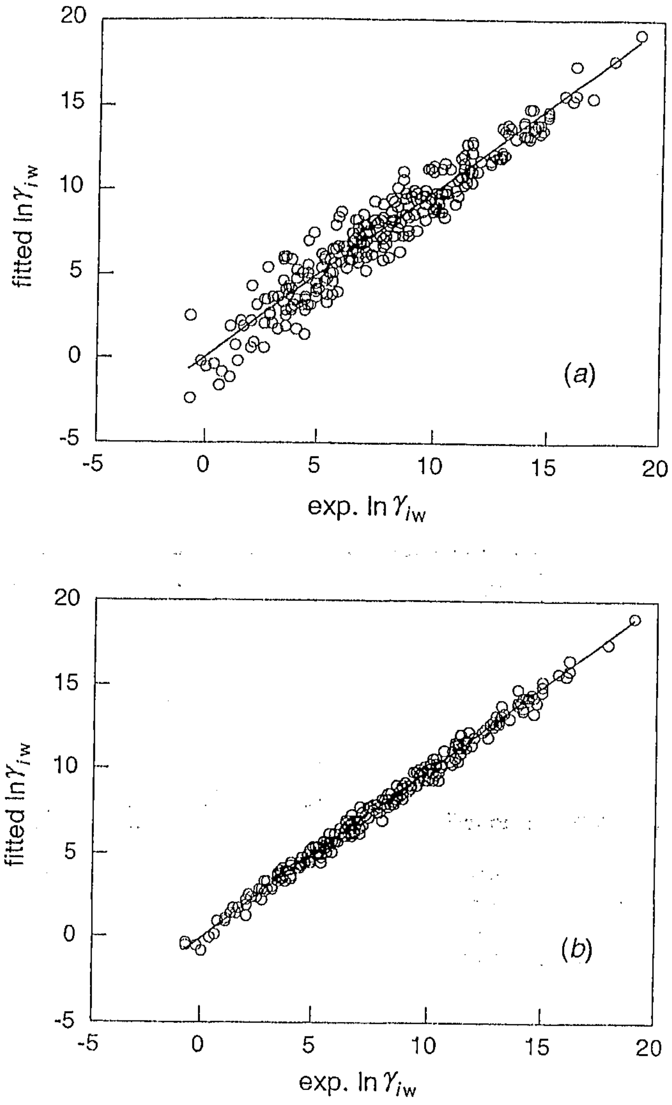


Figure 5.3 Plot of experimental versus fitted $\ln\gamma_{iw}$ values for 266 compounds covering a wide variety of compound classes. *(a)* Fit without using the polarizability parameter π_i (Eq. 5-20). *(b)* Fit including π_i (Eq. 5-21). The fitting parameters for case (*b*) are given in Eq. 5-22.

compound (e.g., Platts et al., 2000), its activity coefficient and therefore also its liquid aqueous solubility (Eqs. 5-7 and 5-12) can be predicted from Eq. 5-22 within a factor of 2 to 3.

It should be noted that when replacing the London dispersive interactions term by other properties such as, for example, the air–hexadecane partition constant, by expressing the surface area in a more sophisticated way, and/or by including additional terms, the predictive capability could still be somewhat improved. From our earlier discussions, we should recall that we do not yet exactly understand all the molecular factors that govern the solvation of organic compounds in water, particularly with respect to the entropic contributions. It is important to realize that for many of the various molecular descriptors that are presently used in the literature to model γ_{iw} or related properties (see Section 5.5), it is not known exactly how they contribute to the excess free energy of the compound in aqueous solution. Therefore, when also considering that some of the descriptors used are correlated to each other (a fact that

Table 5.5 Some Representative π_i Values

Compound or Group of Compounds	π_i [a]	Compound or Group of Compounds	π_i [a]
Alkanes	0.00	1,2,3-Trimethylbenzene	0.61
Cycloalkanes	0.10	1,3,5-Trimethylbenzene	0.52
1-Alkenes	0.08	Naphthalene	0.92
1-Alkines	0.23	Acenaphthene	1.04
Aliphatic ethers (ROR')	0.25	Chlorobenzene	0.65
Aliphatic aldehydes (RCHO)	0.65	1,2-Dichlorobenzene	0.76
Aliphatic ketones (RCOR')	0.68	1,4-Dichlorobenzene	0.75
Aliphatic carboxylic acid esters (RCOOR')	0.55-0.60	1,2,3-Trichlorobenzene	0.86
Aliphatic amines (RNH_2)	0.35	1,3,5-Trichlorobenzene	0.73
Primary aliphatic alcohols ($R\text{-}CH_2OH$)	0.42	1,2,3,4-Tetrachlorobenzene	0.92
Secondary aliphatic alcohols (RR'CHOH)	0.36	1,2,4,5-Tetrachlorobenzene	0.86
Aliphatic carboxylic acids (RCOOH)	0.63	Benzaldehyde	1.00
Trichloromethane	0.49	Benzonitrile	1.11
Tetrachloromethane	0.38	Nitrobenzene	1.11
1,1,2,2-Tetrachloroethane	0.76	Phenol	0.89
Tetrachloroethene	0.42	Alkylphenol	0.80-0.90
Tribromomethane	0.68	2-Chlorophenol	0.88
Benzene	0.52	4-Chlorophenol	1.08
Toluene	0.52	2-Nitrophenol	1.05
1,2-Dimethylbenzene	0.56	4-Nitrophenol	1.72
1,4-Dimethylbenzene	0.52		

[a] Data from Abraham et al. (1994a).

is often not recognized in the literature!), our policy should be to use as few and as *clearly defined* parameters as possible. There is certainly still room for further improvements in this area of research. Nevertheless, as is demonstrated by the examples discussed in Illustrative Example 5.2, Eq. 5-22 is very useful to assess which molecular factors primarily determine the aqueous activity coefficient (or the excess free energy in water) of a given compound.

A very important conclusion that we can draw from our effort to use insights on intermolecular interactions to develop a means to estimate γ_{iw} is that this important compound property is very sensitive to changes in the structure of a compound. Hence, as we will also notice in the following chapters, in any simple structure–property or property–property relationship involving γ_{iw} (or $C_{iw}^{sat}(L)$), we have to be careful to confine a given equation to a set of compounds for which structural differences either are not reflected, or are proportionally reflected in the type of molecular descriptors used in Eq. 5-22. Otherwise, we are in danger of mixing apples with oranges (and grapes!). For example, as already addressed above, it is common practice to try to correlate the aqueous activity coefficient (or the liquid aqueous solubility as in Fig. 5.2) with the size (molar volume, total surface area) of the organic molecule. As is illustrated by Fig. 5.2, good correlations can be expected only for sets of compounds that fulfill the above-mentioned criteria. Fig. 5.2*a* shows, for example, that even sets of quite closely related compounds such as *n*-alkanes and highly branched alkanes, or primary, secondary, and tertiary aliphatic alcohols, exhibit different linear relationships between liquid aqueous solubility and molar volume. In the case of the apolar alkanes (i.e., $\pi_i = \alpha_i = \beta_i = 0$), the differences must be due to the different shapes of the *n*-alkanes as compared to the highly branched ones. In the case of the aliphatic alcohols, the differences between the three sets of compounds can be found primarily in the polar interaction terms of the alcohol moieties. Within each series, however, very good correlations are obtained. Two other examples where quite satisfying correlations are obtained, are shown in Fig. 5.2*b*. The rather good correlation found for the apolar, rigid chlorinated benzenes (i.e., $\alpha_i = \beta_i = 0$) does not come as a surprise, because these compounds exhibit also very similar π_i values (Table 5.5). In the case of the PAHs, however, the correlation does hold only because the polar parameters (i.e., π_i and β_i) increase both with increasing size. Finally, Fig. 5.2*c* shows a group of compounds, the polyhalogenated C_1- and C_2-compounds, for which, intuitively, we might have expected a much better result. A closer inspection of the polar parameters of the various compounds shows, however, that the rather large scatter could have been anticipated. For example, the π_i, α_i and β_i values of the similarly sized 1,1,2,2-tetrachloroethane and tetrachloroethene differ substantially (0.76, 0.16, 0.12 versus 0.42, 0.0, 0.0, respectively), which is reflected in the 20-times-higher liquid aqueous solubility of 1,1,2,2-tetrachloroethane as compared to tetrachloroethene. This example should remind us again that such simple one-parameter correlations work, in general, only for limited sets of "structurally closely related" compounds for which they may, however, be very powerful predictive tools. Obviously, as shown by the examples in Fig. 5.2, it may not always be clear whether two compounds are structurally closely related with respect to the factors that govern their aqueous activity coefficients. In such cases inspection of the type of parameters used in Eq. 5-22 may be very helpful for selecting appropriate reference compounds.

Illustrative Example 5.2 Evaluating the Factors that Govern the Aqueous Activity Coefficient of a Given Compound

Problem

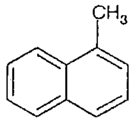
Calculate the activity coefficients as well as the excess free energies of *n*-octane (Oct), 1-methylnaphthalene (1-MeNa), and 4-*t*-butylphenol (4-BuPh) in aqueous solution at 25°C using Eq. 5-22. Compare and discuss the contributions of the various terms in Eq. 5-22.

Answer

n-octane (Oct)

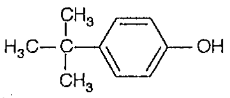
$p^*_{iL} = 1826$ Pa
$V_{ix} = 123.6\ \text{cm}^3\ \text{mol}^{-1}$
$n_{Di} = 1.397$
$\pi_i = \alpha_i = \beta_i = 0$

Get the p^*_{iL} values from the data given in Appendix C. Note that 4-BuPh (T_m = 99°C) is a solid at 25°C (use Eq. 4-40 to estimate p^*_{iL} from p^*_{is}). Calculate V_{ix} using the method described in Box 5.1. Get the n_{Di} values of the compounds from Lide (1995). Use the α_i, and β_i, and π_i values given in Tables 4.3 and 5.5. The resulting data sets for the three compounds are given in the margin. Recall that $G^E_{iw} = RT \ln \gamma_{iw}$. Insertion of the respective values into Eq. 5-22 yields the following result:



1-methyl-naphthalene (1-MeNa)

$p^*_{i\text{L}} = 8.33$ Pa
$V_{ix} = 122.6\ \text{cm}^3\ \text{mol}^{-1}$
$n_{Di} = 1.617$
$\pi_i = 0.90$
$\alpha_i = 0$
$\beta_i = 0.20$



4-*t*-butyl-phenol

$p^*_{i\text{L}} = 6.75$ Pa
$V_{ix} = 133.9\ \text{cm}^3\ \text{mol}^{-1}$
$n_{Di} = 1.517$
$\pi_i = 0.89$
$\alpha_i = 0.56$
$\beta_i = 0.39$

	Oct		1-MeNa		4-BuPh	
Term	$\Delta \ln \gamma_{iw}$ –	(G^E_{iw}) (kJ·mol^{-1})	$\Delta \ln \gamma_{iw}$ –	(G^E_{iw}) (kJ·mol^{-1})	$\Delta \ln \gamma_{iw}$ –	(G^E_{iw}) (kJ·mol^{-1})
$-\ln p^*_{i\text{L}}$	+4.00	(+9.9)	+9.40	(+23.3)	+9.61	(+23.8)
– vdW[a]	–3.42	(–8.5)	–4.94	(–12.2)	–4.53	(–11.2)
$-5.78\ \pi_i$	0		–5.20	(–12.9)	–5.14	(–12.7)
$-8.77\ \alpha_i$	0		0		–4.91	(–12.2)
$-11.12\ \beta_i$	0		–2.22	(– 5.5)	–4.33	(–10.7)
$+0.0472\ V_{ix}$	+5.83	(+14.4)	+5.7	(+14.3)	+6.32	(+15.7)
+ constant	+9.49	(+23.5)	+9.49	(+23.5)	+9.49	(+23.5)
$\ln \gamma_{iw}\ (G^E_{iw})$	15.9	(39.3)	12.2	(30.5)	6.51	(16.2)
exp. value	16.0		12.5		7.15	

[a] dispersive vdW $= 0.572 \left[(V_{ix})^{2/3} \left(\dfrac{n^2_{Di} - 1}{n^2_{Di} + 2} \right) \right]$

First, you note that, although the three compounds are of comparable size, there are significant differences in their γ_{iw} (i.e., G^E_{iw}) values.

As is evident, the lack of any polar interactions with the water molecules is the major cause for the large hydrophobicity of Oct, although this compound exhibits the highest vapor pressure (which facilitates the transfer of Oct from the pure liquid into another phase as compared to the other two compounds). Comparison of 1-MeNa with Oct reveals that the lower activity coefficients (i.e., the higher liquid water solubilities) of aromatic compounds as compared to aliphatic compounds of similar size are primarily due to the relatively large polarizability term (π_i) of aromatic structures. Finally, from comparing 4-BuPh with 1-MeNa it can be seen that H-bond interactions (α_i, β_i-terms) may decrease γ_{iw} by several orders of magnitude (note that for these two compounds, all other terms contribute similarly to the overall γ_{iw}).

5.4 Effect of Temperature and Solution Composition on Aqueous Solubility and Activity Coefficient

So far, we have focused on how differences in molecular structure affect the solubilities and activity coefficients of organic compounds in pure water at 25°C. The next step is to evaluate the influence of some important environmental factors on these properties. In the following we consider three such factors: temperature, ionic strength (i.e., dissolved salts), and organic cosolutes. The influence of pH of the aqueous solution, which is most important for acids and bases, will be discussed in Chapter 8.

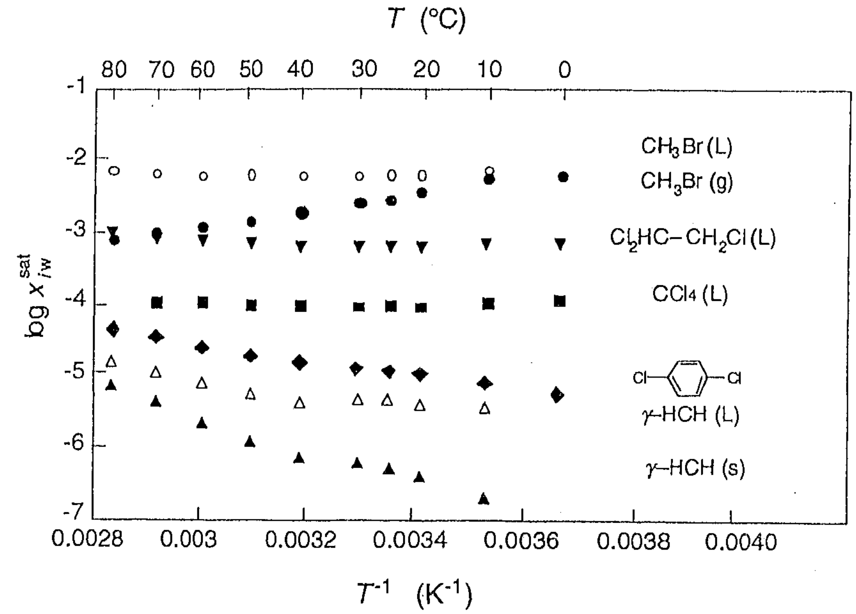


Figure 5.4 Effect of temperature on the mole fraction solubility in water of some halogenated hydrocarbons. γ-HCH is γ-1,2,3,4,5,6-hexachlorocyclohexane (lindane; for structure see Illustrative Example 5.1). Data from Horvath (1982).

Temperature

Let us consider the temperature dependence of the mole fraction solubility of organic *liquids*. Since $x_{iw}^{sat} / x_{iL} \cong x_{iw}^{sat}$ ($x_{iL} \cong 1$) represents the partitioning constant between the aqueous phase and the pure liquid, for a narrow temperature range, its temperature dependence is given by (Section 3.4):

$$\ln x_{iw}^{sat}(L) = -\frac{H_{iw}^{E}}{R} \cdot \frac{1}{T} + \text{constant} \tag{5-23}$$

When expressing aqueous solubility in molar units we may write Eq. 5-23 as:

$$\ln C_{iw}^{sat}(L) = -\frac{H_{iw}^{E}}{R} \cdot \frac{1}{T} + \text{constant}' \tag{5-24}$$

Now constant' = constant –log $\bar{V}_w$ and we assume a temperature-independent molar volume ($\bar{V}_w$) of the aqueous solution (see Section 3.4).

For the majority of the (subcooled) liquid compounds, the excess enthalpy, H_{iw}^{E}, is quite small and may even be negative at 25°C (Table 5.3). Thus, for a temperature range between 0 and 80°C, the change in the liquid solubility with increasing temperature is therefore rather small (Fig. 5.4). For some compounds like CH_3Br(L), $CHCl_2$–CH_2Cl, and CCl_4, a solubility minimum is found at ambient temperatures. This occurs because, at low temperatures, H_{iw}^{E} is negative and, in general, H_{iw}^{E} becomes more positive with increasing temperature [in contrast to $\Delta_{vap}H_i$, which decreases with increasing temperature (see Chapter 4)]. This observation can be explained by the fact that at elevated temperatures, some of the hydrogen bonds among the water molecules forming the hydration shell are broken, which leads to a more positive excess enthalpy. Thus, when applying Eqs. 5-23 or 5-24, we know that H_{iw}^{E}

is not constant over the whole ambient temperature range and we can see some curvature in the plots of $\log x_{iw}^{sat}$ versus $1/T$ (Fig. 5.4). This is, however, not too much of a problem since the temperature effect is small anyway. For most com-pounds x_{iw}^{sat} (L) (or C_{iw}^{sat} (L)) will vary less than a factor of 2 between 0 and 30°C. Only for the larger, rigid, apolar compounds such as PAHs, PCBs, and polychlorinated dibenzodioxines (PCDDs), is the effect of temperature on the liquid aqueous solubility significant [see Illustrative Example 5.3, case (b)].

When we are interested in the actual solubilities of *solids or gases*, however, the effect of temperature becomes much more important (e.g., $CH_3Br(g)$ and γ-HCH(s) in Fig. 5.4). Now we must consider the total enthalpy change when transferring a molecule from the solid or gas phase, respectively, to water. This total enthalpy change includes the sum of the enthalpy of the phase change (i.e., conversion of a solid into a subcooled liquid or a gas into a superheated liquid at the temperature of interest) and the excess enthalpy of solution. Hence, for solids the temperature dependence of solubility over a narrow temperature range is given by:

$$\ln C_{iw}^{sat}(s) = -\frac{\Delta_{fus}H_i + H_{iw}^{E}}{R}\cdot\frac{1}{T} + \text{constant} \qquad (5\text{-}25)$$

and for gases:

$$\ln C_{iw}^{1bar}(g) = -\frac{-\Delta_{vap}H_i + H_{iw}^{E}}{R}\cdot\frac{1}{T} + \text{constant} \qquad (5\text{-}26)$$

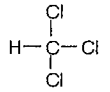
Note that, in general, the resulting enthalpy change will be positive in the case of solids (due to the large positive $\Delta_{fus}H_i$) and negative (dominating positive $\Delta_{vap}H_i$) in the case of gases. Consequently, the solubility of solids increases with increasing temperature, since the "cost" of melting decreases with increasing temperature (and becomes zero at the melting point). Conversely, the difficulty in condensing gaseous organic compounds increases with increasing temperature; thus, heating an aqueous solution tends to diminish solubilities of (organic) gases through this term. Some applications of Eqs. 5-23 to 5-26 are given in the Illustrative Example 5.3.

Illustrative Example 5.3

Evaluating the Effect of Temperature on Aqueous Solubilities and Aqueous Activity Coefficients

Problem

Estimate the solubilities, C_{iw}^{sat}, the activity coefficients, γ_{iw}^{sat}, and the excess enthalpies, H_{iw}^{E}, in water of (a) trichloromethane at 5°C, (b) dibenzofuran at 10°C, and (c) chloroethene (vinyl chloride) at 40°C.



$H-\overset{Cl}{\underset{Cl}{C}}-Cl$

trichoromethane
(chloroform)

$T_m = -63°C$

Answer (a)

Since trichloromethane is a liquid at ambient temperatures, the magnitude of change in its solubility with solution temperature is dictated by its excess enthalpy, H_{iw}^{E} (Eq. 5-23). Generally, for low-molecular-weight compounds, you can expect that H_{iw}^{E} will not be too different from zero (± 10 kJ·mol^{-1}; see Table 5.3). Hence, at 5°C both

C_{iw}^{sat} and γ_{iw}^{sat} should not differ too much from the corresponding values at 25°C. In fact, inspection of the experimental data reported by Horvath (1982) shows that between 0 and 30°C the mole fraction solubility of trichloromethane *decreases*, but only about 20% (see margin). Since H_{iw}^{E} increases with increasing temperature, use only the two x_{iw}^{sat} values given at 0 and 10°C to estimate x_{iw}^{sat} at 5°C (Eq. 5-23):

T / (°C)	$x_{iw}^{\text{sat}\ a}$
0	0.001514
10	0.001366
20	0.001249
25	0.001203
30	0.001168

[a] Data from Horvath (1982).

$$\ln x_{iw}^{\text{sat}} = \frac{799}{T} - 9.418 \qquad (1)$$

Note again that the excess enthalpy of solution of trichloromethane between 0 and 10°C is slightly negative, i.e., $H_{iw}^{\text{E}} = -(799\ \text{K})\,(8.31) = -6.6\ \text{kJ}\cdot\text{mol}^{-1}$.

Insertion of $T = 278.2$ K into Eq. 1 yields $x_{iw}^{\text{sat}}(5°\text{C}) = 0.001436$ or, in molar concentrations (Eq. 3-43):

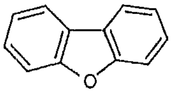
$$C_{iw}^{\text{sat}}(5°\text{C}) = x_{iw}^{\text{sat}} \,/\, \overline{V}_{\text{w}} = (0.001436)\,/\,(0.018) = 8.0 \times 10^{-2}\ \text{mol}\cdot\text{L}^{-1}$$

The aqueous activity coefficient is given by $1 / x_{iw}^{\text{sat}}$ (trichloromethane is a liquid; see Eq. 5.6):

$$\gamma_{iw}^{\text{sat}}(5°\text{C}) = 1\,/\,(0.001436) = 7.0 \times 10^{2}$$

Answer (b)

Dibenzofuran is a solid at ambient temperatures. Hence, the enthalpy of solution ($\Delta_{\text{ws}}H_i$) is given by the sum of the enthalpy of fusion ($\Delta_{\text{fus}}H_i$) and the excess enthalpy in aqueous solution (H_{iw}^{E}) (Fig. 5.1 and Eq. 5-25). In a paper by Shiu et al. (1997) you find aqueous solubility data expressed in $\text{g}\cdot\text{m}^{-3}$ for dibenzofuran at various temperatures (see margin). For simplicity, assume that $\overline{V}_{\text{w}}$ is temperature independent.



dibenzofuran

$M_i = 168.2\ \text{g}\cdot\text{mol}^{-1}$
$T_{\text{m}} = 87°\text{C}$

T / (°C)	$C_{iw}^{\text{sat}\ a}$ / (g·m^{-3})
5	1.92
15	3.04
25	4.75
35	7.56
45	11.7

[a] Data from Shiu et al. (1997).

Calculate $1/T$ in K^{-1} and log C_{iw}^{sat}:

$1/T$ (K^{-1})	0.003597	0.003472	0.003356	0.003247	0.003145
log C_{iw}^{sat} / (g·m^{-3})	0.282	0.483	0.677	0.879	1.069

and perform a least square fit of log C_{iw}^{sat} versus $1/T$:

$$\log C_{iw}^{\text{sat}} / (\text{g}\cdot\text{m}^{-3}) = -\frac{1742}{T} + 6.536 \qquad (2)$$

From the slope one obtains an average $\Delta_{\text{ws}}H_i$ [= (1742) (2.303) (8.31)] value of 33.4 kJ·mol^{-1}. Note that because we use decadic logarithms, the slope in Eq. 2 is equal to $\Delta_{\text{ws}}H_i\,/(2.303)\,R$. Hence, the aqueous solubility increases by about a factor of 1.6 per 10 degrees increase in temperature (Table 3.5). Insertion of $T = 283.2$ K into Eq. 2 yields:

$$\log C_{iw}^{\text{sat}}\ (10°\text{C}) = 0.385 \text{ or } C_{iw}^{\text{sat}}\ (10°\text{C}) = 2.43\ \text{g}\cdot\text{m}^{-3}$$

or, in molar concentrations:

$$C_{iw}^{\text{sat}}\ (10°\text{C}) = \frac{(2.43 \times 10^{-3})}{(168.2)} = 1.44 \times 10^{-5}\ \text{mol} \cdot \text{L}^{-1}$$

To get the activity coefficient, estimate first the aqueous solubility of subcooled liquid dibenzofuran at 283 K (Eq. 5-12). To the end, estimate $\Delta_{\text{fus}}G_i$ at 10°C from T_m using Eq. 4-41:

$$\Delta_{\text{fus}}G_i\ (10°\text{C}) = (56.5 + 0 - 19.2 \log 2)\ (77) = 3.9\ \text{kJ} \cdot \text{mol}^{-1}$$

Insertion into Eq. 5-13 yields

$$C_{iw}^{\text{sat}}\ (\text{L}, 10°\text{C}) = (1.44 \times 10^{-5})\ (5.3) = 7.6 \times 10^{-5}\ \text{mol} \cdot \text{L}^{-1}$$

and thus (Eq. 5-12)

$$\gamma_{iw}^{\text{sat}}\ (10°\text{C}) = 1 / (7.6 \times 10^{-5})\ (0.018) = 7.3 \times 10^{5}$$

To estimate H_{iw}^{E}, assume a constant $\Delta_{\text{fus}}H_i$ below the melting point:

$$\Delta_{\text{fus}}H_i \cong \Delta_{\text{fus}}H_i\ (T_m) = T_m \cdot \Delta_{\text{fus}}S_i\ (T_m)$$

Use Eq. 4-39 to estimate $\Delta_{\text{fus}}S_i\ (T_m)$:

$$\Delta_{\text{fus}}S_i\ (T_m) = (56.5 + 0 - 19.2 \log 2) = 50.8\ \text{J} \cdot \text{mol}^{-1}\ \text{K}^{-1}$$

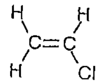
This yields

$$\Delta_{\text{fus}}H_i = (50.8)\ (360) = 18.3\ \text{kJ} \cdot \text{mol}^{-1}$$

and

$$H_{iw}^{\text{E}} = \Delta_{\text{ws}}H_i - \Delta_{\text{fus}}H_i = 33.4 - 18.3 = 15.1\ \text{kJ} \cdot \text{mol}^{-1}$$

Note that this H_{iw}^{E} value represents an average value for the ambient temperature range.



chloroethene
(vinyl chloride)

$T_b = -13.4°\text{C}$

T / (°C)	$x_{iw}^{\text{sat}\ a}$	p_{iL}^{*} / bar ^{a}
0	0.00158	1.70
25	0.000798	3.86
50	0.000410	7.69

[a] Data from Horvath (1982).

Answer (c)

Chloroethene (vinyl chloride) is a gas at the temperature considered. Hence, the enthalpy of solution ($\Delta_{\text{wa}}H_i$) is given by the sum of the enthalpy of condensation ($\Delta_{\text{cond}}H_i$, which is equal to the negative enthalpy of vaporization) and the excess enthalpy in aqueous solution (H_{iw}^{E}) (Fig. 5.1 and Eq. 5-26). Horvath et al. (1982) gives the solubilities of chloroethene at 0°C, 25°C, and 50°C and 1 bar partial pressure. Also given are the vapor pressures of the superheated liquid at these three temperatures.

After conversion of °C to K, perform a least square fit of $\ln\ x_{iw}^{\text{1bar}}$ versus $1 / T$:

$$\ln\ x_{iw}^{\text{1bar}} = +\frac{2375}{T} - 15.134 \qquad (3)$$

From the slope you obtain a $\Delta_{\mathrm{wa}}H_i$ [= − (2375) (8.31)] value of −19.7 kJ·mol^{-1}, meaning that the solubility of chloroethene decreases by about a factor of 1.3 per 10 degrees increase in temperature (Table 3.5). Insertion of T = 313.2 K into Eq. 3 yields x_{iw}^{1bar} (40°C) = 0.000526 or in molar concentration (Eq. 3-43):

$$C_{iw}^{\mathrm{1bar}}\ (40°\mathrm{C}) = 2.9 \times 10^{-2}\ \mathrm{mol \cdot L^{-1}}$$

To get the activity coefficient of chloroethene (Eq. 5-15) calculate its vapor pressure at 40°C using the least square fit of ln p_{iL}^{*} versus 1 / T:

$$\ln\ p_{iL}^{*} / \mathrm{bar} = -\frac{2662}{T} + 10.283 \tag{4}$$

Insertion of T = 313.2 K into Eq. 4 yields a p_{iL}^{*} value of 5.95 bar, which yields a $\gamma_{iw}^{\mathrm{sat}}$ value of (Eq. 5-16):

$$\gamma_{iw}^{\mathrm{1bar}}\ (40°\mathrm{C}) = \frac{1}{(0.000526)} \cdot \frac{1\ \mathrm{bar}}{5.95\ \mathrm{bar}} = 3.2 \times 10^{2}$$

From the slope in Eq. 4 you can obtain $\Delta_{\mathrm{vap}}H_i$ [= (2662) (8.31)] = 22.1 kJ·mol^{-1}. Thus, one obtains an average H_{iw}^{E} value of:

$$H_{iw}^{\mathrm{E}} = \Delta_{\mathrm{wa}}H_i + \Delta_{\mathrm{vap}}H_i = -19.7 + 22.1 = +2.4\ \mathrm{kJ \cdot mol^{-1}}$$

which means that the activity coefficient of chloroethene is more or less constant over the ambient temperature range.

Dissolved Inorganic Salts

When considering saline environments (e.g., seawater, salt lakes, subsurface brines), we have to consider the effects of dissolved inorganic salt(s) on aqueous solubilities and on activity coefficients of organic compounds. Although the number of studies that have been devoted to this topic is rather limited, a few important conclusions can be drawn. Qualitatively, it has been observed that the presence of the predominant inorganic ionic species found in natural waters (i.e., $\mathrm{Na^+}$, $\mathrm{K^+}$, $\mathrm{Mg^{2+}}$, $\mathrm{Ca^{2+}}$, $\mathrm{Cl^-}$, $\mathrm{HCO_3^-}$, $\mathrm{SO_4^{2-}}$) generally decrease the aqueous solubility (or increase the aqueous activity coefficient) of nonpolar or weakly polar organic compounds. Furthermore, it has been found that the magnitude of this effect, which is commonly referred to as *salting-out*, depends on the compound and on the type of ions present.

Long ago, Setschenow (1889) established an *empirical* formula relating organic compound solubilities in saline aqueous solutions ($C_{iw,\mathrm{salt}}^{\mathrm{sat}}$) to those in pure water (C_{iw}^{sat}):

$$\log\left(\frac{C_{iw}^{\mathrm{sat}}}{C_{iw,\mathrm{salt}}^{\mathrm{sat}}}\right) = K_i^{\mathrm{s}}[\mathrm{salt}]_{\mathrm{tot}}$$

or: (5-27)

$$C_{iw,\mathrm{salt}}^{\mathrm{sat}} = C_{iw}^{\mathrm{sat}} \cdot 10^{-K_i^{\mathrm{s}}[\mathrm{salt}]_{\mathrm{tot}}}$$

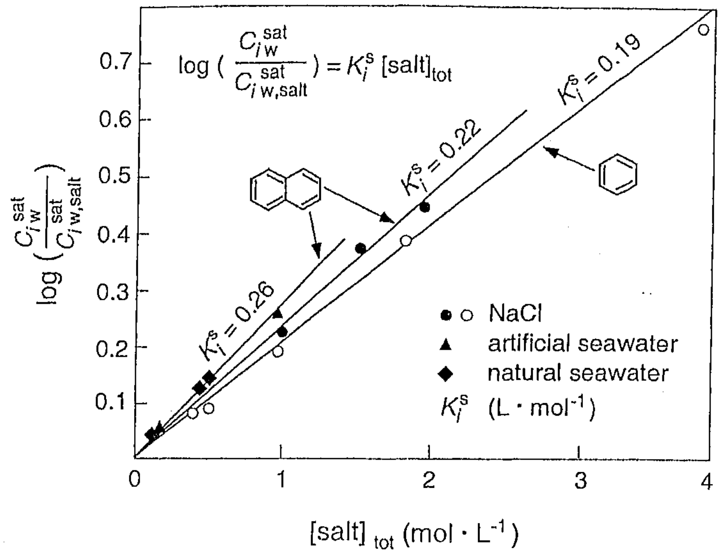


Figure 5.5 Effect of salt concentrations on the aqueous solubility of benzene (McDevit and Long, 1952), and naphthalene (Gordon and Thorne, 1967a).

where $[\text{salt}]_{tot}$ is the total *molar* salt concentration and K_i^s is the *Setschenow* or *salting constant* (unit M^{-1}). This salting constant relates the effectiveness of a particular salt or combination of salts to the change in solubility of a given compound *i*. For a particular salt (e.g., NaCl) or salt mixture (e.g., seawater; for composition see Table 5.6), Eq. 5-27 is valid over a wide range of salt concentrations (Fig. 5.5). Note that the "salting-out" effect increases exponentially with increasing salt concentration. K_i^s-values for a given organic solute and salt composition can be determined experimentally by linear regression of experimental solubilities measured at various salt concentrations (i.e., plots of log C_{iw}^{sat} versus $[\text{salt}]_{tot}$). We should point out that at very high salt concentrations, the effect of the dissolved salts on the molar volume of the solution has to be taken into account. However, as a first approximation, in many cases (e.g., seawater) we may neglect the effect. Written in terms of activity coefficients, Eq. 5-27 is:

$$\gamma_{iw,\text{salt}} = \gamma_{iw} \cdot 10^{+K_i^s [\text{salt}]_{tot}} \qquad (5\text{-}28)$$

Hence $\gamma_{iw,\text{salt}}$ increases exponentially with increasing salt concentration.

Note that if K_i^s has been determined from solubility measurements, $\gamma_{iw,\text{salt}}$ is strictly valid only for saturated conditions. For dilute solutions $\gamma_{iw,\text{salt}}$ can be determined from measurements of air–water or organic solvent–water partition constants at different salt concentrations. From the few compounds for which $\gamma_{iw,\text{salt}}$ has been determined by both solubility and air–water or solvent–water partitioning experiments, because of the large scatter in the data, it is not clear whether K_i^s varies with organic solute concentration. It can, however, be concluded that, if there is an effect, it is not very large.

Before we inspect K_i^s values of a variety of organic compounds for seawater (the most important natural saline environment), we first take a look at the salting-out efficiencies of various ion combinations. Since it is very difficult to quantify the contribution of individual ions, salting constants are available only for combined salts. Nevertheless, the data in Table 5.6 illustrate that smaller ions that form

Table 5.6 Salt Composition of Seawater and Salting Constants for Benzene, Naphthalene, and 1-Naphthol at 25°C for Some Important Salts

	Mole fraction in seawater[b]		Salting constant[a]		
Salt	Weight ($g \cdot mol^{-1}$)	x_{salt}	K_i^s (benzene) ($L \cdot mol^{-1}$)	K_i^s (naphthalene) ($L \cdot mol^{-1}$)	K_i^s (1–naphthol) ($L \cdot mol^{-1}$)
NaCl	58.5	0.799	0.19	0.22	0.21
$MgCl_2$	95.3	0.104		0.30	0.33
Na_2SO_4	142.0	0.055	0.53	0.72	
$CaCl_2$	110.0	0.020		0.32	0.35
KCl	74.5	0.017	0.16	0.19	0.18
$NaHCO_3$	84.0	0.005		0.32	
KBr				0.13	0.13
CsBr				0.01	
$(CH_3)_4NCl$					–0.36
$(CH_3)_4NBr$			–0.15		

[a] Data from McDevit and Long (1952), Gordon and Thorne (1967a,b), Almeida et al. (1983), and Sanemasa et al, (1984). [b] Gordon and Thorne (1967a,b).

hydration shells with more water molecules (e.g., Na^+, Mg^{2+}, Ca^{2+}, Cl^-) have a bigger effect than larger ions that tend to bind water molecules only very weakly (e.g., Cs^+, $N(CH_3)_4^+$, Br^-). In fact, larger organic ions such as tetramethyl-ammonium ($N(CH_3)_4^+$) can even have an opposite effect; that is, they promote solubility (or decrease the activity coefficient). Note that such *salting-in* effects can also be observed for very polar compounds that may strongly interact with certain ions (Almeida et al., 1984). In a simple way, we can rationalize the salting-out of nonpolar and weakly polar compounds by imagining that the dissolved ions compete (successfully) with the organic compound for solvent molecules. Many of the environmentally relevant ions bind water molecules quite tightly in aqueous solution, which can be seen even macroscopically in that the volume of the aqueous solution is reduced. As a consequence, the freedom of some water molecules to solvate an organic molecule is disrupted, and depending on the type of salt and/or compound present, may lead to a loss or gain in solubility (Leberman and Soper, 1995). Furthermore, the solvation of an organic compound, particularly when it is large and nonpolar, requires a large number of water molecules. Hence, we may intuitively anticipate that larger nonpolar organic compounds will exhibit higher K_i^s values as compared to smaller and/or more polar compounds.

Let us now inspect the K_i^s values of some organic compounds in seawater. Using the data given in Table 5.6 we can make our own artificial seawater (at least with respect to the major ion composition) by dissolving an appropriate amount of the corresponding salts in water. The weight of 1 mole of "seawater salt" is given by $(0.799)(58.5) + (0.104)(95.3) + (0.055)(142) + (0.02)(110) + (0.017)(74.5) + (0.005)(84) = 68.35$ g. Hence, if we dissolve 34.17 g of seawater-salt in 1 L, we obtain a seawater with a salinity of 34.2‰, which corresponds to a total molar salt concentration ($[\text{salt}]_{\text{tot}}$ in Eq. 5-27) of 0.5 M. As has been demonstrated by various studies, the differences between K_i^s values determined in artificial and real seawater are usually only marginal. Furthermore, since seawater is dominated by one salt, that is, NaCl (Table 5.6), as a first approximation K_i^s values determined for sodium chloride can be used as a surrogate. Let us illustrate this by calculating $K_{i,\text{seawater}}^s$ for naphthalene using the data given in Table 5.6. If we assume that naphthalene does not specifically interact with any of the inorganic ions present, we may estimate $K_{i,\text{seawater}}^s$ by summing up the contributions of the various salts present (Gordon and Thorne, 1967a,b):

$$K_{i,\text{seawater}}^s \cong \sum_k K_{i,\text{salt}\,k}^s \cdot x_k \tag{5-29}$$

where x_k is the mole fraction and $K_{i,\text{salt}\,k}^s$ is the salting constant of salt k in the mixture. For naphthalene we then obtain (Table 5.6):

$$K_{i,\text{seawater}}^s = (0.799)\,(0.22\ \text{M}^{-1}) + (0.104)\,(0.30\ \text{M}^{-1}) + (0.055)\,(0.72\ \text{M}^{-1}) + (0.02)\,(0.32\ \text{M}^{-1}) + (0.01)\,(0.19\ \text{M}^{-1}) + (0.005)\,(0.32\ \text{M}^{-1}) = 0.26\ \text{M}^{-1}$$

which compares very favorably with the experimental value for seawater (average value 0.27 M^{-1}). The K_i^s value of naphthalene for NaCl is 0.22 M^{-1}. Hence, the contribution of the other salts is only 0.04. With insertion of the two K_i^s values into Eq. 5-28 and assuming a $[\text{salt}]_{\text{tot}} = 0.5$ M (typical seawater), we obtain $\gamma_{iw,\text{salt}} / \gamma_{iw}$ ratios of 1.66 for $K_i^s = 0.22$ and 1.84 for $K_i^s = 0.265$, respectively. In general, the error introduced when using $K_{i,\text{NaCl}}^s$ instead of $K_{i,\text{seawater}}^s$ is only in the order of 10%, which is often well within the experimental error of K_i^s measurements. Therefore, in the data set given in Table 5.7, some K_i^s values determined for NaCl have been included. Some more data can be found in the review by Xie et al. (1997).

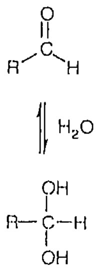
A few general comments on the data given in Table 5.7 are necessary. First, where available, average K_i^s values taken from different studies are reported. The ranges indicated for these values show that in general, one has to expect rather large uncertainties (i.e., up to ± 20%) in the reported K_i^s values. Furthermore, it should also be noted that Table 5.7 contains values determined from solubility as well as from partitioning (i.e., air–water, organic solvent–water) experiments. Finally, the results of the few studies in which the effect of temperature on salting-out has been investigated (Whitehouse, 1984; Zhou and Mopper, 1990; Dewulf et al., 1995; Alaee et al., 1996) suggest that K_i^s increases somewhat with decreasing temperature. Unfortunately, due to the relatively large scatter in the data, no quantitative relationship can be derived. As a first approximation, the data given in Table 5.7 should, however, also be applicable at temperatures other than 25°C.

Inspection of Table 5.7 shows that our conclusion drawn above from our simple picture of the salting effect, which is that smaller and/or polar compounds should exhibit smaller K_i^s values as compared to larger, nonpolar compounds, is more or less confirmed by the experimental data. When considering the rather limited experimental data set, and the relatively large uncertainty in the data, it is, however, presently not feasible to derive any reliable quantitative relationship using molecular descriptors that would allow prediction of K_i^s values of other compounds. One

Table 5.7 Salting Constants for Some Organic Compounds for Seawater

Compound	K_i^s (L·mol^{-1})	Compound	K_i^s (L·mol^{-1})
Halogenated C_1- and C_2-Compounds [a,b,c,d]		*Substituted Benzenes and Phenols* [b,d,e,f,h]	
Trichloromethane	0.2	Benzene	0.20 (±0.02)
Tetrachloromethane	0.2	Toluene	0.24 (±0.03)
Methylbromide	0.15	Ethylbenzene	0.29 (±0.02)
Dichlorodifluoromethane	0.29	1,2-Dimethylbenzene	0.30
Trichlorofluoromethane	0.30	1,3-Dimethylbenzene	0.29
1,1-Dichloroethane	0.2	1,4-Dimethylbenzene	0.30
1,2-Dichloroethane	0.2	*n*-Propylbenzene (NaCl)	0.28
1,1,1-Trichloroethane	0.25	Chlorobenzene (NaCl)	0.23
Trichloroethene	0.21 (±0.01)	1,4-Dichlorobenzene (NaCl)	0.27
Tetrachloroethene	0.24 (±0.02)	Benzaldehyde	0.20 (±0.04)
		Phenol	0.13 (±0.02)
Miscellaneous Aliphatic Compounds [e,f]		2-Nitrophenol	0.13 (±0.01)
Pentane (NaCl)	0.22	3-Nitrophenol	0.15
Hexane (NaCl)	0.28	4-Nitrophenol	0.17
1-Butanal	0.3	4-Nitrotoluene	0.16
1-Pentanal	0.3	4-Aminotoluene	0.17
1-Hexanal	0.4		
1-Heptanal	0.5	*Polycyclic Aromatic Compounds* [e,h,i,j,k,l]	
1-Octanal	0.6	Naphthalene	0.28 (±0.04)
1-Nonanal	~ 1.0	Fluorene (NaCl)	0.27
1-Decanal	~ 1.0	Phenanthrene	0.30 (±0.03)
Dimethylsulfide	0.17	Anthracene	0.30 (±0.02)
2-Butanone	0.20	Fluoranthene (NaCl)	0.34
		Pyrene	0.30 (±0.02)
PCBs [e,g]		Chrysene (NaCl)	0.34
Biphenyl	0.32 (±0.05)	Benzo[a]pyrene	0.34
Various PCBs (dichloro to hexachloro)	0.3–0.4	Benzo[a]anthracene (NaCl)	0.35
		1-Naphthol (NaCl)	0.23

[a] Warner and Weiss (1995). [b] Dewulf et al. (1995). [c] DeBruyn and Saltzman (1997). [d] Peng and Wang (1998). [e] Sanemasa et al. (1984). [f] Zhou and Mopper (1990). [g] Brownawell (1986). [h] Hashimoto et al. (1984). [i] Eganhouse and Calder (1975). [j] Whitehouse (1984). [k] Gordon and Thorne (1967b). [l] Almeida et al. (1983).



a geminal diol

class of compounds that does not quite fit the qualitative picture is the *n*-alkanals (Table 5.7). One possible cause for the unexpectedly high salting constants of these compounds is their tendency to form diols in aqueous solution (Bell and McDougall, 1960). For example, acetaldehyde (R = CH_3, see margin) forms about 50% diol in pure water. If, in saltwater, the aldehyde/diol ratio is changed in favor of the aldehyde, one would expect a stronger salting-out effect, because it can be assumed that the diol form is more easily accommodated in water as compared to the aldehyde form. An additional reason for the large K_i^s values of the larger-chain aldehydes could be the fact that the effect of salt on the activity coefficients of flexible molecules is larger than the effect on the more rigid compounds. However, there are presently no reliable data available to verify this hypothesis.

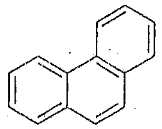
In summary, we can conclude that at moderate salt concentrations typical for seawater (~ 0.5 M), salinity will affect aqueous solubility (or the aqueous activity coefficient) by a factor of between less than 1.5 (small and/or polar compounds) and about 3 (large, nonpolar compounds, *n*-alkanals). Hence, in marine environments for many compounds, salting-out will not be a major factor in determining their partitioning behavior. Note, however, that in environments exhibiting much higher salt concentrations [e.g., in the Dead Sea (5 M) or in subsurface brines near oil fields], because of the exponential relationship (Eq. 5-28), salting-out will be substantial (see also Illustrative Example 5.4).

Illustrative Example 5.4

Quantifying the Effect of Inorganic Salts on Aqueous Solubility and Aqueous Activity Coefficients

Problem

Estimate the solubility and the activity coefficient of phenanthrene in (a) seawater at 25°C and 30‰ salinity, and (b) a salt solution containing 117 g NaCl per liter water.



i = phenanthrene

C_{iw}^{sat} (25°C) $= 6.3 \times 10^{-6}$ mol $\cdot$ L^{-1}
$T_m = 101$°C
γ_{iw}^{sat} (25°C) $= 2.0 \times 10^{6}$
(see Table 5.2)

Answer (a)

At 25°C phenanthrene is a solid. Because the free energy contributions of phase change (i.e., melting, or condensation in the case of a gas) to the overall free energy of solution are not affected by salts in the solution, it is the aqueous activity coefficient that is increased as salt concentration increases (Eq. 5-28). Hence, the actual solubility C_{iw}^{sat} decreases by the same factor (Eq. 5-27). The K_i^s value of phenanthrene is 0.30 M^{-1} (Table 5.7). Since 34.2‰ salinity corresponds to a total salt concentration of 0.5 M (see text), [salt]$_{tot}$ for 30‰ is equal to 0.44 M. Insertion of these values into Eq. 5-28 yields:

$$\gamma_{iw}^{sat} \cdot 10^{+(0.30)\,(0.44)} = (1.34)\,\gamma_{iw}^{sat} = 2.7 \times 10^{6}$$

The aqueous solubility in 30‰ seawater is then given by:

$$C_{iw,salt}^{sat} = C_{iw}^{sat} \,/\, (1.34) = 4.7 \times 10^{-6} \ \mathrm{mol \cdot L^{-1}}$$

Hence, in 30‰ seawater γ_{iw}^{sat} increases (C_{iw}^{sat} decreases) by about 30% as compared to pure water.

Answer (b)

Use the K_i^s value given for seawater as a surrogate for the NaCl solution. 117 g NaCl per liter correspond to a molar concentration of 2 M. Thus:

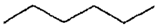
$$\gamma_{iw,NaCl}^{sat} = \gamma_{iw}^{sat} \cdot 10^{+(0.30)(2.0)} = (4.0)\,\gamma_{iw}^{sat} = 8.0 \times 10^{6}$$

and

$$C_{iw,salt}^{sat} = 1.6 \times 10^{-6} \ \mathrm{mol \cdot L^{-1}}$$

Problem

At oil exploitation facilities it is common practice to add salt to the wastewater in order to decrease the solubility of the oil components, although in the wastewater treatment one then has to cope with a salt problem. Calculate how much NaCl you have to add to 1 m^3 of water in order to increase the activity coefficient of *n*-hexane by a factor of ten. How much Na_2SO_4 would be required to do the same job?



$i = n$ - hexane

Answer

In order to increase the activity coefficient of a given compound by a factor of ten, the exponent in Eq. 5-28 has to be equal to 1:

$$K_i^s\,[\text{salt}]_{\text{tot}} = 1$$

The K_i^s value for hexane for NaCl is 0.28 M^{-1} (Table 5.7). Then a total salt concentration $[\text{salt}]_{\text{tot}} = 1 / 0.28\ M^{-1} = 3.57$ M is needed, which corresponds to an amount of *208.8* $kg \cdot m^{-3}$.

For estimating the amount of Na_2SO_4 required, assume a similar relative K_i^s value (relative to NaCl) as determined for benzene (i.e., 0.53 M^{-1} for Na_2SO_4 versus 0.19 M^{-1} for NaCl, see Table 5.6):

$$K_i^s\,(\text{hexane}, Na_2SO_4) = (0.28)\,(0.53) / (0.19) = 0.78\ M^{-1}$$

Thus in the case of Na_2SO_4, the required $[\text{salt}]_{\text{tot}}$ is 1 / 0.78 M^{-1} = *1.28* M or *181.8* $kg \cdot m^{-3}$, which is about the same amount as the NaCl needed although, on a molar base, Na_2SO_4 is much more potent as a salting-out agent.

Advanced Topic

Organic Cosolvents

So far we have considered only situations in which a given organic compound was present as the sole *organic* solute in an aqueous solution. Of course, in reality, in any environmentally relevant aquatic system there will be numerous other natural and/or anthropogenic organic chemicals present that may or may not affect the solubility or, even more important, the activity coefficient of the compound of interest to us. We will treat this issue of organic cosolutes in Chapter 7 when discussing the organic phase–water partitioning of organic compounds present in complex mixtures (e.g., gasoline, oil, PCBs). In this section we will focus on the effect of highly water-soluble organic compounds (i.e., *organic cosolvents*) that *may completely change the solvation properties* of an "aqueous" phase. We may encounter such situations in industrial waste waters or at waste disposal sites where, because of careless dumping procedures, leachates may contain a high portion of organic solvent(s). Furthermore, one of the remediation techniques for contaminated soils is to "wash" the soil with mixtures of water and water-miscible cosolvents (Li et al., 1996). Finally, from an analytical point of view, knowledge of how cosolvents influence the activity coefficient of a given organic compound in organic solvent–water mixtures is pivotal for choosing appropriate mobile phases in reversed-phase liquid chromatography.

Let us start with some comments on the experimental data available on effects of cosolvents on the aqueous solubility and aqueous activity coefficient of organic pollutants. First we should point out that the majority of the systematic studies on this topic have focused on the effects of *completely water-miscible organic solvents* (CMOSs, e.g., methanol, ethanol, propanol, acetone, dioxane, acetonitrile, dimethylsulfoxide, dimethylformamide, glycerol, and many more) and on the *solubility* of sparingly soluble organic *solids*. A large portion of the available data has been collected for drugs and has been published in the pharmaceutical literature. With respect to environmentally more relevant compounds, most investigations have been confined to PAHs (Morris et al., 1988; Dickhut et al., 1989; Li et al., 1996; Fan and Jafvert, 1997) and PCBs (Li and Andren, 1994). Few studies have investigated the impact of CMOSs on the solubility (Groves, 1988) or on the activity coefficient in dilute solution (Munz and Roberts, 1986; Jayasinghe et al., 1992) of *liquid* organic compounds. Note that solubility experiments involving organic liquids are more difficult to interpret because of the partitioning of the cosolvent(s) into the liquid organic phase, which may lead to significant changes in its composition (Groves, 1988). In certain cases, the composition of the liquid phase may even affect the crystal structure of a solid compound, thus complicating the interpretation of solubility data (Khossravi and Connors, 1992). Finally, only very limited data are available on the effect of *partially miscible organic solvents* (PMOSs, e.g., *n*-alcohols ($n > 3$), ethers, halogenated C_1- and C_2-compounds, substituted benzenes) on the aqueous solubility or aqueous activity coefficient of organic pollutants in the presence (Pinal et al., 1990 and 1991) or in the absence (Li and Andren, 1994; Coyle et al., 1997) of a CMOS. Thus, our following discussion will be devoted primarily to water–CMOS systems.

Let us first look at some qualitative aspects of how CMOSs affect the activity coefficient, and thus the solubility and partitioning behavior, of a given organic compound when present in a water/CMOS mixture. The following general conclusions are illustrated by the examples given in Figs. 5.6 to 5.8 and in Table 5.8.

First, we point out that, in general, the activity coefficient of an organic solute, $\gamma_{i\ell}$, decreases (i.e., solubility increases) in an *exponential way* with increasing volume fraction of CMOS. (Note that we use the subscript ℓ to denote that we are dealing with a liquid solution, and, in the following, we do not distinguish between $\gamma_{i\ell}$ values at saturated and dilute solutions.) Second, a significant effect (i.e., > factor 2) is observed only at cosolvent volume fractions greater than 5 to 10% (depending on the solvent). Below 1%, the effect can more or less be neglected (see below). Hence, when conducting experiments, we do not have to worry about significant changes in the activities of organic solutes in an aqueous phase when adding a small amount of a CMOS, as is, for example, common practice when spiking an aqueous solution with a sparingly soluble organic compound dissolved in an organic solvent. Third, the magnitude of the cosolvent effect, as well as its dependence on the amount of cosolvent present, is a function of both the type of cosolvent (Fig. 5.7, Table 5.8) and the type of organic solute (Figs. 5.6 and 5.8) considered. For example, the activity coefficient (or the mole fraction solubility) of naphthalene decreases (increases) by a factor of about 15 when going from pure water to a 40% methanol/60% water mixture, while the effect is about 3 times smaller or 20 times larger when glycerol or acetone, respectively, are the cosolvents (Table 5.8). Furthermore, as can be seen from Fig. 5.8, in 20% methanol/80% water (volume

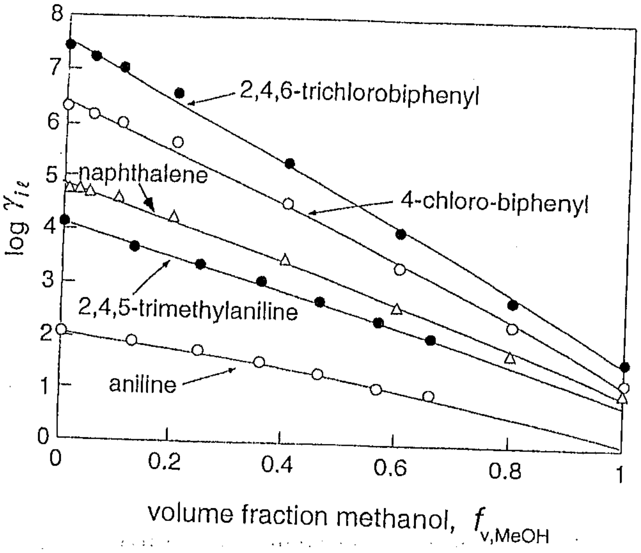


Figure 5.6 Illustration of the effect of a completely water-miscible solvent (CMOS, i.e., methanol) on the activity coefficient of organic compounds in water–organic solvent mixtures: decadic logarithm of the activity coefficient as a function of the volume fraction of methanol. Note that the data for naphthalene (Dickhut et al., 1989; Fan and Jafvert, 1997) and for the two PCBs (Li and Andren, 1994) have been derived from solubility measurements; whereas for the anilins (Jayasinghe et al., 1992), air–water partition constants determined under dilute conditions have been used to calculate $\gamma_{i\ell}$.

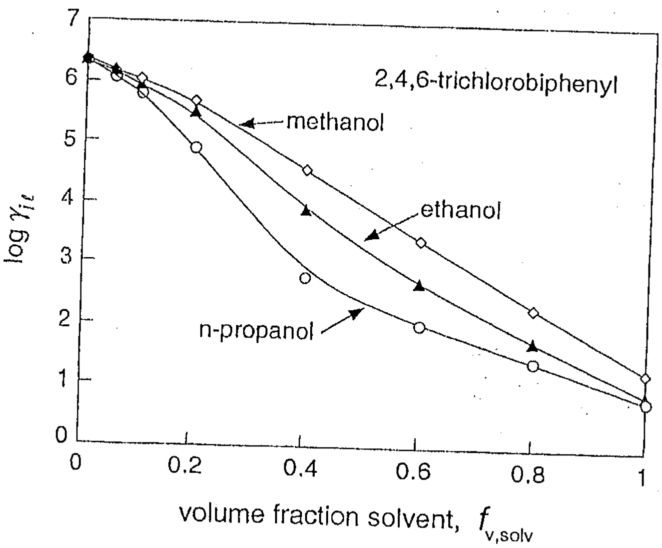


Figure 5.7 Effect of three different CMOSs (i.e., methanol, ethanol, propanol) on the activity coefficient of 2,4,6-trichlorobiphenyl. Data from Li and Andren (1994).

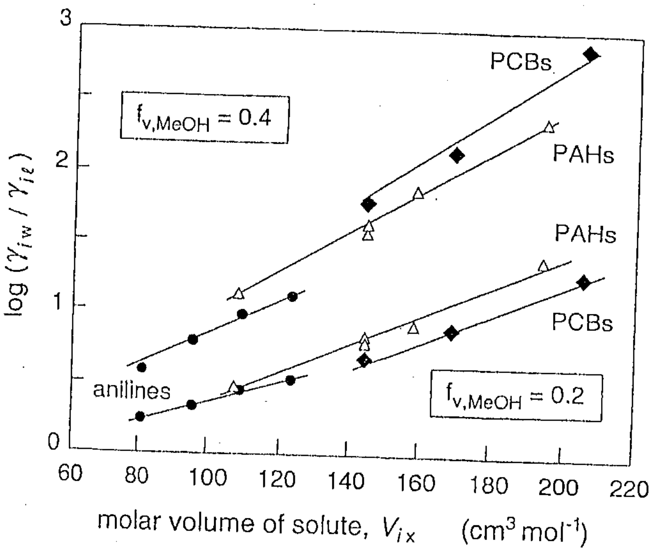


Figure 5.8 Ratio of the activity coefficient in water (γ_{iw}) and in methanol/water [20% (v : v) and 40% (v : v) methanol] as a function of the molar volume (V_{ix}, see Box 5.1) of the solute: $\log(\gamma_{iw}^{sat} / \gamma_{i\ell}^{sat}) = a \cdot V_{ix} + b$. The three compound classes include the following compounds:

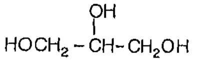
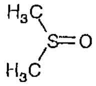
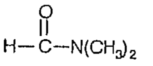
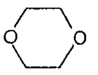
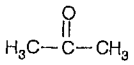
Anilines: aniline, 4-methyl-aniline, 3,4-dimethyl-aniline, 2,4,5-trimethyl-aniline; $f_{v,MeOH} = 0.2$: $a = 0.00700$, $b = -0.309$; $f_{v,MeOH} = 0.4$: $a = 0.0128$, $b = -0.432$.

PAHs: naphthalene, anthracene, phenanthrene, pyrene, perylene; $f_{v,MeOH} = 0.2$: $a = 0.0104$, $b = -0.668$; $f_{v,MeOH} = 0.4$: $a = 0.0147$, $b = -0.469$.

PCBs: 4-chlorobiphenyl, 2,4,6-trichlorobiphenyl, 2,2',4,4',6,6'-hexachlorobipheny; $f_{v,MeOH} = 0.2$: $a = 0.0955$, $b = -0.704$; $f_{v,MeOH} = 0.4$: $a = 0.0180$, $b = -0.848$.

Data from Morris et al. (1988), Jayasinghe et al. (1992), Li and Andren (1994), Fan and Jafvert (1997).

Table 5.8 Effect of Various CMOSs on the Activity Coefficient or Mole Fraction Solubility, Respectively, of Naphthalene at Two Different Solvent/Water Ratios ($f_{v,solv}$ = 0.2 and 0.4)

			Naphthalene[a] $\gamma_{iw}^{sat} / \gamma_{i\ell}^{sat} = x_{i\ell}^{sat} / x_{iw}^{sat}$	
Cosolvent	Structure	Solubility[b] Parameter $(\mathrm{M\,Pa})^{1/2}$	$f_{v,solv} = 0.2$ (σ_i^c)[c]	$f_{v,solv} = 0.4$
Glycerol	 $HOCH_2-CH(OH)-CH_2OH$	36.2	2.5 (2.0)	5.5
Ethyleneglycol	$HOCH_2-CH_2OH$	34.9	3 (2.4)	9
Methanol	CH_3OH	29.7	3.5 (2.7)	14
Dimethylsulfoxide (DMSO)		26.7	5.5 (3.7)	3.6
Ethanol	H_3CCH_2OH	26.1	7 (4.2)	48
Propanol	$H_3CCH_2CH_2OH$	24.9	17 (6.2)	180
Acetonitrile	$H_3C-C{\equiv}N$	24.8	14 (5.7)	140
Dimethylformamide	 $H-C(=O)-N(CH_3)_2$	24.8	15 (5.9)	130
1,4-Dioxane		20.7	14 (5.7)	180
Acetone	 $H_3C-C(=O)-CH_3$	19.7	20 (6.5)	270

[a] Data from Dickhut et al. (1989), Li et al. (1996), and Fan and Jafvert (1997). [b] Hildebrand solubility parameter taken from Barton (1991). The parameter is defined as the square root of the ratio of the enthalpy of vaporization and the molar volume of the liquid. [c] Cosolvency power for the range 0 < $f_{v,solv}$ < 0.2; see Eq. 5-30.

fractional methanol, $f_{v,MeOH} = 0.2$) the activity coefficients of aniline ($V_{ix} = 82\ \mathrm{cm^3\,mol^{-1}}$) and 2,2',4,4',6,6'-hexachlorobiphenyl ($V_{ix} = 206\ \mathrm{cm^3\,mol^{-1}}$) are smaller by a factor of about 2 and 20, respectively, as compared to pure water, while at 40% methanol/60% water ($f_{v,MeOH} = 0.4$) the corresponding factors are 4 and 750, respectively. In general, we may assume that for a given cosolvent–water system, the effect of the cosolvent on $\gamma_{i\ell}$ will be larger for large, nonpolar solutes that are only sparingly soluble in water (e.g., PCBs, PAHs) as compared to more polar, small molecules (e.g., aniline) exhibiting higher water solubilities. Finally, with respect to the "cosolvency-power" of CMOSs, we can see from Table 5.8 that, qualitatively, the more "water-like" solvents such as glycerol, ethylene glycol, or methanol, have a much smaller impact on the activity coefficient of an organic solute as compared to organic solvents for which hydrogen bonding is important, but not the overall dominating factor. Note that the (Hildebrand) solubility parameter given in Table 5.8 (see footnote for explanation) is a measure of the cohesive forces among the molecules in the pure solvent. As can be seen, qualitatively, there is a trend that solvents exhibiting higher cohesive forces in their pure liquid tend to have a smaller cosolvent effect when mixed with water.

Before we address cosolvency in a more quantitative way, it is useful to try to picture how a cosolvent affects the solvation of an organic solute on a molecular level. From the examples given in Table 5.8 we can see that CMOSs are relatively small molecules with strong H-acceptor and/or H-donor properties. When mixed with water, they are, therefore, able to break up some of the hydrogen bonds between the water molecules and thus form a new H-bonded "mixed solvent" that will change its property in a rather complex way as a function of the nature and of the relative amount of the cosolvent. As we have seen in Section 5.3, for smaller and/or more polar organic compounds, the excess free energy in pure aqueous solution is dominated by the entropic contribution. Only for larger, particularly for nonpolar solutes, is the enthalpy term also significant (Table 5.3). Hence, it is reasonable to assume and is supported by experimental data (e.g., Bustamante et al., 1998) that in water-rich mixtures (i.e., $f_{\mathrm{v,\,solv}} < 0.5$), the observed decrease in excess free energy (increase in solubility) of organic compounds with increasing CMOS/water ratio is primarily due to a substantial increase in the excess entropy, which may even compensate possible increases in excess enthalpy. Since these changes in excess enthalpy and entropy with changing cosolvent–water composition are, in general, not linearly correlated with each other, a nonlinear relationship between excess free energy (or log $\gamma_{i\ell}$) and $f_{\mathrm{v,solv}}$ can be expected and, as illustrated by Fig. 5.7, is actually found for many organic solute/CMOS/water systems.

Considering the rather complex factors that determine the excess free energy of an organic solute in a CMOS/water mixture, it is not too surprising that any quantitative models developed for describing cosolvent effects have only rather limited predictive capabilities. The models are, however, quite well suited for fitting experimental data, and for estimating activity coefficients of structurally closely related compounds in a given CMOS/water system for which experimental data are available.

For a discussion of the various approaches taken to quantify cosolvent effects we refer to the literature (e.g., Li and Andren, 1995; Li et al., 1996; Fan and Jafvert, 1997). For our purpose here, we adopt the most simple empirical approach where we assume a *log-linear* relationship between activity coefficient (or mole fraction solubility) of a given compound and volume fraction of the CMOS over a narrow $f_{\mathrm{v,solv}}$-range (i.e., $\Delta f_{\mathrm{v,solv}} = 0.2$) confined by $f^1_{\mathrm{v,solv}}$ and $f^2_{\mathrm{v,solv}}$. Hence, for a given organic solute i and a given CMOS/water system, we get (note that we omit the subscript "solv" to indicate the CMOS):

$$\log \gamma_{i\ell}(f_{\mathrm{v}}) = \log \gamma_{i\ell}\,(f^1_{\mathrm{v}}) - \sigma^{\mathrm{c}}_i \cdot (f_{\mathrm{v}} - f^1_{\mathrm{v}}) \qquad (5\text{-}30)$$

or:

$$\log x^{\mathrm{sat}}_{i\ell}(f_{\mathrm{v}}) = \log x^{\mathrm{sat}}_{i\ell}\,(f^1_{\mathrm{v}}) + \sigma^{\mathrm{c}}_i \cdot (f_{\mathrm{v}} - f^1_{\mathrm{v}}) \qquad (5\text{-}31)$$

where the slope σ^{c}_i, which is dependent on both the solute and the cosolvent, is given by $[\log \gamma_{i\ell}\,(f^1_{\mathrm{v}}) - \log \gamma_{i\ell}\,(f^2_{\mathrm{v}})]\,/\,(f^2_{\mathrm{v}} - f^1_{\mathrm{v}})$, and $f^1_{\mathrm{v}} \le f_{\mathrm{v}} \le f^2_{\mathrm{v}}$. σ^{c}_i is commonly referred to as the cosolvency power of the solvent for the solute i. Note, however, that σ_i^c is not a constant, but changes with increasing f_v. If $f_v^1 = 0$, that is, if we consider only the range between pure water and a given cosolvent fraction f_v^2 (e.g., 0.2), Eq. 5-30 simplifies to:

$$\log \gamma_{i\ell}(f_v) = \log \gamma_{iw} - \sigma_i^c \cdot f_v \qquad (5\text{-}32)$$

with $\sigma_i^c = [\log\gamma_{iw} - \log\gamma_{i\ell}(f_v^2)] / f_v^2$. Eq. 5-32 can also be written as:

$$\gamma_{i\ell}(f_v) = \gamma_{iw} \cdot 10^{-\sigma_i^c \cdot f_v} \qquad (5\text{-}33)$$

Hence, this approach is very similar to the one used for describing the effect of salt on aqueous solubility and aqueous activity coefficient (Eqs. 5-27 and 5-28). Some example calculations using Eq. 5-30 or 5-31, respectively, are given in Illustrative Example 5.5. Finally, we should note that the mole fractions of two solvents in a binary mixture are related to the volume fractions by:

$$x_1 = \frac{1}{1 + \dfrac{(1-f_{v1})}{f_{v1}} \cdot \dfrac{\overline{V}_1}{\overline{V}_2}} \quad \text{and} \quad x_2 = 1 - x_1 \qquad (5\text{-}34)$$

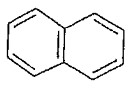
We conclude this section with some brief comments on the cosolvent effects of partially miscible organic solvents (PMOSs). These solvents include very polar liquids such as *n*-butanol, *n*-butanone, *n*-pentanol, or *o*-cresol, but also nonpolar organic compounds such as benzene, toluene, or halogenated methanes, ethanes, and ethenes. For the polar PMOS, a similar effect as for the CMOS can be observed; that is, these solvents decrease the activity coefficient of an organic solute when added to pure water or to a CMOS/water mixture (Pinal et al., 1990; Pinal et al., 1991; Li and Andren, 1994). For the less polar PMOS there is not enough data available to draw any general conclusions.

Illustrative Example 5.5

Estimating the Solubilities and the Activity Coefficients of Organic Pollutants in Organic Solvent –Water Mixtures

Problem

Estimate the solubility and the activity coefficient of (a) naphthalene, and (b) benzo(a)pyrene in a 30% methanol/70% water (v : v) mixture at 25°C.



i = naphthalene

C_{iw}^{sat} (25°C) = 2.5×10^{-4} mol · L^{-1}
T_m = 80.2°C
γ_{iw}^{sat} (25°C) = 6.7×10^4
(see Table 5.2)

Answer (a)

As in the case of inorganic salts (Illustrative Example 5.4) the free energy contributions of phase change to the overall free energy of solution are not affected by CMOS (with some exceptions in which the solvent changes the crystal structure of a solid, see text). Hence, you need only estimate the effect of the CMOS on the activity coefficient. Use the $\gamma_{iw}^{sat} / \gamma_{i\ell}^{sat}$ ratios given for naphthalene in Table 5.8 for $f_{v,\text{MeOH}} = 0.2$ and $f_{v,\text{MeOH}} = 0.4$ to estimate $\gamma_{i\ell}^{sat}$ for $f_{v,\text{MeOH}} = 0.3$ by interpolation, using the log-linear relationship Eq. 5-30. Calculate first the log $\gamma_{i\ell}^{sat}$ values for $f_{v,\text{MeOH}} = 0.2$ and 0.4, respectively:

$$\log \gamma_{i\ell}^{\text{sat}}(f_{\text{v,MeOH}} = 0.2) = \log (\gamma_{iw}^{\text{sat}}) / 3.5) = 4.28$$

$$\log \gamma_{i\ell}^{\text{sat}}(f_{\text{v,MeOH}} = 0.4) = \log (\gamma_{iw}^{\text{sat}}) / 14) = 3.68$$

The slope σ_i^c in Eq. 5-30 is then obtained by:

$$\sigma_i^c = (4.28 - 3.68) / (0.2) = 3.0$$

which yields (Eq. 5-30):

$$\log \gamma_{i\ell}^{\text{sat}}(f_{\text{v,MeOH}} = 0.3) = 4.28 - (3.0)\ (0.1) = 3.98$$

or:

$$\gamma_{i\ell}^{\text{sat}}(f_{\text{v,MeOH}} = 0.3) = 9.5 \times 10^3$$

which is about a factor of 7 smaller than γ_{iw}^{sat}. This also means that the mol fraction solubility of naphthalene will be about a factor of 7 larger (Eq. 5-31), that is:

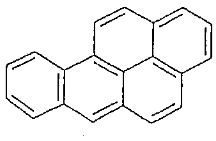
$$x_{i\ell}^{\text{sat}} = (7)\ (2.5 \times 10^{-4})\ (0.018) = 3.2 \times 10^{-5}.$$

The mole fraction of methanol in a 30% methanol/70% water mixture is 0.16 (Eq. 5-34). The molar volume of methanol is 0.0406 L·mol^{-1}. Hence, the molar volume of the mixture can be calculated as (Eq. 3-43, note that we assume additivity):

$$V_{i\ell} = (0.16)\ (0.0406) + (0.84)\ (0.018) = 0.022\ \text{L} \cdot \text{mol}^{-1}$$

Hence, the molar solubility of naphthalene in the mixture is:

$$C_{i\ell}^{\text{sat}}(f_{\text{v,MeOH}} = 0.3) = (3.2 \times 10^{-5}) / (0.022) = 1.45 \times 10^{-3}\ \text{mol} \cdot \text{L}^{-1}$$



i = benzo(a)pyrene

C_{iw}^{sat} (25°C) $= 7.2 \times 10^{-9}$ mol·L^{-1}
$T_{\text{m}} = 176.5$°C
γ_{iw}^{sat} (25°C) $= 3.2 \times 10^8$
(see Table 5.2)

Answer (b)

For benzo(a)pyrene there are no experimental data available. Estimate $\gamma_{iw}^{\text{sat}} / \gamma_{i\ell}^{\text{sat}}$ for $f_{\text{v,MeOH}} = 0.2$ and 0.4, respectively using the data given for other PAHs in Fig. 5.8. From the original data sets reported in the literature, derive the corresponding linear relationships between $\log \gamma_{iw}^{\text{sat}} / \gamma_{i\ell}^{\text{sat}}$ and the molar volume, V_{ix} (in cm^3 mol^{-1}), calculated by the method described in Box 5.1 (see caption Fig. 5.8):

$$f_{\text{v,MeOH}} = 0.2: \quad \log (\gamma_{iw}^{\text{sat}} / \gamma_{i\ell}^{\text{sat}}) = (0.0104)\ V_{ix} - 0.668 \tag{1}$$

$$f_{\text{v,MeOH}} = 0.4: \quad \log (\gamma_{iw}^{\text{sat}} / \gamma_{i\ell}^{\text{sat}}) = (0.0147)\ V_{ix} - 0.469 \tag{2}$$

Insertion of $\log \gamma_{iw}^{\text{sat}}$ and V_{ix} (195.0 cm^3 mol^{-1}) of benzo(a)pyrene into Eqs. 1 and 2 yields:

$$\log \gamma_{i\ell}^{\text{sat}}(f_{\text{v,MeOH}} = 0.2) = 7.15$$

$$\log \gamma_{i\ell}^{\text{sat}}(f_{\text{v,MeOH}} = 0.4) = 6.10$$

which yields a slope $\sigma_i^c = (7.15 - 6.10) / (0.2) = 5.25$ demonstrating that the effect of the cosolvent methanol is more pronounced for the more hydrophobic benzo(a)pyrene as compared to the less hydrophobic naphthalene ($\sigma_i^c = 3.0$, see above). Insertion of the according values into Eq. 5-28 then yields:

$$\log \gamma_{i\ell}^{\text{sat}}(f_{\text{v,MeOH}} = 0.3) = 7.15 - (5.25)\,(0.1) = 6.63$$

or

$$\gamma_{i\ell}^{\text{sat}}(f_{\text{v,MeOH}} = 0.3) = \mathit{4.2 \times 10^6}$$

which is about 75 times smaller than γ_{iw}^{sat}. Hence, the corresponding mole fraction solubility is about a factor of 75 larger (Eq. 5-31), that is:

$$x_{i\ell}^{\text{sat}} = (75)\,(7.2 \times 10^{-9})\,(0.018) = \mathit{9.7 \times 10^{-9}}$$

and by analogy to case (a):

$$C_{i\ell}^{\text{sat}}(f_{\text{v,MeOH}}) = (9.7 \times 10^{-9}) / (0.022) = \mathit{4.4 \times 10^{-7}}\ \text{mol} \cdot \text{L}^{-1}$$

5.5 Availability of Experimental Data; Methods for Estimation of Aqueous Activity Coefficient and Aqueous Solubility

Experimental Data

We have already seen from our above discussions that organic chemicals cover a very wide range of aqueous solubilities, that is, from completely miscible down to 10^{-10} mol · L^{-1} and below (see Appendix C). Because of these low solubilities and owing to the analytical limitations in the past, many organic substances have acquired the reputation of "being insoluble in water" (e.g., Lide, 1995). From an environmental point of view such a statement is, of course, not correct at all because water is one of the major transport and reaction media for organic compounds in natural systems. Hence, for assessing the behavior and the effects of organic pollutants in the environment, accurate data on aqueous solubilities and aqueous activity coefficients are of utmost importance.

The conventional method of determining *aqueous solubility* is to equilibrate an excess amount of the pure chemical of interest with water in a batch reactor. Equilibrium is achieved by gently shaking or by slowly stirring with a magnetic stirrer. The aim is to prevent formation of emulsions or suspensions and thus avoid extra experimental procedures such a filtration or centrifugation which may be required to ensure that a "true" solution is obtained. This method, which is commonly referred to as *shake flask method* works quite well for more soluble compounds. For more sparingly soluble chemicals such as higher alkanes, PAHs, PCBs, polychlorinated dioxins, and dibenzofurans, however, experimental difficulties can still occur because of the formation of emulsion or microcrystal suspensions, and because of adsorption phenomenon if filtration is necessary. For such compounds, the *generator column method* has been found to produce much more accurate solubility data. In this method, a solid support (e.g., glass bead) is coated with the chemical, packed in an open tubular column, and water is run through at a precise flow rate to achieve equilibrium. Subsequently, the aqueous effluent is assessed for the organic solute by using an appropriate analytical technique. For a more detailed discussion of the various aspects of the experimental determination of aqueous solubilities, we refer to Yalkowsky and Banerjee (1992) and to the handbooks published by Mackay et al. (1992–1997). These latter handbooks also contain large compilations of water solubilities of a variety of important compound classes. Additional experimental data may be found in smaller compilations reported by Ruelle and Kesselring (1997a,b), Montgomery (1997), and Mitchell and Jurs (1998). As with our comments on experimental vapor pressure data (Section 4.4), we should point out that, particularly for sparingly soluble compounds, aqueous solubilities determined by different methods and/or different laboratories may vary by as much as a factor of 2 to 3, and in some cases even by more than an order of magnitude. Such data should, therefore, be treated with the necessary caution. Again, one way of deciding which solubility value should be selected is to compare the experimental data with predicted values using other compound properties or solubility data from structurally related compounds.

Several experimental methods are available to determine activity coefficients of organic compounds in dilute aqueous solution. A critical review of the various direct and indirect measurement methods can be found in the article by Sherman et al. (1996). For compounds exhibiting small γ_{iw} values (i.e., high water solubilities), differential ebulliometry or dewpoint techniques are frequently used. Here, the effect of the solute on the boiling point of the solvent (i.e., water), or on the dewpoint of the solvent vapor, respectively, is determined under constant pressure. The measured changes then allow us to derive the activity coefficient of the compound in the solvent. For compounds that exhibit larger γ_{iw} values, particularly for the more volatile compounds, the techniques of head space gas chromatography and gas stripping seem to provide reliable activity coefficients in dilute aqueous solution. Among the indirect approaches, derivation of γ_{iw} values from experimental evaluation of the partitioning of a compound between an organic solvent (e.g., hexadecane, *n*-octanol) and water is the most widely used method. We will come back to this issue in Chapter 7.

In summary, we can conclude that there is quite a large experimental database on aqueous solubilities and/or aqueous activity coefficients of organic compounds available in the literature. In this context, we should recall that for compounds exhibiting γ_{iw} values greater than about 100, we may assume that γ_{iw} is concentration independent (Section 5.2). Thus, if only γ_{iw} is known for a given compound (either experimentally determined or predicted; see below), we can estimate its aqueous solubility by using Eqs. 5-6, 5-10, or 5-15, respectively (see also Illustrative Example 5.2). If neither the aqueous solubility nor the aqueous activity coefficient is known for a given compound (e.g., for a new chemical), we may use one of the various methods that have been developed for estimating these important compound properties.

Prediction of Aqueous Solubilities and/or Aqueous Activity Coefficients

Any general approach (i.e., any approach that is not restricted to a confined set of structurally related compounds) for prediction of aqueous solubilities and/or aqueous activity coefficients has to cope with the intrinsic difficulty of describing precisely what is happening when introducing an organic compound in water. We have discussed this problem in detail in Section 5.3, where we have also seen that by using molecular descriptors such as the solvatochromic parameters we are able to model the aqueous activity coefficient of any kind of organic compound with reasonable success. The problem with these and similar approaches (Yalkowsky and Banerjee, 1992) is only that often not all required descriptors are readily available for a given compound.

Therefore, similar to the attempts made to estimate vapor pressure (Section 4.4) there have been a series of quite promising approaches to derive topological, geometric, and electronic molecular descriptors for prediction of aqueous activity coefficients from chemical structure (e.g., Mitchell and Jurs, 1998; Huibers and Katritzky, 1998). The advantage of such quantitative structure property relationships (QSPRs) is, of course, that they can be applied to any compound for which the structure is known. The disadvantages are that these methods require sophisticated computer software, and that they are not very transparent for the user. Furthermore, at the present stage, it remains to be seen how good the actual predictive capabilities of these QSPRs are.

A completely different method that has been shown to be particularly useful for estimating activity coefficients in *nonaqueous* solutions is based on a group contribution approach. The best known and most widely used version of this approach is the UNIFAC method (Hansen et al., 1991; Kan and Tomson, 1996). A similar approach that is, however, focused on aqueous solutions is referred to as AQUAFAC (Myrdal et al., 1993). The basic idea of this type of approach is to express enthalpic and entropic contributions to the excess free energy by summing up interactive terms of parts of the solute and solved molecules, particularly of their functional groups. A large number of such interaction parameters have been derived from a statistical analysis of experimental data on vapor–liquid partitioning. As already mentioned above, UNIFAC works best for nonaqueous mixtures or mixtures that contain only a very limited amount of water. When dealing with solutions exhibiting significant amounts of water, the present limitations of UNIFAC, but also of AQUAFAC (Sherman et al., 1996; Fan and Jafvert, 1997), are probably due primarily to the difficulties in properly expressing the entropic contributions resulting from the unique properties of the solvent water.

We conclude our short discussion of estimation methods for aqueous solubilities and aqueous activity coefficients by restating that simple one-parameter relationships [e.g., relationships between liquid aqueous solubility and molar volume (Table 5.4) or octanol–water partition constant (Section 7.4)] may also be quite powerful predictive tools, provided that we confine a given equation to a set of *structurally closely related* compounds. In this context, we should emphasize again (and again!) that only with a sufficient understanding of the molecular interactions that determine the excess free energy of a given compound in a given molecular environment (here in aqueous solution) will we be able to define which compounds are structurally related with respect to a given partitioning process. This will become even more evident in the following chapters.

5.6 Questions and Problems

Questions

Q 5.1

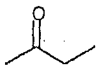
What is meant by the term *water solubility* or *aqueous solubility* of a given compound? What is the range of aqueous solubilities encountered when dealing with environmentally relevant compounds?

Q 5.2

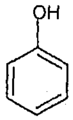
How is the aqueous activity coefficient of a compound related to the aqueous solubility, if the compound is (a) a liquid, (b) a solid, and (c) a gas under the prevailing conditions? Comment on any assumptions that you make when answering this question.

Q 5.3

The excess enthalpy in aqueous solution (H_{iw}^{E}) of 2-butanone is smaller than that of the similarly sized phenol (Table 5.3), although one can assume that phenol has stronger polar interactions with the water molecules. Try to explain these findings.



2-butanone

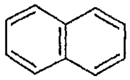


phenol

Q 5.4

The excess entropy in aqueous solution (S_{iw}^{E}) of *n*-hexane is significantly more negative as compared to the similarly sized naphthalene (Table 5.3). Try to explain this difference.

n-hexane



naphthalene

Q 5.5

Figure 5.2 and Table 5.4 show that, for a given class of strucurally closely related compounds, a linear relationship exists between liquid aqueous solubility and size of the molecule (Eq. 5-18). Note that in both Fig. 5.2 and Table 5.4 decadic instead of natural logarithms are used:

$$\log C_{iw}^{\text{sat}}(\text{L}) = -c \cdot V_{ix} + d$$

Try to answer the following questions:

(a) Why are the slopes c of the regression lines quite similar for the *n*-alkanes and the alkanols (Fig. 5.2*a*), and why do these two groups of compounds exhibit such different intercepts d? Why are there any significant differences in the intercepts between primary, secondary, and tertiary alkanols?

(b) Why do the chlorobenzenes and PAHs (Fig. 5.2*b*) exhibit different slopes?

(c) Why is there such a large scatter in the data of the halogenated C_1- and C_2-compounds (Fig. 5.2*c*)?

Q 5.6

Explain qualitatively how the aqueous solubility of a (a) liquid, (b) solid, and (c) gaseous compound changes with temperature. Which thermodynamic quantity(ies) do you need to know for quantifying this temperature dependence?

Q 5.7

Explain in words how environmentally relevant inorganic salts affect the aqueous solubility of a (a) liquid, (b) solid, and (c) gaseous compound. Is it true that the effect is linearly related to the concentration of a given salt? What is the magnitude of the effect of salt on the aqueous activity coefficient of organic compounds in typical seawater?

Q 5.8

Explain in words how organic cosolvents affect the activity coefficients in water-solvent mixtures? Which organic solvents are most effective? Is it true that the effect of an organic cosolvent is linearly related to its volume fraction in the solvent–water mixture? Below which volume fraction can the effect of an organic cosolvent be neglected?

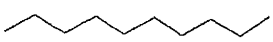
Q 5.9

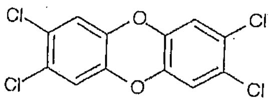
Derive Eq. 5-34 by realizing that the number of moles of a given compound present in a given volume, V_L, of the pure liquid of that compound is given by $V_L / \bar{V}_L$.

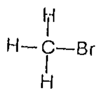
Problems

P 5.1 *Calculating Aqueous Activity Coefficients and Excess Free Energies in Aqueous Solution from Experimental Solubility Data*

Calculate the aqueous activity coefficients, γ_{iw}^{sat}, and the excess free energies in aqueous solution, G_{iw}^{E} (in $kJ \cdot mol^{-1}$), of (a) *n*-decane ($n\text{-}C_{10}H_{22}$), (b) 2,3,7,8-tetrachlorodibenzo-p-dioxin, and (c) bromomethane (CH_3Br) at 25°C using the data provided in Appendix C.


n-decane


2,3,7,8-tetrachloro-dibenzo-*p*-dioxin


bromomethane

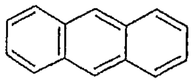
P 5.2 *A Tricky Stock Solution*

You work in an analytical laboratory and you are asked to prepare 250 mL of a 0.5 M stock solution of anthracene in toluene (ρ^{20} (toluene) = 0.87 $g \cdot cm^{-3}$) as solvent. You look up the molar mass of anthracene, go to the balance, weigh out 22.3 g of this compound, put it into a 250 mL volumetric flask, and then fill the flask with toluene. To your surprise, even after several hours of intensive shaking, there is still a substantial portion of undissolved anthracene present in the flask, although your intuition tells you that these two aromatic compounds should form a near-ideal liquid mixture.

(a) What is the problem?

(b) Give an estimate of how much anthracene has actually been dissolved (in grams).

(c) What is anthracene's concentration (in molar units) in the stock solution (at 20°C)? The necessary data can be found in Appendix C.



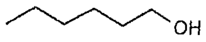
anthracene
$T_m = 217.5$ °C
$T_b = 341.0$ °C

P 5.3 *Explaining the Differences in Aqueous Solubility Between n-Hexane, di-n-Propylether, and n-Hexanol*

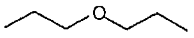
As can be seen from the data in Appendix C, the aqueous solubilities of *n*-hexanol ($C_{iw}^{sat} = 6.2 \times 10^{-2}\ \text{mol} \cdot \text{L}^{-1}$) and di-*n*-propylether ($C_{iw}^{sat} = 3.0 \times 10^{-2}\ \text{mol} \cdot \text{L}^{-1}$) exceed that of *n*-hexane ($C_{iw}^{sat} = 1.5 \times 10^{-4}\ \text{mol} \cdot \text{L}^{-1}$) by more than two orders of magnitude.

(a) Try to explain the differences in C_{iw}^{sat} between the three compounds based on their abilities to undergo intermolecular interactions.

(b) Use Eq. 5-22 to evaluate the various factors that determine the aqueous solubilities of the three compounds. You can find all necessary data in Tables 4.3 and 5.5 and in Appendix C.



n-hexanol
$n_{Di} =$ 1.418

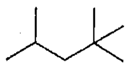


di-*n*-proylether
1.381

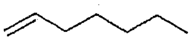
n-hexane
1.375

P 5.4 *Estimating Aqueous Solubilities Using Solubility Data of Structurally Related Compounds (adapted from Roberts, 1995).*

As will be discussed in Chapter 7, for estimating the aqueous saturation concentration of a given component of a complex mixture when this mixture is in equilibrium with water (e.g., after a gasoline spill), one needs to know the liquid aqueous solubility of the pure compound of interest. Shown below are the aqueous solubilities of some hydrocarbons present in gasoline that are all liquids at 25°C. Estimate the aqueous solubilities (in molar units) of the two gasoline compounds isooctane (2,2,4-trimethylpentane) and 1-heptene using the experimental data reported below and/or using one of the equations given in Table 5.4. Comment on the selection of the set of reference compounds that you use for your estimates.



isoctane



1-heptene

Compound	M_i (g·mol^{-1})	T_b (°C)	C_{iw}^{sat} (25°C) (mg·L^{-1})
1-pentene	70.1	30.0	148
2-methyl-1-pentene	84.2	60.7	78
1-hexene	84.2	63.4	50
4-methyl-1-pentene	84.2	53.9	48
2,2-dimethylbutane	86.2	49.7	12.8
2,2-dimethylpentane	100.2	79.2	4.4
2,2,3-trimethylbutane	100.2	80.9	4.4
3-methylhexane	100.2	92.0	3.3
1-octene	112.2	121.3	2.7
2-methylheptane	114.2	117.6	0.85
1-nonene	126.3	146.9	1.12
3-methyloctane	128.3	143.0	1.42
2,2,5-trimethylhexane	128.3	124.0	1.15

P 5.5 *Evaluating the Effect of Temperature on the Aqueous Solubility and on the Aqueous Activity Coefficient of a Solid Compound*

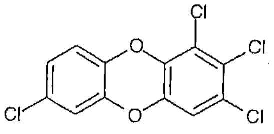
Living in a cold area, you want to know the aqueous solubility and the aqueous activity coefficient of organic compounds at 1°C rather than at 25°C.

(a) Estimate C_{iw}^{sat} (in molar units) and γ_{iw}^{sat} of 1,2,3,7-tetrachlorodibenzo-*p*-dioxin at 1°C using aqueous solubilities of this compound determined at more elevated temperatures by Friesen and Webster (1990):

(b) Also calculate the average excess enthalpy (H_{iw}^{E}) of the compound in water for the temperature range considered (in kJ·mol^{-1}). Why are you interested in this quantity? Comment on any assumption that you make.

T / °C	7.0	11.5	17.0	21.0	26.0
C_{iw}^{sat} / mol·L^{-1}	7.56×10^{-10}	8.12×10^{-10}	12.5×10^{-10}	14.9×10^{-10}	22.6×10^{-10}

Hint: You can solve this problem without any lengthy calculations!



1,2,3,7-tetrachloro-*p*-dibenzodioxin

$M_i = 322.0$ g·mol^{-1}

$T_m = 175.0$ °C

P 5.6 *Evaluating the Effect of Temperature on the Solubility and/or the Activity Coefficient of a Gaseous Compound (Freon 12) in Freshwater and in Seawater*

For an assessment of the global distribution of persistent volatile halogenated hydrocarbons, the solubility and activity coefficients of such compounds in natural waters need to be known. Warner and Weiss (1985) have determined the solubilities of dichlorodifluoromethane (Freon 12) at 1 bar partial pressure at various temperatures in freshwater and in seawater (35.8‰ salinity):

Freshwater:					
T / °C	0.9	9.6	19.9	29.9	40.7
$C_{iw}^{1\text{bar}}$ / mol·L^{-1}	9.0×10^{-3}	5.6×10^{-3}	3.5×10^{-3}	2.5×10^{-3}	1.8×10^{-3}
Seawater:					
T / °C	4.8	9.2	20.4	29.6	39.9
$C_{iw}^{1\text{bar}}$ / mol·L^{-1}	4.9×10^{-3}	4.0×10^{-3}	2.4×10^{-3}	1.7×10^{-3}	1.3×10^{-3}

(a) Estimate the solubilities (in molar units) of Freon 12 in freshwater and in seawater at 1 bar partial pressure at 5 and 25°C.

(b) Calculate the activity coefficients of Freon 12 in freshwater and seawater at these temperatures by using the vapor pressure data given in Problem 4.2.

(c) Derive the average excess enthalpy (H_{iw}^{E} in kJ·mol) of Freon 12 in freshwater and seawater for the ambient temperature range (i.e., 0 – 40°C).

(d) Comment on any differences found between freshwater and seawater.

P 5.7 *A Small Bet with an Oceanographer*

A colleague of yours who works in oceanography bets you that both the solubility as well as the activity coefficient of naphthalene are larger in seawater (35‰ salinity) at 25°C than in distilled water at 5°C. Is this not a contradiction? How much money do you bet? Estimate C_{iw}^{sat} and γ_{iw}^{sat} for naphthalene in seawater at 25°C and in distilled water at 5°C. Discuss the result. Assume that the average enthalpy of solution ($\Delta_{ws}H_i$, Fig. 5.1) of naphthalene is about 30 kJ·mol^{-1} over the ambient temperature range. All other data can be found in Tables 5.3 and 5.7 and in Appendix C.

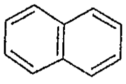
P 5.8 *Evaluating the Effect of Different Cosolvents on the Retention Time of Organic Compounds in Reversed-Phase Liquid Chromatography*

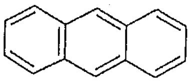
The retention time of an organic compound in reversed-phase liquid chromatography is heavily influenced by the activity coefficient of the compound in the mobile phase, which commonly consists of a CMOS/water mixture.

(a) Estimate by what factor the activity coefficients of naphthalene and anthracene change when switching the mobile phase from 30% methanol / 70% water (v : v) to 30% acetonitrile / 70% water.

(b) What is the effect on the absolute and relative retention times of the two compounds when leaving all other parameters invariant?

In the literature (Pinal et al., 1991) you find data showing that the activity coefficient of anthracene is 400 times smaller in 40% acetonitrile / 60% water (v : v) as compared to pure water. All other necessary data can be found in Table 5.8, Illustrative Example 5.5, and Appendix C.


naphthalene


anthracene

Chapter 7

ORGANIC LIQUID–WATER PARTITIONING

7.1 Introduction

In this chapter we will focus on the equilibrium partitioning of neutral organic compounds between aqueous solutions and *water-immiscible, well-defined* organic liquids. Our focus will be on situations in which the organic compound is present at a low enough concentration that it does not have a significant impact on the properties of either bulk liquid.

As will be discussed in Chapters 9 to 11, the distribution of neutral organic compounds between water and natural solids (e.g., soils, sediments, and suspended particles) and organisms can in many cases be viewed as a partitioning process between the aqueous phase and organic phases present in those solids. This conceptualization even applies somewhat to "solids" that are alive! As early as 1900, investigators studying the uptake of nonpolar drugs by organisms discovered that they could use water-immiscible organic solvents like olive oil or *n*-octanol as a reasonable surrogate for organisms insofar as accumulation of pharmaceutically important organic molecules from the water was concerned (Meyer, 1899; Overton, 1899). Although the extent of uptake from water into these solvents was not identical to that into organisms, it was proportional. That is, *within a series of compounds*, higher accumulation into an organism corresponded to more favorable partitioning into the organic solvent. More recently, environmental chemists have found similar correlations with soil humus and other naturally occurring organic phases (Chapter 9).

Furthermore, knowledge of the molecular factors that determine the partitioning of an organic compound between a liquid organic phase and water is of great interest in environmental analytical chemistry. This is particularly important when dealing with enrichment (i.e., extraction from water samples) or separation steps (i.e., reversed-phase liquid chromatography). Finally, understanding pure solvent–water partitioning will also be applicable to the problem of dissolving organic compounds in water when those organic substances are present in complex mixtures. In practice, we need such knowledge when dealing with contamination of the environment by mixtures such as gasoline, petroleum, or PCBs (Section 7.5).

We start, however, with some general thermodynamic considerations (Section 7.2). Then, using our insights gained in Chapter 6, we compare solvent–water partition constants of a series of model compounds for different organic solvents of different polarity (Section 7.3). Finally, because *n*-octanol is such a widely used organic solvent in environmental chemistry, we will discuss the octanol–water partition constant in somewhat more detail (Section 7.4).

7.2 Thermodynamic Considerations

The Organic Solvent–Water Partition Constant

In Section 3.4, we derived the equilibrium partition constant of a compound between two bulk liquid phases (Eq. 3-40). Denoting the organic phase with a subscript ℓ, we express the organic solvent–water partition constant on a mole fraction basis (superscript prime) as:

$$K'_{i\ell w} = \frac{x_{i\ell}}{x_{iw}} = \frac{\gamma_{iw}}{\gamma_{i\ell}} \tag{7-1}$$

Hence, $K'_{i\ell w}$ is simply given by the ratio of the activity coefficients of the compound in water and in the organic phase. Note that this result applies whether the partitioning compound is a gas, liquid, or solid as a pure substance under the conditions of interest because the dissolved molecules exist in a liquid-like form in both phases. For many of the compounds of interest to us, we know that γ_{iw} can be quite large (e.g., 10^2 to $>10^8$, see Table 5.2). In contrast, in most organic solvents, organic compounds exhibit rather small activity coefficients (e.g., < 1 to 10^2, see Tables 3.2 and 6.1). Consequently, we can expect that in many cases, the magnitudes of organic solvent–water partition constants will be dominated by γ_{iw}. As a result, within a series of structurally related compounds, we may *generally find increasing organic solvent–water partition constants with decreasing (liquid) water solubilities* [recall that $\gamma_{iw} \cong \gamma_{iw}^{\text{sat}}$ is given by $(\overline{V}_w \cdot C_{iw}^{\text{sat}}(\text{L}))^{-1}$; Section 5.2].

A more common way of expressing organic solvent–water partition constants is to use molar concentrations in both phases (Eq. 3-45):

$$K_{i\ell w} = \frac{C_{i\ell}}{C_{iw}} = \frac{\overline{V}_w}{\overline{V}_\ell} \cdot \frac{\gamma_{iw}}{\gamma_{i\ell}} \tag{7-2}$$

where $\overline{V}_w$ and $\overline{V}_\ell$ are the molar volumes of water and the organic solvent, respectively. Note that in Eq. 7-2 we have to use the molar volumes of the mutually saturated liquid phases (e.g., water which contains as much octanol as it can hold and water-saturated octanol). Considering the rather limited water solubility of most water-immiscible organic solvents, we can assume that we can often justifiably use the molar volume of pure water (i.e., 0.018 L·mol^{-1} at 25°C). Similarly for apolar and weakly polar organic solvents, we may use the molar volume of the water-free solvent. Only for some polar organic solvents, may we have to correct for the presence of water in the organic phase (e.g., water-wet *n*-octanol has a $\overline{V}_\ell$ value of 0.13 L·mol^{-1} as compared to 0.16 L·mol^{-1} for "dry" octanol).

If we may assume that the mutual saturation of the two liquid phases has little effect on γ_{iw} and $\gamma_{i\ell}$, we may relate $K_{i\ell w}$ to the respective air–solvent and air–water partition constants (see Eq. 6-11):

$$K_{i\ell w} = \frac{K_{iaw}(= C_{ia} / C_{iw})}{K_{ia\ell}(= C_{ia} / C_{i\ell})} \tag{7-3}$$

Effect of Temperature and Salt on Organic Solvent–Water Partitioning

As for any partition constant, over a temperature range narrow enough that the enthalpy of transfer may be assumed nearly constant, we may express the temperature dependence of $K_{i\ell w}$ by:

$$\ln K_{i\ell w} = -\frac{\Delta_{\ell w} H_i}{R} \cdot \frac{1}{T} + \text{constant} \tag{7-4}$$

where $\Delta_{\ell w}H_i$ is the enthalpy of transfer of i from water to the organic solvent. This enthalpy difference is given by the difference between the excess enthalpies of the compound in the two phases:

$$\Delta_{\ell w}H_i = H_{i\ell}^{E} - H_{iw}^{E} \tag{7-5}$$

The magnitude of the excess enthalpy of a given compound in the organic phase depends, of course, on the natures of both the solvent and the solute. For many compounds H_{iw}^{E} has a fairly small absolute value (e.g., Table 5.3). Substantial deviation from zero (i.e., $|H_{iw}^{E}| > 10\ \text{kJ}\cdot\text{mol}^{-1}$) occurs for some small monopolar compounds (e.g., diethylether, $H_{iw}^{E} = -20\ \text{kJ}\cdot\text{mol}^{-1}$) and for large apolar or weakly monopolar compounds (e.g., PCBs, PAHs which exhibit positive H_{iw}^{E} values, Table 5.3). Typically, $H_{i\ell}^{E}$ for organic solutes and organic solvents does not exceed $\pm 10\ \text{kJ}\cdot\text{mol}^{-1}$ (Section 6.3). Exceptions include small bipolar compounds in apolar solvents (e.g., the excess enthalpy of solution for ethanol in hexadecane is $+26\ \text{kJ}\cdot\text{mol}^{-1}$, see Table 3.3). Since, at the same time, such compounds tend to have negative H_{iw}^{E} values, the $\Delta_{\ell w}H_i$ value may become substantial (e.g., $+36\ \text{kJ}\cdot\text{mol}^{-1}$ for hexadecane–water partitioning of ethanol, Table 3.4). However, for the majority of cases we are interested in, we can assume that organic solvent–water partitioning is only weakly dependent on temperature.

Using a similar approach, one may deduce how other factors should influence organic liquid–water partitioning. For example, we know that the addition of common salts (e.g., NaCl) to water containing organic solutes causes the aqueous activity coefficients of those organic solutes to increase. Since ionic substances are not compatible with nonpolar media like apolar organic solvents, one would not expect salt to dissolve in significant amounts in organic solvents. Consequently, the influence of salt on activity coefficients of organic solutes in organic solvents would likely be minimal. Combining these insights via Eq. 7.2, we can now calculate that the influence of salt on organic liquid–aqueous solution partitioning of organic compounds will entirely correspond to the impact of this factor on the aqueous activity coefficient, and hence (see Eq. 5-28):

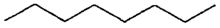
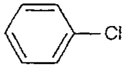
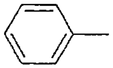
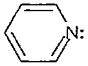
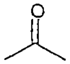
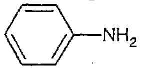
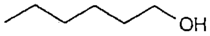
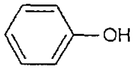
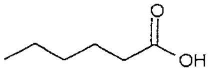
$$K_{i\ell w,\text{salt}} = K_{i\ell w} \cdot 10^{+K_i^{s}[\text{salt}]_{\text{tot}}} \tag{7-6}$$

7.3 Comparison of Different Organic Solvent–Water Systems

General Comments

Since the organic solvent–water partition constant of a given compound is determined by the ratio of its activity coefficients in the two phases (Eq. 7-2), we can rationalize how different compounds partition in different organic solvent–water systems. Consider the values of log $K_{i\ell w}$ for a series of compounds i partitioning into five organic solvents ℓ exhibiting different polarities (Table 7.1). First, focus on the partitioning behavior of the apolar and weakly monopolar compounds (octane, chlorobenzene, methylbenzene). These undergo primarily vdW interactions (i.e., *n*-octane, chlorobenzene, methylbenzene for which α_i and β_i are small or even zero). In general, such compounds partition very favorably from water into organic

Table 7.1 Organic Solvent–Water Partition Constants of a Series of Compounds for Various Organic Solvents at 25°C [a]

Compound i (Solute) (α_i/β_i) [b]	Structure	n-Hexane (0.00/0.00) [b, c] log K_{ihw}	Methylbenzene (Toluene) (0.00/0.14) [b, c] log K_{itw}	Diethylether (0.00/0.45) [b, c] log K_{idw}	Trichloromethane (Chloroform) (0.15/0.02) [b, c] log K_{icw}	n-Octanol (0.37/0.48) [b, c] log K_{iow}
n-Octane (0.00/0.00)		6.08	5.98	6.03	6.01	5.53
Chlorobenzene (0.00/0.07)		2.91			3.40	2.78
Methylbenzene (0.00/0.14)		2.83	3.14	3.07	3.43	2.66
Pyridine (0.00/0.52)		–0.21	0.29	0.08	1.43	0.65
Acetone (0.04/0.51)		–0.92	–0.31	–0.21	0.72	–0.24
Aniline (0.26/0.41)		0.01	0.78	0.85	1.23	0.90
1-Hexanol (0.037/0.48)		0.45	1.29	1.80	1.69	2.03
Phenol (0.60/0.31)		–0.89	0.12	1.58	0.37	1.49
Hexanoic Acid (0.60/0.45)		–0.14	0.48	1.78	0.71	1.95

[a] Data from Hansch and Leo (1979). [b] (α_i / β_i); Abraham et al. (1994a). [c] The α_i and β_i values correspond to the values of the solvents when present as solute! They are not necessarily identical when the compounds act as solvent. However, they give at least a good qualitative idea of the polar properties of the solvent.

solvents. This is not too surprising since these compounds have rather large γ_{iw}-values (Chapter 5). Furthermore, their log $K_{i\ell w}$, values do not vary much among the different organic solvents. For example, *n*-octane's partition coefficients vary only by about a factor of 4 for the five solvents shown in Table 7.1. For the strictly apolar solutes, lower values of log $K_{i\ell w}$, can be expected in bipolar solvents such as *n*-octanol. In the case of such a bipolar solvent, some solvent:solvent polar interactions have to be overcome when forming the solute cavity.

In contrast, partitioning from water into organic solvents may be somewhat enhanced if the solvents exhibit complementary polarity to monopolar solutes. One example is the partitioning of methylbenzene (toluene) between water and trichloromethane (Table 7.1). Each additional polar effect may become very substantial if the solute is strongly monopolar. This is illustrated by the trichloromethane–water partition constants of pyridine and acetone. Both of these solutes are quite strong H-acceptors or electron donors (i.e., $\beta_i \cong 0.5$). This causes these solutes to be strongly attracted to trichloromethane's hydrogen and results in significantly higher log K_{icw} values of these two compounds than for the other solvent–water systems. Note that the electron-accepting properties of trichloromethane (and of other polyhalogenated methanes and ethanes, e.g., dichloromethane, see Table 6.1) make such solvents well suited for the extraction of electron-donating solutes from water or other environmentally relevant matrices including soil or sediment samples.

When considering bipolar solutes (e.g., aniline, 1-hexanol, phenol, hexanoic acid), we can see that depending on the relative magnitudes of the solvent's α_i and β_i values, solute:solvent interactions may become quite attractive. For example, for aniline, for which $\alpha_i < \beta_i$, trichloromethane is still the most favorable solvent, whereas for phenol ($\alpha_i > \beta_i$), diethylether wins over the others. Finally, due to the lack of polar interactions in hexane, bipolar solutes partition rather poorly from water into such apolar solvents (Table 7.1).

LFERs Relating Partition Constants in Different Solvent–Water Systems

Often we may want to quantitatively extrapolate our experience with one organic solvent–water partitioning system to know what to expect for new systems. This is typically done using a linear free energy relationship of the form:

$$\log K_{i1w} = a \cdot \log K_{i2w} + b \tag{7-7}$$

where partitioning of solute, *i*, between some organic liquid, 1, and water is related to the partitioning of the same solute between another organic liquid, 2, and water. However, we should recall from our qualitative discussion of the molecular factors that govern organic solvent–water partitioning that such simple LFERs as shown in Eq. 7-7 will not always serve to correlate $K_{i\ell w}$ values of a large variety of compounds for structurally diverse solvent–water systems. Nonetheless, there are numerous special cases of groups of compounds and/or pairs of organic solvents for which such LFERs may be applied with good success. Obvious special cases include all those in which the molecular interactions of a given group of compounds are similar in nature in both organic phases. This is illustrated in Fig. 7.1 for the two solvents hexadecane and octanol (subscripts h and o, respectively). In this case, a

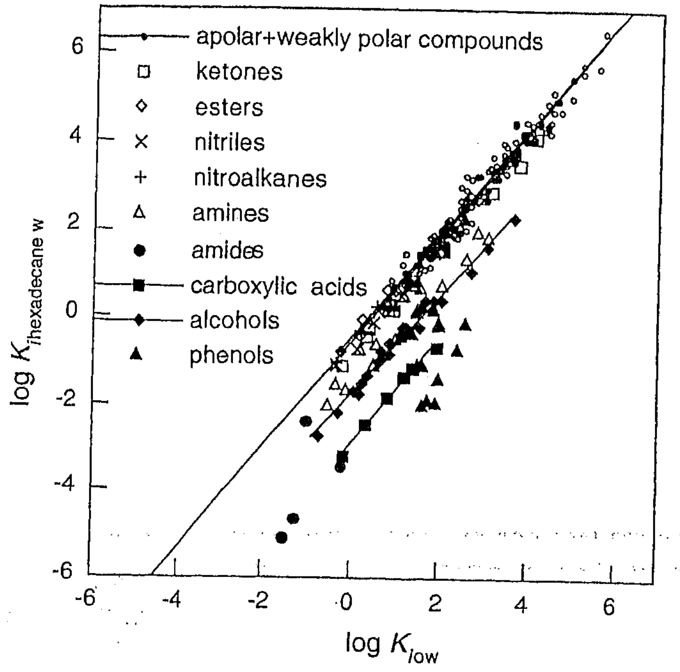


Figure 7.1 Plot of the decadic logarithms of the hexadecane–water partition constants versus the octanol–water constants for a variety of apolar, monopolar, and bipolar compounds. Data from Abraham (1994b). The a and b values for some LFERs (Eq. 7-7) are: apolar and weakly monopolar compounds (a = 1.21, b = 0.43; Eq. 7-8), aliphatic carboxylic acids (a = 1.21; b = −2.88), and aliphatic alcohols (a = 1.12, b = −1.74).

good correlation is found for all *apolar* and *weakly polar* compounds, for which the vdW interactions are the dominating forces in both organic solvents:

$$\log K_{ihw} = 1.21\ (\pm\ 0.02) \cdot \log K_{iow} - 0.43\ (\pm\ 0.06)$$

$$(N = 89,\ R^2 = 0.97) \qquad (7\text{-}8)$$

The slope of greater than 1 in Eq. 7-8 indicates that structural differences in the solutes have a somewhat greater impact on their partitioning behaviors in the hexadecane–water, as compared to the octanol–water system. This can be rationalized as arising from the different free-energy costs related to the cavity formation in the two solvents, which is larger in the bipolar octanol (see discussion in Chapter 6).

A second important feature shown in Fig. 7.1 is that, for the two organic solvents considered, the more polar compounds do not fit well in the LFER expressed in Eq. 7-8. This is particularly true for bipolar solutes. Here, LFERs may be found only for structurally related compounds. For example, good correlations exist for a homologous series of compounds such as the aliphatic carboxylic acids or the aliphatic alcohols. In these cases, within the series of compounds, the polar contribution is constant; that is, the compounds differ only in their ability to undergo dispersive vdW interactions. This example shows that we have to be careful when applying one-parameter LFERs to describe systems in which more than one intermolecular interaction is varying. Such is the case when we are dealing with diverse groups of partitioning chemicals and/or with structurally complex organic phases including natural organic matter (Chapter 9) or parts of organisms (Chapter 10). If we are, however, aware of the pertinent molecular interactions that govern the partitioning of a given set of organic compounds in the organic phase–water systems considered, appropriately applied one-parameter LFERs of the type Eq. 7-7 may be extremely useful predictive tools.

Model for Description of Organic Solvent–Water Partitioning

Multiparameter LFERs for description of air–organic solvent (Eq. 6-13, Table 6.2) and air–water (Eq. 6-21) partition constants have been developed. If we can assume that dissolution of water in the organic solvent and of the organic solvent in the water have no significant effects on the partitioning of a given compound, the organic solvent–water partition constant, $K_{i\ell\mathrm{w}}$, is equal to $K_{i\mathrm{aw}}$ divided by $K_{i\mathrm{a}\ell}$ (Eq. 7-3). Consequently, we can develop a multiparameter equation for $K_{i\ell\mathrm{w}}$ and immediately deduce the coefficients from these earlier LFERs:

$$\ln K_{i\ell\mathrm{w}} = s\left[V_{i\mathrm{x}}^{2/3}\left(\frac{n_{D_i}^2 - 1}{n_{D_i}^2 + 2}\right)\right] + p(\pi_i) + a(\alpha_i) + b(\beta_i) + v(V_{i\mathrm{x}}) + \text{constant} \qquad (7\text{-}9)$$

In this case, the coefficients s, p, a, b, v, and constant in Eq. 7-9 reflect *the differences* of the solvent interaction parameters (i.e., dispersive, polar, H-donor, H-acceptor properties, and cavity formation) for water and organic solvent considered. As for the other multiparameter LFERs discussed in earlier chapters, for a given solvent–water system, these coefficients can be obtained by fitting an appropriate set of experimental $K_{i\ell\mathrm{w}}$ values using the chemical property parameters V_{ix}, n_{Di}, π_i, α_i, and β_i. If such experimental data are not available, but if a multiparameter LFER has been established for the corresponding air–organic solvent system (Eq. 6-13, Table 6.2), Eq. 7-9 can be derived by simply subtracting Eq. 6-13 from Eq. 6-21, provided that we are dealing with water-immiscible organic solvents. Conversely, a multiparameter LFER for air–solvent partitioning can be obtained by subtracting Eq. 7-9 from Eq. 6-21. When doing so, one has to be careful to use equations that have been established with the same molecular parameter sets (e.g., the same calculated molar volumes (see Box 5.1), as well as the same compilations of published π_i, α_i, and β_i values. Furthermore, the equations that are combined should preferably cover a similar range of compounds used for their derivation. Finally, we should note again that we are assuming that dissolution of water in the organic solvent and of the organic solvent in the water have no significant effect on the partitioning of a given compound (Section 6.3).

Such multiparameter LFERs have been developed for a few organic solvent–water systems (Table 7.2.) The magnitudes of the fitted coefficients, when combined with an individual solute's V_{ix}, n_{Di}, π_i, α_i, β_i values, reveal the importance of each intermolecular interaction to the overall partitioning process for that chemical. To interpret the various terms, we note that these coefficients reflect the differences of the corresponding terms used to describe the partitioning of the compounds from air to water and from air to organic solvent, respectively (see Chapter 6). Some applications of Eq. 7-9 are discussed in Illustrative Example 7.1.

Table 7.2 Organic Solvent–Water Partitioning: Multiparameter LFERs Eq. 7-8 for Some Selected Organic Solvents at 25°C [a]

	Coefficient for Parameter								
	vdW	(π_i)	(α_i)	(β_i)	V_{ix}		ln $K_{i\ell w}$		
Solvent	*s*	*p*	*a*	*b*	*v*	constant	range [b]	R^2	*n* [c]
n-Hexadecane (apolar)	0.75	–3.61	–8.06	–11.41	0.069	–0.16	–10.0 to 6.11	0.99	302
Trichloromethane	–0.01	0.01	–3.45	–3.38	0.042	0.30	–2.1 to 3.7	1.00	40
Diethylether	–0.11	–0.12	–0.49	–10.54	0.100	–0.10	–0.5 to 5.6	0.97	35
n-Octanol	0.62	–2.53	–0.35	–7.88	0.063	–0.25	–3.2 to 13.0	0.98	260

[a] Data from Abraham et al. (1994*a*,*b*). [b] Range of $K_{i\ell w}$ values that were used to establish the LFER. [c] Number of compounds.

Illustrative Example 7.1 Evaluating the Factors that Govern the Organic Solvent–Water Partitioning of a Compound

Problem

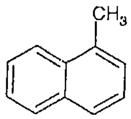
Calculate the *n*-hexadecane–water (ln $K_{i\text{hw}}$) and the *n*-octanol–water (ln $K_{i\text{ow}}$) partition constants at 25°C of *n*-octane (Oct), 1-methylnaphthalene (1-MeNa), and 4-*t*-butylphenol (4-BuPh) using the polyparameter LFER, Eq. 7-9, with the coefficients given in Table 7.2. Compare and discuss the contributions of the various terms in Eq. 7-9 for the three compounds in the two solvent–water systems. Note that the three compounds have already been used in Illustrative Example 5.2 to evaluate the polyparameter LFER describing the aqueous activity coefficient.

Answer

Get the n_{Di} values of the compounds from Lide (1995). Use the α_i, β_i and π_i values given in Tables 4.3 and 5.5. The resulting data sets for the three compounds are given in the margin. Insertion of the respective values into Eq. 7-9 with the appropriate coefficients (Table 7.2) yields the following results:

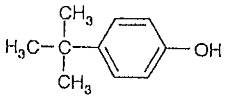
n-octane (Oct)

p^*_{iL} = 1826 Pa
V_{ix} = 123.6 cm^3 mol^{-1}
n_{Di} = 1.397
π_i = 0
α_i = 0
β_i = 0



1-methylnaphthalene (1-MeNa)

p^*_{iL} = 8.33 Pa
V_{ix} = 122.6 cm^3 mol^{-1}
n_{Di} = 1.617
π_i = 0.90
α_i = 0
β_i = 0.20



4-*t*-butylphenol (4-BuPh)

p^*_{iL} = 6.75 Pa
V_{ix} = 133.9 cm^3 mol^{-1}
n_{Di} = 1.517
π_i = 0.89
α_i = 0.56
β_i = 0.39

Term	Oct		1-MeNa		4-BuPh	
	Δ ln $K_{i\text{hw}}$	Δ ln $K_{i\text{ow}}$	Δ ln $K_{i\text{hw}}$	Δ ln $K_{i\text{ow}}$	Δ ln $K_{i\text{hw}}$	Δ ln $K_{i\text{ow}}$
$s \cdot$ disp. vdW [a]	+4.47	+3.70	+6.47	+5.35	+5.94	+4.91
$+p \cdot (\pi_i)$	0	0	−3.25	−2.28	−3.21	−2.25
$+a \cdot (\alpha_i)$	0	0	0	0	−4.51	−0.20
$+b \cdot (\beta_i)$	0	0	−2.28	−1.58	−4.45	−3.07
$+v \cdot (V_{ix})$	+8.52	+7.78	+8.46	+7.72	+9.24	+8.44
+ constant	−0.16	−0.25	−0.16	−0.25	−0.16	−0.25
ln $K_{i\ell\text{w}}$	12.8	11.2	9.24	8.96	2.85	7.58
observed	13.3	11.9	9.21	9.19	2.20	7.23

[a] dispersive vdW attractions = $\left[(V_{ix})^{2/3}\left(\frac{n_{Di}^2-1}{n_{Di}^2+2}\right)\right]$

First, note that the three compounds are of similar size. Hence, the two terms that reflect primarily the differences in the energy costs for cavity formation and the differences in the dispersive interactions of the solute (i.e., $v \cdot V_{ix}$ and $s \cdot$disp. vdW) in water and in the organic solvent are of comparable magnitudes for the three compounds. Note that the values in the table reflect variations on a natural logarithm scale. So, for example, the effect of the product, $v \cdot V_{ix}$, is to vary $K_{i\text{ow}}$ by a factor of 5 between these compounds and the product, $s \cdot$disp vdW, also contributes a factor of 5 variation to these compounds' $K_{i\text{ow}}$ values. Because of the higher costs of cavity formation in the water as compared to *n*-hexadecane and *n*-octanol, both terms promote partitioning into the organic phase (i.e., they have positive values). This promoting effect is somewhat larger in the *n*-hexadecane–water system than in the *n*-octanol–water system because of the somewhat higher costs of forming a cavity in the bipolar solvent, *n*-octanol.

Significant differences in the partition constants of the three compounds, in particular for the *n*-hexadecane–water system, are also due to the polar interactions, also including the dipolarity/polarizability parameter, π_i. For the two organic solvent–water systems considered, due to the strong polar interactions of mono- and bipolar compounds in the water as compared to the organic phase, all these terms are negative. Therefore, these polar intermolecular interactions decrease the $K_{i\ell w}$ value. These polar effects are more pronounced in the *n*-hexadecane–water system (e.g., 1-MeNa partitioning reduced by a factor of 26) as compared to the *n*-octanol–water system (e.g., 1-MeNa partitioning reduced by a factor of 10).

Finally, with respect to the H-acceptor properties of the solvents (*a*-term), water and *n*-octanol are quite similar. Therefore, for a hydrogen-bonding solute like 4-BuPh, the corresponding product, $a \cdot (\alpha_i)$, is close to zero. This is not the case for the hexadecane–water system where loss of hydrogen bonding in this alkane solvent causes both the H-acceptor and H-donor terms to contribute factors of about 100 to 4-BuPh's value of K_{ihw}.

7.4 The *n*-Octanol–Water Partition Constant

General Comments

Because *n*-octanol is still the most widely used organic solvent for predicting partitioning of organic compounds between natural organic phases and water, we need to discuss the octanol–water partition constant, K_{iow}, in more detail. Note that in the literature, K_{iow} is often also denoted as P or P_{ow} (for *p*artitioning). From the preceding discussions, we recall that *n*-octanol has an *amphiphilic* character. That is, it has a substantial apolar part as well as a bipolar functional group. Thus, in contrast to smaller bipolar solvents (e.g., methanol, ethylene glycol), where more hydrogen bonds have to be disturbed when creating a cavity of a given size, the free-energy costs for cavity formation in *n*-octanol are not that high. Also, the presence of the bipolar alcohol group ensures favorable interactions with bipolar and monopolar solutes. Hence, *n*-octanol is a solvent that is capable of accommodating any kind of solute. As a result, the activity coefficients in octanol (Fig. 7.2) of a large number of very diverse organic compounds are between 0.1 (bipolar small compounds) and 10 (apolar or weakly polar medium-sized compounds). Values of γ_{io} exceeding 10 can be expected only for larger hydrophobic compounds, including highly chlorinated biphenyls and dibenzodioxins, certain PAHs, and some hydrophobic dyes (Sijm et al., 1999). Therefore, the K_{iow} values of the more hydrophobic compounds (i.e., $\gamma_{iw} >> 10^3$) are primarily determined by the activity coefficients in the aqueous phase.

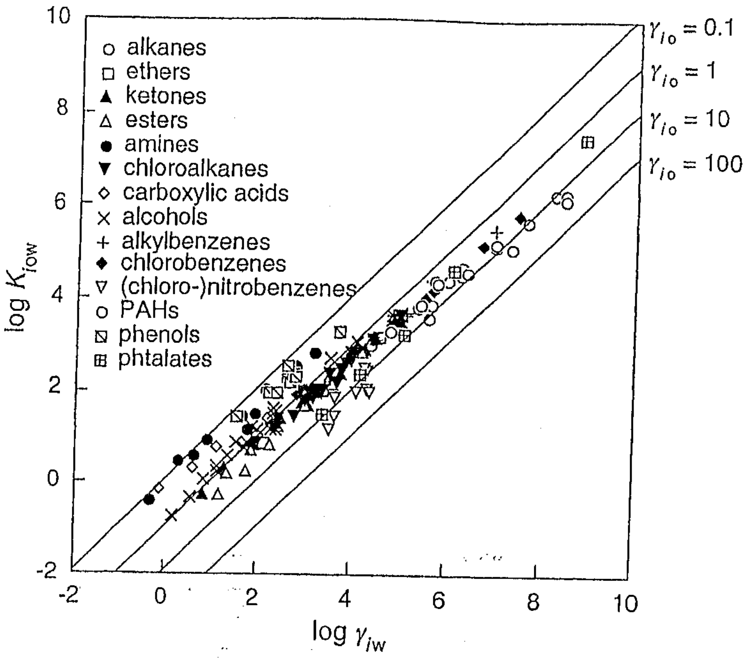


Figure 7.2 Plot of the decadic logarithms of the octanol–water partition constants versus the aqueous activity coefficients for a variety of apolar, monopolar, and bipolar compounds. The diagonal lines show the location of compounds with activity coefficients in octanol (calculated using Eq. 7-2) of 0.1, 1, 10, and 100, respectively.

For sets of compounds with the same functional group and variations in their apolar structural portion, we can also see that γ_{io} is either constant or varies proportionally to γ_{iw} (Fig. 7.2). Thus, for such groups of compounds, we find one-parameter LFERs of the type:

$$\log K_{iow} = a \cdot \log \gamma_{iw} + b \tag{7-10}$$

Since γ_{iw} is more or less equal to γ_{iw}^{sat} for many low solubility compounds ($\gamma_{iw} >$ *ca.* 50), we have $\gamma_{iw} = (\bar{V}_w \cdot C_{iw}^{\text{sat}}(\text{L}))^{-1}$. Considering such sets of compounds, we can rewrite Eq. 7-10 as:

$$\log K_{iow} = -a \cdot \log C_{iw}^{\text{sat}}(\text{L}) + b' \tag{7-11}$$

where $b' = b - a \cdot \log \bar{V}_w = b + 1.74\,a$ (at 25°C). Note that in Eq. 7-11, $C_{iw}^{\text{sat}}(\text{L})$ is expressed in $\text{mol} \cdot \text{L}^{-1}$.

Such correlation equations have been derived for many classes of compounds (Table 7.3). These examples illustrate that very good relationships are found when only members of a specific compound class are included in the LFER. One can also reasonably combine compound classes into a single LFER if only compounds that exhibit similar intermolecular interaction characteristics are used (e.g., alkyl and chlorobenzenes; aliphatic ethers and ketones; polychlorinated biphenyls and polychlorinated dibenzodioxins).

When properly applied, LFERs of these types may be quite useful for estimating K_{iow} from γ_{iw} or $C_{iw}^{\text{sat}}(\text{L})$. Additionally, these relationships can be used to check new K_{iow} and/or $C_{iw}^{\text{sat}}(\text{L})$ values for consistency.

Table 7.3 LFERs Between Octanol–Water Partition Constants and Aqueous Activity Coefficients or Liquid Aqueous Solubilities at 25°C for Various Sets of Compounds: Slopes and Intercepts of Eqs. 7-10 and 7-11

Set of Compounds	a [a,b]	b [a]	b' [b]	log K_{iow} range [c]	R^2	n [d]
Alkanes	0.85	–0.87	0.62	3.0 to 6.3	0.98	112
Alkylbenzenes	0.94	–1.04	0.60	2.1 to 5.5	0.99	15
Polycyclic aromatic hydrocarbons	0.75	–0.13	1.17	3.3 to 6.3	0.98	11
Chlorobenzenes	0.90	–0.95	0.62	2.9 to 5.8	0.99	10
Polychlorinated biphenyls	0.85	–0.70	0.78	4.0 to 8.0	0.92	14
Polychlorinated dibenzodioxins	0.84	–0.79	0.67	4.3 to 8.0	0.98	13
Phthalates	1.09	–2.16	–0.26	1.5 to 7.5	1.00	5
Aliphatic esters (RCOOR')	0.99	–1.27	(0.45) [e]	–0.3 to 2.8	0.98	15
Aliphatic ethers (R–O–R')	0.91	–0.90	(0.68) [e]	0.9 to 3.2	0.96	4
Aliphatic ketones (RCOR')	0.90	–0.89	(0.68) [e]	–0.2 to 3.1	0.99	10
Aliphatic amines (R—NH_2, R–NHR')	0.88	+0.03	(1.56) [e]	–0.4 to 2.8	0.96	12
Aliphatic alcohols (R–OH)	0.94	–0.76	(0.88) [e]	–0.7 to 3.7	0.98	20
Aliphatic carboxylic acids (R–COOH)	0.69	–0.10	(1.10) [e]	–0.2 to 1.9	0.99	5

[a] Eq. 7-10. [b] Eq. 7-11. [c] Range of experimental values for which the LFER has been established. [d] Number of compounds used for LFER. [e] Only for compounds for which log $K_{iow} > \sim 1$.

Availability of Experimental Data

The most common experimental approaches for determination of octanol–water partition constants are quite similar to those for water solubility. These employ shake flask or generator column techniques (Mackay et al., 1992-1997). The "shake flask method," in which the compound is partitioned in a closed vessel between given volumes of octanol and water, is restricted to compounds with K_{iow} values of less than about 10^5. The reason is that for more hydrophobic compounds the concentration in the aqueous phase becomes too low to be accurately measured, even when using very small octanol-to-water volume ratios. Hence, for more hydrophobic compounds "generator columns," coupled with solid sorbent cartridges, are commonly used. Briefly, large volumes of octanol-saturated water (up to 10 L) are passed through small columns, packed with beads of inert support material that are coated with octanol solutions (typically 10 mL) of the compound of interest. As the water passes through the column, an equilibrium distribution of the compound is established between the immobile octanol solutions and the slowly flowing water. By collecting and concentrating the chemical of interest with a solid sorbent cartridge from large volumes of the effluent water leaving the column, enough material may be accumulated to allow accurate quantification of the trace level water load. This result, along with knowledge of the volume of water extracted and the concentration of the compound in the octanol, ultimately provides the K_{iow} value.

As for vapor pressure and aqueous solubility, there is quite a large experimental database on octanol–water partition constants available in the literature (see, e.g., Mackay et al., 1992–1997; Hansch et al., 1995). Up to K_{iow} values of about 10^6, the experimental data for neutral species are commonly quite accurate. For more hydrophobic compounds, accurate measurements require meticulous techniques. Hence, it is not surprising to find differences of more than an order of magnitude in the K_{iow} values reported by different authors for a given highly hydrophobic compound. Such data should, therefore, be treated with the necessary caution. Again, as with other compound properties, one way of deciding which value should be selected is to compare the experimental data with predicted values using other compound properties or K_{iow} data from structurally related compounds.

One-parameter LFERs for Estimation of Octanol–Water Partition Constants

There are also various methods for *estimating* the K_{iow} of a given compound. This can be done from other experimentally determined properties and/or by using molecular descriptors derived from the structure of the compound. We have already discussed some of the approaches (and their limitations) when evaluating the one-parameter LFERs correlating K_{iow} with aqueous solubility (Eq. 7-11, Table 7.3) or with other organic solvent–water partition constants (Eqs. 7-7 and 7-8). A related method that is quite frequently applied is based on the retention behavior of a given compound in a liquid-chromatographic system [high-performance liquid chromatography (HPLC) or thin-layer chromatography (TLC)]. Here, the organic solute is transported in a polar phase (e.g., water or a water/methanol mixture) through a porous stationary phase which commonly consists of an organic phase that is bound to a silica support (e.g., C_2–C_{18} alkyl chains covalently bound to silica beads). As the compounds of interest move through the system, they partition between the organic phase and the polar mobile phase.

Hence, in analogy to organic solvent–water systems, particularly for sets of structurally related apolar or weakly polar compounds for which solute hydrophobicity primarily determines the partitioning behavior, good correlations between K_{iow} and the *s*tationary-phase/*m*obile-phase partition constant, K_{ism}, of a given compound may be obtained. Since, in a given chromatographic system, the travel time or *retention time*, t_i, of a solute i is directly proportional to K_{ism}, an LFER of the following form is obtained:

$$\log K_{iow} = a \cdot \log t_i + b \tag{7-12}$$

To compare different chromatographic systems, however, it is more useful to use the *relative retention time* (also called the *capacity factor*, k_i'). This parameter is defined as the retention of the compound relative to a nonretained chemical species, such as a very polar organic compound or an inorganic species such as nitrate:

$$k_i' = [(t_i - t_0) / t_0] \tag{7-13}$$

where t_0 is the travel time of the nonretained species in the system. Eq. 7-12 is then written as:

$$\log K_{iow} = a \cdot \log\left(\frac{t_i - t_0}{t_0}\right) + b'$$

or:

$$\log K_{iow} = a \cdot \log k_i' + b' \tag{7-14}$$

It should be pointed out that the coefficients a and b or b' in Eqs. 7-12 and 7-14 must be determined using appropriate reference compounds for *each* chromatographic system. With respect to the choice of the organic stationary phase and reference compounds (type, range of hydrophobicity) and the goodness of the LFER, in principle the same conclusions as drawn earlier for organic solvent–water systems are valid. For a given set of structurally related compounds, reasonably good correlations may be obtained. Finally, we should note that when using an organic solvent–water mixture as mobile phase, the (rather complex) effect of the organic cosolvent on the activity coefficient of an organic compound in the mobile phase (Section 5.4) has to be taken into account when establishing LFERs of the type Eqs. 7-12 and 7-14.

In summary, appropriate use of chromatographic systems for evaluating the partitioning behavior of organic compounds between nonaqueous phases and water (e.g., octanol–water) offers several advantages. Once a chromatographic system is set up and calibrated, many compounds may be investigated at once. The measurements are fast. Also, accurate compound quantification (which is a prerequisite when using solvent–water systems) is not required. For more details and additional references see Lambert (1993) and Herbert and Dorsey (1995).

Polyparameter LFERs for Estimation of the Octanol–Water Partition Constant

It is also possible to estimate K_{iow} via polyparameter LFERs such as Eq. 7-9 (with the coefficients in Table 7.2), provided that all the necessary parameters are known for the compound of interest. Note that such polyparameter LFERs are also used to characterize stationary phases in chromatographic systems such as the ones described above (Abraham et al., 1997). Such information provides the necessary knowledge about the molecular interactions between a given set of compounds and a given stationary phase. This understanding is very helpful for establishing logical one-parameter LFERs (Eqs. 7-12 and 7-14) for prediction of K_{iow} values.

The Atom/Fragment Contribution Method for Estimation of the Octanol–Water Partition Constant

Finally, the fragment or group contribution approach is widely used for predicting K_{iow} values solely from the structure of a given compound. We have already introduced this approach in very general terms in Section 3.4 (Eqs. 3-57 and 3-58), and we have discussed one application in Section 6.4 when dealing with the prediction of the air–water partition constants (Eq. 6-22, Table 6.4). We have also pointed out that any approach of this type suffers from the difficulty of quantifying electronic and steric effects between functional groups present within the same molecule. Therefore, in addition to simply adding up the individual contributions associated with the various structural pieces of which a compound is composed, numerous correction factors have to be used to account for such *intramolecular* interactions. Nevertheless, because of the very large number of experimental octanol–water partition constants available, the various versions of fragment or group contribution methods proposed in the literature for estimating K_{iow} (e.g., Hansch et al., 1995; Meylan and Howard, 1995) are much more sophisticated than the methods available to predict other partition constants, including K_{iaw}.

The classical and most widely used fragment or group contribution method for estimating K_{iow} is the one introduced originally by Rekker and co-workers (Rekker, 1977) and Hansch and Leo (Hansch and Leo, 1979; Hansch and Leo, 1995; Hansch et al., 1995). The computerized version of this method (known as the CLOGP program; note again the P is often used to denote K_{iow}) has been initially established by Chou and Jurs (1979) and has since been modified and extended (Hansch and Leo, 1995). The method uses primarily single-atom "fundamental" fragments consisting of isolated types of carbons, hydrogen, and various heteroatoms, plus some multiple-atom "fundamental" fragments (e.g., –OH, –COOH, –CN, $-NO_2$). These fundamental fragments were derived from a limited number of simple molecules. Therefore, the method also uses a large number of correction factors including unsaturation and conjugation, branching, multiple halogenation, proximity of polar groups, and many more (for more details see Hansch et al., 1995).

In the following, the atom/fragment contribution method (AFC method) developed by Meylan and Howard (1995) is used to illustrate the approach. This method is similar to the CLOGP method, but it is easier to see its application without using a computer program. Here, we confine ourselves to a few selected examples of fragment coefficients and correction factors. This will reveal how the method is applied and how certain important substructural units quantitatively affect the *n*-octanol–water partitioning of a given compound. For a more detailed treatment of this method including a discussion of its performance, we refer to the literature (Meylan and Howard, 1995).

Using a large database of K_{iow} values, fragment coefficients and correction factors were derived by multiple linear regression (Tables 7.4 and 7.5 give selected values of fragment coefficients and of some correction factors reported by Meylan and Howard, 1995). For estimating the log K_{iow} value of a given compound at 25°C, one simply adds up all fragment constants, f_k, and correction factors, c_j, according to the equation

$$\log K_{iow} = \sum_k n_k \cdot f_k + \sum_j n_j \cdot c_j + 0.23 \tag{7-15}$$

where n_k and n_j are the frequency of each type of fragment and specific interaction, respectively, occurring in the compound of interest.

The magnitudes of the individual atom/fragment coefficients give us a feeling for the contribution of each type of substructural unit (e.g., a functional group) to the overall K_{iow} of a compound. Recall that in most cases, the effect of a given subunit on K_{iow} is primarily due to its effect on the aqueous activity coefficient of the compound, and to a lesser extent on γ_{io}. First, we note that any aliphatic, olefinic, or aromatic carbon atom has a positive fragment coefficient and therefore increases log K_{iow}. For aliphatic carbons, the coefficient decreases with increased branching. This can be rationalized by the smaller size of a branched versus nonbranched compound resulting in reduced cavity "costs." Furthermore, because of the higher polarizability of π-electrons, olefinic and aromatic carbon atoms have a somewhat smaller coefficient as compared to the corresponding aliphatic carbon. Except for aliphatically bound fluorine, all halogens increase K_{iow} significantly. This *hydrophobic* effect of the halogens increases, as expected, with the size of the halogens (i.e., I > Br > Cl > F), and it is more pronounced for halogens bound to aromatic carbon as compared to halogens on aliphatic carbon. The latter fact can be explained by the interactions of the nonbonded electrons of the halogens with the π-electron system, causing a decrease in the polarity of the corresponding carbon–halogen bond.

With respect to the functional groups containing oxygen, nitrogen, sulfur and phosphorus (see also Chapter 2), in most cases, such polar groups decrease log K_{iow} primarily due to hydrogen bonding. This *hydrophilic* effect is, in general, more pronounced if the polar group is aliphatically bound. Again, interactions of nonbonded or π-electrons of the functional group with the aromatic π-electron system (i.e., by resonance, see Chapter 2) are the major explanation for these findings. Note that in the case of isolated double bonds, this resonance effect is smaller. It is only one-third to one-half of the effect of an aromatic system.

As illustrated by the examples in Table 7.5, application of correction factors is necessary in those cases in which electronic and/or steric interactions of functional groups within a molecule influence the solvation of the compound. A positive correction factor is required if the interaction decreases the overall H-donor and/or

Table 7.4 Selected Atom/Fragment Coefficients, f_k for log K_{iow} Estimation at 25°C (Eqs. 7-15 and 7-16) [a]

Atom/Fragment	f_k	Atom/Fragment	f_k
Carbon		*Carbonyls*	
–CH$_3$	0.55	al–CHO	–0.94
–CH$_2$–	0.49	ar–CHO	–0.28
–CH<	0.36	al–CO–al	–1.56
>C<	0.27	ol–CO–al	–1.27
=CH$_2$	0.52	ar–CO–al	–0.87
=CH– or =C<	0.38	ar–CO–ar	–0.20
C$_{ar}$	0.29	al–COO– (ester)	–0.95
		ar–COO– (ester)	–0.71
Halogens		al–CON< (amide)	–0.52
al–F	0.00	ar–CON< (amide)	0.16
ar–F	0.20	>N–COO– (carbamate)	0.13
al–Cl	0.31	>N–CO–N< (urea)	1.05
ol–Cl	0.49	al–COOH	–0.69
ar–Cl	0.64	ar–COOH	–0.12
al–Br	0.40		
ar–Br	0.89	*Nitrogen-Containing Groups*	
al–I	0.81	al–NH$_2$	–1.41
ar–I	1.17	al–NH–	–1.50
		al–N<	–1.83
Aliphatic Oxygen		ar–NH$_2$, ar –NH–, ar–N<	–0.92
al–O–al	–1.26	al–NO$_2$	–0.81
al–O–ar	–0.47	ar–NO$_2$	–0.18
ar–O–ar	0.29	ar–N=N–ar	0.35
al–OH	–1.41	al–C≡N	–0.92
ol–OH	–0.89	ar–C≡N	–0.45
ar–OH	–0.48		
al–O–(P)	–0.02	*Sulfur-Containing Groups*	
ar–O–(P)	0.53	al–SH	
		ar–SH	
Heteroatoms in Aromatic Systems		al–S–al	–0.40
		ar–S–al	0.05
Oxygen	–0.04	al–SO–al	–2.55
Nitrogen in five-member ring	–0.53	ar–SO–al	–2.11
Nitrogen in six-member ring	–0.73	al–SO$_2$–al	–2.43
Nitrogen at fused ring location	0.00	ar–SO$_2$–al	–1.98
Sulfur	0.41	al–SO$_2$N<	–0.44
		ar–SO$_2$N<	–0.21
Phosphorus		ar–SO$_3$H	–3.16
⩾P=O	–2.42		
⩾P=S	–0.66		

[a] Data from Meylan and Howard (1995); total number of fragment constants derived: 130; al = aliphatic attachment, ol = olefinic attachment; ar = aromatic attachment.

Table 7.5 Examples of Correction Factors, c_j, for log K_{iow} Estimation at 25°C (Eqs. 7-15 and 7-16) [a]

Description	c_j	Description	c_j
Factors Involving Aromatic Ring Substituent Positions [b]			
o–OH/–COOH	1.19	*o*–N< /two arom. N	1.28
o–OH/–COO–(ester)	1.26	*o*–CH_3/–CON< (amide)	–0.74
o–N /–CON< (amide)	0.62	2 × *o* –CH_3/–CON< (amide)	–1.13
o–OR/arom. N	0.45	*p*–N /–OH	–0.35
o–OR/two arom. N	0.90	*o,m,p*–NO_2/–OH or –N<	0.58
o–N< /arom. N	0.64	*p*–OH/COO–(ester)	0.65
Miscellaneous Factors			
More than one aliph. –COOH	–0.59	Symmetric triazine ring	0.89
More than one aliph. –OH	0.41	Fused aliphatic ring connection [c]	–0.34
α-Amino acid	–2.02		

[a] Data from Meylan and Howard (1995); total number of correction factors derived: 235.
[b] *o* = *ortho*, *m* = *meta*, *p* = *para* substitution. [c] See Illustrative Example 7.2.

H-acceptor capability of the compound. The factor is negative, if the opposite is true. Examples of the former case are *ortho*-substitutions in aromatic systems leading to *intramolecular* H-bonding (e.g., –COOH/–OH; –COOR/–OH; –OH/–OH), or substituents in any position that decrease the electron density at a polar group (e.g., –OH or –N< with –NO_2). Examples in which negative correction factors have to be applied include *ortho*-substitutions in aromatic systems that cause a disturbance of the resonance of a polar group with the aromatic system (the attachment has a more aliphatic character, e.g., –CH_3/–$CONH_2$), or the presence of several polar groups leading to a higher overall polarity of the molecule. For a more comprehensive collection of all the 235 correction factors derived for this method, see the paper by Meylan and Howard (1995). Some examples of the use of Eq. 7-15 are given in Illustrative Example 7.2.

Finally, one should recognize that if the log K_{iow} value of a structurally related compound (rel.compd) is known, the estimation expression is simplified and the accuracy of the result is improved using:

$$\log K_{iow} = \log K_{iow}(\text{rel.compd}) - \sum_k n_k \cdot f_k + \sum_k n_k \cdot f_k - \sum_j n_j \cdot c_j + \sum_j n_j \cdot c_j \quad (7\text{-}16)$$

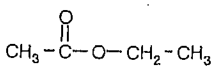
fragments corrections
removed added removed added

Some applications of Eq. 7-16 are given in Illustrative Example 7.3.

Illustrative Example 7.2 Estimating Octanol–Water Partition Constants from Structure Using the Atom/Fragment Contribution Method

Problem

Estimate the K_{iow} values at 25°C of (a) ethylacetate, (b) 2,3,7,8-tetrachlorodibenzodioxin, (c) the herbicide 2-*s*-butyl-4,6-dinitrophenol (Dinoseb), (d) the insecticide parathion, and (e) the hormone testosterone using solely the fragment coefficients and correction factors given in Tables 7.4 and 7.5 (Eq. 7-15).



$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3$

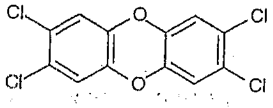
ethyl acetate

Answer (a)

Fragment	f_k	×	n_k	=	Value
$-CH_3$	0.55		2		1.10
$-CH_2-$	0.49		1		0.49
al–COO–(ester)	–0.95		1		–0.95
					+0.23

log K_{iow} (est.) *0.87*

(exp.) 0.73



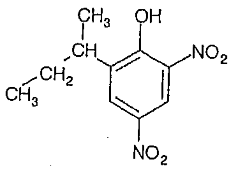
2,3,7,8-tetrachlorodibenzodioxin

Answer (b)

Fragment	f_k	×	n_k	=	Value
C_{ar}	0.29		12		3.48
ar–Cl	0.64		4		2.56
ar–O–ar	0.29		2		0.58
					+0.23

log K_{iow} (est.) *6.85*

(exp.) 6.53



2-*s*-butyl-4,6-dinitrophenol (Dinoseb)

Answer (c)

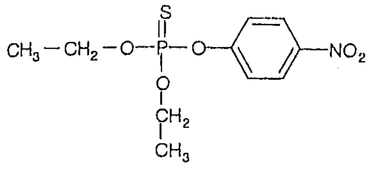
Fragment	f_k	×	n_k	=	Value
$-CH_3$	0.55		2		1.10
$-CH_2-$	0.49		1		0.49
–CH<	0.36		1		0.36
C_{ar}	0.29		6		1.65
ar–OH	–0.48		1		–0.48
ar–NO_2	–0.18		2		–0.36

Corr. Factor	c_j	×	n_j	=	Value
o,m,p–NO_2/OH	0.58		1		0.58
					+0.23

log K_{iow} (est.) *3.57*

(exp.) 3.56

Note: Since it is not clear whether in the case of two nitro substituents the correction factor has to be applied twice, both scenarios have been calculated. Comparison with the experimental value suggests that the correction factor has to be applicated only once.

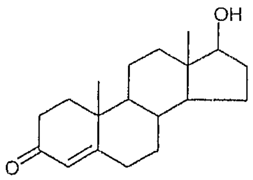


parathion

Answer (d)

Fragment	f_k	×	n_k	=	Value
$-CH_3$	0.55		2		1.10
$-CH_2-$	0.49		2		0.98
al–O–P	−0.02		2		−0.04
P=S	−0.66		1		−0.66
ar–O–P	+0.53		1		0.53
C_{ar}	0.29		6		1.74
ar–NO_2	−0.18		1		−0.18
					+0.23

log K_{iow} (est.) *3.70*
(exp.) 3.83



testosterone

Answer (e)

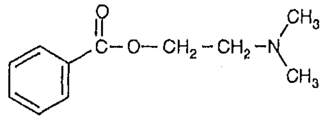
Fragment	f_k	×	n_k	=	Value
$-CH_3$	0.55		2		1.10
$-CH_2-$	0.49		8		3.92
–CH<	0.36		4		1.44
>C<	0.27		2		0.54
=CH– or =C<	0.38		2		0.76
al–OH	−1.41		1		−1.41
ol–CO–al	−1.27		1		−1.27
Corr. Factor	c_j	×	n_j	=	Value
fused aliph ring.corr.	−0.34		6		−2.04
					+0.23

log K_{iow} (est.) *3.27*
(exp.) 3.32

Illustrative Example 7.3 **Estimating Octanol–Water Partition Constants Based on Experimental K_{iow}'s of Structurally Related Compounds**

Problem

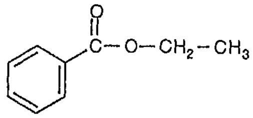
Estimate the K_{iow} values at 25°C of the following compounds based on the experimental K_{iow} values of the indicated structurally related compounds: (a) benzoic acid dimethylaminoethyl ester from benzoic acid ethyl ester (log K_{iow} = 2.64), (b) the insecticide methoxychlor from DDT (log K_{iow} = 6.20), (c) the insecticide fenthion from parathion [log K_{iow} = 3.83, see Ill. Ex. 7.2, Answer (d)], and (d) the hormone estradiol from testosterone [log K_{iow} = 3.32, see Ill. Ex. 7.2, Answer (e)].



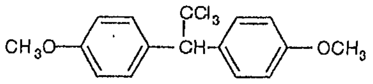
benzoic acid dimethylaminoethylester

Answer (a)

	Fragment	f_k	×	n_k	=	Value
Starting	K_{iow}					2.64
Add	$-CH_2-$	0.55		1		0.49
	$-CH_3$	0.55		1		0.55
	al–N<	−1.83		1		−1.83
				log K_{iow}	(est.)	*1.85*
					(exp.)	2.06



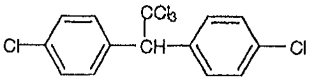
benzoic acid ethylester



methoxychlor

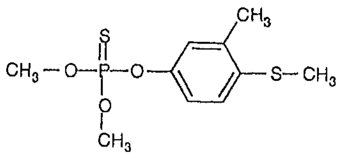
Answer (b)

	Fragment	f_k	×	n_k	=	Value
Starting	K_{iow}					6.20
Remove	ar–Cl	0.64		2		−1.28
Add	$-CH_3$	0.55		2		1.10
	al–O–ar	−0.47		2		−0.94
				log K_{iow}	(est.)	*5.08*
					(exp.)	5.08



DDT

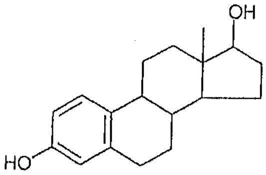
Hence, by substitution of 2 chlorine atoms by two methoxy groups the K_{iow} value is lowered by one order of magnitude. Such insights are used by chemical manufacturers to adjust chemical properties to suit specific purposes.



fenthion

Answer (c)

	Fragment	f_k	×	n_k	=	Value
Starting	K_{iow}					3.83
Remove	$-CH_2-$	0.49		2		−0.98
	ar–NO_2	−0.18		1		+0.18
Add	$-CH_3$	0.55		2		+1.10
	ar–S–al	0.05		1		+0.05
				log K_{iow}	(est.)	*4.18*
					(exp.)	4.10



estradiol

Answer (d)

	Fragment/ Corr. Factor	f_k/c_j	×	n_k/n_j	=	Value
Starting	K_{iow}					3.32
Remove	$-CH_3$	0.55		1		–0.55
	$-CH_2-$	0.49		2		–0.98
	>C<	0.27		1		–0.27
	=CH– or =C<	0.38		2		–0.76
	ol–CO–al	–1.27		1		+1.27
	fused aliph. ring.corr.	–0.34		2		+0.68 ?
Add	C_{ar}	0.29		6		+1.74
	ar–OH	0.48		1		–0.48
				log K_{iow} (est.)		*3.97*
					or	*3.29*

Advanced Topic 7.5 Dissolution of Organic Compounds in Water from Organic Liquid Mixtures—Equilibrium Considerations

There are numerous cases of environmental contaminations in which we need to know how organic compounds present in *liquid organic mixtures* partition into an aqueous phase. Such cases include the dissolution of compounds from the mixtures into water from so-called *l*ight *n*on *a*queous *p*hase *l*iquids (LNAPLs, e.g., gasoline, diesel fuel, heating oil) or *d*ense non aqueous phase liquids (DNAPLs, e.g., coal tars, creosotes, chlorinated solvent mixtures, PCBs, hydraulic oils containing PCBs). The density distinction is made because if the liquid mixture density is greater than that of water, then the mixture tends to "fall" through water bodies and reside at loci like bedrock underlying aquifers or at river bottoms. In contrast, LNAPLs float on water tables or at the air–water interface.

In this section, we evaluate the factors that determine the concentration of a given component of an LNAPL or DNAPL in an adjacent aqueous phase that is *in equilibrium* with the organic mixture. Hence, we consider a snapshot of the situation where we assume a constant composition of the liquid organic mixture. Of course, in reality, when exposed continuously to "clean" water, the composition of an LNAPL or DNAPL may change significantly with time, because a given mixture will become depleted in the more water-soluble compounds. Furthermore, depending on the contact time and contact area between the organic phase and the water, equilibrium may not be established. Therefore, a mass transfer approach has to be taken to describe the dissolution process. However, even for modeling the dissolution kinetics, the equilibrium partitioning of a given compound needs to be known to quantify the mass transfer gradient (see Part IV).

As a starting point for describing the equilibrium partitioning of a given compound *i* between a liquid organic mixture (subscript "mix") and an aqueous phase (subscript "w"), we rewrite Eq. 7-1 as:

$$x_{iw} = x_{i\text{mix}} \cdot \gamma_{i\text{mix}} \cdot \gamma_{iw}^{-1} \tag{7-17}$$

or in terms of molar concentrations (Eq. 7-2):

$$C_{iw} = C_{i\text{mix}} \cdot \overline{V}_{\text{mix}} \cdot \gamma_{i\text{mix}} \cdot \left(\gamma_{iw} \cdot \overline{V}_{\text{w}}\right)^{-1} \tag{7-18}$$

In order to calculate the aqueous concentration of compound i at equilibrium, one needs to know its mole fraction, $x_{i\text{mix}}$, in the mixture (or its molar concentration, $C_{i\text{mix}}$, and the molar volume, $\overline{V}_{\text{mix}}$, of the mixture), as well as its activity coefficients in the organic ($\gamma_{i\text{mix}}$) and the aqueous (γ_{iw}) phases. Very often, when dealing with complex mixtures, $\overline{V}_{\text{mix}}$ is not known and has to be estimated. At a first approximation, this can be done from the density, ρ_{mix}, of the liquid mixture, and by assuming an average molar mass, $\overline{M}_{\text{mix}}$, of the mixture components:

$$\overline{V}_{\text{mix}} \cong \frac{\overline{M}_{\text{mix}}}{\rho_{\text{mix}}} \tag{7-19}$$

For example, the molar mass of gasoline has been estimated as near 110 g·mol^{-1} and that of coal tar as near 150 g·mol^{-1} (Masters, 1998; Picel et al., 1988).

Let us now consider the various factors that may influence the equilibrium partitioning of an organic compound between an organic mixture and water. First, there are some cases in which the organic mixture originally contains a significant amount of a highly water–soluble compound that, at equilibrium with a water phase, may have dissolved to a great extent into the water leading to a cosolvent effect as discussed in Section 5.4. Prominent examples include the presence of oxygenated compounds such as methyl-*t*-butyl ether (MBTE), methanol, or ethanol in gasoline (Cline et al., 1991; Poulsen et al., 1992; Heermann and Powers, 1998). We recall from Section 5.4 that we can neglect the cosolvent effect in the water if the volume fraction of the organic solvent does not exceed 0.01 (1%). However, in some countries, by law, such polar compounds may make up 10 to 20% of the gasoline. In these cases, cosolvent effects in the "aqueous" phase may be significant (for more details see, e.g., Heermann and Powers, 1998). To illustrate, the activity coefficient of naphthalene in a 20% ethanol/80% water mixture is 7 times smaller than in pure water (Table 5.8). In the following, we will focus on those cases for which we may assume that the effect of other dissolved mixture constituents on the *aqueous* activity coefficient of a given compound is minimal. Furthermore, we also neglect the effect of salts on γ_{iw} (which has the opposite effect of a cosolvent, see Section 5.4, Eq. 5-28), which we would need to consider when dealing with the pollution of the marine environment or groundwater brines. Thus, for compounds for which $\gamma_{iw} \cong \gamma_{iw}^{\text{sat}}$ (Section 5.2), we may substitute the term $(\gamma_{iw}\overline{V}_{\text{w}})^{-1}$ in Eq. 7-18 by the *liquid* aqueous solubility, $C_{iw}^{\text{sat}}(\text{L})$, of the compound:

$$C_{iw} = C_{i\text{mix}} \cdot \overline{V}_{\text{mix}} \cdot \gamma_{i\text{mix}} \cdot C_{iw}^{\text{sat}}(\text{L}) \tag{7-20}$$

or with $x_{i\text{mix}} = C_{i\text{mix}} \cdot \overline{V}_{\text{mix}}$:

$$C_{iw} = x_{i\text{mix}} \cdot \gamma_{i\text{mix}} \cdot C_{iw}^{\text{sat}}(\text{L}) \tag{7-21}$$

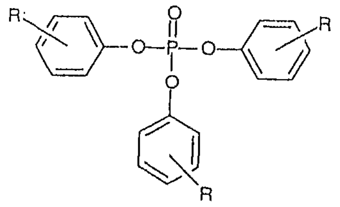
By rearranging Eq. 7-20, we may then also express the organic mixture–water partition coefficient, $K_{i\mathrm{mix\,w}}$, as:

$$K_{i\mathrm{mix\,w}} = \frac{C_{i\mathrm{mix}}}{C_{iw}} = \frac{1}{\gamma_{i\mathrm{mix}} \cdot \overline{V}_{\mathrm{mix}} \cdot C_{iw}^{\mathrm{sat}}(\mathrm{L})} \qquad (7\text{-}22)$$

Let us now evaluate in which cases we may, as a first approximation, assume that *Raoult's law* is valid. Said another way, in what cases may we set $\gamma_{i\mathrm{mix}}$ in Eqs. 7-20 to 7-22 equal to 1? From our earlier discussions on the molecular factors that determine the magnitude of the activity coefficient of an organic compound in an organic liquid, we would expect more or less ideal behavior, that is, $\gamma_{i\mathrm{mix}}$ values not too different from 1 for (i) apolar compounds in mixtures in which the major components undergo primarily vdW interactions, and (ii) monopolar compounds in the same situation, but with the restriction that in the mixture there are no major constituents exhibiting a significant complementary polarity. As confirmed by experimental data and by model calculations using approaches such as the UNIFAC method (e.g., Peters et al., 1999b), examples meeting the above criteria include aliphatic hydrocarbons and BTEX compounds (Fig. 2.13) present in most gasolines and in other fuels (Cline et al., 1991; Hemptinne et al., 1998; Heermann and Powers, 1998; Garg and Rixey, 1999), the components of mixtures of chlorinated solvents (Broholm and Feenstra, 1995), PAHs present in diesel fuels, coal tars, and creosotes (Lane and Loehr, 1992; Lee et al., 1992a,b), and PCB congeners present in pure PCB mixtures (e.g., Aroclor 1242) or in hydraulic oils consisting of other types of compounds [e.g., trialkylphenylphosphates (Luthy et al., 1997a); see also Illustrative Example 7.4]. In all these cases, the $\gamma_{i\mathrm{mix}}$ values determined were found to meet the Raoult's law criteria within less than a factor of 2 to 3, and, therefore, for practical purposes, $\gamma_{i\mathrm{mix}}$ can be approximated as 1.

We should note that, particularly for bipolar compounds such as, for example, certain additives in gasoline (e.g., phenolic compounds, aromatic amines, see Chapter 2), larger deviations from ideal behavior have to be expected (Schmidt et al., 2002). In addition, it should be pointed out that in mixtures containing major quantities of polar compounds, the activity coefficients of the various mixture compounds may change with time if these polar constituents are depleted during the dissolution process. Furthermore, when using organic mixture–water partition coefficients as defined by Eq. 7-22, changes in the molar volume of the mixture as a consequence of the preferential dissolution of the more water-soluble components may have to be considered. Finally, we should be aware that the preferential dissolution of more soluble compounds in a mixture leads to a higher concentration of the less soluble compounds and thus to increasing concentrations in the aqueous phase. This has to be taken into account when evaluating the long-term dynamics of complex organic mixtures in the environment (e.g., Mackay et al., 1996; Peters et al., 1999a).

Illustrative Example 7.4 Estimating the Concentrations of Individual PCB Congeners in Water that Is in Equilibrium with an Aroclor and an Aroclor/Hydraulic Oil Mixture



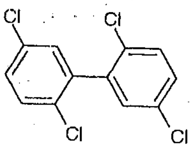
Fyrquel 220

Chemical structure of Fyrquel 220 hydraulic oil (R is primarily *n*-butyl)

Aroclor 1242 is a commercial PCB mixture with an average chlorine content of 42%, an average molar mass $\overline{M}_{\text{Aroclor}}$ of about 265 $\text{g} \cdot \text{mol}^{-1}$, and a density ρ_{Aroclor} of 1.39 $\text{g} \cdot \text{cm}^{-3}$ at 25°C. Luthy et al. (1997a) have determined the composition of a pure Aroclor 1242 mixture, and they have measured the aqueous concentrations of some individual congeners established at 25°C in equilibrium with (a) the real Aroclor 1242 mixture and (b) a mixture of 5% (v/v) Aroclor 1242 in a hydraulic oil (Fyrquel 220) consisting of trialkyl-phenylphosphates (see margin), with an average molar mass $\overline{M}_{\text{Fyrquel}}$ of about 380 $\text{g} \cdot \text{mol}^{-1}$ at a density r_{Fyrquel} of 1.14 $\text{g} \cdot \text{cm}^{-3}$ at 25°C.

Problem

Among the congeners investigated was 2,2',5,5'-tetrachlorobiphenyl (TeClBP), which was determined to be present in the Aroclor 1242 mixture at about 3.2 mass percent (i.e., mass fraction $m_{i\,\text{Aroclor}} = 0.032\ \text{g}_i \cdot \text{g}_{\text{Aroclor}}^{-1}$). The measured aqueous concentrations for this compound were 1.11 $\mu\text{g} \cdot \text{L}^{-1}$ (case a) and 0.10 $\mu\text{g} \cdot \text{L}^{-1}$ (case b), respectively. Are these concentrations reasonable? What aqueous TeClBP concentrations would you have predicted from the above information, when assuming that Raoult's law is valid in both cases?



i - 2,2'5,5'-tetrachlorobiphenyl (TeClBP)

$M_i = 292.0\ \text{g} \cdot \text{cm}^{-3}$

$T_m = 86.5°\text{C}$

$C_{iw}^{\text{sat}} = 10^{-7}\ \text{mol} \cdot \text{L}^{-1}$

(see Appendix C)

Answer (a)

Convert the mass fraction ($m_{i\,\text{Aroclor}} = 0.032$) of TeClBP in the Aroclor 1242 mixture into the mole fraction by using the average molar mass, $\overline{M}_{\text{Arcolor}}$, of 265 $\text{g} \cdot \text{mol}^{-1}$:

$$x_{i\,\text{Aroclor}} = m_{i\,\text{Aroclor}} \cdot \frac{\overline{M}_{\text{Aroclor}}}{M_i} = (0.032)\frac{(265)}{(292)} = 0.029$$

Estimate the liquid aqueous solubility of TeClBP from its aqueous solubility using T_m (Eqs. 139 5-13 and p.124 4-41). The resulting $C_{iw}^{\text{sat}}(\text{L})$ value is $3.5 \times 10^{-7}\ \text{mol} \cdot \text{L}^{-1}$. Insert this value together with the above calculated $x_{i\,\text{Aroclor}}$ value and $\gamma_{i\,\text{Aroclor}} = 1$ into Eq. 7-~~19~~ 21 to get the estimated aqueous concentration of TeClBP:

$$C_{iw} = (0.029)(1)(3.5 \times 10^{-7}) = \mathit{1.0} \times \mathit{10}^{-8}\,\text{mol} \cdot \text{L}^{-1}$$

or about *3* $\mu\text{g} \cdot \text{L}^{-1}$. This value is three times higher than the measured one, but it is well within the same order of magnitude. Since it is rather unlikely that the apolar TeClBP has a $\gamma_{i\,\text{Aroclor}}$ value significantly smaller than 1, the discrepancy is more likely to be due to uncertainties in the measured mole fraction in the Aroclor 1242 mixture, in the aqueous concentration, and/or in the subcooled liquid solubility of TeClBP.

Answer (b)

Calculate the molar volumes of Aroclor 1242 and Fyrquel from the corresponding average molar masses and densities:

$$\overline{V}_{\text{Aroclor}} = \frac{265}{1.39} = 191\ \text{cm}^3\ \text{mol}^{-1} = 0.191\ \text{L}\cdot\text{mol}^{-1}$$

$$\overline{V}_{\text{Fyrquel}} = \frac{380}{1.14} = 333\ \text{cm}^3\ \text{mol}^{-1} = 0.333\ \text{L}\cdot\text{mol}^{-1}$$

Consider now one liter of the 5% (v/v) Aroclor/Fyrquel mixture. In this liter there are (0.05)/(0.191) = 0.262 moles total PCBs and (0.95)/(0.333) = 2.85 moles Fyrquel compounds, which yield a total number of 3.11 moles. The mole fraction of TeClBP in this mixture is then given by [recall that $x_{i\,\text{Aroclor}} = 0.029$, see Answer (a)]:

$$x_{i\,\text{mix}} = \frac{(0.029)(0.262)}{(3.11)} = 0.0024$$

Insertion of this value together with $C_{iw}^{\text{sat}}(\text{L}) = 3.5 \times 10^{-7}\ \text{mol}\cdot\text{L}^{-1}$ and $\gamma_{i\,\text{mix}} = 1$ into Eq. 7-19 yields

$$C_{iw} = (0.0024)\ (1)\ (3.5 \times 10^{-7}\ \text{mol}\cdot\text{L}^{-1}) = \mathit{8 \times 10^{-9}}\ \text{mol}\cdot\text{L}^{-1}$$

or about *0.25* $\mu\text{g}\cdot\text{L}^{-1}$. Again, this value is about 3 times higher than the measured one, which is very consistent with the result obtained for the pure Aroclor 1242 mixture. This suggests that the activity coefficients of TeClBP in Aroclor 1242 and in the Aroclor 1242/Fyrquel mixture are quite similar. From a molecular interaction point of view, this conclusion seems also reasonable, since the phosphate esters making up the Fyrquel mixtures are monopolar and exhibit about the same π_i values as the apolar PCBs (Abraham et al., 1994b).

7.6 Questions and Problems

Questions

Q 7.1

Give several reasons why it is important to know something about the partitioning behavior of a given compound between organic solvents and water.

Q 7.2

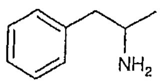
Which is(are) the dominating factor(s) determining the organic solvent–water partitioning of the majority of organic compounds of environmental concern?

Q 7.3

Why is the effect of temperature on organic solvent–water partitioning of organic compounds in many cases not very significant? What maximum $|\Delta_{\ell w}H_i|$ values would you expect? Give examples of solutes and organic solvents for which you would expect (a) a substantial positive (i.e., > 10 $\text{kJ}\cdot\text{mol}^{-1}$) and (b) a substantial negative (i.e., < $-10\ \text{kJ}\cdot\text{mol}^{-1}$) $\Delta_{\ell w}H_i$ value.

Q 7.4

When comparing the $K_{i\ell w}$ values of the stimulant amphetamine for the solvents trichloromethane (chloroform, log K_{icw} = 2.20), *n*-octanol (log K_{iow} = 1.80), and *n*-heptane (log K_{ihw} = 0.40), one can see that they differ quite substantially. Try to explain these differences.



i = amphetamine
(2-aminopropylbenzene)

Q 7.5

Imagine a compound for which $\Delta_{\ell w}G_i$ is equal to zero ($G_{i\ell}^{\mathrm{E}} = G_{iw}^{\mathrm{E}}$) in each of the solvent–water systems trichloromethane (chloroform)–water, *n*-octanol–water, and *n*-hexadecane–water. A friend of yours claims that the $K_{i\ell w}$ ($= C_{i\ell} / C_{iw}$) values of such a compound are 0.22, 0.11, and 0.06, respectively, for the three solvent–water systems. Another friend disagrees and claims that the $K_{i\ell w}$ values are all equal to 1. Who is right and why?

Q 7.6

What are the prerequisites for a successful estimation of $K_{i\ell w}$ (e.g., K_{iow}) by liquid chromatography?

Q 7.7

What are the major difficulties of any atom/fragment contribution method for estimation of solvent–water partition constants from structure?

Q 7.8

What are the major factors determining the aqueous concentration of a constituent of a liquid organic mixture (LNAPL, DNAPL) that is in equilibrium with an aqueous phase? Explain Raoult's law and give some practical examples of (a) cases in which you can apply it to estimate the concentration of a given LNAPL or DNAPL constituent in water that is in equilibrium with the organic liquid, and (b) cases in which Raoult's law does not hold.

Q 7.9

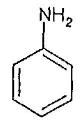
When flushing a gasoline-contaminated soil in a laboratory column with clean water, Mackay et al. (1996) observed that after 5 pore volumes (i.e., after 5 times replacing the water in the column), the benzene concentration in the effluent decreased from initially 370 to about 75 $\mu g \cdot L^{-1}$, while the 1,2-dimethylbenzene concentration increased from 1200 to 1400 $\mu g \cdot L^{-1}$. Try to explain these findings.

Problems

P 7.1 *Estimating Activity Coefficients of Organic Compounds in Organic Solvents*

Calculate the activity coefficients of (a) *n*-octane, and (b) aniline in water-saturated (see Table 5.1) *n*-hexane (γ_{ih}), toluene (γ_{it}), diethylether (γ_{id}), chloroform (γ_{ic}), *n*-octanol (γ_{io}), and in water γ_{iw} from the $K_{i\ell w}$ values given in Table 7.1. The aqueous solubilities of the two compounds are given in Appendix C. Compare and discuss the results.

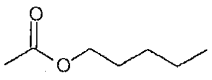
n-octane



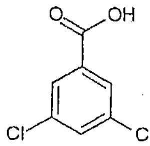
aniline

P 7.2 *Some Additional K_{iow} Estimation Exercises Using the Atom/Fragment Contribution Method*

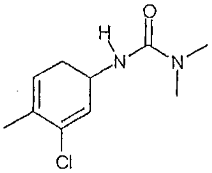
Estimate the K_{iow} values of the four compounds indicated below (a) by using only fragment constants and correction factors (Eq. 7-15), and (b) by starting with the K_{iow} value of a structurally related compound (Eq. 7-16) that you choose from Appendix C. Discuss the results by comparing them with the indicated experimental K_{iow} values.



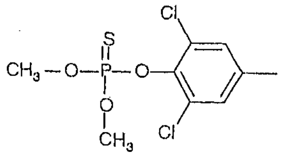
n-pentyl acetate
(exp. log K_{iow} = 2.23)



3,5-dichloro benzoic acid
(exp. log K_{iow} = 3.00)



chlortoluron
(exp. log K_{iow} = 2.41)



tolclofos-methyl
(exp. log K_{iow} = 4.56)

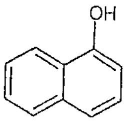
P 7.3 *Extraction of Organic Pollutants from Water Samples*

For analyzing organic pollutants in water, the compounds are commonly preconcentrated by adsorption, stripping (see Problem 6.6), or extraction with an organic solvent. You have the job to determine the concentration of 1-naphthol in a contaminated groundwater by using gas chromatography. You decide to extract 20 mL water samples with a convenient solvent. In the literature (Hansch and Leo, 1979) you find the following $K_{i\ell w}$ value for a series of solvents:

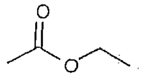
Solvent ℓ	$\log K_{i\ell w}$
n-hexane	0.52
benzene	1.89
trichloromethane (chloroform)	1.82
ethyl acetate (acetic acid ethyl ester)	2.60
n-octanol	2.90

Are you surprised to find such big differences in the $K_{i\ell w}$ values of 1-naphtol for the various solvents? If not, try to explain these differences. You choose ethyl acetate as solvent for the extraction. Why not n-octanol?

Now you wonder how much ethyl acetate you should use. Calculate the volume of ethyl acetate that you need at minimum if you want to extract at least 99% of the total 1-naphthol present in the water sample. Are you happy with this preconcentration step? Somebody tells you that it would be much wiser to extract the sample twice with the goal to get each time 90% of the total compound out of the water (which would also amount to 99%), and then pool the two extracts. How much total ethyl acetate would you need in this case? Finally, another colleague suggests to add 3.56 g NaCl to the 20 mL sample in order to improve the extraction efficiency. How much less ethyl acetate would be required in the presence of the salt? (*Hint:* Consult Table 5.7.) Is there any other effect that the addition of NaCl would have on the extraction, and is this effect favorable for the analytical procedure chosen?



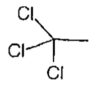
i = 1-naphthol



ethyl acetate

P 7.4 *A Small Accident in Your Kitchen*

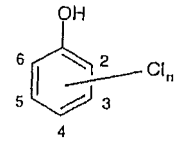
In your kitchen ($T = 25°\text{C}$) you drop a small bottle with 20 mL of the solvent 1,1,1-trichloroethane (methyl chloroform, MCF) that you use for cleaning purposes. The bottle breaks and the solvent starts to evaporate. The doors and the windows are closed. On your stove there is an open pan containing 2 L of cold olive oil. Furthermore, on the floor there is a large bucket that is filled with 50 L of water. The air volume of the kitchen is 30 m³. Calculate the concentration of MCF in the air, in the water in the bucket, and in the olive oil at equilibrium by assuming that the adsorption of MCF to any other phases/surfaces present in the kitchen can be neglected. Consider MCF as an apolar compound. You can find some important physical–chemical data in Appendix C and in Fig. 6.7. Comment on any assumption that you make.



1,1,1-trichloroethane
(methyl chloroform, MCF)

P 7.5 *Evaluating Partition Constants of Chlorinated Phenols in Two Different Organic Solvent-Water Systems*

Kishino and Kobayashi (1994) determined the *n*-octane–water ($K_{i\text{octw}}$) and *n*-octanol–water ($K_{i\text{ow}}$) partition constants of a series of chlorinated phenols (see Table below). Plot the log $K_{i\text{octw}}$ values versus the log $K_{i\text{ow}}$ values of the 13 compounds. Inspect the data and derive meaningfull LFERs of the type Eq. 7-7 for subsets of compounds. Discuss your findings in terms of the molecular interactions that govern the partitioning of the chlorinated phenols in the two different solvent–water systems.



chlorinated phenols

	compound	log $K_{i\text{octw}}$	log $K_{i\text{ow}}$ [a]
1	Phenol	–0.99	1.57
2	2-Chlorophenol	0.74	2.29
3	3-Chlorophenol	–0.31	2.64
4	4-Chlorophenol	–0.41	2.53
5	2,3-Dichlorophenol	1.27	3.26
6	2,4-Dichlorophenol	1.21	3.20
7	2,5-Dichloropehol	1.31	3.36
8	2,6-Dichlorophenol	1.48	2.92
9	3,5-Dichlorophenol	0.41	3.60
10	2,4,5-Trichlorophenol	1.76	4.02
11	2,4,6-Trichlorophenol	2.05	3.67
12	2,3,4,6-Tetrachlorophenol	2.58	4.24
13	Pentachlorophenol	3.18	5.02

[a] Values given in Appendix C may differ somewhat from the ones determined by Kishino and Kobayashi (1994).

P 7.6 *Assessing the Dissolution Behavior of Gasoline Components*

Gasoline is a mixture of primarily aliphatic (>50%) and aromatic (~ 30%) hydrocarbons with an average molar mass, $\overline{M}_{\text{gas}}$, of about 105 $\text{g}\cdot\text{mol}^{-1}$ and a density of about 0.75 $\text{g}\cdot\text{m}^{-3}$ (Cline et al., 1991). In addition it contains a variety of additives including, for example, oxygenates (see Section 7.5), antioxidants, corrosion inhibitors, detergents, antifreezing agents, dyes, and many more (Owen, 1989).

You are confronted with a gasoline spill underneath a gas station. Among the compounds that are of great concern with respect to groundwater pollution are benzene and 3,4-dimethylaniline (DMA). You know that the spilled gasoline contains 2 volume percent benzene and 10 $mg \cdot L^{-1}$ DMA. Furthermore, in the literature you find experimental gasoline–water partition coefficients (Eq. 7-22) of 300 $L_w \cdot L^{-1}_{gasoline}$ for benzene (Cline et al., 1991) and 30 $L_w \cdot L^{-1}_{gasoline}$ for DMA [determined by Schmidt et al. (2002) at pH8 where DMA is present primarily as neutral species (see Chapter 8)]. Note that these coefficients have been determined for other brands of gasoline. Answer now the following questions.

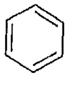
(a) Using the gasoline–water partition coefficients reported in the literature (see above), calculate the activity coefficients of benzene and DMA in the gasoline mixture of interest. Which of the two values do you trust more?

(b) What benzene and DMA concentration would you expect in groundwater that is in equilibrium with a large pool of the spilled gasoline at 25°C (i.e., assume that the gasoline composition is not altered significantly by the dissolution of the components in the aqueous phase).

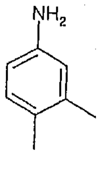
(c) In the aqueous phase that is in equilibrium with the spilled gasoline, you measure a naphthalene concentration of 1 $mg \cdot L^{-1}$. How much naphthalene does the gasoline contain? Comment on any assumption that you make.

You find all necessary data in Appendix C.

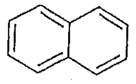
Hint: To estimate the mole fraction of a given gasoline component from its volume fraction, use Eq. 5-34 by assuming a binary mixture of the component with a solvent that has the average molar volume of the whole gasoline mixture.



benzene



3,4-dimethylaniline
(3,4-DMA)



naphthalene