

Chapter 9

SOLUBILITY (C_{iw}^{sat}) AND ACTIVITY COEFFICIENT (γ_{iw}^{sat}) IN WATER; AIR–WATER PARTITION CONSTANT (K_{iaw})

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9.1 Introduction and Thermodynamic Considerations

Whether an organic compound “likes” or “dislikes” being surrounded by liquid water, or alternatively, whether water “likes” or “dislikes” accommodating a given organic solute, determines the environmental behavior and toxic effects of the compound. Due to its small size and strong H-bonding characteristics, water is the most unusual solvent on the planet. Here and in Chapter 10, we discuss and try to visualize the molecular factors associated with partitioning an organic compound between a nonaqueous bulk phase (i.e., air, organic solvent) and an aqueous solution. We also consider how these factors determine a compound’s partition constants in the system considered. Fig. 9.1 summarizes the systems that concern us in our treatment of bulk phase partitioning between well-defined media. We have already briefly addressed partitioning involving organic solvents (right side of the scheme) in Chapter 7, where we have considered the compound to be in a (infinitely) diluted solution (superscript “ ∞ ”). We come back to this topic in more depth in Chapter 10. The left side of the scheme in Fig. 9.1 depicts the situation where equilibrium partitioning of the pure compound (liquid, “L” or solid, “s”) to air or water leads to a saturated vapor (Chapter 8) or a saturated aqueous solution, respectively. The latter, which is commonly referred to as the *water solubility* or the *aqueous solubility* of the compound (denoted as $C_{iw}^{\text{sat}}(\text{L}, \text{s})$), is the main focus of this chapter. This compound property, which has been determined experimentally for many compounds, not only tells us the maximum concentration of a given chemical that can be dissolved in pure water at a given temperature, but it also allows us to calculate the compound’s aqueous activity coefficient *at saturation*, γ_{iw}^{sat} , and, thus, the excess free energy in saturated aqueous solution. We also explore when we can use γ_{iw}^{sat} in place of the activity coefficient of a compound in *dilute* aqueous solution, γ_{iw}^{∞} , which represents a more relevant situation in the environment. Assuming ideal behavior in the gas phase, this is equivalent to assessing when we can approximate the air–water partition constant, K_{iaw}^{∞} , by the “saturated” air–water partition constant calculated from vapor pressure and aqueous solubility, K_{iaw}^{sat} (see thermodynamic cycles in Fig. 9.1). Finally, we address the effect

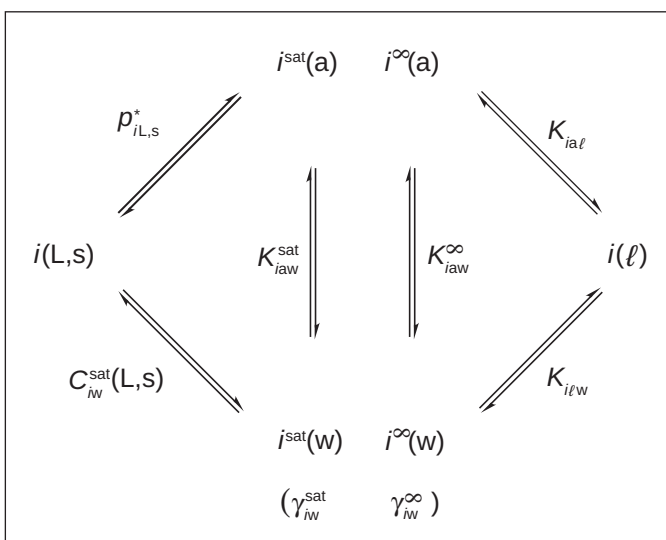


Figure 9.1 Thermodynamic cycles relating partition constants between air (a), water (w), pure organic liquid (L) or solid (s), and an organic solvent (ℓ) at saturated (superscript “sat,” left) and (infinitely) dilute (superscript “ ∞ ,” right) conditions.

of temperature, dissolved salts, and pH on the aqueous activity coefficient, and, thus, also on the air–water partition constant of a given organic compound.

Solubilities and Aqueous Activity Coefficients of Organic Liquids, Solids, and Gases

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. 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 4, Section 4.2):

$$\begin{aligned}\mu_{iL} &= \mu_{iL}^* + RT \ln \gamma_{iL} x_{iL} \\ \mu_{iw} &= \mu_{iL}^* + RT \ln \gamma_{iw} x_{iw}\end{aligned}\quad (9-1)$$

where we still use the subscript L to indicate the pure liquid organic phase, although in this case it contains some water molecules. Since in both expressions we relate chemical potential to the same reference potential, μ_{iL}^* , the difference in chemical potentials of the “product” (solute in aqueous solution) minus the “reactant” (i in its pure liquid) molecules at any time during the experiment is given by:

$$\mu_{iw} - \mu_{iL} = RT \ln \gamma_{iw} x_{iw} - RT \ln \gamma_{iL} x_{iL} \quad (9-2)$$

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. We then obtain:

$$\ln \frac{x_{iw}^{\text{sat}}}{x_{iL}} = \frac{RT \ln \gamma_{iL} - RT \ln \gamma_{iw}^{\text{sat}}}{RT} \quad (9-3)$$

where we now use the superscript “sat” to indicate that we are dealing with a saturated aqueous solution of the compound. In Eq. 9-3, we 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, $RT \ln \gamma_i$, is a free energy term per 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 to the mole

fraction of the compound itself; that is, x_{iL} remains approximately 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, Eq. 9-3 simplifies to:

$$\ln x_{iw}^{\text{sat}} = -\frac{RT \ln \gamma_{iw}^{\text{sat}}}{RT} = -\frac{G_{iw}^{\text{E, sat}}}{RT} \quad (9-4)$$

where $G_{iw}^{\text{E, sat}}$ is the *excess free energy* of the compound in *saturated* aqueous solution for the case when one chooses the pure liquid ($x_{iL} = 1$) as the reference state (see Chapter 4). Now we can see a key result; for an organic liquid, the aqueous activity coefficient is simply given by the inverse of its aqueous mole fraction solubility:

$$\gamma_{iw}^{\text{sat}} = \frac{1}{x_{iw}^{\text{sat}}} \quad (9-5a)$$

or in molar units (Eq. 4-26):

$$C_{iw}^{\text{sat}}(\text{L}) = \frac{1}{\bar{V}_w \gamma_{iw}^{\text{sat}}} \quad \text{for organic liquids} \quad (9-5b)$$

where \bar{V}_w is the molar volume of water (0.0181 L mol⁻¹).

When thermodynamically describing the solubility of a *solid organic compound* in water, conceptually, we can imagine first converting the solid to the liquid state and then proceeding as for a liquid compound. As discussed in Chapter 8, the free energy cost involved in the solid-to-liquid conversion is referred to as the free energy of fusion, $\Delta_{\text{fus}} G_i$, which can be derived from vapor pressure data (Eq. 8-9):

$$\Delta_{\text{fus}} G_i = RT \ln \frac{p_{iL}^*}{p_{is}^*} \quad (9-6)$$

In analogy to Eq. 9-2, we can now express the difference in chemical potential as:

$$\begin{aligned} \mu_{iw} - \mu_{is} &= \mu_{iw} - (\mu_{iL} - \Delta_{\text{fus}} G_i) \\ &= RT \ln \gamma_{iw} x_{iw} - (RT \ln \gamma_{iL} x_{iL} - \Delta_{\text{fus}} G_i) \end{aligned} \quad (9-7)$$

At equilibrium, we then obtain:

$$\gamma_{iw}^{\text{sat}} = \frac{1}{x_{iw}^{\text{sat}}(\text{s})} e^{-\Delta_{\text{fus}} G_i / RT} \quad (9-8a)$$

or in molar units: for organic solids

$$C_{iw}^{\text{sat}}(\text{s}) = \frac{1}{\bar{V}_w \gamma_{iw}^{\text{sat}}} e^{-\Delta_{\text{fus}} G_i / RT} \quad (9-8b)$$

Eq. 9-8b clearly shows that the solubility of an organic solid in water is dependent on both the compatibility of the chemical with the water *and* the ease with which the solid is converted to a liquid. Recalling the concept of a *subcooled* liquid compound as one that has cooled below its freezing temperature without becoming solid (Chapter 8, Fig. 8.2), we may evaluate the solubility of such a hypothetical liquid, $C_{iw}^{\text{sat}}(\text{L})$, as:

$$\gamma_{iw}^{\text{sat}} = \frac{1}{\bar{V}_w C_{iw}^{\text{sat}}(\text{L})} \quad (9-9)$$

where the liquid compound solubility is related to the actual experimental solubility of the solid compound using Eq. 9-8:

$$C_{iw}^{\text{sat}}(\text{L}) = C_{iw}^{\text{sat}}(\text{s}) e^{+\Delta_{\text{fus}} G_i / RT} \quad (9-10)$$

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 4, 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. 4.2d). Therefore, by equating chemical potential or fugacity expressions for a compound in both the gas phase and an equilibrated aqueous solution phase, we have:

$$p_i = \gamma_{iw} x_{iw} p_{iL}^* \quad (9-11)$$

We can now express the mole fraction solubility of a gaseous organic substance as a function of the partial pressure p_i :

$$x_{iw}^{p_i} = \frac{1}{\gamma_{iw}^{p_i}} \cdot \frac{p_i}{p_{iL}^*} \quad (9-12a)$$

or in molar units:

for gases

$$C_{iw}^{p_i} = \frac{1}{\bar{V}_w \gamma_{iw}^{p_i}} \cdot \frac{p_i}{p_{iL}^*} \quad (9-12b)$$

The activity coefficient, $\gamma_{iw}^{p_i}$, is not necessarily constant with varying p_i . In fact, evaluation of the air–water equilibrium distribution ratio as a function of p_i or $C_{iw}^{p_i}$ is one of the methods that can be used to assess the concentration dependence of an organic compound's activity coefficient, regardless of whether the compound is a gas, liquid, or solid at the temperature considered. If, for sparingly soluble gases, we assume that

$\gamma_{iw}^{p_i}$ is independent of concentration (even at saturation, where $p_i = p_i^*$ and 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:

$$C_{iw}^{\text{sat}}(\text{L}) = C_{iw}^{p_i} \frac{p_{iL}^*}{p_i} \quad (9-13)$$

Concentration Dependence of the Aqueous Activity Coefficient

From an environmental point of view, knowing the activity coefficient of an organic compound in *dilute* aqueous solution is of the most interest as it describes a concentration at which the solute molecules do not “feel” each other. This activity coefficient is commonly denoted as γ_{iw}^∞ and is referred to as the *limiting* activity coefficient or *infinite dilution* activity coefficient. As previously shown, an activity coefficient can be deduced from aqueous solubility (together with vapor pressure or melting data, as necessary). However, in using this “saturation” 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. Table 9.1 shows a comparison of γ_{iw}^{sat} values obtained from solubility measurements (Eqs. 9-5 and 9-8) with γ_{iw}^∞ values determined by various methods (including studies on the concentration dependence of air–water partitioning) 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 assume that γ_{iw} is independent of the concentration of the compound. As such, we 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. In other words, we assume that the solvation of a given organic molecule by water molecules is not influenced by the other molecules of that compound present. In Section 9.3, we introduce limited cases where this assumption is not valid.

Air–Water Partitioning: “The” Henry’s Law Constant

Following the previous discussion on the aqueous solubility of gases, we can now rearrange Eq. 9-12 to obtain the air–water partition constant, commonly referred to as “the” Henry’s law constant:

$$K_{iH} = \frac{p_i}{C_{iw}} = \gamma_{iw} p_{iL}^* \bar{V}_w \quad (9-14)$$

K_{iH} is commonly expressed in $\text{bar L}_w \text{ mol}^{-1}$ or $\text{Pa L}_w \text{ mol}^{-1}$. The “dimensionless” Henry constant, denoted as K_{iaw} , is related to K_{iH} by:

$$K_{iaw} = K_{iH}/RT \quad (9-15)$$

Table 9.1 Comparison of Activity Coefficients and Corresponding Excess Free Energies of a Series of Organic Compounds in Dilute and Saturated Aqueous Solution at 25°C ($G_{iw}^E = RT \ln \gamma_{iw}$)

Compound	γ_{iw}^{sat}	$G_{iw}^{E,\text{sat}a}$ (kJ mol ⁻¹)	γ_{iw}^{∞}	$G_{iw}^{E,\infty b}$ (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	2.3×10^2	13.5
1-Hexanol	9.0×10^2	16.9	8.0×10^2	16.6
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 (PCE)	6.5×10^4	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	27.4	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	36.0	1.7×10^6	35.6
Anthracene	2.5×10^6	36.5	2.7×10^6	36.7
Hexachlorobenzene	4.3×10^7	43.6	3.5×10^7	43.1
2,4,4'-Trichlorobiphenyl	5.6×10^7	44.2	4.7×10^7	43.8
2,2',5,5'-Tetrachlorobiphenyl	7.0×10^7	44.8	7.5×10^7	44.9
Benzo(a)pyrene	3.2×10^8	48.5	2.7×10^8	48.1

^aData from Appendix C using enthalpy and entropy of fusion values given by Hinckley et al. (1990) and Lide (1995).

^bData from Sherman et al. (1996); Staudinger and Roberts (1996); and Mitchell and Jurs (1998).

where R has to be expressed in the respective units, i.e., 0.0831 bar L_w mol⁻¹ K⁻¹ or 8310 Pa L_w mol⁻¹ K⁻¹.

Strictly speaking, the Henry's law constant is defined for solutes at infinite dilution. However, as discussed earlier, in most cases, we may assume that the aqueous activity coefficient is approximately independent of concentration (see Table 9.1). We may therefore replace γ_{iw} in Eq. 9-14 by γ_{iw}^{sat} :

$$K_{iH} \cong \gamma_{iw}^{\text{sat}} p_{iL}^* \bar{V}_w \cong \frac{p_{iL}^*}{C_{iw}^{\text{sat}}(\text{L})} \quad (9-16)$$

For solid compounds:

$$K_{iH} \cong \frac{p_{is}^*}{C_{iw}^{\text{sat}}(\text{s})} \quad (9-17)$$

because the free energy terms relating the liquid and solid vapor pressure and the liquid and solid aqueous solubility, Eqs. 9-6 and 9-10, cancel when dividing the two entities. From a practical point of view, Eqs. 9-16 and 9-17 are very useful because they tell us that we may estimate the Henry's law constant of a compound directly from its vapor pressure and aqueous solubility. In fact, many of the K_{iH} or K_{iaw} values listed in data compilations, including much of the data given in Appendix C, have been derived in this way. Comparison of calculated with experimental K_{iaw} values (see review and compilation of a large data set published by Sander, 2015) shows that, in most cases, Eqs. 9-16 and 9-17 yield quite satisfactory estimates with less than a factor of 2 deviation.

9.2 Molecular Interactions Governing the Aqueous Activity Coefficient and the Air–Water Partition Constant

Enthalpic and Entropic Contributions to the Excess Free Energy in Water and to the Free Energy of Air–Water Partitioning

As pointed out in the previous section, water is a very unusual solvent in that water molecules exhibit an extraordinary H-bonding capacity in relation to their molecular size, which is reflected in the high cohesive energy of water. In our simple cavity model of partitioning (Fig. 7.1), at least part of these H-bonds have to be disrupted when inserting an organic solute. However, since the water molecules are comparably small and, therefore, a large number of them are involved in forming the cavity, they conceivably may arrange themselves around the cavity with as little loss in H-bonding as possible. Unfortunately, even after decades of research trying to uncover the “secrets” of water, it is still unclear exactly how water molecules accommodate an organic molecule and how the size, shape, and polarity of the organic solute influence the rearrangement. To gain at least a few insights, one still relies on bulk observations that yield data such as enthalpy and entropy changes when partitioning an organic compound between air or an organic solvent and water.

In the following, we compare the standard enthalpy and entropy changes observed for some of our companion chemicals and other organic compounds for the following phase transfers (see also Fig. 9.2):

- (1) from water to air ($\Delta_{aw}H_i$, $\Delta_{aw}S_i$),
- (2) from the pure liquid to air ($\Delta_{vap}H_i$, $\Delta_{vap}S_i$), and
- (3) from the pure liquid to water (H_{iw}^E , the excess enthalpy; S_{iw}^E , the excess entropy in water; see Chapter 4, Eqs. 4-17 and 4-18).

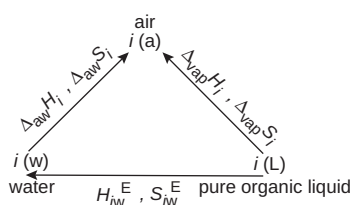


Figure 9.2 Standard enthalpy and entropy changes for the transfer of an organic compound from water to air (aw), and from the pure organic liquid to air (vap) and water (w) respectively.

The corresponding values are summarized in Table 9.2. The reported data are averages from various studies and, therefore, contain quite a large error (± 5 kJ mol⁻¹). Also, using the thermodynamic cycle, i.e., $\Delta_{aw}H_i = -\Delta_{vap}H_i + H_{iw}^E$, and $\Delta_{aw}S_i = -\Delta_{vap}S_i + S_{iw}^E$, some of the values have been adjusted to make the data set internally consistent. Nevertheless, we can draw some important general conclusions.

Table 9.2 Standard Enthalpy and Entropy Changes for the Transfer from Water to Air (aw), and from the Pure Organic Liquid to Air (vap) or Water (w) for Some Selected Organic Compounds^a

Compound	water to air			pure liquid to air			pure liquid to water			
	$\Delta_{\text{aw}} G_i^{(1)}$ (kJ mol ⁻¹)	$= \Delta_{\text{aw}} H_i$ (kJ mol ⁻¹)	$- T \Delta_{\text{aw}} S_i$ (kJ mol ⁻¹)	$\Delta_{\text{vap}} G_i^{(2)}$ (kJ mol ⁻¹)	$= \Delta_{\text{vap}} H_i$ (kJ mol ⁻¹)	$- T \Delta_{\text{vap}} S_i$ (kJ mol ⁻¹)	$G_i^{\text{E}(3)}$ (kJ mol ⁻¹)	$= H_{\text{w}}^{\text{E}}$ (kJ mol ⁻¹)	$- TS_{\text{w}}^{\text{E}}$ (kJ mol ⁻¹)	S_i^{E} (J K ⁻¹ mol ⁻¹)
pentane	-28	28	56	1	26	25	29	-2	-31	-104
hexane	-28	32	60	4	32	28	32	0	-32	-107
octane	-29	37	66	10	42	32	39	5	-34	-114
decane	-31	41	72	16	52	36	47	9	-36	-121
1-hexanol	0	67	67	17	62	45	17	-5	-22	-74
1-octanol	-1	74	75	22	71	49	23	-3	-26	-87
MTBE	-9	49	58	3	30	27	12	-19	-31	-104
PCE	-18	42	60	9	40	31	27	-2	-29	-97
benzene	-12	32	46	5	34	29	17	2	-17	-57
phenol	8	58	50	18	58	40	10	0	-10	-33
3-methylphenol	8	58	50	21	62	41	13	4	-9	-30
naphthalene	-6	45	51	20	58	38	26	13	-13	-44
phenanthrene	-2	54	56	34	69	35	36	15	-21	-70
anthracene	-2	50	52	36	68	32	38	18	-20	-67
pyrene	2	59	57	42	74	32	40	15	-25	-83
benzo(a)pyrene	8			58			50			
chlorobenzene	-13	29	42	10	41	31	23	12	-11	-37
1,3,5-trichlorobenzene	-16	34	50	18	50	32	34	16	-18	-60
hexachlorobenzene	-9	46	55	33	75	42	42	29	-13	-44
lindane (γ -HCH)	5	54	49	35	70	35	30	16	-14	-47
PCB 15	-5	54	59	35	72	37	40	18	-22	-74
PCB 153	-5	70	75	47	90	43	52	20	-32	-107
D5	-36	80	116	20	60	40	56	-20	-76	-255
D6	-36	92	128	26	65	39	62	-27	-89	-299

¹ $\Delta_{\text{aw}} G_i = -RT \ln p_i/x_i$; ⁽²⁾ $\Delta_{\text{vap}} G_i = -RT \ln p_i^*$; ⁽³⁾ $G_i^{\text{E}} = -RT \ln \gamma_{\text{w}}$

^a Data compiled and averaged from Shiu et al. (1997); Goss and Schwarzenbach (1999); Bamford et al. (2000); Beyer et al. (2002); Arey et al. (2005); Kühne et al. (2005); Goss (2006); Mintz et al. (2007); and Lei et al. (2010).

First, let us compare the relative importance of the entropy versus enthalpy contributions to the standard free energy of the three phase transfer processes. As seen in Chapter 8 (Fig. 8.5) and as is evident from Table 9.2, for vaporization at 25°C, the enthalpy contribution is always larger than the entropy contribution. A similar picture is obtained for the transfer of an organic compound between an organic solvent (*l*) and air (see Chapter 10). In contrast, when transferring an organic compound from water to the gas phase (air), the entropy term becomes much more important, and in most cases, is even the dominant term. This is due to the large excess entropy of organic chemicals in water, which disfavors their presence in the aqueous phase.

Looking at the transfer from pure liquid to water, for some of the smaller compounds (e.g., hexane, octane, PCE, benzene, 1-hexanol, phenol, 3-methylphenol in Table 9.2), the enthalpy that has to be “spent” to isolate the molecules from their pure liquid is about equal to the enthalpy gained when inserting the compound in water; the excess enthalpy is close to zero. For the monopolar compound MTBE, the excess enthalpy is even significantly negative because the MTBE molecules may undergo H-bonding in aqueous solution but not in their pure liquid phase. For larger compounds such as the PAHs or polychlorinated aromatic compounds, the excess enthalpy becomes larger, but the entropy term is still an important factor in determining the “dislike” of the compound for the aqueous phase. This entropic effect explains what is often referred to as “hydrophobicity.” An extreme case involves the monopolar cyclic polydimethylsiloxanes (D5, D6); these compounds exhibit a negative excess enthalpy but also an extremely large negative entropy term. The net result is that they are highly hydrophobic. In summary, when transferring a compound to or from water, the entropy effect primarily determines the “dislike” of the aqueous phase (i.e., making G_i^E positive).

The reasons for these large unfavorable entropy terms are not easy to rationalize because, as already stated, exactly how the water molecules arrange themselves around a given organic molecule is not clear. Conceivably, the water molecules forming a hydration shell around the organic compound lose some of their freedom of motion as compared to the bulk water molecules. More likely, however, the major contribution to this entropy term is the loss of freedom that the compound itself experiences when being transferred from its pure liquid into an environment that is more “rigid;” 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 conformational freedom, see Box 8.1) could also explain the quite substantial differences in excess entropy found between rigid aromatic (e.g., naphthalene, $S_{iw}^E = -44 \text{ J mol}^{-1} \text{ K}^{-1}$) and aliphatic (e.g., decane, $S_{iw}^E = -121 \text{ J mol}^{-1} \text{ K}^{-1}$) compounds of the same carbon number (Table 9.2), the latter having more degrees of conformational freedom in the gas or liquid phase. When compared to the entropies of freezing (negative entropy of fusion) of the two compounds at their melting points, one finds remarkably similar values, i.e., $\Delta_{\text{fus}} S_i(T_m) = -53$ and $-118 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively (Table 8.2). Inspecting the excess entropies of other compounds included in Table 9.2 shows the same qualitative picture, in that the more rigid compounds (i.e., PAHs, chlorobenzenes, and lindane) exhibit

distinctly lower excess entropies than the compounds with a less rigid structure (i.e., PCBs and cyclic polydimethylsiloxanes). Finally, we note that introducing a bipolar group such as an OH diminishes the excess entropy of both rigid and more flexible compounds, as is illustrated by phenol or 3-methylphenol versus benzene and by 1-hexanol and 1-octanol versus hexane and octane respectively. Due to H-bonding, the entropy of bipolar compounds in their pure liquid is lower as compared to the entropy of the structurally related apolar or monopolar compounds, thus leading to a comparably smaller loss in entropy when they transfer into water. The same reasoning explains their higher entropies of vaporization (Table 9.2), as we have already discussed in Section 8.2 when introducing the Fishtine constant (Eq. 8-16) for estimation of the entropy of vaporization of organic compounds at their boiling point.

9.3 LFERs for Estimating Air–Water Partition Constants and Aqueous Activity Coefficients/Aqueous Solubilities

Air–Water Partition Constant

pp-LFER. Using the *pp-LFER* approach described in Section 7.4, we may apply an equation published by Goss (2006) for estimating the air–water partition constant at 25°C:

$$\log K_{iaw} (298K) = 2.55V_i - 0.48L_i - 2.07S_i - 3.67A_i - 4.87B_i + 0.59 \quad (9-18)$$

(number of chemicals = 390; $r^2 = 0.99$; S.D. = 0.12)

From the examples given in Table 9.3 and other applications reported in the literature (e.g., Goss, 2006), we may conclude that Eq. 9-18 allows prediction of air–water partition constants within a factor of 2 to 3.

Table 9.3 illustrates how the different terms in Eq. 9-18 contribute to the overall air–water partition constant of some selected compounds. Let us first compare all compounds that contain six carbon atoms (i.e., from hexane to phenol), that is, compounds of a similar size. For both the aliphatic (the first seven) as well as for the aromatic (the next three) compounds in Table 9.3, the $(\nu V_i - IL_i)$ term, which encompasses the free energy contributions of cavity formation, London dispersive vdW interactions, and entropy effects (see Chapter 7), is positive, thus favoring the gas phase. However, the total of these terms is larger for aliphatic as compared to aromatic compounds, which can be partly explained by the larger entropy gain when transferring a more flexible aliphatic compound from water to air as compared to transferring a more rigid aromatic compound (see Table 9.2). A much smaller or even negative $(\nu V - IL)$ term is found for the larger, more rigid PAHs. In contrast, for the large, flexible telomer alcohols (e.g., 8:2 FTOH) or polydimethylsiloxanes (e.g., D5), which also exhibit weak vdW interactions, this term is very large.

Looking for other terms in Table 9.3 that favor the aqueous phase, we find that the polarizability term (sS) is particularly important for PAHs. Furthermore, as we would

Table 9.3 Contribution of the Different Terms in Eq. 9-18 to the Calculated Air–Water Partition Constant for Some Selected Compounds^a at 25°C

Compound	$\log K_{iaw}^b$	$\log K_{iaw} = (\text{Eq. 9-18})$	$+2.55V_i - 0.48L_i$	$-2.07S_i$	$-3.67A_i$	$-4.87B_i$	$+0.59$
<i>n</i> -hexane	+1.74	+1.73	+1.14	0.00	0.00	0.00	+0.59
di- <i>n</i> -propyl ether	−0.97	−0.96	+1.16	−0.52	0.00	−2.19	+0.59
1-hexanal	−2.06	−2.09	+0.86	−1.35	0.00	−2.19	+0.59
2-hexanone	−2.43	−2.39	+0.91	−1.41	0.00	−2.48	+0.59
<i>n</i> -hexylamine	−2.90	−2.77	+0.92	−0.72	−0.59	−2.97	+0.59
1-hexanol	−3.23	−3.13	+0.85	−0.87	−1.36	−2.34	+0.59
<i>n</i> -hexanoic acid	−4.56	−4.28	+0.85	−1.30	−2.28	−2.14	+0.59
benzene	−0.65	−0.67	+0.50	−1.08	0.00	−0.68	+0.59
aniline	−4.03	−4.14	+0.20	−1.99	−0.95	−2.00	+0.59
phenol	−4.79	−4.74	+0.18	−1.84	−2.20	−1.46	+0.59
naphthalene	−1.73	−1.80	+0.28	−1.80	0.00	−0.88	+0.59
phenanthrene	−2.76	−3.11	+0.06	−2.59	0.00	−1.17	+0.59
pyrene	−3.27	−3.79	−0.19	−2.98	0.00	−1.22	+0.59
benzo(a)pyrene	−4.51	−5.22	−0.53	−3.77	0.00	−1.51	+0.59
8:2 FTOH	+0.58	+0.51	+4.00	−0.29	−2.28	−1.51	+0.59
D5	+3.15	+3.32	+4.96	+0.20	0.00	−2.44	+0.59

^aThe solute parameters of the compounds are given in Appendix C.^bExperimentally derived $\log K_{aw}$ values given in Appendix C.

expect, the air–water partition constants of polar compounds are significantly determined by their H-bonding properties. In the case of bipolar functional groups such as hydroxyl or amino groups, we note that the relative importance of the H-donor (*aA*) versus H-acceptor (*bB*) term is quite different for aliphatic versus aromatic compounds (e.g., 1-hexanol versus phenol or *n*-hexylamine versus aniline). Because of resonance with the aromatic ring, the nonbonding electrons in phenol or aniline are weaker H-acceptors, whereas the H atoms bound to the oxygen or nitrogen atom, respectively, are more acidic and thus better H-donors in the aromatic versus aliphatic compounds (see also Chapter 4, Section 4.4).

Bond Contribution Method. In addition to the more sophisticated pp-LFER method, we now briefly address a simple LFER approach to estimate K_{iaw} values that is based solely on chemical structure. The underlying idea of this LFER, which was introduced by Hine and Mookerjee (1975) and expanded by Meylan and Howard (1991), is similar to the fragment contribution method (Section 7.3, Eq. 7-6). In this method, each bond type (e.g., a C–H bond) is taken to have a substantially constant effect on $\Delta_{aw}G_i$, regardless of the compound in which the bond occurs. This assumption is reasonably valid for simple molecules with no significant interactions between functional groups. Therefore, the method is interesting from a didactic point of view as we can directly see how certain substructural units affect air–water partitioning.

Table 9.4 summarizes bond contribution values derived by Meylan and Howard (1991) from a large data set at a temperature of 25°C. Some included values are for a singly bonded aliphatic carbon bound to hydrogen (C–H, 0.1197), an aromatic carbon bound to chlorine (C_{ar}–Cl, –0.3335), and an aliphatic carbon bound to a doubly bonded (olefinic) carbon (C–C_d, –0.0635). Such values can be used to calculate log K_{iaw} by simple addition:

$$\log K_{iaw}(25^\circ\text{C}) = \sum_k (\text{number of bonds type } k)(\text{contribution of bond type } k) \quad (9-19)$$

By looking at the signs and values of each bond contribution, we readily see that units such as C–H bonds, and, particularly, C–F bonds tend to encourage molecules to partition into the air, while other units, like O–H or those groups containing oxygen or nitrogen, strongly induce molecules to remain associated with water. These tendencies correspond to the expected behaviors deduced qualitatively from our previous discussion of intermolecular interactions of organic molecules with water.

For simple molecules, this contribution approach is usually accurate to within a factor of 2 or 3. One major drawback, however, is that it does not account for special intermolecular or intramolecular interactions that may be unique to the molecule in which a particular bond type occurs. Therefore, additional correction factors may have to be applied (Meylan and Howard, 1991). Furthermore, we stress the limited applicability of this simple approach for prediction of K_{iaw} values of more complex molecules.

9.4 Effect of Temperature, Dissolved Salts, and pH on the Aqueous Activity Coefficient/Aqueous Solubility and on the Air–Water Partition Constant

So far, we have focused on how differences in molecular structure affect aqueous solubility, activity coefficients, and air–water partitioning 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 this section, we consider three such factors: temperature, ionic strength (i.e., dissolved salts), and pH.

Effect of Temperature

Solubility and Aqueous Activity Coefficient. In Chapter 4 (Section 4.2), we have seen that, when assuming a constant $\Delta_{12}H_i$ over a narrow temperature range, the temperature dependence of any partition constant can be expressed by:

$$\ln K_{i12} = -\frac{\Delta_{12}H_i}{R} \cdot \frac{1}{T} + \text{constant} \quad (9-22)$$

Table 9.4 Bond Contributions^a for Estimation of log K_{iaw} at 25°C

Bond ^b	Bond Contribution	Bond ^b	Bond Contribution
C – H	+0.1197	C _{ar} – OH	–0.5967 ^c
C – C	–0.1163	C _{ar} – O	–0.3473 ^c
C – C _{ar}	–0.1619	C _{ar} – N _{ar}	–1.6282
C – C _d	–0.0635	C _{ar} – S _{ar}	–0.3739
C – C _t	–0.5375	C _{ar} – O _{ar}	–0.2419
C – CO	–1.7057	C _{ar} – S	–0.6345
C – N	–1.3001	C _{ar} – N	–0.7304
C – O	–1.0855	C _{ar} – I	–0.4806
C – S	–1.1056	C _{ar} – F	+0.2214
C – Cl	–0.3335	C _{ar} – C _d	–0.4391
C – Br	–0.8187	C _{ar} – CN	–1.8606
C – F	+0.4184	C _{ar} – CO	–1.2387
C – I	–1.0074	C _{ar} – Br	–0.2454
C – NO ₂	–3.1231	C _{ar} – NO ₂	–2.2496
C – CN	–3.2624	CO – H	–1.2102
C – P	–0.7786	CO – O	–0.0714
C = S	+0.0460	CO – N	–2.4261
C _d – H	+0.1005	CO – CO	–2.4000
C _d = C _d	–0.0000 ^d	O – H	–3.2318
C _d – C _d	–0.0997	O – P	–0.3930
C _d – CO	–1.9260	O – O	+0.4036
C _d – Cl	–0.0426	O = O	–1.6334
C _d – CN	–2.5514	N – H	–1.2835
C _d – O	–0.2051	N – N	–1.0956 ^e
C _d – F	+0.3824	N = O	–1.0956 ^e
C _t – H	–0.0040	N = N	–0.1374
C _t ≡ C _t	–0.0000 ^d	S – H	–0.2247
C _{ar} – H	+0.1543	S – S	+0.1891
C _{ar} – C _{ar}	–0.2638 ^f	S – P	–0.6334
C _{ar} – C _{ar}	–0.1490 ^g	S = P	+1.0317
C _{ar} – Cl	+0.0241		

^aData from Meylan and Howard (1991).^bC: single-bonded aliphatic carbon (note that for linear and branched alkanes a correction term of +0.75 has to be added to Eq. 9.19 (Meylan and Howard, 1991); C_d: olefinic carbon; C_t: triple-bonded carbon; C_{ar}: aromatic carbon; N_{ar}: aromatic nitrogen; S_{ar}: aromatic sulfur; O_{ar}: aromatic oxygen; CO: carbonyl (C = O); CN: cyano (C ≡ N). Note: the carbonyl, cyano, and nitrofunctions are treated as single atoms.^cTwo separate types of aromatic carbon-to-oxygen bonds have been derived: (a) the oxygen is part of an –OH function, and (b) the oxygen is not connected to hydrogen.^dThe C = C and C ≡ C bonds are assigned a value of zero by definition (Hine and Mookerjee, 1975).^eValue is specific for nitrosamines.^fIntra-ring aromatic carbon to aromatic carbon.^gExternal aromatic carbon to aromatic carbon (e.g., biphenyl).

Recalling from Chapter 4 that we use the pure organic liquid as the reference state, we omit the Δ -notation, and we now express the temperature dependence of the aqueous solubility of liquid, solid, and gaseous compounds respectively as:

$$\ln C_{iw}^{\text{sat}}(\text{L}) = -\frac{H_{iw}^{\text{E}}}{R} \cdot \frac{1}{T} + \text{constant} \quad \text{for liquids} \quad (9-23a)$$

$$\ln \gamma_{iw}^{\text{sat}} = +\frac{H_{iw}^{\text{E}}}{R} \cdot \frac{1}{T} + \text{constant}' \quad (9-23b)$$

$$\ln C_{iw}^{\text{sat}}(\text{s}) = -\frac{\Delta_{\text{fus}}H_i + H_{iw}^{\text{E}}}{R} \cdot \frac{1}{T} + \text{constant} \quad \text{for solids} \quad (9-24)$$

$$\ln C_{iw}^{\text{sat}}(\text{g}) = -\frac{-\Delta_{\text{vap}}H_i + H_{iw}^{\text{E}}}{R} \cdot \frac{1}{T} + \text{constant} \quad \text{for gases} \quad (9-25)$$

In Eqs. 9-23 to 9-25, we use molar concentrations instead of mole fractions, as we assume that the molar volume of the aqueous solution is temperature-independent over the temperature range considered.

Let us first consider the temperature dependence of the *liquid* aqueous solubility (Eq. 9-23a) and of the linked aqueous activity coefficient (Eq. 9-23b). We recall from Chapter 4 (Table 4.3) that a $\Delta_{12}H_i$ value of $\pm 30 \text{ kJ mol}^{-1}$ means a factor of approximately 1.5 change in K_{i12} . Inspection of Table 9.2 shows that for many compounds, H_{iw}^{E} is rather small and may even be negative. Even for very large molecules, H_{iw}^{E} never exceeds $\pm 30 \text{ kJ mol}^{-1}$. Therefore, in contrast to vaporization or air–water partitioning (see Table 9.2 and subsequent discussion), the change in liquid aqueous solubility, and thus in the aqueous activity coefficient, with increasing/decreasing temperature is rather small. Furthermore, at temperatures above about 40°C , H_{iw}^{E} becomes increasingly more positive because the number of hydrogen bonds among the water molecules decreases. In fact, we cannot actually assume that H_{iw}^{E} is constant over the ambient temperature range, which is, however, not too much of a problem for solubility approximations since the temperature effect is small anyway. If we want to extrapolate H_{iw}^{E} values determined at high temperatures (i.e., $\gg 40^\circ\text{C}$) to the ambient temperature range, we have to be cautious.

When we are interested in the solubilities of *solids or gases*, the effect of temperature becomes much more important. Now, we must consider the total enthalpy change when transferring a molecule from the solid or gas phase 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 (Eqs. 9-24 and 9-25 respectively). In general, the resulting enthalpy change will be positive in the case of solids, due to the large positive $\Delta_{\text{fus}}H_i$, and negative in the case of gases, from the positive $\Delta_{\text{vap}}H_i$. 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 decrease the solubility of organic gases.

Air–Water Partition Constant. For the air–water partition constant, the effect of temperature is given by:

$$\ln K_{iaw} = -\frac{\Delta_{aw}H_i}{R} \cdot \frac{1}{T} + \text{constant} \quad (9-26)$$

where $\Delta_{aw}H_i = \Delta_{vap}H_i - H_{iw}^E$ (Fig. 9.2). We recall from Chapter 4 that the molar volume of gases is temperature dependent and if K_{i12} is expressed in molar concentrations, $\Delta_{12}H_i$ has to be replaced by $\Delta_{12}H_i + RT_{av}$, where T_{av} is the average temperature (in K) of the temperature range considered (see Atkinson and Curthoys, 1978). However, because RT_{av} is only about 2.5 kJ mol⁻¹, we neglect this term. From the examples given in Table 9.2, we can see that $\Delta_{aw}H_i$ is similar or smaller than $\Delta_{vap}H_i$ for most compounds. For compounds exhibiting a relatively large negative H_{iw}^E and a large $\Delta_{vap}H_i$ (e.g., D5, D6), the temperature effect can be as much as a factor of 3 to 4 per 10°C temperature change.

Mintz et al. (2008) have published a pp-LFER (Eq. 9-27) that allows one to estimate $\Delta_{aw}H_i$ values:

$$\Delta_{aw}H_i \text{ (kJ mol}^{-1}\text{)} = 17.3V_i + 1.4L_i - 0.73S_i + 33.6A_i + 43.5B_i + 8.4 \quad (9-27)$$

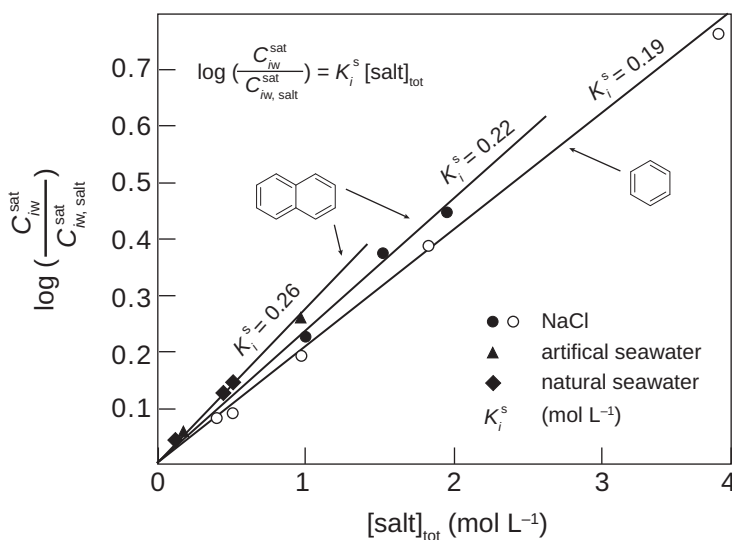
(number of chemicals = 368; $r^2 = 0.94$; S.D. = 4.7)

The scatter in this relation is somewhat large, which could be explained by the fact that the relative enthalpy and entropy contributions to the standard free energy of air–water partitioning differ between different compound classes (Table 9.2). A more uniform proportionality between enthalpy and entropy, which we have encountered for vaporization (Fig. 8.5), would be necessary to get a better predictive tool. Nevertheless, Eq. 9-27 allows us to predict $\Delta_{aw}H_i$ values within about ± 10 kJ mol⁻¹ (± 2 S.D.), which, for practical purposes, is often quite sufficient. Another alternative to estimate the effect of temperature on K_{iaw} is to use pp-LFERs, like Eq. 9-18, with the temperature-dependent system descriptors reported in Goss (2006).

Effect of Dissolved Inorganic Salts

When considering saline environments (e.g., seawater, salty lakes, or subsurface brines), we have to consider the effects of dissolved inorganic salts on aqueous solubilities, aqueous activity coefficients, and, consequently, on all partitioning processes involving water. Although the number of studies that have been devoted to this topic is still rather small, a few important conclusions can be drawn. Qualitatively, one observes that the presence of the predominant inorganic ionic species found in natural waters (i.e., Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, HCO₃⁻, HCO₃⁻, SO₄²⁻) generally decreases the aqueous solubility and increases the aqueous activity coefficient. Thus, the air–water partition constant, particularly of larger nonpolar or weakly polar organic compounds,

Figure 9.3 Effect of salt concentration on the aqueous solubility of benzene and naphthalene. Data from McDevit and Long (1952) and Gordon and Thorne (1967a).



is increased with increasing dissolved salt. 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 ($C_{iw,salt}^{sat}$) to those in pure water (C_{iw}^{sat}):

$$\log \frac{C_{iw}^{sat}}{C_{iw,salt}^{sat}} = K_i^s [\text{salt}]_{\text{tot}}$$

or

(9-28)

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

where $[\text{salt}]_{\text{tot}}$ is the total *molar* salt concentration and K_i^s is the *Setschenow* or *salting constant* (units M^{-1}). The salting constant relates the effectiveness of a particular salt or combination of salts to change the solubility of a given compound i . As salt concentration increases, the salting-out effect exponentially increases (Fig. 9.3). For a particular salt (e.g., NaCl) or salt mixture (e.g., seawater; for composition see Table 9.5), Eq. 9-28 is valid over a wide range of salt concentrations. 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 $[\text{salt}]_{\text{tot}}$). We assume the effect of salt on the molar volume of the solution is minor and $\gamma_{iw,salt}$, the activity coefficient in saline solution, is valid for saturated and dilute conditions.

Written in terms of activity coefficients, Eq. 9-28 is:

$$\gamma_{iw,salt} = \gamma_{iw} \cdot 10^{+K_i^s [\text{salt}]_{\text{tot}}} \quad (9-29)$$

Table 9.5 Salt Composition of Seawater and Salting Constants for Benzene, Naphthalene, and 1-Naphthol at 25°C for Some Important Salts

Salt	Weight (g mol ⁻¹)	Mole fraction in seawater ^b x_{salt}	Salting constant ^a		
			K_i^s (benzene) (L mol ⁻¹)	K_i^s (naphthalene) (L mol ⁻¹)	K_i^s (1-naphthol) (L mol ⁻¹)
NaCl	58.5	0.799	0.19	0.22	0.21
MgCl ₂	95.3	0.104		0.30	0.33
Na ₂ SO 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	119.0			0.13	0.13
CsBr	212.8			0.01	
(CH ₃) ₄ NCl	109.6				-0.36
(CH ₃) ₄ NBr	154.1		-0.15		

^aData from McDevitt and Long (1952); Gordon and Thorne (1967a,b); Almeida et al. (1983); and Sanemasa et al. (1984).^bData from Gordon and Thorne (1967a,b). The mole fraction refers to the mole fraction of the total salt, that is, $\sum x_{\text{salt}} = 1$.

and, similarly, for the air–water partition constant:

$$K_{i\text{aw,salt}} = K_{i\text{aw}} \cdot 10^{+K_i^s[\text{salt}]_{\text{tot}}} \quad (9-30)$$

Therefore, $\gamma_{i\text{w,salt}}$ and $K_{i\text{aw,salt}}$ increase exponentially with increasing salt concentration. For a given salt concentration, the standard free energy of transferring a solute from pure water to the salt solution, $\Delta_{\text{w,salt}} G_i$, is related to K_i^s by:

$$\Delta_{\text{w,salt}} G_i = RT \ln \gamma_{i\text{w,salt}} / \gamma_{i\text{w}} = 2.303RT K_i^s [\text{salt}]_{\text{tot}} \quad (9-31)$$

Before we inspect K_i^s values of a variety of organic compounds for seawater, we first take a look at the salting-out efficiencies of various ion combinations. Salting constants are available only for combined salts, not single ions. Nevertheless, the data in Table 9.5 illustrate that smaller ions (e.g., Na⁺, Mg²⁺, Ca²⁺, Cl⁻), which form hydration shells with more water molecules, have a bigger effect on solubility than larger ions (e.g., Cs⁺, N(CH₃)₄⁺, Br⁻) that tend to weakly bind water molecules. In fact, larger organic ions such as tetramethyl-ammonium (N(CH₃)₄⁺) can even have a positive effect, a *salting-in* effect; that is, they promote solubility and a decrease in the activity coefficient. Such salting-in effects can also be observed for very polar compounds that may strongly interact with certain ions (Almeida et al., 1983). In a simple way, we can rationalize the salting-out of nonpolar and weakly polar compounds by imagining that the dissolved ions successfully compete with the organic compound for solvent molecules. Many environmentally relevant ions bind water molecules quite tightly in aqueous solution, which can even be seen macroscopically when the volume of the aqueous solution reduces upon dissolution. As a consequence, the number of “free” water molecules to solvate an organic molecule is changed, which depending

on the type of salt or compound present, may lead to a loss or gain in solubility. Also, the compound itself may lose further translational, rotational, and conformational freedom. In fact, the rather restricted number of studies on the thermodynamics of the transfer of organic compounds from pure water to saltwater (Eq. 9-31) report very small positive or even negative $\Delta_{w,salt}H_i$ values, thus suggesting a negative entropy effect to be primarily responsible for the salting-out effect (Gold and Rodriguez, 1989; Prak and O'Sullivan, 2009; Aria-Gonzalez et al., 2010). The small $\Delta_{w,salt}H_i$ values also mean that, over the ambient temperature range, we may assume a constant K_i^s .

Let us now look at the effect of the various salts on the overall salting-out constant of an organic compound in seawater, the most important natural saline environment. We chose naphthalene as a model compound. First, using the data given in Table 9.5, we can make our own artificial seawater 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 total volume, we obtain seawater with a salinity of about 34‰, which corresponds to a total molar salt concentration ($[\text{salt}]_{\text{tot}}$) of about 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 (see Xie et al., 1997). Furthermore, since seawater is dominated by one salt, that is, NaCl (Table 9.5), as a first approximation, K_i^s values determined for sodium chloride can be used as a surrogate.

Let us calculate $K_{i,\text{seawater}}^s$ for naphthalene using the data given in Table 9.5. We estimate $K_{i,\text{seawater}}^s$ by summing up the contributions of the various salts present (Gordon and Thorne, 1967a,b):

$$K_{i,\text{seawater}}^s \cong \sum_k K_{i,\text{salt } k}^s \cdot x_k \quad (9-32)$$

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:

$$K_{i,\text{seawater}}^s = (0.799)(0.22 \text{ M}^{-1}) + (0.104)(0.30 \text{ M}^{-1}) + (0.055)(0.72 \text{ M}^{-1}) \\ + (0.02)(0.32 \text{ M}^{-1}) + (0.017)(0.19 \text{ M}^{-1}) + (0.005)(0.32 \text{ M}^{-1}) = 0.26 \text{ M}^{-1}$$

which is close to 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 M^{-1} . With insertion of the two K_i^s values into Eqs. 9-29 and 9-30 and assuming a $[\text{salt}]_{\text{tot}} = 0.5 \text{ M}$ (typical seawater, see also Chapter 5), we obtain $\gamma_{iw,\text{salt}}/\gamma_{iw}$ and $K_{iaw,\text{salt}}/K_{iaw}$ ratios of 1.3 for $K_{i,\text{NaCl}}^s$ and 1.35 for $K_{i,\text{seawater}}^s$. In general, the error introduced when using $K_{i,\text{NaCl}}^s$ instead of $K_{i,\text{seawater}}^s$ is only on the order of 10%, which is often well within the experimental error of K_i^s measurements. Therefore, many K_i^s values available in the literature have been determined for NaCl, used as a reasonable surrogate for seawater. Larger compilations of K_i^s values can be found in Ni and Yalkowsky (2003) and Endo et al. (2012). In addition, a series of K_i^s values of

Table 9.6 Experimental and Estimated (Eq. 9-33) K_i^s values of NaCl Solutions or Seawater (sw) of Some Selected Compounds^a

Compound	K_i^s exp. ^b	$K_{i,\text{NaCl}}^s = \text{calc.}$	$+0.21V_i - 0.013L_i$	$-0.031S_i$	$-0.049A_i$	$-0.057B_i$	$+0.103$
<i>n</i> -hexane	0.28	0.27	+0.17	0.00	0.00	0.00	+0.10
2-hexanone	0.20	0.21	+0.16	−0.02	0.00	−0.03	+0.10
1-hexanol	0.23	0.21	+0.17	−0.01	−0.02	−0.03	+0.10
<i>n</i> -hexanoic acid	0.22	0.19	+0.17	−0.02	−0.03	−0.03	+0.10
2-decanone	0.31	0.30	+0.25	−0.02	0.00	−0.03	+0.10
benzene	0.19	0.18	+0.11	−0.02	0.00	−0.01	+0.10
phenol	0.11	0.14	+0.12	−0.03	−0.03	−0.02	+0.10
naphthalene	0.22	0.22	+0.16	−0.03	0.00	−0.01	+0.10
phenanthrene	0.27	0.26	+0.21	−0.04	0.00	−0.01	+0.10
	0.30 (sw)						
pyrene	0.32	0.26	+0.22	−0.04	0.00	−0.02	+0.10
	0.30 (sw)						
benzo(a)pyrene	0.33	0.29	+0.27	−0.06	0.00	−0.02	+0.10
	0.34 (sw)						
6:2 FTOH	0.38	0.39	+0.34	−0.01	−0.03	−0.01	+0.10
D5	n.a.	0.62	+0.55	+0.00	0.00	−0.03	+0.10

^aThe solute parameters of most compounds are given in Appendix C; 2-decanone parameters from UFZ-LSER database (Endo et al., 2014).^bExperimental K_i^s data from Ni and Yalkowsky (2003) and Endo et al. (2012).

a diverse set of organic compounds for ammonium sulfate ((NH₄)₂SO₄)), including a pp-LFER as given below for NaCl, is reported by Wang et al. (2014).

Table 9.6 gives experimental K_i^s values for NaCl solutions for some representative compounds including some of our companion compounds. Also included in Table 9.6 are estimated values using a pp-LFER derived by Endo et al. (2012) and Endo (2014, personal communication):

$$K_{i,\text{NaCl}}^s (\text{M}^{-1}) = 0.21V_i - 0.013L_i - 0.031S_i - 0.049A_i - 0.057B_i + 0.103 \quad (9-33)$$

(number of chemicals = 43; $r^2 = 0.84$; S.D. = 0.031)

We recall that K_i^s is directly related to a free energy term (Eq. 9-31), and therefore, its description by a pp-LFER is feasible. We should note, however, that Eq. 9-33 has been derived from a rather small, although structurally diverse, set of compounds. Nevertheless, Eq. 9-33 is a useful tool to estimate K_i^s values of organic compounds, and it allows us to see how compound characteristics affect K_i^s .

Some general trends can be seen by analyzing the data in Table 9.6. First, K_i^s values of organic compounds for NaCl solutions cover a range of between 0.1 and 0.6, and they tend to increase with increasing size. Second, mono- and bipolar substituents decrease K_i^s , most likely by diminishing the number of “free” water molecules. This is evident when comparing 2-hexanone, 1-hexanol, and *n*-hexanoic acid with *n*-hexane,

or phenol with benzene. Third, aliphatic compounds tend to have significantly higher K_i^s values than aromatic compounds exhibiting the same number of carbon atoms (e.g., hexane versus benzene). Similarly, with increasing size, K_i^s values of aliphatic compounds increase much more pronounced as compared to aromatic compounds (e.g., 2-decanone as compared to 2-hexanone versus naphthalene compared to benzene). Consequently, within a compound class, the range of K_i^s is larger for compounds exhibiting aliphatic moieties as compared to aromatic compounds. For example, for PAHs ($K_i^s = 0.22\text{--}0.36$) or chlorinated benzenes ($K_i^s = 0.2\text{--}0.3$), the range covers less than 0.2, whereas for the dialkyl phthalates ($K_i^s = 0.2\text{--}0.6$), the range is much larger (Endo et al., 2012). This difference between aromatic and aliphatic compounds is primarily due to the difference between the cavity formation term ($+0.21V_i$), which promotes salting-out, and the vdW and polarizability terms ($-0.013L_i - 0.031S_i$). Therefore, similar to the air–water partition constant (Table 9.3), large K_i^s values can be expected for large compounds exhibiting weak vdW and polarizability interactions, such as the polyfluorinated telomer alcohols (e.g., 6:2 FTOH), and particularly, the polydimethylsiloxanes (e.g., D5).

In summary, we can conclude that at moderate salt concentrations typical for seawater (~ 0.5 M), salinity will affect aqueous solubility, the aqueous activity coefficient, and air– or organic solvent–water partition constants by a factor of between 1.1 ($K_i^s = 0.1$; small, rigid polar compounds) and about 2 ($K_i^s = 0.6$; large, flexible compounds exhibiting low vdW interactions). Hence, in marine environments, salting-out will not be a major factor in determining the partitioning behavior of many compounds. However, in environments exhibiting much higher salt concentrations (e.g., in the Dead Sea (5 M) or in subsurface brines near oil fields), salting-out can be substantial because of the exponential relationship (Eqs. 9-28 to 9-30).

Effect of pH on Aqueous Solubility and Air–Water Partitioning of Organic Acids and Bases

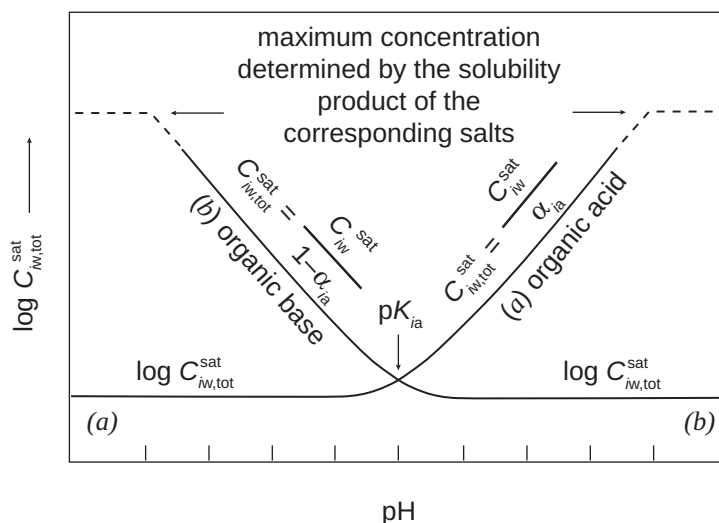
The water solubility of the ionic form (salt) of an organic acid or base is generally several orders of magnitude higher than the solubility of the neutral species (C_{iw}^{sat}) of the compound. The *total* concentration of the compound, that is, the sum of non-dissociated (HA and BH^+ for acids and bases, respectively) and dissociated (A^- and B, respectively) forms at saturation, $C_{iw,\text{tot}}^{\text{sat}}$, is, therefore, in contrast to neutral compounds, strongly pH-dependent. As has been demonstrated for pentachlorophenol (Arcand et al., 1995) and as illustrated schematically for an organic acid in Fig. 9.4 (line *a*), at low pH, the saturation concentration is given by the solubility of the neutral compound. At higher pH values, $C_{iw,\text{tot}}^{\text{sat}}$ is determined by the fraction in HA form, α_{ia} :

$$C_{iw,\text{tot}}^{\text{sat}} = \frac{C_{iw}^{\text{sat}}}{\alpha_{ia}} \quad \text{for organic acids} \quad (9-33)$$

where, as we recall from Chapter 4 (Eq. 4-59):

$$\alpha_{ia} = \frac{1}{1 + 10^{\text{pH} - \text{p}K_{ia}}} \quad (4-59)$$

Figure 9.4 Schematic representation of the total aqueous solubility of (a) an organic acid and (b) an organic base as a function of pH. For simplicity, the same pK_a values and maximum solubilities of the neutral and charged (salt) species have been assumed.



Equation 9-33 is valid only up to the solubility product of the salt of the ionized organic species, which is dependent on the type of counterions present. Unfortunately, solubility data of organic salts are rather scarce.

In the case of an organic base, the situation is symmetrical to the one shown in Fig. 9.4 (line a), in that the BH^+ form dominates at low pH. Hence, $C_{iw,tot}^{sat}$ is given by [Fig. 9.4 (line b)]:

$$C_{iw,tot}^{sat} = \frac{C_{iw}^{sat}}{1 - \alpha_{ia}} \quad \text{for organic bases} \quad (9-34)$$

When considering the air–water equilibrium partitioning of an organic acid or base, we may, in general, assume that the ionized species will not be present in the gas phase. The air–water distribution ratio of an organic acid, D_{iaw} (note that we speak of a ratio and not of a partition constant since we are dealing with more than one species), is then given by:

$$D_{iaw} = \frac{[HA]_a}{[HA]_w + [A^-]_w} \quad (9-35)$$

Multiplication of Eq. 9-35 with $[HA]_w / [HA]_w (= 1)$ and rearrangement shows that D_{iaw} is simply given by the product of the fraction in the HA form (α_{ia}) and the air–water partition constant of the neutral compound (K_{iaw}):

$$D_{iaw} = \frac{[HA]_w}{[HA]_w + [A^-]_w} \cdot \frac{[HA]_a}{[HA]_w} = \alpha_{ia} K_{iaw} \quad \text{for organic acids} \quad (9-36)$$

By analogy, we obtain:

$$D_{iaw} = (1 - \alpha_{ia}) K_{iaw} \quad \text{for organic bases} \quad (9-37)$$

9.5 Questions and Problems

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

Questions

Q9.1

What is meant by the term *water solubility* or *aqueous solubility* of a given compound? What is the range of aqueous solubilities encountered when considering environmentally relevant organic chemicals? Is there such a thing as a *water insoluble compound*, as often stated in handbooks?

Q9.2

How is the aqueous activity coefficient of a compound related to the aqueous solubility, if the compound is a (a) liquid, (b) solid, (c) gas under the prevailing conditions? Comment on any assumption that you make when answering this question.

Q9.3

Frequently, the air–water partition constant of a given organic compound is estimated from its vapor pressure and its aqueous solubility. What are the assumptions made when using this approximation? Are there cases in which this approach is questionable? If yes, in which cases?

Q9.4

What could be the reason why the excess enthalpy of MTBE in water is so much more negative than the excess enthalpy of 1-hexanol, which has a similar size? The values are given in Table 9.2.

Q9.5

Explain the following observations (see also Table 9.2):

- (a) the excess entropies in water of alkanes are generally much larger than those of aromatic compounds of similar size, and
- (b) the excess entropies in water of phenol and hexanol are smaller than those of benzene and hexane respectively.

Q9.6

Explain qualitatively how the aqueous solubility of a (a) liquid, (b) solid, and (c) gaseous compound changes with temperature. Which thermodynamic quantities do you need to know to quantify this temperature dependence?

Q 9.7

In many cases, the temperature dependence of the air–water partition constant of a given compound has not been experimentally determined. Describe two different approaches how this temperature dependence can be estimated.

Q 9.8

Explain in words how environmentally relevant inorganic dissolved salts affect the aqueous solubility of an organic 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 (a) the aqueous activity coefficient, and (b) on the air–water partition constant of organic compounds in seawater?

Q 9.9

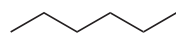
Which compound characteristics primarily determine the magnitude of the salting constant (Setschenow constant) of a given compound in a sodium chloride solution?

Q 9.10

Consider the air–water partitioning of an organic acid and an organic base both exhibiting a K_{iaw} value of $0.01 \text{ L}_w\text{L}_a^{-1}$ (neutral compound) and a $\text{p}K_{ia}$ value of 6 (note that for the base this is the $\text{p}K_{ia}$ of the conjugated acid, see Chapter 4). What is their air–water distribution ratio at pH 4 and 7, respectively?

Problems**P 9.1* Deriving Aqueous Activity Coefficients from Experimental Solubility Data and Using pp-LFERs**

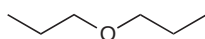
Calculate the aqueous activity coefficients, γ_{iw}^{sat} , of the companion compounds MTBE, atrazine, and methyl bromide at 25°C from (a) experimental solubility data, and (b) using only pp-LFERs. Compare the results. All necessary data is provided in Appendix C. Comment on any assumption that you make.



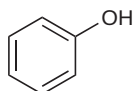
$i = n\text{-hexane}$



$i = \text{benzene}$



$i = \text{di-}n\text{-propyl ether}$



$i = \text{phenol}$

P 9.2* Estimating Air–Water Partition Constants by the Bond Contribution Method

Estimate the K_{iaw} values at 25°C of (a) *n*-hexane, (b) benzene, (c) di-*n*-propyl ether, and (d) phenol using the bond contribution values given in Table 9.4. Compare these values with the experimental air–water partition constants given in Table 9.3. Remember that for a linear or branched alkane (i.e., hexane) a correction factor of +0.75 log units has to be added (footnote *b* in Table 9.4).

P 9.3* A Tricky Stock Solution

You work in an analytical laboratory and are asked to prepare 250 mL of a 0.5 M stock solution of anthracene using toluene as solvent (the density of toluene is 0.87 g cm^{-3} at 20°C). 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. Although your intuition tells you that these two aromatic compounds should form a near-ideal liquid mixture, to your surprise, even after several hours of

intensive shaking, a substantial portion of the anthracene remains undissolved in the flask.

What is the problem? What is anthracene's concentration in molar units in your stock solution? Give an estimate of how much anthracene has actually been dissolved (in g).

P 9.4 Evaluating the Effect of Temperature on the Aqueous Solubility and Aqueous Activity Coefficient of a Solid Compound

As you live in a cold area, you want to know the aqueous solubility and aqueous activity coefficient of organic compounds at 1°C rather than at 25°C. Estimate C_{iw}^{sat} (in molar units) and γ_{iw}^{sat} of 1,2,3,7-tetrachlorodibenzo-*p*-dioxin ($T_m = 175^\circ\text{C}$) at 1°C using aqueous solubilities of this compound determined at more elevated temperatures by Friesen and Webster (1990). Also estimate the average excess enthalpy of the compound in water for the temperature range considered. Why are you interested in this quantity? Comment on any assumption that you make.

$T(^{\circ}\text{C})$	7.0	11.5	17.0	21.0	26.0
$C_{iw}^{\text{sat}} \times 10^{10} (\text{mol L}^{-1})$	7.56	8.12	12.5	14.9	22.6

P 9.5 Quantifying the Effect of Inorganic Salts on Aqueous Solubility and Aqueous Activity Coefficient

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

(b) 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 m³ of water in order to decrease the water solubility of n-hexane by a factor of ten. How much Na₂SO₄ would roughly be required to do the same job (assume a factor of 3 times larger K_i^s for Na₂SO₄ as compared to NaCl, see Table 9.6)?

P 9.6 A Small Bet with an Oceanographer

An oceanography colleague 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. You know that aqueous solubility and the aqueous activity coefficient are inversely related, so would you put money on the 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 of (solid) naphthalene is about 30 kJ mol⁻¹ over the ambient temperature range.

P 9.7 Evaluation the Direction of Air–Water Exchange at Different Temperature

What is the direction of the air–water exchange (into or out of water?) of benzene in a well-mixed shallow pond located in the center of a big city in each of the following seasons: (a) summer ($T = 25^\circ\text{C}$), and (b) winter ($T = 5^\circ\text{C}$)? In both cases, the

concentrations detected in air and water are $C_{ia} = 0.05 \text{ mg m}^{-3}$ and $C_{iw} = 0.4 \text{ mg m}^{-3}$, respectively. Assume that the temperature of the water and the air is the same. Note: The direction of the flux can be assessed from an equilibrium consideration; the rate of air–water exchange will be discussed in Chapter 19.

P9.8 Finding the Original Concentration of Tetrachloroethene (PCE) in Water Samples

You are the head of an analytical laboratory, and you check the numbers reported by one of your co-workers from the analysis of tetrachloroethene (PCE, $\text{Cl}_2\text{C}=\text{CCl}_2$) in water samples of very different origins, namely (a) moderately contaminated groundwater, (b) seawater ($[\text{salt}]_{\text{tot}} \cong 0.5 \text{ M}$), and (c) water from a subsurface brine ($[\text{salt}]_{\text{tot}} \cong 5.0 \text{ M}$). For all samples, your laboratory reports the same PCE concentration of $10 \mu\text{g L}^{-1}$. You read the report more carefully, and you realize that the sample flasks were not completely filled. The 1 L flasks were filled with only 200 mL liquid, and stored at 25°C before analysis. What were the original concentrations (in $\mu\text{g L}^{-1}$) of PCE in the three samples?

P9.9 Raining Out of Pesticides

The increasing pollution of the atmosphere by organic chemicals is creating a growing concern about the quality of rainwater. This concern makes it important to know how pesticides that are present in gaseous form in the atmosphere are scavenged by rainfall. Although for a quantitative description of this process more sophisticated models are required, some simple equilibrium calculations are already quite helpful (see also Chapter 15).

Assume that the pesticides methyl bromide, atrazine, and 2,4-dinitro-6-methylphenol (DNOC) are present in the atmosphere at low concentrations. Consider now a drop of water of 0.1 mL volume and a pH of 6 in a volume of 100 L of air, which corresponds to about the air–water ratio of a cloud (Seinfeld and Pandis, 2006). Calculate the fraction of the total amount of each compound present in the water drop at 25°C and 5°C assuming equilibrium between the two phases. Comment on any assumptions that you make. What do the results tell you about the potential of the three compounds to be scavenged from the atmosphere by rain? Note: DNOC is a weak acid with a $\text{p}K_{ia}$ value of 4.31; see Appendix C for all other data.

P9.10 Air–Water Equilibrium Distribution of Organic Acids and Bases in Fog

Represent graphically the approximate fraction of (a) total 2,3,4,5-tetrachlorophenol and (b) total aniline present in the water phase of a dense fog (air–water volume ratio about 10^5) as a function of pH (pH-range 2 to 7) at 5 and 25°C . Neglect any adsorption to the surface of the fog droplet. Assume a $\Delta_{aw}H_i$ value of about 70 kJ mol^{-1} for 2,3,4,5-tetrachlorophenol, and 50 kJ mol^{-1} for aniline. All other data can be found in Appendix C.

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