

CHAPTER 3: PHASE EQUILIBRIA

3.1 Introduction

Multiphase and solution thermodynamics deal with the composition of two or more phases in equilibrium. Thus, the maximum concentration of a species in an aqueous stream in contact with an organic stream can be estimated by these calculations. This can establish the contaminant levels obtained in various wastewater streams. A second major application is in partitioning of a pollutant into various phases in the environment. These multiphase thermodynamic calculations are important in design of heterogeneous reactors. In this section, we provide some basic definitions and illustrate the applications of thermodynamic models to waste minimization.

First, we provide various definitions for thermodynamic equilibrium and then illustrate them with applications.

3.2 Vapor-Liquid Equilibrium

The ratio of the composition measure such as (mole fraction) in the vapor phase to that in the liquid phase at equilibrium is referred to as the K-value. Note that K_y is dimensionless.

$$K_{yi} = \left(\frac{y_i}{x_i} \right)_{eq} \quad (1)$$

where y_i is the mole fraction of species i in the vapor phase and x_i is the liquid.

For ideal solutions, the Raoult's law applies. This can be stated as follows. At equilibrium the partial pressure of a species in the gas phase, P_i , is equal to the mole fraction of the species in the liquid phase, x_i , multiplied by its vapor pressure, P_i^{vap} , at the given temperature. It is also equal to the product of the mole fraction in the gas phase, y_i , and total pressure, P .

$$P_i = x_i P_i^{vap} = y_i P \quad (2)$$

Hence, Raoult's law can also be stated as:

$$y_i = x_i \frac{P_i^{vap}}{P} \quad (3)$$

Therefore, the K-factor for ideal mixtures is:

$$K_{yi} = \frac{P_i^{vap}}{P} \quad (4)$$

For non-ideal solutions, the K-factors can be calculated using the activity coefficients. However, for many environmental applications, one can use experimentally reported K-factors. These calculations are, for example, useful to find the composition of the vapor phase in contact with the liquid in the reactor. If there is a fugitive emission, then we can estimate the amount of the toxic chemicals that has inadvertently escaped to the atmosphere. Vapor-liquid equilibrium is also useful in estimating the maximum concentration of VOC in a mixture.

For dilute solutions, or for gaseous species, Henry's law, given by Eq. (5) is more convenient.

$$x_i = \bar{H}_i y_i P \quad (5)$$

where H_i is the Henry's law constant, (atm^{-1}) and P (atm) is the total pressure. With this definition, we find that K_{yi} -factor is

$$K_{yi} = \frac{1}{\bar{H}_i P} \quad (6)$$

Vapor pressure data is often needed to estimate the levels of VOC emissions at various temperatures. The data for pure liquids are well represented by the Antoine equation.

$$\log_{10} P^* = A - \frac{B}{T + C} \quad (7a)$$

or by an empirical extended Antoine is equation:

$$\ln P^{vap} = k_1 + \frac{k_2}{k_3 + T} + k_4 T + k_5 \ln T + k_6 T^{k_7} \quad (7b)$$

3.3 Gas-Liquid Systems

Phase equilibrium between a dissolving gas, A, and its dissolved concentration, $[A \cdot H_2O]$ or $[A]$, in water is often expressed (for dilute systems) through the equilibrium constant K_A

$$K_A = \frac{[A \cdot H_2O]}{P_A} \text{ (mol } L^{-1} \text{ atm}^{-1}) \quad (8)$$

which is a function of temperature

$$\frac{d \ln K_A}{dT} = \frac{\Delta H_{A_{ab}}}{RT^2} \quad (9)$$

where

$$\Delta H_{A_{ab}} = \tilde{H}_{A_{solution}} - \tilde{H}_{A_{gas}} \text{ is the heat of absorption. Typically } \Delta H_{A_{ab}} < 0$$

so that as temperature increases the absorption equilibrium constant decreases. Actually, this equilibrium constant is called Henry's constant in environmental chemistry and is independent of composition for dilute solutions.

$$[A \cdot H_2O] = H_A P_A \quad H_A [M \text{ atm}^{-1}] \quad (10)$$

Note that the units of H_A are now (mole/L atm) and M means mole/liter.

Large H_A implies a very soluble gas. Low H_A is a slightly soluble gas. (**Attention: some books define the reciprocal of H_A as Henry's constant**). The solubility in water of various gases is indicated in Table 3.1.

A dimensionless Henry's constant, \hat{H}_A , is obtained if gas concentration is used in its definition instead of partial pressure, i.e. $[A]_g = P_A / RT$

$$\hat{H}_A = H_A RT = \frac{[A \cdot H_2O]}{[A]_g} \quad (11)$$

Note that depending on the composition measures used to define equilibrium, Henry's constants appear with different units e.g. \bar{H}_A (atm^{-1}), H_A ($M \text{ atm}^{-1}$), \hat{H}_A (-). It is unfortunate that the chemical engineering and some environmental engineering literature use the reciprocal of the above defined Henry's constant under the same name! We have adopted here the definitions prevalent in the

environmental chemistry literature although the chemical engineering approach is the older and the better established one. A website posted as part of the course gives the various definitions and conversion factors (<http://www.mpch-mainz.mpg.de/~sander/res/henry.html>).

The following relationship holds between the above constants

$$\bar{H}_A = \frac{K_A}{C_{LTOT}} = \frac{H_A}{C_{LTOT}} = \frac{\hat{H}_A}{C_{LTOT} RT} \quad (12)$$

where C_{LTOT} is the total liquid molar concentration.

TABLE 3.1: Henry's Law coefficients of atmospheric gases dissolving in liquid water^a

Gas	$H, \text{ M atm}^{-1} (298 \text{ K})$
O ₂	1.3×10^{-3}
NO	1.9×10^{-3}
C ₂ H ₄	4.9×10^{-3}
O ₃ ^d	9.4×10^{-3}
NO ₂ ^b	1×10^{-2}
N ₂ O	2.5×10^{-2}
CO ₂ ^c	3.4×10^{-2}
SO ₂ ^c	1.24
HNO ₂ ^c	49
NH ₃ ^c	62
HCl	2.5×10^3
HCHO ^f	6.3×10^3
H ₂ O ₂	7.1×10^4 ^e
HNO ₃ ^c	2.1×10^5

^aAdapted from Schwartz (1983) and Martin (1984a).
^bPhysical solubility only. Dissolved NO₂ reacts with liquid water.
^cPhysical solubility only. These species participate in acid-base equilibria that are not reflected in the values of H given.
^dOzone is actually a reacting solute in water (Roth and Sullivan, 1981). For our purposes here we will use only the Henry's law coefficient as presented here and as a function of temperature in Table 5.4. The Henry's law coefficient of Roth and Sullivan is presented as $H = 3.84 \times 10^7 [\text{OH}^-]^{0.035} \exp(-2428/T)$ [atm mole fraction⁻¹], defined by $P_A = H_A x_A$.
^eA more recent measurement of the H₂O₂ Henry's law constant is that of Yoshizumi et al. (1984) who report $H_{\text{H}_2\text{O}_2} = 1.42 \times 10^5 \text{ M atm}^{-1}$ at 293 K.
^fHCHO exists in solution primarily in the gem-diol form: $\text{HCHO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{C}(\text{OH})_2$. The Henry's law coefficient given in the table includes both dissolved HCHO and H₂C(OH)₂.

3.3.1 Water Ionization

The ionization or recombination reaction for water is for all practical purposes infinitely fast



so that equilibrium is always established

$$K_w' = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = 1.82 \times 10^{-16} \text{ M at } 298 \text{ K} \quad (14)$$

Since molar concentration of water is constant, we get

$$K_w = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = 1.0 \times 10^{-14} \text{ M}^2 \text{ at } 298 \text{ K} \quad (15)$$

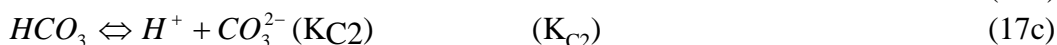
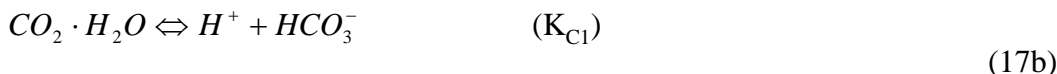
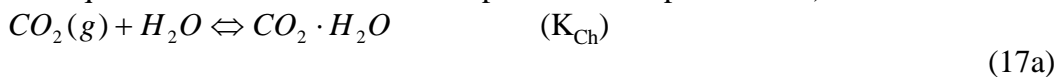
For pure water $[H^+] = [OH^-] = 1.0 \cdot 10^{-7}$ M. Recall that

$$pH = -\log [H^+] \quad (16)$$

so that $pH = 7$ for pure water at 298K.

3.3.2 Carbon Dioxide/Water Equilibria

Carbon dioxide is prevalent in the atmosphere and undergoes the following equilibrations in water (with equilibrium constant for each step indicated in parentheses)



We can express now the concentration of dissolved carbon containing species (ions) in terms of these constants

$$[CO_2 \cdot H_2O] = K_{Ch} p_{CO_2} = H_{CO_2} p_{CO_2} \quad (18a)$$

$$[HCO_3^-] = \frac{K_{C1} [CO_2 \cdot H_2O]}{[H^+]} = \frac{H_{CO_2} K_{C1} p_{CO_2}}{[H^+]} \quad (18b)$$

$$[CO_3^{2-}] = \frac{K_{C2} [HCO_3^-]}{[H^+]} = \frac{H_{CO_2} K_{C1} K_{C2} p_{CO_2}}{[H^+]^2} \quad (18c)$$

We also must always satisfy the electroneutrality relation

$$[H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \quad (19)$$

Upon substitution of the above expressions into the electroneutrality equation we get:

$$[H^+] = \frac{H_{CO_2} K_{C1} p_{CO_2}}{[H^+]} + \frac{2 H_{CO_2} K_{C1} K_{C2} p_{CO_2}}{[H^+]^2} + \frac{K_w}{[H^+]} \quad (19a)$$

Upon rearrangement a cubic equation for $[H^+]$ results

$$[H^+]^3 - [K_w + H_{CO_2} K_{C1} p_{CO_2}][H^+] - 2 H_{CO_2} K_{C1} K_{C2} p_{CO_2} = 0 \quad (20)$$

Given the temperature, T , and partial pressure of CO_2 , p_{CO_2} , the hydrogen ion concentration $[H^+]$ can be calculated from the above equation and pH obtained. (For temperature dependence see Table 3.2).

At $p_{CO_2} = 330$ ppm ($= 3.3 \times 10^{-4}$ atm) at 283°K the solution pH = 5.6 ($[H^+] = 2.51 \times 10^{-6}$ mol/L). This is often called the pH of "pure" rain water.

TABLE 3.2: Thermodynamic data for calculating temperature dependence of aqueous equilibrium constants

Equilibrium	ΔH_{298} , kcal mole ⁻¹	K at 298 K, M
$H_2O \rightleftharpoons H^+ + OH^-$	13.345	1.008×10^{-14}
$CO_2 \cdot H_2O \rightleftharpoons H^+ + HCO_3^-$	1.825	4.283×10^{-7}
$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	3.55	4.687×10^{-11}
$NH_3 \cdot H_2O \rightleftharpoons NH_4^+ + OH^-$	8.65	1.709×10^{-5}
$SO_2 \cdot H_2O \rightleftharpoons H^+ + HSO_3^-$ ^a	-4.161	1.29×10^{-2}
$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$ ^a	-2.23	6.014×10^{-8}

^aMaahs (1982) has reviewed the data on SO_2/H_2O equilibria and has recommended the following values of K_{hs} , K_{s1} , and K_{s2} :

$$\log K_{hs} = \frac{1376.1}{T} - 4.521$$

$$\log K_{s1} = \frac{853}{T} - 4.74$$

$$\log K_{s2} = \frac{621.9}{T} - 9.278$$

3.3.3 Sulfur Dioxide/Water Equilibrium

The scenario is similar as in the case of CO_2 absorption



The concentrations of dissolved species are

$$[SO_2 \cdot H_2O] = H_{SO_2} p_{SO_2} \quad (22a)$$

$$[HSO_3^-] = \frac{H_{SO_2} K_{S1} p_{SO_2}}{[H^+]} \quad (22b)$$

$$[SO_3^{2-}] = \frac{H_{SO_2} K_{S1} K_{S2} p_{SO_2}}{[H^+]^2} \quad (22c)$$

Satisfying the electroneutrality relation requires

$$[H^+]^3 - (K_w + H_{SO_2} K_{S1} p_{SO_2}) [H^+] - 2 H_{SO_2} K_{S1} K_{S2} p_{SO_2} = 0 \quad (23)$$

The total dissolved sulfur in oxidation state + 4 is S(IV) and its concentration is given by

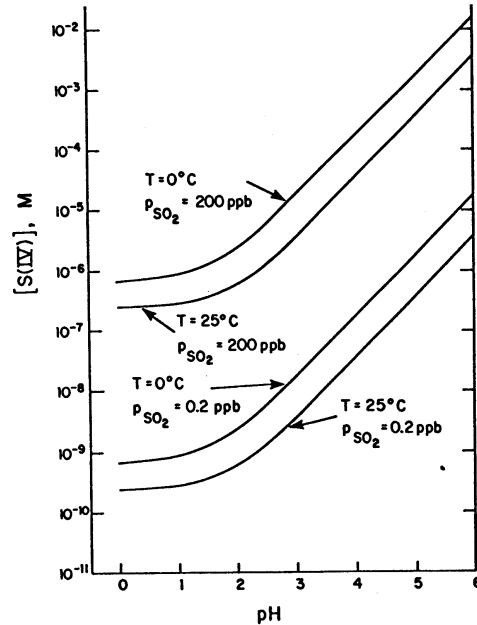
$$[S(IV)] = H_{SO_2} p_{SO_2} \left[1 + \frac{K_{S1}}{[H^+]} + \frac{K_{S1} K_{S2}}{[H^+]^2} \right] = H_{S(IV)}^* p_{SO_2} \quad (24)$$

where $H_{S(IV)}^*$ is the modified Henry's constant which we can express as

$$H_{S(IV)}^* = H_{SO_2} \left[1 + 10^{pH} K_{S1} + 10^{2pH} K_{S1} K_{S2} \right] \quad (25)$$

Clearly the modified constant H^* is dependent on pH. The larger the pH, i.e. the more alkaline the solution, the larger the equilibrium content of $S(IV)$. This is illustrated in Figure 3.2 for $p_{SO_2} = 0.2$ ppb and 200 ppb.

FIGURE 3.2: Equilibrium dissolved S(IV) as a function of pH, gas-phase partial pressure of SO_2 and temperature



Let us express now mole fractions of various dissolved sulfur species as function of pH (really these are mole ratios, i.e. moles of a particular sulfur species divided by total moles of $S(IV)$ or mole fractions on water free basis since water is the dominant component.

$$\alpha_0 = X_{SO_2 \cdot H_2O} = \frac{[SO_2 \cdot H_2O]}{[S(IV)]} = \left[1 + K_{S1} 10^{pH} + K_{S1} K_{S2} 10^{2pH} \right]^{-1} \quad (26a)$$

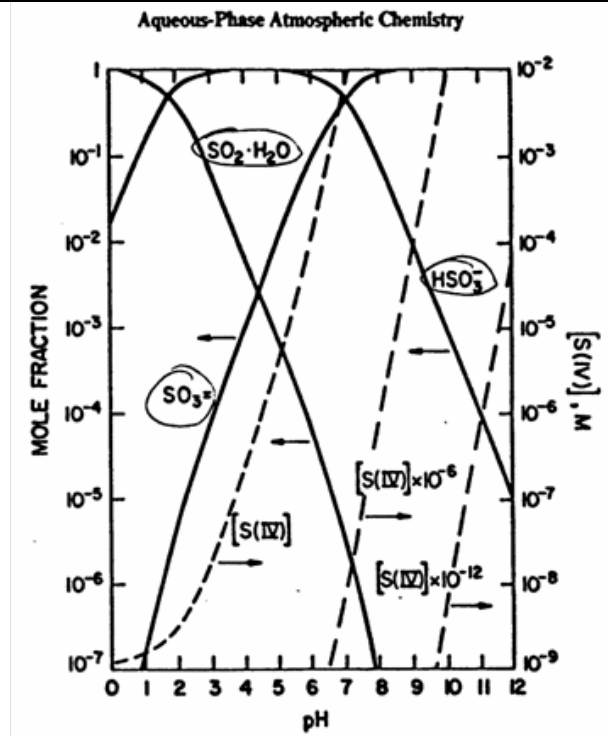
$$\alpha_1 = X_{HSO_3^-} = \frac{[HSO_3^-]}{[S(IV)]} = \left[1 + K_{S1}^{-1} 10^{-pH} + K_{S2} 10^{pH} \right]^{-1} \quad (26b)$$

$$\alpha_3 = X_{SO_3^{2-}} = \frac{[SO_3^{2-}]}{[S(IV)]} = \left[1 + K_{S2}^{-1} 10^{-2pH} + (K_{S1} K_{S2})^{-1} 10^{-2pH} \right]^{-1} \quad (26c)$$

Common notation for these are $\alpha_0, \alpha_1, \alpha_2$ in aquatic chemistry.

Figure 3.3 illustrates the above three mole fractions for $p_{SO_2} = 10^{-9}$ atm (1 ppb). Since these species have different reactivities pH will affect reaction rates. At low pH $SO_2 \cdot H_2O$ dominates, at high pH all $S(IV)$ is in the form of SO_3^{2-} . Intermediate pH contains mainly HSO_3^- .

FIGURE 3.3: Mole fractions and concentrations of the three dissolved S(IV) species, $SO_2 \cdot H_2O$, HSO_3^- , and SO_3^{2-} , as a function of pH at $T = 298\text{ K}$, and $p_{SO_2} = 10^{-9}\text{ atm}$ (1ppb).



3.3.4 Abundance of Liquid Water in the Atmosphere

Liquid water content is expressed in (g water/m³ air) or (m³ water/m³ air). Let L be the second dimensionless measure. Then

clouds	$L = 10^{-7}$ to 10^{-6}
fog	$L = 10^{-8}$ to 5×10^{-7}
aerosols	$L = 10^{-11}$ to 10^{-10}

The distribution of a species A between gas and aqueous phases, in say a cloud, can be expressed as

$$\frac{\text{moles of } A \text{ in solution per m}^3 \text{ of air}}{\text{moles of } A \text{ in air per m}^3 \text{ of air}} = \frac{H_A P_A L}{\frac{P_A}{RT}} = H_A R T L \quad (27)$$

$$H_A R T L \ll 1$$

species A is mainly in the gas

$$H_A R T L \gg 1$$

species A mainly in the liquid

$$\text{For } L = 10^{-6}, (R T L)^{-1} \approx 4 \times 10^4 \text{ M atm}^{-1}$$

Hence for

$$H_A \ll 4 \times 10^4 \text{ M atm}^{-1}$$

species A in the gas

$$H_A \gg 4 \times 10^4 \text{ M atm}^{-1}$$

species A in the liquid

Table 3.1 indicates that, with exception of $HC\ell$, $HCHO$ and especially H_2O_2 and HNO_3 , other species will remain mainly confined to the gas phase.

For SO_2 at $pH = 4$, $H_{S(IV)}^* \approx 10^2$ and at $L = 10^{-6}$ $H_{S(IV)}^* \leq (RTL)^{-1}$ and most of (almost all of) the $S(IV)$ is in the gas phase. In contrast for HNO_3 the modified Henry's constant is

$H^* = 10^{10}$ and all of nitric acid is in solution.

Maximum Solubility

For example, the equilibrium dissolved concentration of A is given by $[A_e] = H_A P_A$ but the total amount of species present in a closed system (i.e. system with fixed boundaries over which no exchange of matter occurs with the surroundings) is:

$$\begin{aligned} N_{totA} &= C_{A_g} V_g + C_{A_L} V_L \\ &= V_g \left[C_{A_g} + C_{A_L} \frac{V_L}{V_g} \right] = V_g \left[\frac{P_A}{RT} + C_{A_L} L \right] \end{aligned} \quad (28)$$

Dividing by air volume, V_g , we get:

$$\frac{N_{totA}}{V_g} = C_{A_{so}} = \frac{P_{A_{so}}}{RT} = \frac{P_A}{RT} + C_{A_L} L \quad (29)$$

Since the following relationship holds

$$C_{A_L} = H_A P_A \quad (30)$$

Substituting eq. (30) into eq. (29) yields

$$\frac{P_{A_{so}}}{RT} = P_A \left[\frac{1}{RT} + H_A L \right] = \frac{P_A}{RT} [1 + H_A RTL] \quad (31)$$

Solving for the partial pressure of A gives:

$$P_A = \frac{P_{A_o}}{1 + H_A RTL} \quad (32)$$

Using eq. (30) we get the concentration of dissolved A in water:

$$C_{A_L} = \frac{H_A P_{A_o}}{1 + H_A RTL}$$

Then, when gas solubility is very high so that $H_A RTL \gg 1$ the maximum concentration of dissolved A is:

$$C_{A_{Lmax}} = \frac{P_{A_o}}{RTL} = [A]_{max} \quad (33)$$

Thus, essentially all of the soluble gas is in the liquid phase!

Clearly, then, in a closed system for a very highly soluble gas we must take precautions in calculating the equilibrium composition not to violate the mass balance, (i.e. "not to dissolve more gas than there is available") as the concentration of eq. (33) cannot be exceeded. For example, if $P_A = 10^{-9}$ atm (1 ppb) and $L = 10^{-6}$, $[A]_{\max} = 4 \times 10^{-5}$ M. Regardless of the value of H , since for highly soluble species with $H = 10^{10}$ the equilibrium dissolved concentration is $[A]_{\text{eq}} = 10$ M. However, clearly the six orders of magnitude $[A]_{\max}$ cannot be exceeded. $[A]_{\max}$ can only be exceeded if the water droplets are brought into contact with much larger volume of air not just the volume containing L amount of water.

3.4 Liquid-Liquid Systems

For immiscible liquid-liquid systems, the K-factors are known more commonly as the distribution coefficients.

$$K_{D,l} = \frac{x_i^{(1)}}{x_i^{(2)}} \quad (34)$$

where (1) and (2) refer to liquid phases 1 and 2 with x_i as the mole fraction of species i in the corresponding phase. For gas-solid or liquid-solid systems the equilibrium is described by adsorption equilibrium constants which will be addressed in a subsequent chapter.

Liquid-liquid equilibria can also be expressed in terms of a ratio of concentrations $K = C_o/C_w$ where C_o is the concentration in the organic phase and C_w is the concentration in the water phase.

One important parameter widely used in environmental engineering is the octanol-water partition coefficient usually denoted K_{ow} . This is defined as the ratio of concentration of the solute in n-octanol to that in water. The essential idea behind the use of this parameter is that n-octanol can be viewed as representative of the lipid phase in tissues and, hence, this quantity is a measure of how the solute gets incorporated into the tissues. Hence, accurate estimates or experimental values of this parameter is of importance in estimating the bio-toxicity of a compound. A related parameter is the bio-concentration factor BCF which is defined as follows:

$$\log BCF = 0.79 \log (K_{ow}) - 0.40 \quad (35)$$

Thus, BCF is proportional to K_{ow} . If BCF is greater than 1000 then the compound is considered to have a high potential for bioaccumulation. If BCF is less than 250 then the compound is assumed to have low potential to accumulate in aquatic organisms.

Predictive methods based on group contributions are available for K_{ow} and these are useful as a first estimate for a new compound in the absence of measured values.

Example: Phenol has a $\log (K_{ow})$ value of 1.46. What is its bio-concentration potential?

Answer: Using the equation above we find $\log (BCF) = 0.7771$ and $BCF = 10^{0.7771}$ which is less than 250.

Hence phenol has low bio-accumulation potential.

3.5 Multiphase Distribution

Situations where multiphase equilibria, when more than two phases co-exists, need to be assessed and are illustrated by Figure 3.5 taken from Seader and Henley (1998) where 7 phases are reported.

Air
<i>n</i> -hexane-rich liquid
Aniline-rich liquid
Water-rich liquid
Phosphorous liquid
Gallium liquid
Mercury liquid

Figure 3.5 Seven Phases in Equilibrium

In some applications of multiphase systems, three or more phases coexist. Figure 3.5 is a schematic diagram of an experiment taken from Hildebrand (1970), which shows seven phases in equilibrium at near-ambient temperature. The phase on top is air, followed by six liquid phases in order of increasing density: hexane-rich, aniline-rich, water-rich, phosphorous, gallium and mercury. Each phase contains all components in the seven-phase mixture, but the mole fractions in many cases are extremely small. For example, the aniline-rich phase contains on the order of 10 mol % *n*-hexane, 20 mol % water, but much less than 1 mol % each of dissolved air, phosphorous, gallium and mercury. Note that even though the hexane-rich phase is not in direct contact with the water-rich phase, an equilibrium amount of water (approximately 0.06 mol %) is present in the hexane-rich phase. This is so because each phase is in equilibrium with each of the other phases as attested by the equality of component fugacities:

$$f_i^{(1)} = f_i^{(2)} = f_i^{(3)} = f_i^{(4)} = f_i^{(5)} = f_i^{(6)} = f_i^{(7)} \quad 36$$

(This is true for all i (i.e. all components in the system)).

Note that the fugacity of a component must be the same in all phases if the phases are to be in equilibrium. In f_i^j the superscript j denotes the phase and subscript i the chemical component.

3.6 Partitioning of pollutants: Level I Model

The environment is divided into four compartments: air, water, soil and biota. Each component is assigned a certain volume denoted by V_i . The concentration distribution of a pollutant discharged into any of the phases (say air), can be calculated by using the concept of fugacity. The fugacity of a component (designated as f here) is the same in all the compartments at equilibrium. For calculation purposes, a concept called “**fugacity capacity**” is more useful. This is defined by the following equation.

$$c_i = z_i f$$

where c_i = pollutant concentration in compartment i
and z_i = fugacity capacity for the compartment i (37)

Now consider an amount of pollutant M_T released to the environment. M_T has units of mass. The release may be to one or more of the compartments. Then, by mass balance, at equilibrium in a closed system one has

$$M_T = \sum c_i V_i \quad (38)$$

Using the definition of fugacity capacity, we have

$$M_T = f \sum z_i V_i \quad (38a)$$

$$\text{Hence } f = \frac{M_T}{\sum z_i V_i} \quad (39)$$

Pollutant concentration in compartment i at equilibrium is equal to

$$c_i = M_T \frac{z_i}{\sum z_i V_i} \quad (40)$$

Pollutant total mass in any compartment i , $M_i = c_i V_i$, is given by

$$M_i = M_T \frac{z_i V_i}{\sum z_i V_i} \quad (41)$$

Percentage distribution to compartment i is then directly calculated as

$$\frac{M_i}{M_T} \times 100 = \left(z_i V_i / \sum z_i V_i \right) \times 100 \quad (42)$$

Note that the fugacity need not be explicitly calculated when using this approach. One needs the information only on the fugacity capacity. We now show how these can be obtained from basic thermodynamic properties. Also note that the above procedure can be repeated for a number of pollutants.

3.6.1 Fugacity capacity in air phase

Fugacity of a component at ideal state in the air phase is equal to its partial pressure p , and the concentration is equal to p/RT . Hence, using the definition of fugacity capacity

$$z_{air} = \frac{1}{RT} \quad (43)$$

which has a value of $4.04 \times 10^{-4} \text{ mol / m}^3 \cdot \text{Pa}$ at 25°C . The fugacity capacity in air is independent of the chemical species and has a constant value at a fixed temperature.

3.6.2 Water phase

In aqueous systems, the fugacity of a chemical is

$$f = x\gamma P^{vap} \quad (44)$$

where x is the mole fraction and γ is the activity coefficient. If the solute is in equilibrium with the gas then $f = p$. By Henry's law $c_i = Hp$.

Hence, we have

$$z_{water} = H \quad (45)$$

where H is the Henry's law constant in $(\text{mol/m}^3 \text{ Pa})$.

3.6.3. Soil phase

Chemicals in soil are almost always adsorbed into the natural organic matter and are in equilibrium with the water phase concentration. Concentration in soil is related to concentration in water by the adsorption equilibrium constant.

$$c_{soil} = K_{soil} c_{water} \quad (46)$$

A measure of K_{soil} is K_{oc} , the organic carbon based distribution coefficient. K_{oc} represents the concentration per unit mass of organic carbon in soil. If ϕ_{soil} represents the mass fraction of carbon in the soil, then a measure of K_{soil} is the product $K_{oc} \phi_{oc}$ where ϕ_{oc} is the mass fraction of carbon.

Hence the fugacity capacity of soil is

$$z_{soil} = HK_{oc} \phi_{soil} \rho_{soil} \quad (47)$$

Further K_{oc} is shown to correlate well with octanol-water partition coefficient K_{ow} with the equality $K_{oc} = 0.41K_{ow}$. With these, we find

$$z_{soil} = 0.41 H K_{ow} \phi_{soil} \rho_{soil} \quad (48)$$

For biota equation (49) below is used

$$z_{biota} = 0.05 K_{ow} H \rho_{biota} \text{ is used.} \quad (49)$$

where ϕ_{biota} is the mass fraction of organic carbon in the biota phase.

Example:

Consider 100 mol of PCP (pentachlorophenol) released into the aqueous phase. Find its distribution in various compartments using the equilibrium (fugacity level 1) model.

Solution:

We need some data for the volumes of various compartments and some thermodynamic properties of PCP.

Assume these volumes. These are typical values used in these calculations

$$V_{air} = 10^{14} \text{ m}^3; \text{ water} = 2 \times 10^{11} \text{ m}^3$$

$$\text{soil} = 9 \times 10^9 \text{ m}^3, \text{ biota} = 2 \times 10^5 \text{ m}^3$$

Thermodynamic data.

Reciprocal of the Henry's law constant $H^{-1} = 0.079 \text{ Pa m}^3/\text{mole}$ (from the literature).

Also $K_{ow} = 112,202$

Now we can calculate the fugacity capacity values for the four phases.

$$z_{air} = \frac{1}{RT} = 4.04 \times 10^{-4} \frac{\text{mol}}{\text{m}^3 \text{ Pa}} \text{ at } 25^\circ \text{C}$$

$$z_{water} = H = 12.66 \text{ mol/m}^3 \text{ Pa}$$

$$z_{soil} = 0.41 H K_{ow} \phi_{soil} \rho_{soil} \cdot$$

ϕ_{soil} = the mole fraction of organic carbon. We use a value of 0.02 here.

$$\rho_{soil} = 2400 \text{ kg/m}^3 \cdot$$

Using these values

$$z_{soil} = 2.8 \times 10^4 \text{ mol/m}^3 \text{ Pa}.$$

Similarly we use $\rho_{biota} = 1000 \text{ kg/m}^3$ and find

$$z_{biota} = 7.1 \times 10^4 \text{ mol/m}^3 \text{ Pa}.$$

With all this information we can find the equilibrium of the pollutant distribution. The calculations can be done conveniently in an excel spreadsheet or using the matlab program shown here.

$$\sum z_i v_i = 2.55 \times 10^4 \text{ mol/m}^3$$

Percentage partition is then calculated as $z_i v_i / \sum z_i v_i$ and the results are
 $air = 1.59 \times 10^{-2} \%$ $water = 0.995 \%$ $soil = 99.4 \%$ $Fish (biota) = 5.58 \times 10^{-3} \%$.

PCP tends to accumulate in soil.

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% MATLAB PROGRAM FOR FUGACITY LEVEL 1 CALCULATIONS.
% 1= air, 2 = water, 3 = soil ; 4 = biota.
% PCP data used here
henry = 0.079 ; % Pa-m^3.mole
kow = 112202 ; % L/kg
phi_soil = 0.02 ; % organic mass fraction in soil
temp = 298.0 ;
% calculation section
volume = [ 1e+14
           2e+11
           9e+09
           2e+05];
rho_soil = 2400.0;
rho_biota = 1000.0 ;
z(1) = 1./8.314 /temp ;
z(2) = 1./henry ;
z(3) = 0.41* phi_soil * rho_soil * kow/henry /1000.;
z(4) = 0.05 * rho_biota * kow/ henry/1000.0 ;
sum = z * volume ;
distribution(1) = z(1) * volume (1) / sum ;
distribution(2) = z(2) * volume (2) / sum ;
distribution(3) = z(3) * volume (3) / sum ;
distribution(4) = z(4) * volume (4) / sum ;
distribution

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References:

Hilderbrand, J.H. *Principles of Chemistry, ed. MacMillian, New York, 1970.

J.D. Seader, Henley, G.J., Separation Process Principles, John Wiley & Sons, Inc., 1998.