

# “Chemical Distribution Among Phases”

Module 1: Basic Concepts, Lecture 3

*Chemical Fate and Transport in the Environment*,  
2nd edition. H.F. Hemond and E.J. Fechner-Levy.  
Academic Press. London. 2000.

## 1.8 Multiple Phases Present in the Environment

- One medium (water, air, or soil) may contain different phases.
- Atmosphere contains gas, water, and solids.
- Surface water contains gas bubbles and particulates.
- Pollutants become distributed between different phases in each medium.

## Examples of Pollutant Phases

- Pure air is an example of a gas phase
- Solid phases include soil grains, solid particles suspended in water or air, plus pure solid chemicals.
- Immiscible liquid (a liquid that doesn't mix freely with water) can form its own nonaqueous phase liquid (NAPL), such as an oil slick on water.
- This chapter considers only equilibrium partitioning, however, the rate of change of partitioning may be an issue for some conditions (such as the loss of volatiles from a spill of crude oil).

## 1.8.1 Solubility and Vapor Pressure

- Aqueous solubility is the concentration of a chemical dissolved in water when that water is both in contact and at equilibrium with the pure chemical.
- Aqueous solubility is temperature dependent, but does not vary greatly over typical environmental temperatures.
- As an example, TCE (trichloroethene) dissolves in water until an aqueous concentration of about 1,000 mg/L is reached.

- Vapor pressure is defined as the partial pressure of a chemical in a gas phase that is in equilibrium with the pure liquid or solid chemical.
- Temperature is very important when determining vapor pressure.
- A sealed bottle containing both air and pure liquid TCE will develop a partial pressure of TCE of about 0.08 atm at 20°C in the headspace. This corresponds to about 0.0033 mol/L.

- The ideal gas law is used to convert the partial pressure to the moles of vapor per unit volume:

$$\frac{n}{V} = \frac{P}{RT}$$

Where  $n/V$  is the number of moles of the chemical per unit volume,  $P$  is the partial pressure,  $T$  is the absolute temperature, and  $R$  is the gas constant: (0.082 liter-atm)/(mol-K).

Hemond and Fechner-Levy 2000, Table 1-3

Chemical	Molecular weight (g/mol) <sup>a</sup>	Density (g/cm <sup>3</sup> ) <sup>b</sup>	Solubility (mg/l) <sup>c</sup>	Vapor pressure (atm) <sup>d</sup>	Henry's law constant (atm-cm <sup>3</sup> /mol) <sup>e</sup>	Henry's law constant (dimensionless) <sup>f</sup>	log $K_{ow}$ <sup>g</sup>	Comments
Acetic acid	60.05	1.05	=					
Aroclor 1254	325.00 <sup>h</sup>	1.30 <sup>h</sup>	$1.3 \times 10^{-1}$	$1 \times 10^{-1}$	$2.7 \times 10^{-1}$	$1.2 \times 10^{-1}$	6.3	Polychlorinated biphenyl mixture (PCB)
Aroclor 1260	371.22 <sup>h</sup>	1.57 <sup>h</sup>	$2.7 \times 10^{-1}$	$3.5 \times 10^{-1}$	$7.1 \times 10^{-1}$	$3.0 \times 10^{-1}$	6.3	Polychlorinated biphenyl mixture (PCB)
Aroclor	215.80 <sup>h</sup>		30 <sup>h</sup>	$4 \times 10^{-1}$	$3 \times 10^{-1}$	$1 \times 10^{-1}$	3.00	Hexachloro
Benzene	78.11	0.88	1780	$1.29 \times 10^{-1}$	$5.5 \times 10^{-1}$	$2.4 \times 10^{-1}$	2.13	Aromatic
Benz[a]anthracene	228.29		$2.5 \times 10^{-4}$	$6.3 \times 10^{-6}$	$5.75 \times 10^{-6}$	$2.4 \times 10^{-6}$	5.01	Polycyclic aromatic hydrocarbon (PAH)
Benz[a]pyrene	252.32		$4.9 \times 10^{-6}$	$2.3 \times 10^{-7}$	$1.20 \times 10^{-6}$	$4.0 \times 10^{-6}$	6.50	PAH
Carbon tetrachloride	153.82	1.59	800	0.13	$2.3 \times 10^{-1}$	$9.7 \times 10^{-1}$	2.83	
Chlorobenzene	112.56	1.11	472	$1.8 \times 10^{-1}$	$3.7 \times 10^{-1}$	$1.65 \times 10^{-1}$	2.82	
Chloroform	119.38	1.48	8000	0.32	$4.8 \times 10^{-1}$	$2.0 \times 10^{-1}$	1.83	
n-Coal	108.14		2700				1.86	
Cyclohexane	84.18	0.78	80	0.13	0.18	7.3	3.44	
1,3-Dichlorobenzene	98.96	1.18	4900	$3.0 \times 10^{-1}$	$6 \times 10^{-1}$	$2.4 \times 10^{-1}$	1.79	
1,2-Dichlorobenzene	98.96	1.28	4500	$0.1 \times 10^{-1}$	10 <sup>-1</sup>	$4.1 \times 10^{-1}$	1.47	

## Example Problem 1-12

- A 70 L fuel tank has a 2 ft x 1.5 in D filler pipe. How much fuel is lost if the cap is left off for a day? Assume;
  - Diffusion coefficient of 0.1 cm<sup>2</sup>/sec
  - Fuel is octane, C<sub>8</sub>H<sub>18</sub>, having a molecular weight of 114
  - Vapor pressure is 0.015 atm at the ambient temperature of 70°F (21°C)
  - The fuel tank is half empty

Headspace octane concentration:

$$\frac{n}{V} = \frac{P}{RT} = \frac{0.015 \text{ atm}}{0.082 \text{ liter} \cdot \text{atm} / (\text{mol} \cdot \text{K}) \cdot (21 + 273) \text{ K}} = 6.2 \times 10^{-4} \text{ M}$$

With a MW of 114, this concentration corresponds to:

$$6.2 \times 10^{-4} \frac{\text{mol}}{\text{L}} \cdot 114 \frac{\text{g}}{\text{mol}} \cdot 7.1 \times 10^{-2} \frac{\text{g}}{\text{L}} \cdot \frac{\text{L}}{10^3 \text{ mL}} = 7.1 \times 10^{-5} \text{ g} / \text{cm}^3$$

The concentration gradient along the filler tube is:

$$\frac{dC}{dX} = \frac{(7.1 \times 10^{-5} \text{ g} / \text{cm}^3 - 0 \text{ g} / \text{cm}^3)}{(2 \text{ ft} \cdot 30.48 \text{ cm} / \text{ft})} = 1.2 \times 10^{-6} \text{ g} / \text{cm}^4$$

Fick's first law used to estimate flux density of octane:

$$J = -D \cdot \frac{dC}{dx} = 0.1 \frac{\text{cm}^2}{\text{sec}} \cdot 1.2 \times 10^{-6} \frac{\text{g}}{\text{cm}^4}$$

The rate of fuel loss is the flux density multiplied by the cross-sectional area:

$$1.2 \times 10^{-7} \frac{\text{g}}{\text{cm}^2 \cdot \text{sec}} \cdot \pi \cdot \left( \frac{1.5 \text{ in}}{2} \cdot \frac{2.54 \text{ cm}}{\text{in}} \right)^2 = 1.3 \times 10^{-6} \frac{\text{g}}{\text{sec}} = 0.11 \frac{\text{g}}{\text{day}}$$

- Can also calculate the loss due to “advective” pumping through a tank vent if the atmospheric pressure decreases from 30.0 to 29.5 in Hg. Assume that the mass of air in the tank is proportional to pressure.

Initially, the air in the tank contains the following octane:

$$35 \text{ liter} \cdot 7.1 \times 10^{-2} \text{ g} / \text{liter} = 2.5 \text{ g}$$

When the pressure drops from 30 to 29.5 in Hg, the mass of air decreases to:

$$\frac{29.5}{30} \cdot 100\% = 98.3\%$$

Therefore, about 1.7% of the air, and thus about 1.7% of the 2.5 g of octane leaves the tank, or 0.041 g.

## 1.8.2 Henry's Law Constants

- A partition coefficient describes how a chemical distributes itself between two different phases.
- The Henry's Law constant, H (or  $K_H$ ), is a partition coefficient defined as the ratio of a chemical's concentration in air to its concentration in water at equilibrium.
- H can be estimated for a chemical by dividing its vapor pressure by its aqueous solubility at the same temperature.
- H generally increases with increasing temperature (vapor pressure changes more rapidly than aqueous solubility with temperature).

- H can be dimensionless (using the same concentration units for the water and air phases), in dimensionless forms, such as atm-L/mol or atm-m<sup>3</sup>/mol. Can be converted:

$$H = \frac{\text{mol} \cdot \text{chemical} / \text{liter} \cdot \text{air}}{\text{mol} \cdot \text{chemical} / \text{liter} \cdot \text{water}} \cdot R \left( \frac{\text{liter} \cdot \text{air} \cdot \text{atm} \cdot \text{chemical}}{\text{mol} \cdot \text{chemical} \cdot K} \right) \cdot T(K)$$

$$= \frac{\text{atm} \cdot \text{chemical}}{\text{mol} \cdot \text{chemical} / \text{liter} \cdot \text{water}} = \frac{\text{atm} \cdot \text{liter}}{\text{mol}}$$

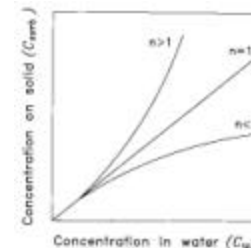
## 1.8.3 Chemical Partitioning to Solids

- Sorption is the term used to describe the chemical partitioning between air and solid phases.
- Adsorption is when the chemical sticks to the two-dimensional surface of a solid.
- Absorption is when the chemical diffuses into a three-dimensional solid.
- Chemical sorption is much more difficult to predict than other forms of partitioning.
- Sorption can include absorption into natural organ matter; adsorption to mineral surfaces via van der Waals, dipole-dipole, and other weak physical intermolecular forces; amongst many other processes.

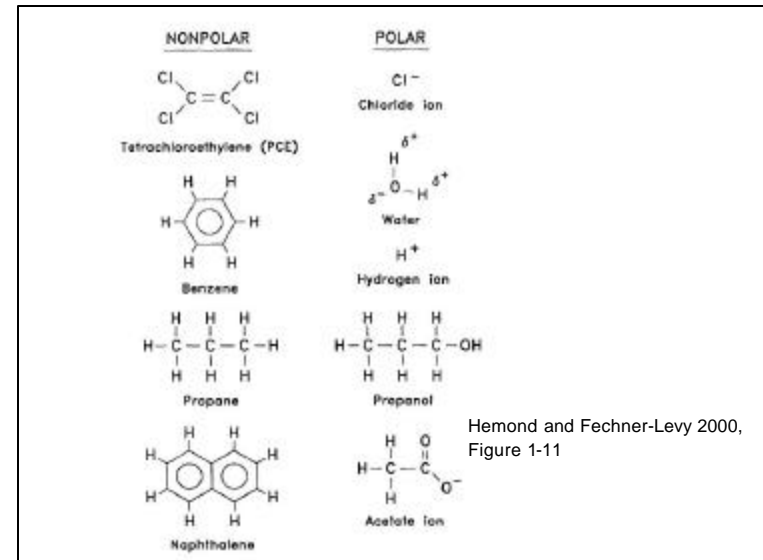
- Sorption isotherms (conducted at a constant temperature) are therefore used to directly measure the partitioning between water and solids.
- Laboratory data usually fitted to the Freundlich isotherm:

$$C_{\text{sorb}} = K_f \cdot (C_w)^n$$

$C_{\text{sorb}}$  is the concentration of the sorbed chemical [M/M]  
 $K_f$  is the Freundlich constant  
 $C_w$  is the concentration of the dissolved chemical [M/L<sup>3</sup>]  
 n reflects non-linearity:



- Laboratory tests needed to determine  $K_d$  (distribution coefficient between water and solids) for inorganic chemicals, and charged organic chemicals which sorb through chemical reactions with solid surfaces.
- For many neutral (uncharged) organic chemicals, can predict  $K_d$  assuming that the absorption is the primary sorption process. They sorb because they are nonpolar.
- Polarity refers to the extent to which the charge is unevenly distributed within a molecule or substance.



- Water is very polar, with an excess of positive charges associated with the hydrogen atoms. Most natural minerals are also polar.
- Because of water's polarity, it readily dissolves other polar (hydrophilic) chemicals.
- The nonpolar (hydrophobic) chemicals tend to avoid the less favorable state (based on free-energy considerations) of being dissolved in water by absorbing into natural organic matter.

- The polarity of a chemical has a strong inverse correlation with the chemical's  $K_{ow}$  (the octanol-water partition coefficient).
- $K_{ow}$  is the ratio of a chemical's concentration in octanol ( $C_7H_{15}CH_2OH$ ) to its concentration in water at equilibrium.
- This ratio was developed by the pharmaceutical industry to predict drug behavior in the body, the ratio mimics partitioning between water and body fat.
- Smaller molecules and more polar molecules dissolve more readily in water and have lower  $K_{ow}$  values.
- Larger molecules and less polar molecules are less soluble in water and have higher  $K_{ow}$  values.
- $K_{ow}$  is therefore a very valuable indicator of how chemicals will behave in the environment.

## Example Problem 1-14

- Partition toluene in a fish (5% fatty tissue, 3% air, 85% water, 7% nonsorptive for toluene).
- Obtain relevant partition coefficients and set up an expression in which all masses of toluene are written as functions of the volume of fish:

Mass of toluene in water of fish =  $(V_{\text{fish}})(0.85)C_w$

Mass of toluene in swim bladder =  $(V_{\text{fish}})(0.03)(H_{\text{toluene}} \times C_w)$

Mass of toluene in fatty tissue =  $(V_{\text{fish}})(0.05)(K_{ow} \times C_w)$

- The fraction of toluene in fatty tissues can be written:

$$\frac{(V_{\text{fish}})(0.05)(K_{ow} \cdot C_w)}{(V_{\text{fish}})(0.05)(K_{ow} \cdot C_w) + (V_{\text{fish}})(0.03)(H_{\text{toluene}} \cdot C_w) + (V_{\text{fish}})(0.85)C_w}$$

$$= \frac{(0.05)(K_{ow})}{(0.05)(K_{ow}) + (0.03)(H_{\text{toluene}}) + (0.85)}$$

$$= \frac{(0.05)(490)}{(0.05)(490) + (0.03)(0.28) + (0.85)}$$

$$= \frac{(25)}{(25) + (0.008) + (0.85)} = 97\%$$