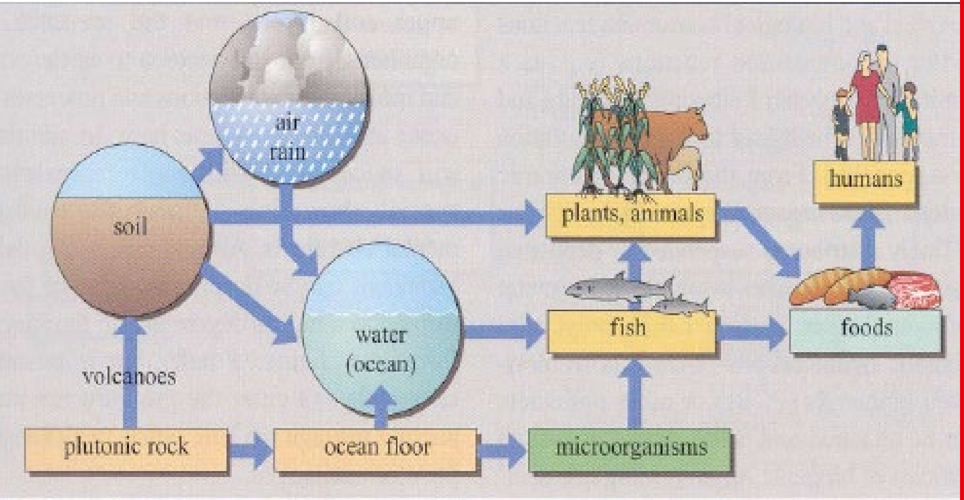

ENV-200 Partitioning

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Learning objectives

You should be able to:

1. Recognize the most common organic functional groups.
2. Understand the derivation of partitioning constants based on the principle of equal chemical potential in different phases.
3. Understand the physical meaning of the most important partitioning constants for environmental chemists: aqueous solubility; vapor pressure; K_{ow}; K_{aw} and K_H; K_{oc}
4. Apply these partitioning constants to determine the distribution of an organic chemical among different phases of interest.
5. Derive partitioning constants based on an LFER with a tabulated parameter or based on a combination of known portioning constants.
6. Calculate partitioning constants under non-standard conditions of temperature and salinity.

Resources

Many graphs, tables and examples are taken from:

Schwarzenbach, Gschwend, Imboden , Environmental Organic Chemistry

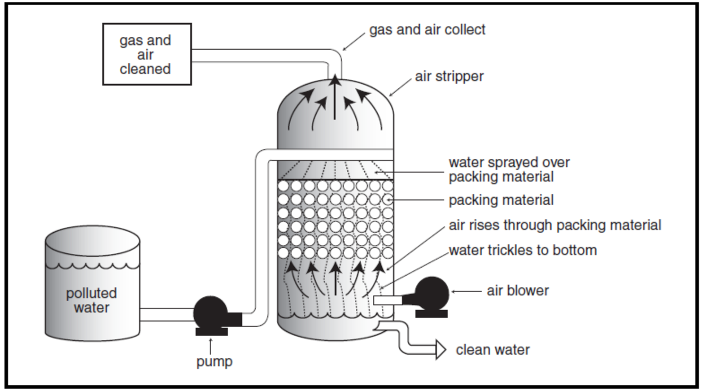
Note that Appendix C of this book is on moodle.

Engineering application: air stripping to clean up groundwater

What is air stripping?

Used for:

- Soil and groundwater remediation, in particular petroleum compounds or chlorinated solvents
- Water treatment (e.g., H_2S)
- Can be applied in-situ or ex-situ (pump and treat)
- Works for compounds with $K_H > 0.01$ atm*m^3 / mol (mostly organic compounds)
- Removal efficency > 99%



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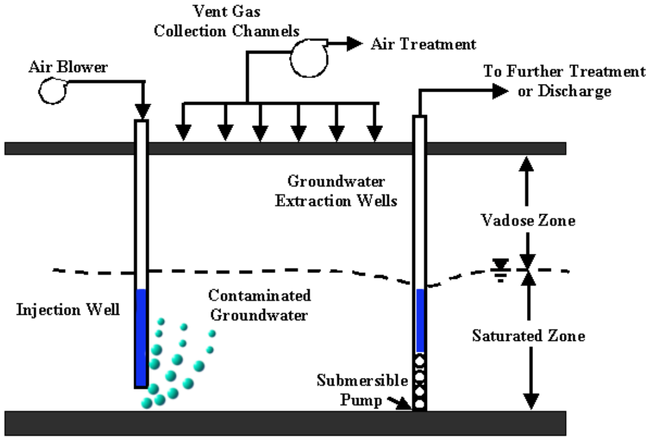
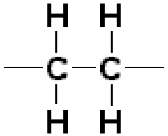


http://www.frtr.gov/matrix2/section4/4-34.html

Roadmap for the partitioning lectures

- Brief introduction
- Some thermodynamics
- Some general partitioning theory
- General liquid-liqud partitioning
  - Special case I: aqueous solubility C_w^{sat}
  - Special case II: octanol water, K_{ow}
- General air-liquid partitioning
  - Henry’s law
  - Special case I: vapor pressure
  - Special case II: « the » Henry’s law constant K_H for air-water partitioning
- Liquid-solid partitioning
  - Isotherms
  - K_d
  - Special case: organic matter partitioning, K_{oc}
- Multiphase distribution

Quick exercise: Organic nomenclature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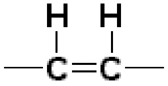
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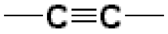
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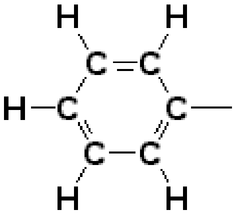
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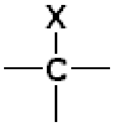
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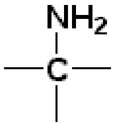
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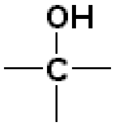
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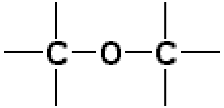
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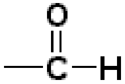
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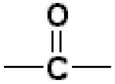
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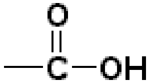
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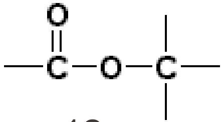
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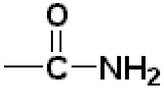
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a: alkane
b: carboxylic acid
c: ketone
e: alkyne
f: phenyl
g: alkyl halide
h: alcohol
i: amide
j: ether
k: amine
l: aldehyde
m: ester
n: alkene

Thermodynamics of partitioning

Big Picture

- Molecules move between different phases (or compartments): water, air, solid, oil, etc.
- This movement is driven by differences in chemical potential (μ)
- At equilibrium: chemical potentials are equal across phases, even if concentrations differ

Classic environmental compartments

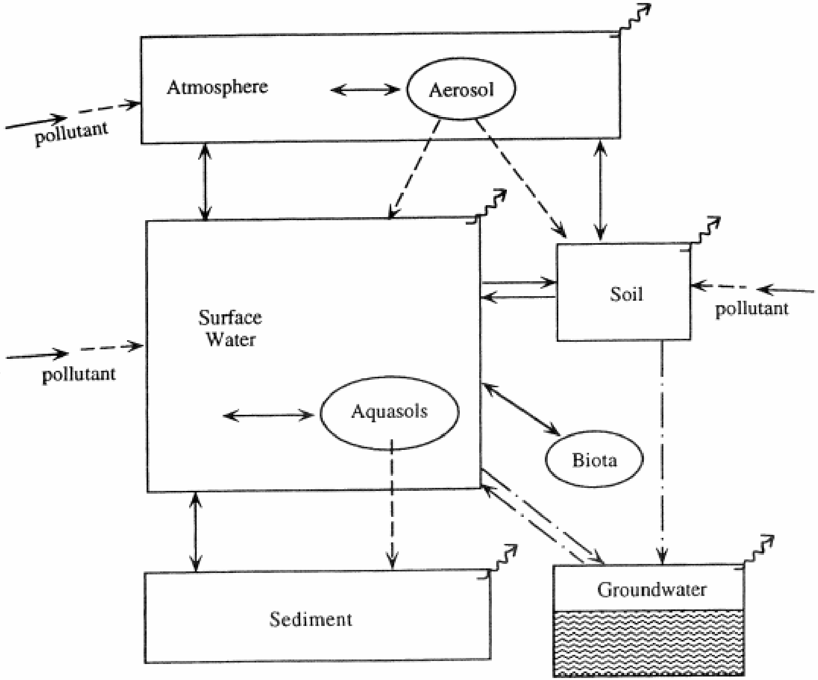


Figure 1.7 Path of a pollutant through the environment. The distribution of a pollutant in the environment is dependent on its specific properties. Of particular ecological relevance is fat solubility or, in other words, lipophilicity, as lipophilic substances accumulate in organisms and the food chain. Biodegradation and chemical or photochemical decomposition (indicated by ∿∿→), on the other hand, decrease residence time and residual concentrations. From Sigg and Stumm.[35]

J.L. Schnoor, 1996

Some more environmental compartments

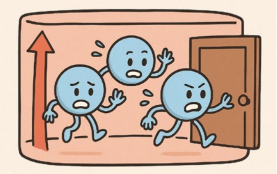
Compartments?
- urban waste materials
- water column
- sediments
- aquatic plants
- fish
- fisherman

Compartments?
- outdoor air
- indoor air
- clay bricks
- straw roofs
- soil
- terrestrial plants

Chemical potential μ

The chemical potential represents the free energy per mole of a compound in a given condition.

Think of it as the molecule's "urge to escape" it's current phase.



The chemical potential is defined as: $\mu_i = \mu_i^0 + RT\ln(x_i\,\gamma_i)$

μ_i^0 = standard chemical potential. The standard is the chemical potential of the pure phase. It depends on the aggregation state. For each compund, we have three different standard potentials: $\mu_{l,s}^0 \neq \mu_{i,l}^0 \neq \mu_{i,g}^0$

x_i = mole fraction of i (moles i / total moles in solution)

γ_i = activity coefficient of i. Defines how «uncomfortable» a chemical is in a given phase, compared to its own, pure phase, i.e., how «non-ideal» a phase is.

The chemical potential cannot be measured in absolute terms, only as the deviation from the standard potential.

Phase types

In a pure phase:

- $x_i = 1$ and $\gamma_i = 1$
- $\mu_i = \mu_i^0$

In an ideal mixture:

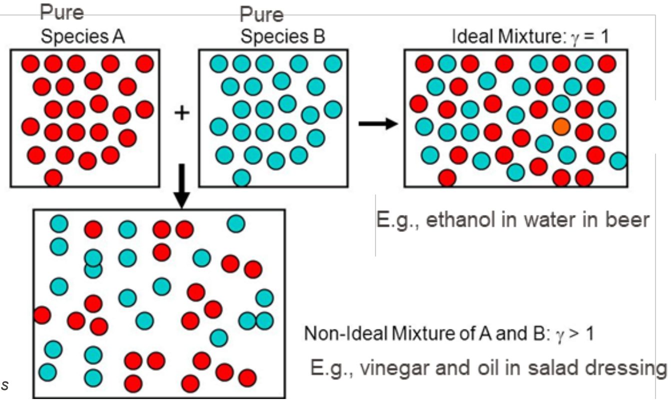
- the compound is in a solvent environment that « feels » like its own pure phase
- molecules interact as if in a pure phase
- $x_i \neq 1$ but $\gamma_i = 1$

In a non-ideal mixture:

- the compound is in a solvent environment that differs from its own
- Molecular interactions differ from pure phase
- $x_i \neq 1$ and $\gamma_i \neq 1$

A phase can be liquid, gas, or solid.

It can represent water, air, soil, oil, sediment, fish, plants, etc.



E.g., ethanol in water in beer

E.g., vinegar and oil in salad dressing

https://edurev.in/t/160337/Ideal-and-Non-ideal-Solutions

Some activity coefficients γ of organic compounds

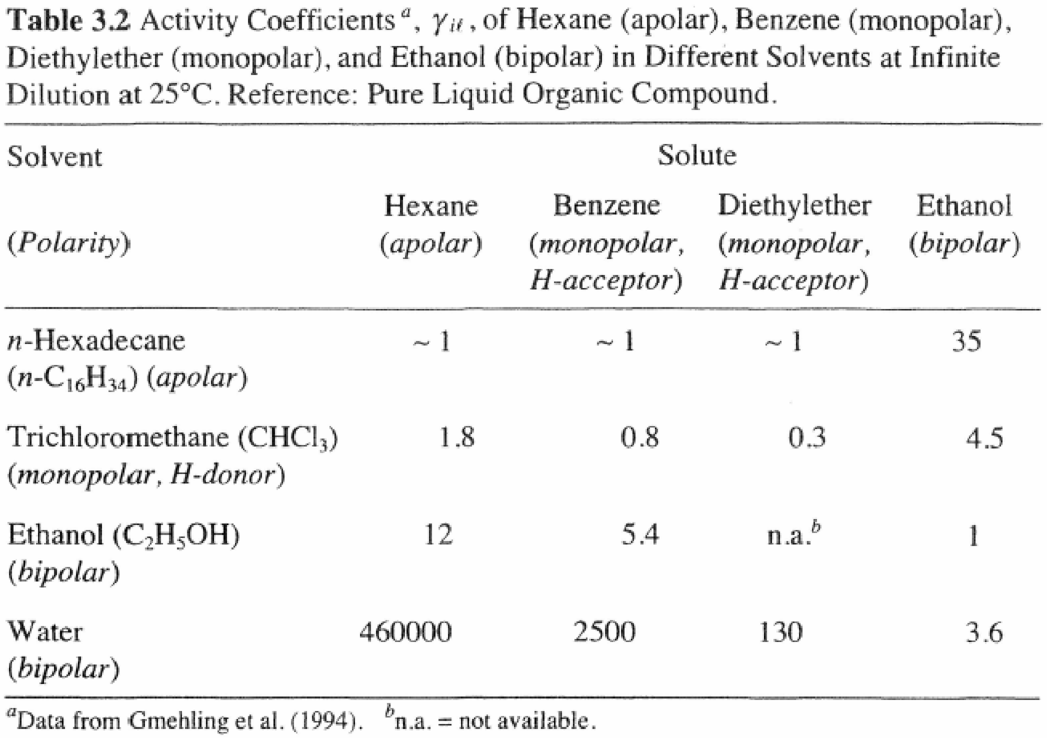


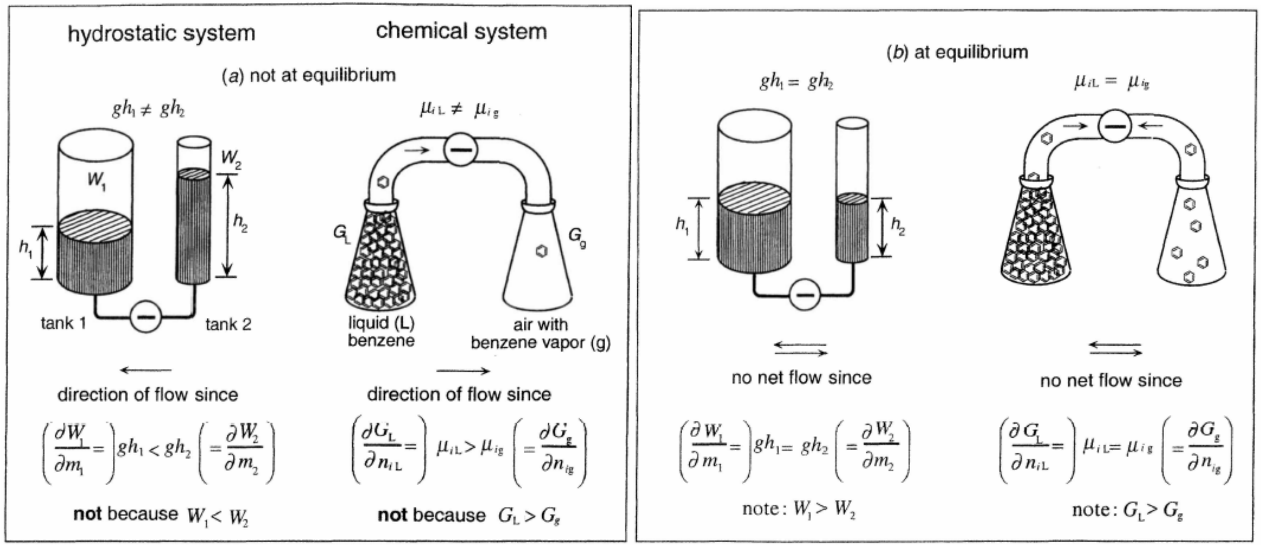
Table 3.2 Activity Coefficients[a], $\gamma_{i\ell}$, of Hexane (apolar), Benzene (monopolar), Diethylether (monopolar), and Ethanol (bipolar) in Different Solvents at Infinite Dilution at 25°C. Reference: Pure Liquid Organic Compound.

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

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

(Schwarzenbach et al. 2003, Table 3.2)

Comparison of hydrostatic and a chemical potentials



(Schwarzenbach et al. 2003, Fig. 3.8).

Left: in the non-equilibrated hydrostatic system, water flows from reservoir 2 of higher hydrostatic potential to reservoir 1 of lower hydrostatic potential. Similarly, benzene molecules move from liquid benzene to the head space in the non-equilibrated chemical system, not because there are more molecules in the flask containing the liquid, but because the molecules initially exhibit a higher chemical potential in the liquid than in the gas phase

Right: at equilibrium, the hydrostatic system is characterised by equal hydrostatic potentials in both reservoirs and the chemical system reflects equal chemical potentials in both flasks (not equal benzene concentrations).

Partitioning equilibrium

Partitioning is the distribution of a compound i between two (or more) phases (compartments). At equilibrium, the chemical potential μ of compound i in both phases is equal. I.e., i wants to «escape» from phase 1 into phase 2 as much as it wants to «escape» from phase 2 back to phase 1:

$$\mu_{i,1} = \mu_{i,2}$$

The partitioning equilibrium is expressed as the distribution of a compound i between two phases: ***$K_{i,12}$*** .

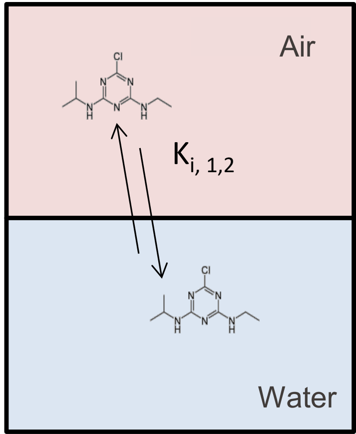
$K_{i,12}$ can be expressed in various ways (note that these K's are not equal!):

$$K_{i,1,2} = \frac{C_{i,1}}{C_{i,2}}$$ Ratio of concentrations

$$K'_{i,1,2} = \frac{x_{i,1}}{x_{i,2}}$$ Ratio of mole fractions

$$K_{H,i} = \frac{p_{i,1}}{C_{i,2}}$$ Ratio of partial pressure and concentration

Example: how does atrazine (a herbicide) distribute between water and air? →



T-dependence of $K_{i,12}$

Partition coefficients $K_{i,12}$ depend on temperature.

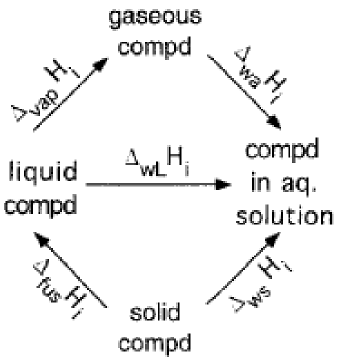
The relationship is given by the integrated van t'Hoff equation:

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

Shortcut!

Δ_{12}H (enthalpy of phase transfer) determines the sensitivity to temperautre.

Δ_{12}H depends on the phase transfer considered. It is often tabulated.



We can use this relationship to determine the $K_{i,12}$ at different temperatures.

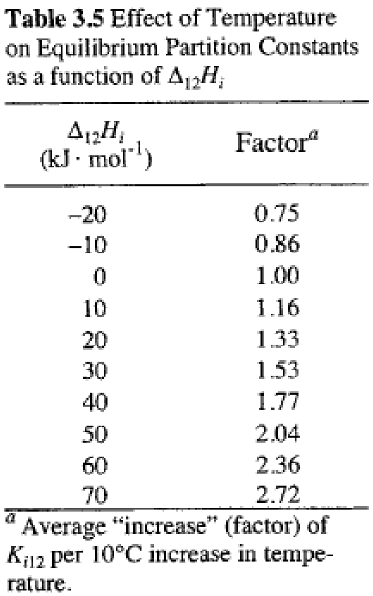


Table 3.5 Effect of Temperature on Equilibrium Partition Constants as a function of $\Delta_{12}H_i$

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

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

System 1: Liquid-liquid partitioning

Lets first consider a system where a compound partitions bewteen two liquids.

Example: atrazine partitioning between water and oil.

As we saw earlier, the following must be true at partitioning equilibrium:

$$\mu_{i,1} = \mu_{i,2}$$

where

$$\mu_{i,1} = \mu_{i,1}^{0} + RT \ln(x_{i,1}\gamma_{i,1})$$

$$\mu_{i,2} = \mu_{i,2}^{0} + RT \ln(x_{i,2}\gamma_{i,2})$$

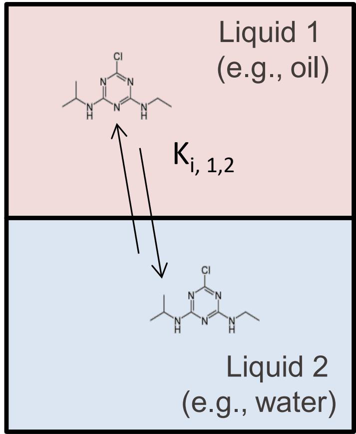
So at equilibrium:

$$\mu_{i,1}^{0} + RT \ln(x_{i,1}\gamma_{i,1}) = \mu_{i,2}^{0} + RT \ln(x_{i,2}\gamma_{i,2})$$

Or

$$\boxed{\mu_{i,1}^{0} - \mu_{i,2}^{0} = -RT \ln \frac{x_{i,1}\gamma_{i,1}}{x_{i,2}\gamma_{i,2}}}$$

On the next slide we'll learn how to get from here to $K_{i,12}$.



System 1: Liquid-liquid partitioning

Both phases are liquid, so the standard chemical potential in both phases is the potential of pure liquid i ($\mu_{i,l}{}^{0}$).

Therefore, $\mu_{i,1}{}^{0} = \mu_{i,2}{}^{0}$ and $\mu^{0}_{i,1} - \mu^{0}_{i,2} = -RT\ln\frac{x_{i,1}\gamma_{i,1}}{x_{i,2}\gamma_{i,2}} = 0$

We can re-write: $RT \ln(x_{i,1}\gamma_{i,1}) = RT \ln(x_{i,2}\gamma_{i,2})$

$$x_{i,1}\,\gamma_{i,1} = x_{i,2}\,\gamma_{i,2}$$

And finally, $K'_{i,1,2} = \frac{x_{i,1}}{x_{i,2}} = \frac{\gamma_{i,2}}{\gamma_{i,1}}$

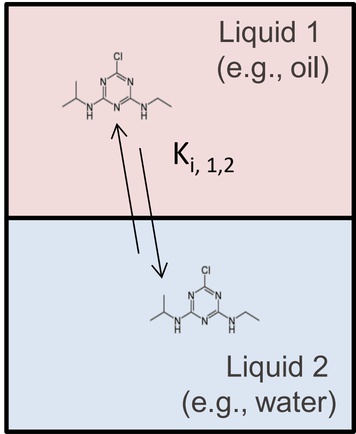
$K'_{1,2}$, is the ratio of mole fractions (x). But we usually prefer $K_{1,2}$ in terms of molar concentration ([i]). We convert:

$$\boxed{K_{i,1,2} = \frac{[i]_1}{[i]_2} = \frac{x_{i,1}}{x_{i,2}}\frac{\bar{v}_2}{\bar{v}_1} = \frac{\gamma_{i,2}}{\gamma_{i,1}}\frac{\bar{v}_2}{\bar{v}_1}}$$

Where $\bar{v}_1$ is the molar volume of phase 1 (see next slide):

$$\bar{v}_1 = \frac{L\ of\ \ phase\,1}{mol\ of\ \ phase\,1} \quad \text{and} \quad [i]_1 \approx \frac{x_{i,1}}{\bar{v}_1}$$

So how is all of this useful? → can use this approach to determine aqueous solubility of i.



Molar volume $\bar{v}$: a quick explanation

The molar volume tells us how much volume 1 mol of a substance (solvent) takes up.

The molar volume for water is: 1L / 55.4 mol = 0.018 L/mol

Note: the molar volume refers not to i, but to the solvent it is in. Many organics are not very soluble in water. You can therefore assume that the total mols are approximately equal to the number of moles of the solvent (water).

Example: benzene (b) in water (w):

x_b = mol b / mol (b+w) ≈ mol b/mol w

$\bar{v}_w$ has units of L/mol w

[b] = x_b / $\bar{v}_w$ = (mol b / mol w) / (L/mol w) = mol b / L

A special case of liquid-liquid partitioning I: Aqueous solubility $C_{i,w}^{sat}$

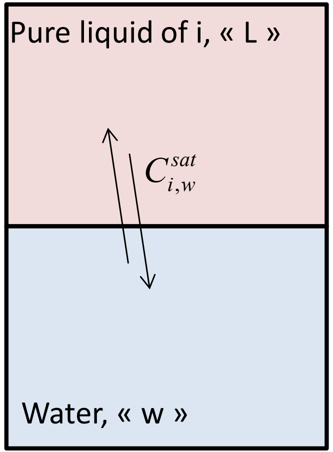
Consider a pure liquid phase of substance i (« L ») in equilibrium with pure water (« w ») (e.g., hexane in equilibrium with water):

$$K_{i,wL}^{'} = \frac{x_{i,w}}{x_{i,L}} = \frac{\gamma_{i,L}}{\gamma_{i,w}}$$

In L (the pure liquid of i), $x_{i,L} = 1$, and $\gamma_{i,L} = 1$. We can simplify: $K_{i,wL}^{'} = \frac{x_{i,w}}{1} = \frac{1}{\gamma_{i,w}}$

The aqueous solubility of i, $C_{i,w}^{sat}$, is the concentration of i in water equilibrated with the pure liquid phase of i:

$$\boxed{C_{i,w}^{sat} = \frac{mol\ of\ i}{L\ water} \approx \frac{x_{i,w}}{\bar{v}_w} = \frac{1}{\gamma_{i,w}\bar{v}_w} = \frac{1}{\gamma_{i,w} 0.018\ L/mol}}$$



So from the aqueous solubility we can determine $\gamma_{i,w}$ and vice versa.

Mechanistic perspective of solubility

A mechanistic perspective of the solubilisation process (various enthalpies involved) for an organic solute in water involves the following steps:

(a) breaking-up of solute-solute intermolecular interactions

(b) breaking-up of solvent-solvent intermolecular interactions to form cavity in solvent phase which is large enough to accommodate solute molecule

(c) formation of solute-solvent intermolecular interactions

(d) reformation of solvent-solvent interactions with solvent reconstruction

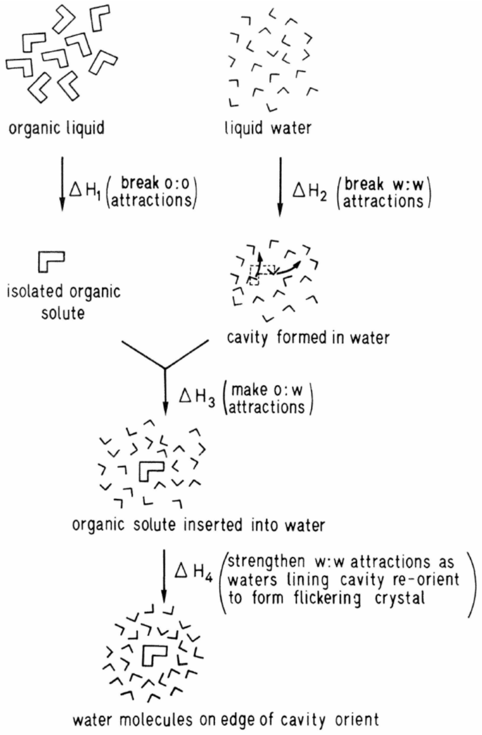
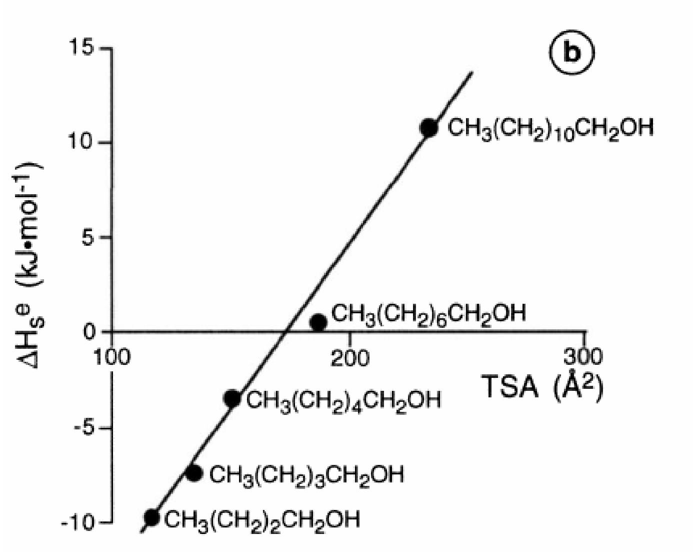


Figure 5.2 Schematic representation of the various enthalpies involved when dissolving a neutral organic molecule in water.

Solubility and cavity formation

Solubility of alcohols of different chain lengths

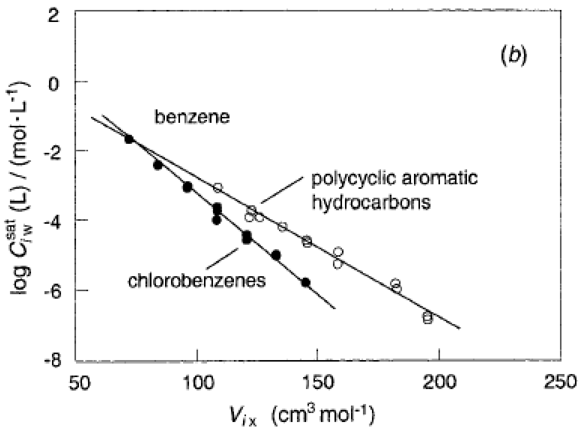


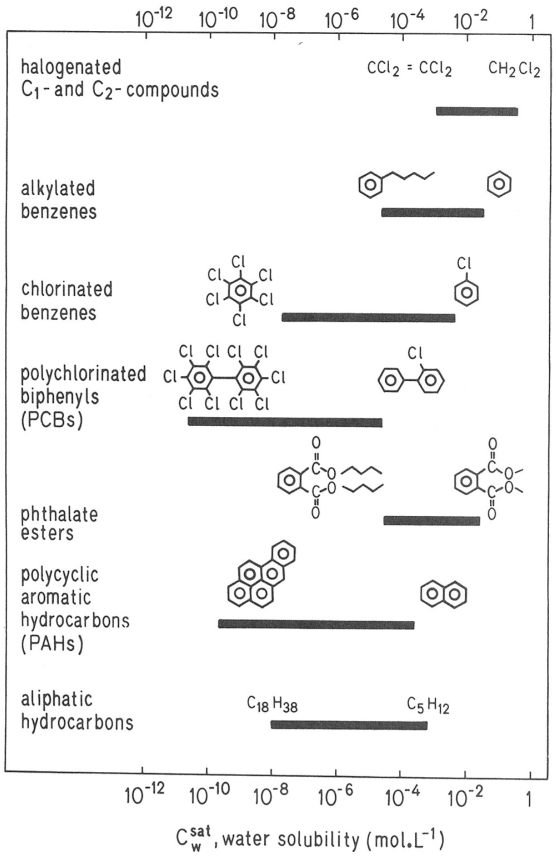
- dissolution is favoured due to alcohol groups in organic molecules (hydrogen donating group)
- however, cavity formation requires energy
- therefore, small alcohols generate heat of dissolution,
- whereas larger molecules consume heat during dissolution

Range of $C_{i,w}^{sat}$ for some organic compounds

C_w^{sat} increases with:

- Decreasing chain length
- Decreasing size
- Decreasing halogenation

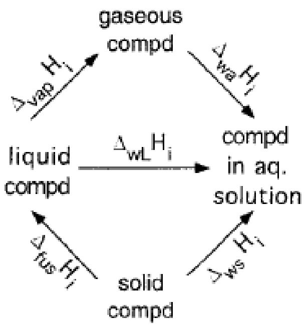


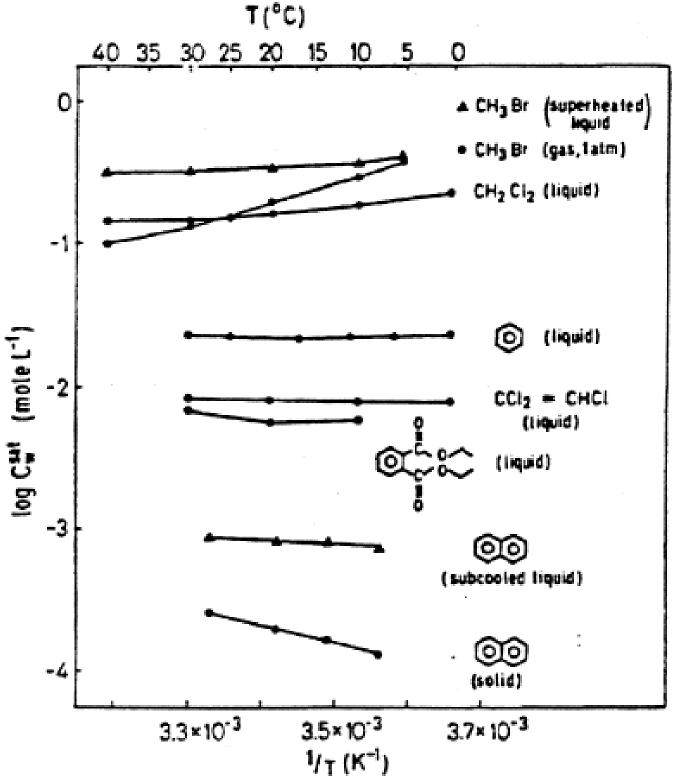


$C_{i,w}^{sat}$: influence of temperature

Recall for the T-dependence: $\ln\frac{K_{12}(T_2)}{K_{12}(T_1)} = \frac{\Delta_{12}H}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$

Here $\Delta_{12}H_i$ is $\Delta_{wL}H_i$. $\Delta_{wL}H_i$ is the energy (enthalpy) needed to get the i from its pure liqid L into water. $\Delta_{wL}H_i$ is often close to zero, so the T-dependence is small!



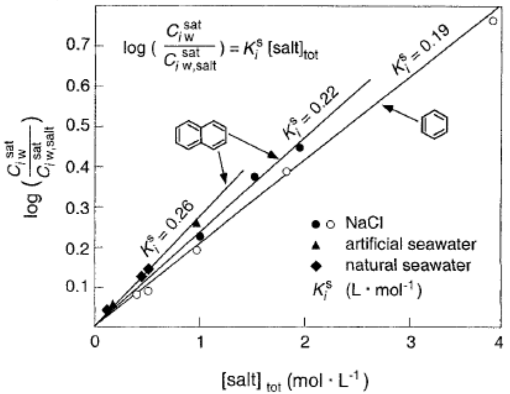


$C_{i,w}^{sat}$: influence of salinity

$C_{i,w}^{sat}$ decreases with increasing salt concentration (« salting out » effect):

$$\boxed{C_{i,w,salt}^{sat} = C_{i,w}^{sat} * 10^{-K_i^s[salt]}}$$

K^s= Setschenow constant, which changes for different salts. The adjacent table shows K_s for seawater or [NaCl] ≈ 0.5 M.



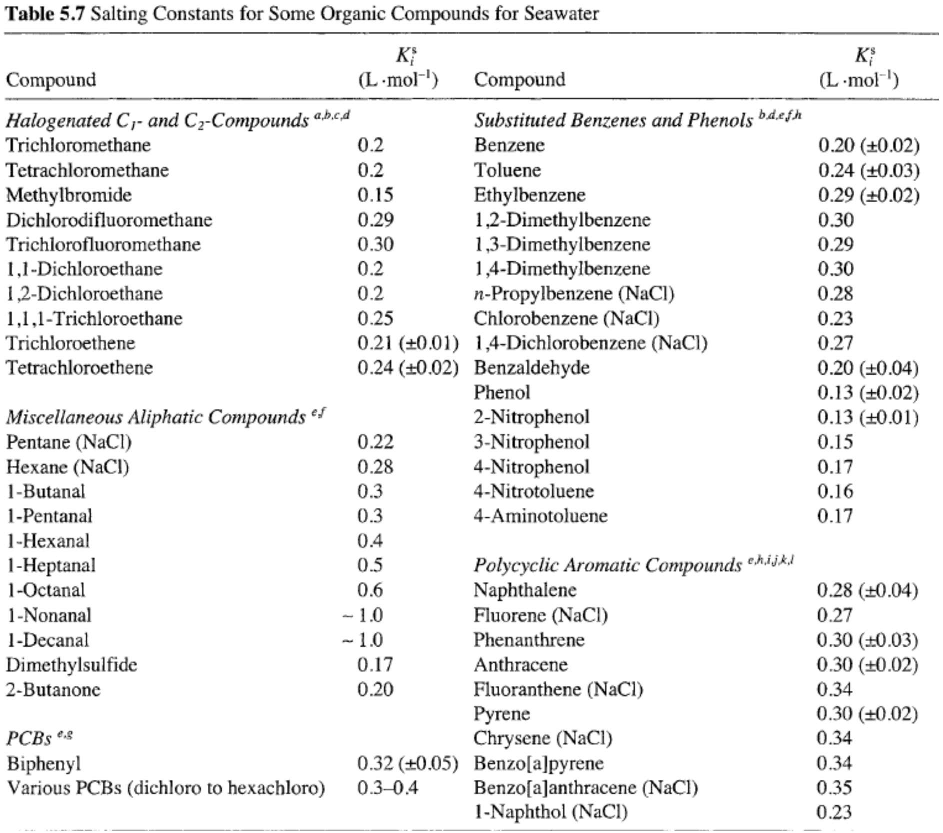


Table 5.7 Salting Constants for Some Organic Compounds for Seawater

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

Exercise 1: influence of salinity on $C_{i,w}^{sat}$

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 during wastewater treatment one then has to deal with a salt problem).

Calculate how much NaCl you have to add to 1 m^3 of water in order to decrease the solubility of hexane (or: increase its activity) by a factor of ten.

Exercise 2 – LNAPL / DNAPL

A gas station leeks 1.5 L benzene into the groundwater. In the aquifer, the benzene is present as a separate phase.

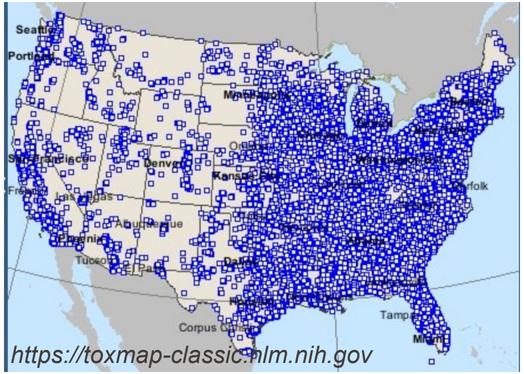
a) Is benzene a DNAPL or an LNAPL? *(**D**ense/**L**ight **N**on-**A**queous **P**hase **L**iquid)*

b) Assuming benzene is in equilibrium with the groundwater, how many liters of water will it take to fully dissolve the benzene?

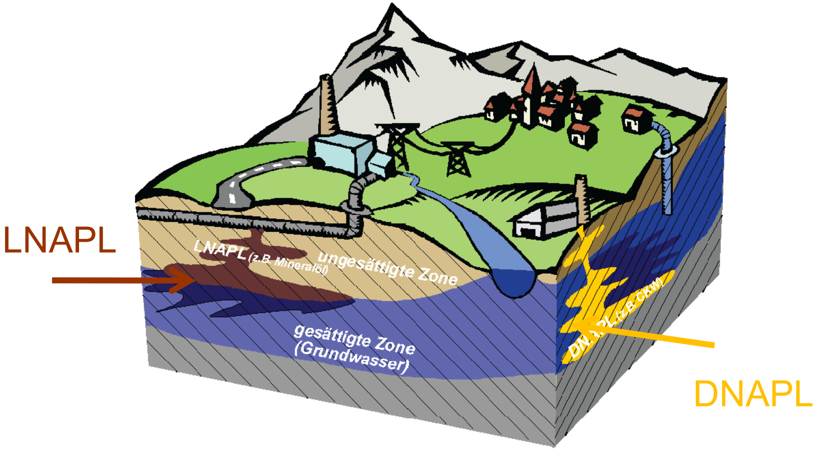
c) How many liters of drinking water can this spill contaminate?

Density of benzene: 0.87 kg/L
Solubility of benzene : 1.8 g/L
Maximum Contaminant Level of benzene : 0.005 mg/L

Toxic release Inventory 2016

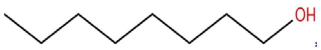


https://toxmap-classic.nlm.nih.gov



A special case of liquid-liquid partitioning II: Octanol-water partitioning constant K_{ow}

Octanol

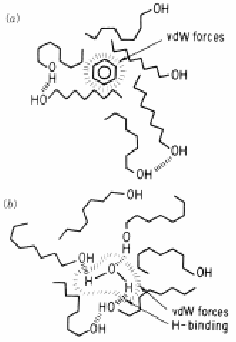


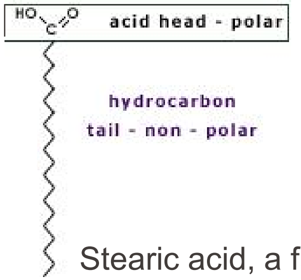
$$K_{i,ow} = \frac{C_{i,o}(mol/L_o)}{C_{i,w}(mol/L_w)}$$

Importance

- Large database of K_{ow} values
- Indicates the **hydrophobic** character of a compound
- Can be used to predict other partitioning constants (e.g, $C_{i,w}^{sat}$) and partitioning of a compound into nonpolar liquids (e.g., oil, gasoline) and nonpolar solids (e.g., natural organic material (NOM), biota (like fish, cells, etc.))

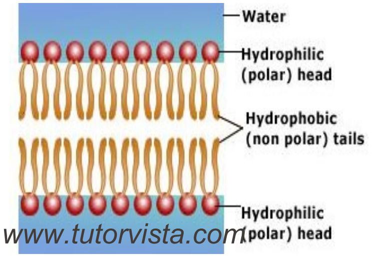
Why octanol? Octanol has both hydrophobic and hydrophilic character ("ampiphilic", similar to a lipid). Therefore a broad range of compounds will have measurable K_{ow} values.



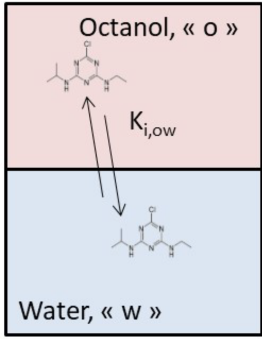


Stearic acid, a fatty acid

A phospholipid bilayer



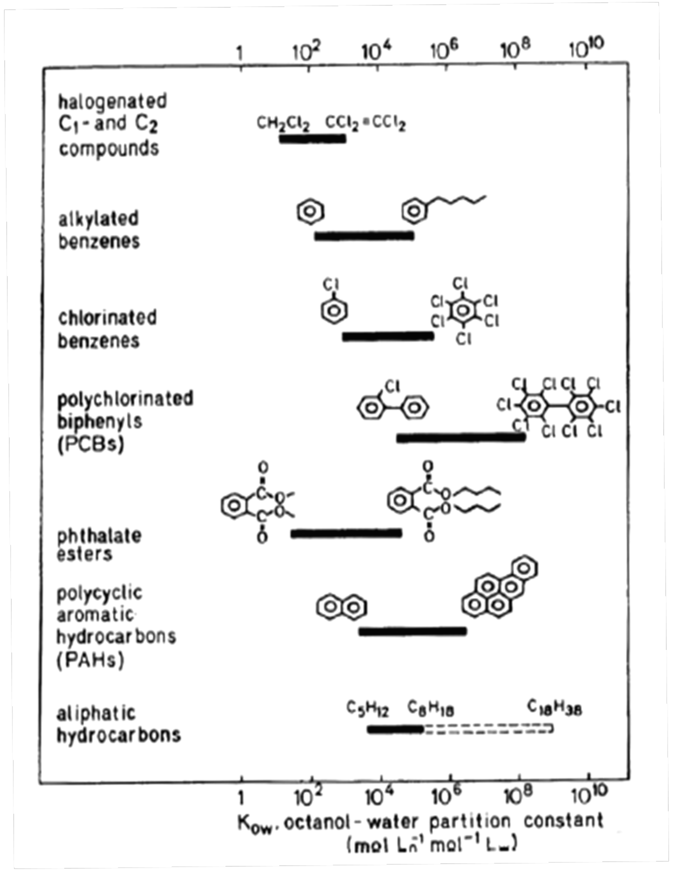
www.tutorvista.com



Range of K_{ow} for some organic compounds

K_{ow} increases with:

- Increasing chain length
- Linearity of the molecule
- Saturation of the molecule
- Increasing halogenation
- Decreasing aqueous solubility



Exercise 3: more complex DNAPLs

Recall the previous example of a benzene spill. Now assume that the benzene isn't pure, but that it contains 1 μM of each one of several organic contaminants given in the table below. Which compounds will be found at the highest concentration in the contaminated groundwater?

Compund	Log K_{ow}
Chloroform	1.97
Dioxine	6.8
DDT	6.19
Naphtalene	3.35
Trichloroethylene	2.42

Relation between K_{ow} and $C_{i,w}^{sat}$

Mix pure water and pure octanol, let come to equilibrium. At equilibrium:

- water contains 8 octanol for every 10^5 water ($\bar{v}_w$ of pure water ≈ $\bar{v}_w$ of octanol-saturated water)
- octanol contains 1 water for every 4 octanol ($\bar{v}_o$ of pure octanol = 0.16 L/mol. $\bar{v}_o$ of water-saturated octanol = 0.12 L/mol)

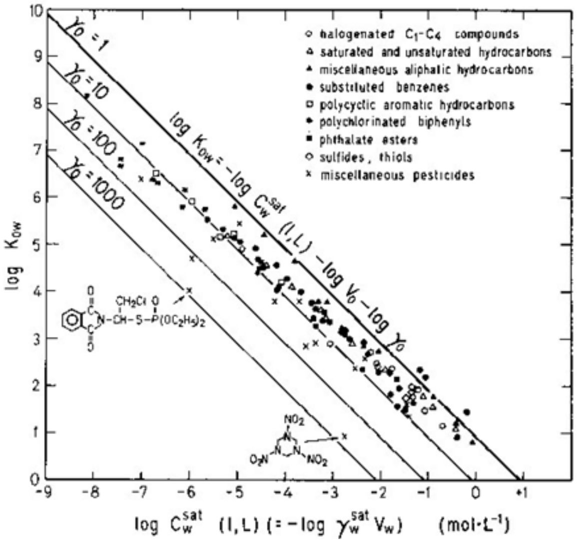
Now add an organic compound *i*. Earlier we derived the K_{12} for the partitioning of *i* in two liquids :

$K_{i,1,2} = \frac{\gamma_{i,2}}{\gamma_{i,1}} \frac{\bar{v}_2}{\bar{v}_1}$. We also learned that $C_{i,w}^{sat} = \frac{1}{\gamma_{i,w} \bar{v}_w}$. So we can write the K_{ow} for compound *i* as:

$$K_{i,ow} = \frac{C_{i,o}}{C_{i,w}} = \frac{\gamma_{i,w}}{\gamma_{i,o}} \frac{\bar{v}_w}{\bar{v}_o} = \frac{1}{C_{i,w}^{sat}} \frac{1}{\gamma_{i,o} \bar{v}_o}$$

Now plot log $K_{i,ow}$ vs. log $C_{i,w}^{sat}$ for several compounds:

$$\log K_{i,ow} = -\log C_{i,w}^{sat} - \log \bar{v}_o - \log \gamma_{i,o} \longrightarrow$$



A few things to note:

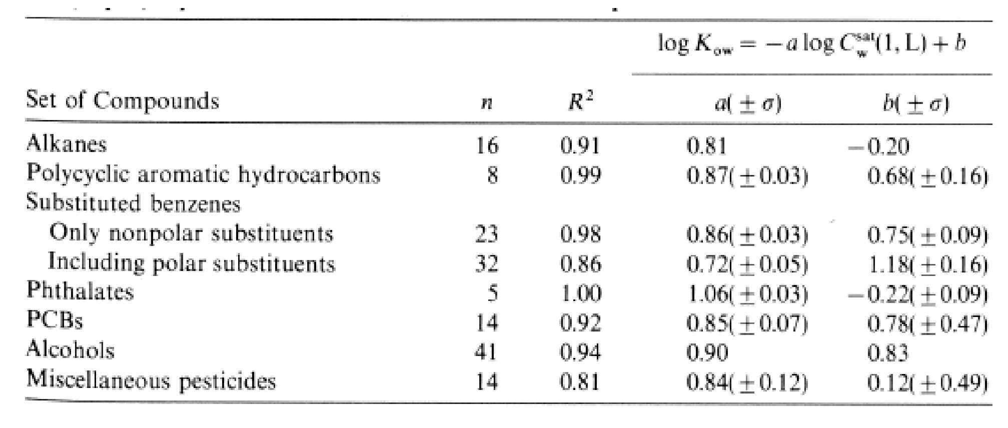
- $\bar{v}_o$ doesn't change much compared to equilibrium with water only
- $\gamma_{i,o}$ is often close to 1 (organics "like" octanol)
- K_{ow} is largely driven by aqueous solubility, except for polar, large compounds

Estimate K_{ow} from $C_{i,w}^{sat}$

K_{ow} can be estimated from the aqueous solubility using a relationship of the following form:

$\log K_{i,ow} = -a * \log C_{i,w}^{sat} + b$ where $C_{i,w}^{sat}$ is in mol/L

The parameters a and b depend on the class of compounds. The table below gives some examples.



			$\log K_{ow} = -a \log C_w^{sat}(1, L) + b$	
Set of Compounds	n	R^2	$a(\pm\sigma)$	$b(\pm\sigma)$
Alkanes	16	0.91	0.81	−0.20
Polycyclic aromatic hydrocarbons	8	0.99	0.87(±0.03)	0.68(±0.16)
Substituted benzenes				
Only nonpolar substituents	23	0.98	0.86(±0.03)	0.75(±0.09)
Including polar substituents	32	0.86	0.72(±0.05)	1.18(±0.16)
Phthalates	5	1.00	1.06(±0.03)	−0.22(±0.09)
PCBs	14	0.92	0.85(±0.07)	0.78(±0.47)
Alcohols	41	0.94	0.90	0.83
Miscellaneous pesticides	14	0.81	0.84(±0.12)	0.12(±0.49)

More generally (and for compounds not in the table above), K_{ow} can also be approximated by empirical equations, such as the one below:

$\log K_{i,ow} = (-\log C_{i,w}^{sat} + 3.70 + \log MW_i)/1.08$

Where MW is the molar weight of the compound of interest, and C_w^{sat} is in units of ppm.

K_{ow}: influence of T and salinity

Because K_{ow} is primarily determined by aqueous solubility, corrections of K_{ow} for T, salt, are made by adjusting C_w^{sat} :

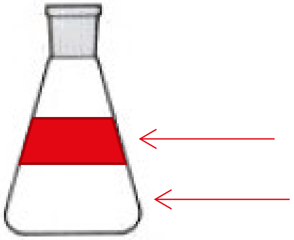
Temperature effects on C_w^{sat} are small, therefore they are also small for K_{ow}.

Salt only affects aqueous phase. So the salt effect of K_{ow} can be expressed based on the effect on C_w^{sat} :

$$K_{i,ow} = \frac{1}{C_{i,w}^{sat}} \frac{1}{\gamma_{i,o} \bar{v}_o} \qquad \log\left[\frac{C_w^{sat}}{C_{w,salt}^{sat}}\right] = K^s[\text{salt}] = \log\left[\frac{K_{ow,salt}}{K_{ow}}\right]$$

Methods of measuring K_{ow}

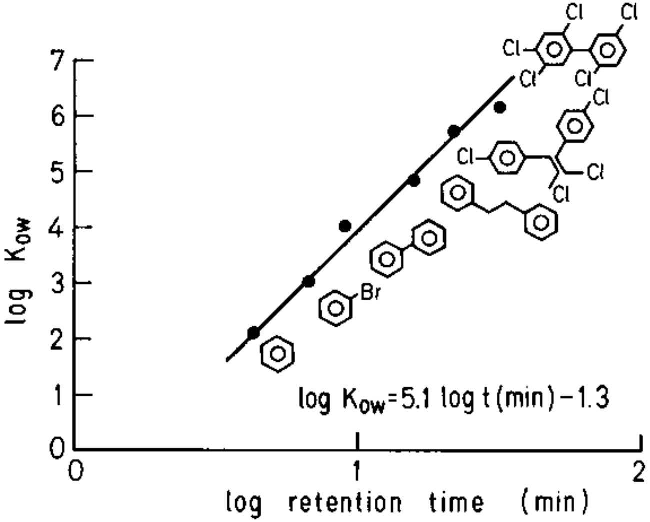
Shake flask method (compounds with log K_{ow} < 5)
Solute is equilibrated between the two phases by shaking:



octanol

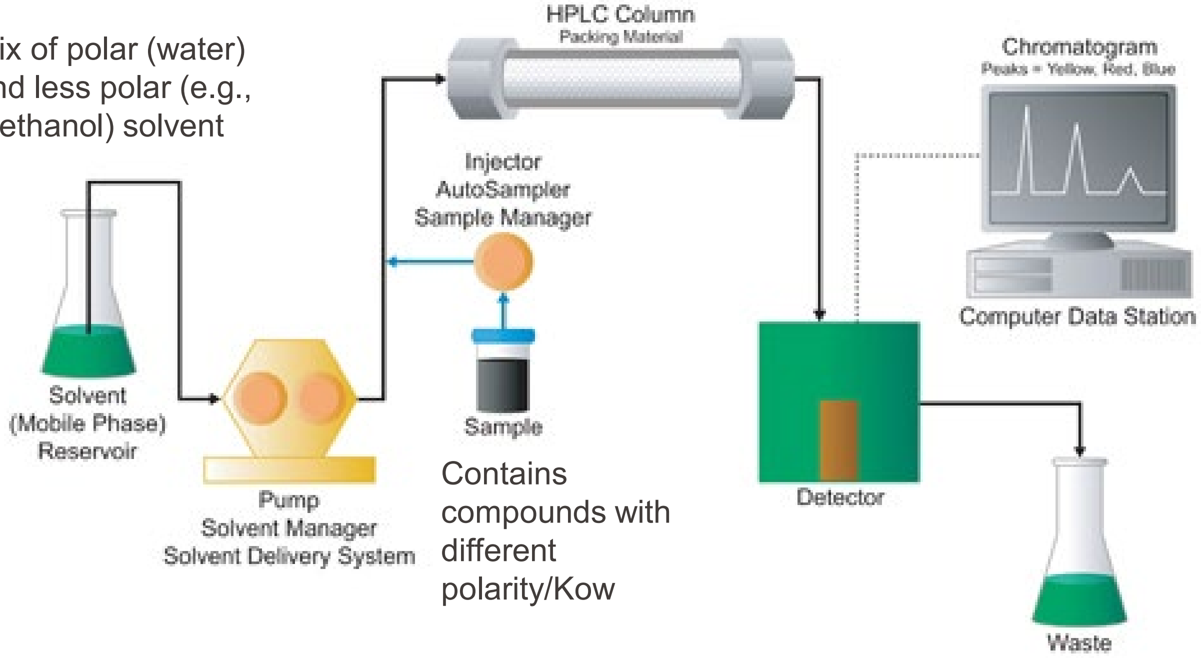
water

Chromatographic data
Relate K_{ow} of known compounds to retention time on a reverse-phase HPLC column.
Measure the retention time for known compounds, develop relationship between K_{ow} and t.



HPLC

High performance liquid chromatography



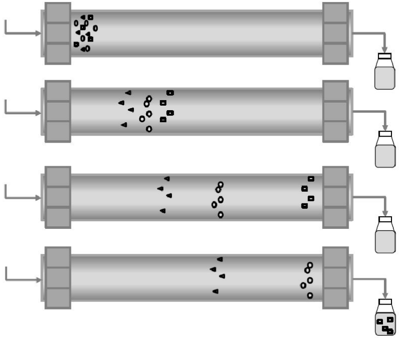
Filled with apolar matrix

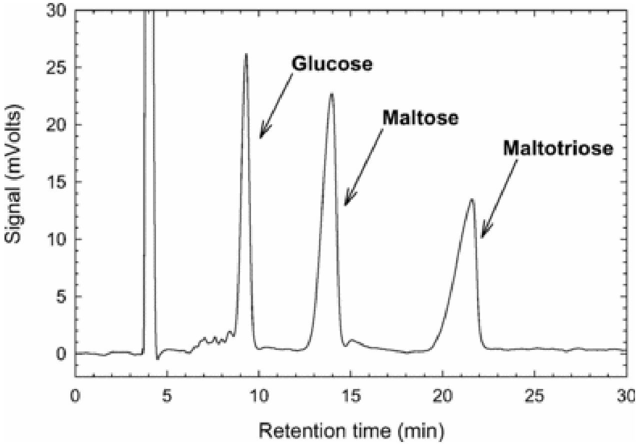
Mix of polar (water) and less polar (e.g., methanol) solvent

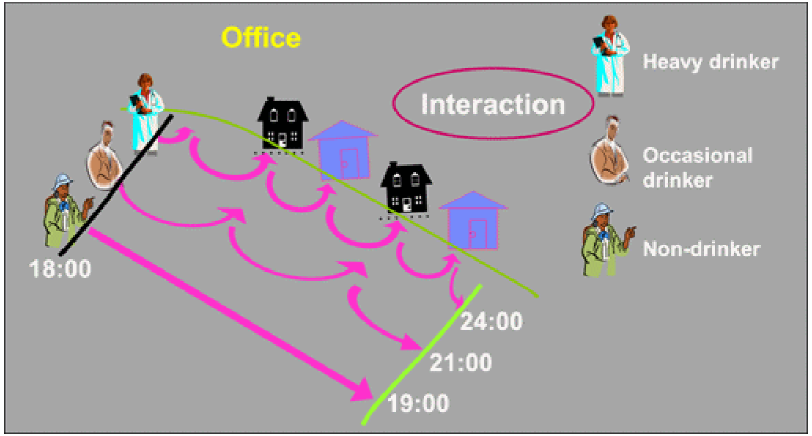
Contains compounds with different polarity/Kow

http://www.pharmacelsus.de/hplc/

HPLC







www.shodex.net

Bar: apolar matrix

Heavy drinker: high K_{ow}

Occasional drinker: medium K_{ow}

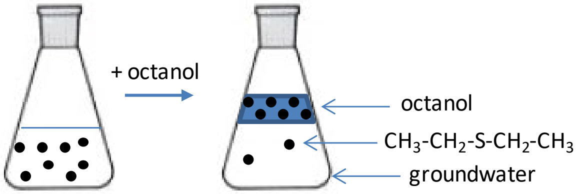
Non-drinker: low K_{ow}

Exercise 4: removal of organics from water

In anaerobic groundwater, CH_3-CH_2-Br can degrade to CH_3-CH_2-S-CH_2-CH_3. Because this product is toxic, you would like to remove as much of it as possible from the groundwater below, and contain it. Your plan is to do a liquid-liquid extraction. This means that you want to add a small amount of octanol to the groundwater, mix it, and then separate the octanol phase from the water. Because CH_3-CH_2-S-CH_2-CH_3 prefers to be in octanol rather than water, most CH_3-CH_2-S-CH_2-CH_3 will be in the octanol phase, which you can then remove and safely discard (see Figure below).

Unfortunately, no one has ever measured the K_{ow} of CH_3-CH_2-S-CH_2-CH_3. However, you do know the following things:

- The partitioning of CH_3-CH_2-S-CH_2-CH_3 between octanol and water is quite similarly to that of alkanes
- The activity coefficient ($\gamma_{CH3\text{-}CH2\text{-}S\text{-}CH2\text{-}CH3}$) in water is 25’000



a) How much octanol do you have to add per L of groundwater to achieve a 90% reduction in the concentration of CH_3-CH_2-S-CH_2-CH_3?

b) A colleague suggests that you could increase the temperature to improve the transfer of CH_3-CH_2-S-CH_2-CH_3 into octanol. Is your colleague correct? Explain your answer.

System 2: Air-liquid partitioning

Generally, the gas-liquid partition constant is:

$$\boxed{K_{i,al} = \frac{C_{i,a}(mol/L\ gas)}{C_{i,l}(mol/L\ liquid)}}$$

Assuming ideal gas behavior (nRT=pV), we can re-write $C_{i,a}$ as $C_{i,a} = \frac{p_{i,a}}{RT}$

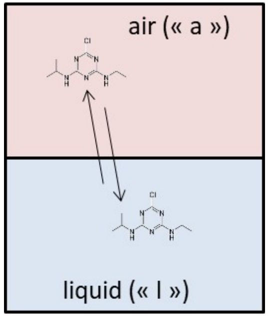
Where $p_{i,a}$ is the partial pressure of i dissolved in a solvent l (so not the pure liquid of i!).

For gases, it is often more practical to work with pressure than concentration.
We therefore define Henry's Law constant as:

$$\boxed{K_{i,H,l} = \frac{p_{i,a}}{C_{i,l}} = K_{i,al}RT}$$

or on a mole fraction basis: $K'_{i,H,l} = \frac{p_{i,a}}{x_{i,l}} = \frac{K_{i,H,l}}{\bar{v}_l}$

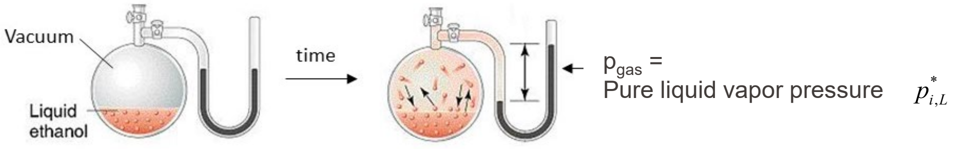
$K_{i,H,l}$ has units of bar/(M) or atm/(M) or Pa*m^3*mol. $K_{i,al}$ is unitless.



A special case of air-liquid partitioning I: pure liquid vapor pressure $p^*_{i,L}$

Recall that in a pure liquid of i (L), the mole fraction $x_{i,L}=1$. Therefore: $K'_{i,H,l} = \frac{p_{i,a}}{x_{i,L}} = p^*_{i,L}$

Where $p^*_{i,L}$ is the pure liquid vapor pressure of compound i. So the pure liquid vapor pressure of i corresponds to the partial pressure of i if air is in equilibrium with the pure liquid of i. (Analogously, $p^*_{i,s}$ is the pure solid vapor pressure.)

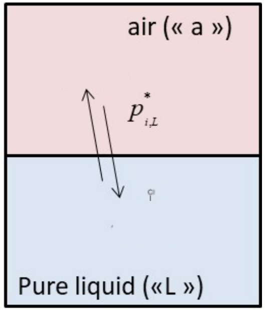


Measurement of vapor pressure of a liquid. After time t, evaporation = condensation, and the system is in equilibrium.
Source: www.csun.edu/~ml727939/coursework/695/vapor%20pressure/Vapor%20Pressure.htm

$p^*_{i,L}$ is widely tabulated for organic compounds, so it is often practical to draw upon relationships with respect to this property.

$p^*_{i,L}$ can also be estimated using various mostly empirical approaches, such as the modified Kistiakowsky- Fishtine expression (K_F is often 1 for non-polar compounds, and T_b is the boiling point):

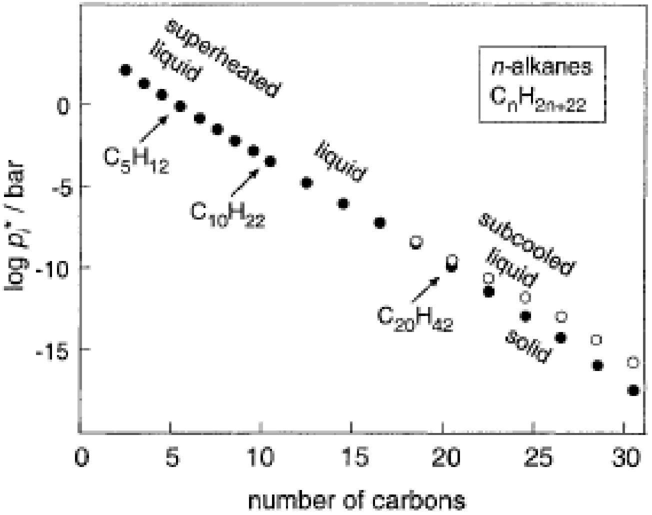
$$\ln\ p^*_{i,L}(bar) = -K_F(4.4+\ln T_b)\left[1.8\left(\frac{T_b}{T}-1\right)-0.8\ln\frac{T_b}{T}\right]$$

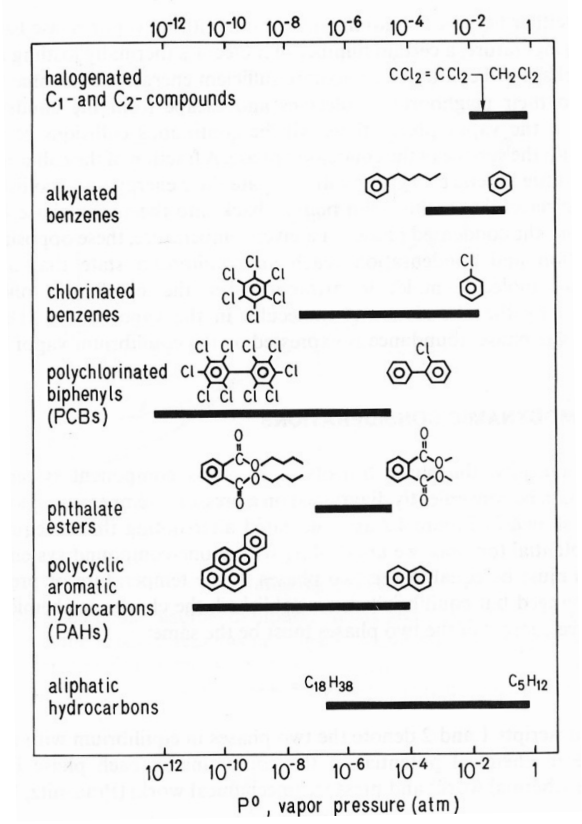


Range of $p^*_{i,L}$ for some organic compounds

$p^*_{i,L}$ increases with:

- Decreasing chain length
- Decreasing size
- Decreasing halogenation





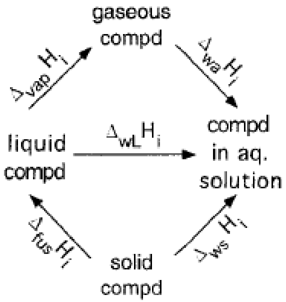
From: Schwarzenbach, Gschwend, Imboden, 2003

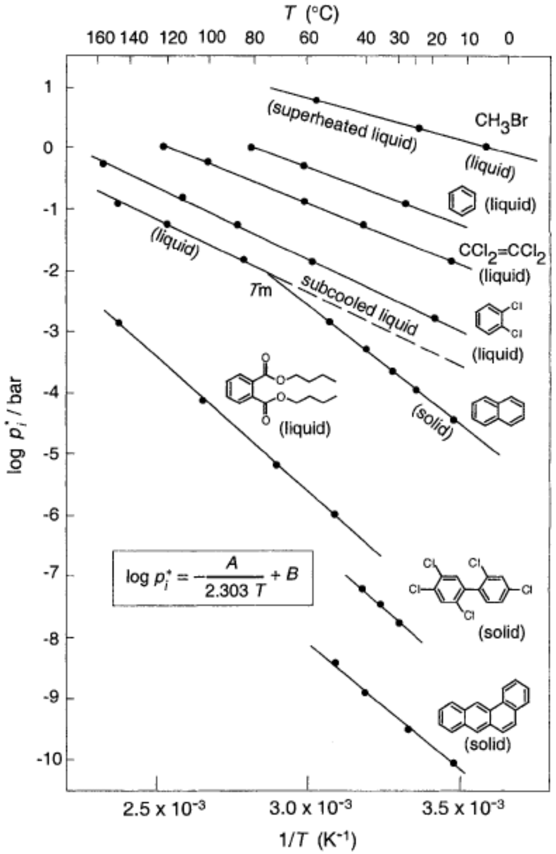
$p^*_{i,L}$: influence of temperature

Recall for the T-dependence: $$\ln \frac{K_{12}(T_2)}{K_{12}(T_1)} = \frac{\Delta_{12}H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Here $\Delta_{12}H_i$ for liquids is $\Delta_{vap}H_i$. $\Delta_{vap}H_i$ is the energy required to convert one mole of pure liquid to gas without an increase in T. (For solids, we first need to melt the solid to a liquid, so $\Delta_{12}H_i = \Delta_{fus}H_i + \Delta_{vap}H_i$.)

$\Delta_{vap}H$ is a function of T. As T approaches the boiling point, $\Delta_{vap}H$ increases rapidly. At T < boiling point, $\Delta_{vap}H$ increases slowly. from 0-40 ◦C, $\Delta_{vap}H$ can be assumed to be constant.





From: Schwarzenbach, Gschwend, Imboden, 2003

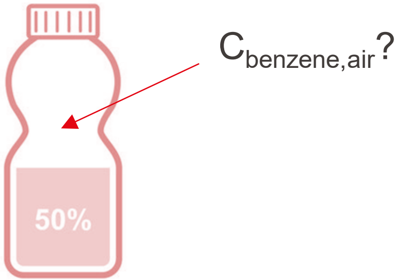
Note that salinity does not affect $p^*_{i,L}$

Exercise 5: $p^*_{i,L}$

Benzene if often used as a cleaning fluid. However, it is quite toxic, so you must be careful not to inhale the benzene vapor.

Assume you have a 1L bottle of benzene in your home, which you store at 25 °C. The bottle contains 0.5 L of liquid benzene. What is the benzene concentration (in M) in the air in the empty half of the bottle?

The $p^*_{i,L}$ of benzene is $10^{4.1}$ Pa.



A special case of air-liquid partitioning II: Air-water

In environmental chemistry, “the” Henry’s law constant usually refers to water as the liquid. If water is the solvent, we omit the subscript w (or l) and just write $K_{i,H}$.

$$K_{i,H} = \frac{p_{i,a}}{C_{i,w}} = K_{i,aw}RT \qquad \text{or} \qquad K'_{i,H} = \frac{p_{i,a}}{x_{i,w}} = \frac{K_{i,H,w}}{\bar{v}_w}$$

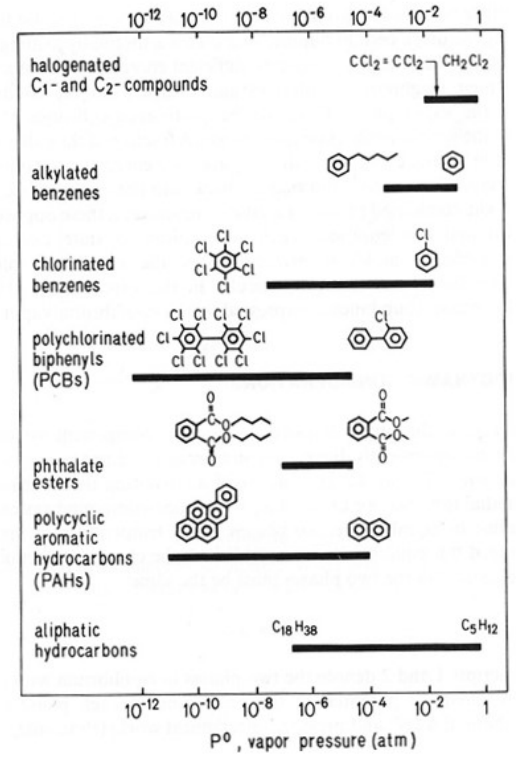
Thermodynamic properties like K_{12} are independent of the reaction pathway and only depend on the starting and end conditions. We can therefore relate the partitioning of a compound between air and liquids to other equilibrium processes. E.g., we can derive “the” Henry’s law constant from the partitioning of i between air-pure phase L and water – pure phase L:

$$K'_{i,H} = \frac{K'_{i,H,L}}{K'_{i,wL}} = \frac{p_{i,a}/x_{iL}}{x_{i,w}/x_{iL}} = \frac{p^*_{i,L}}{x_{iw}}$$

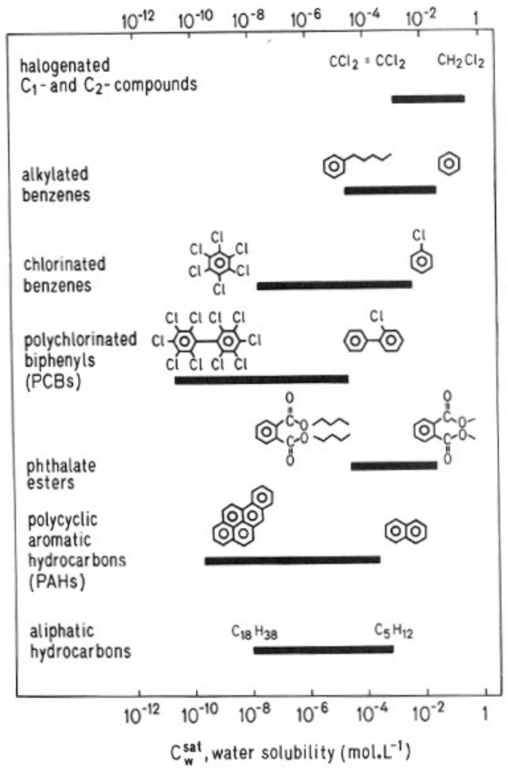
Furthermore, recalling that $\frac{\bar{v}_w}{x_{i,w}} \approx \frac{1}{C^{sat}_{i,w}}$ we can estimate $K_{i,H}$: $\boxed{K_{i,H} = K'_{i,H}\bar{v}_w \approx \frac{p^*_{i,L}}{C^{sat}_{i,w}}}$

So $K_{i,H}$ can be estimated from the(tabulated) vapor pressure and aqueous solubility of i.

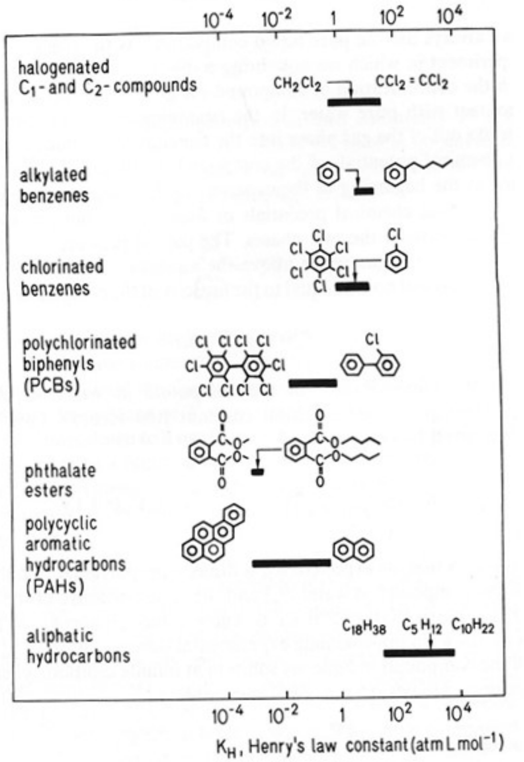
Range of K_H for some organic compounds



Vapor pressure ranges over 10^{12}



Solubility ranges over 10^{12}



K_H ranges over 10^7

Useful website for additional K_H values (attention to units!): *https://henrys-law.org/henry/index.html*

K_H: influence of temperature

The T-dependence of vapor pressure is often much greater than that of solubility, so the T-dependence of $K_{i,H}$ will often mainly be governed by that of the vapor pressure.

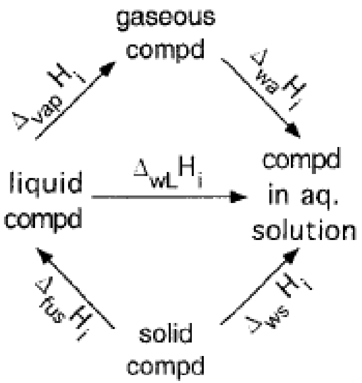
Recall for the T-dependence:

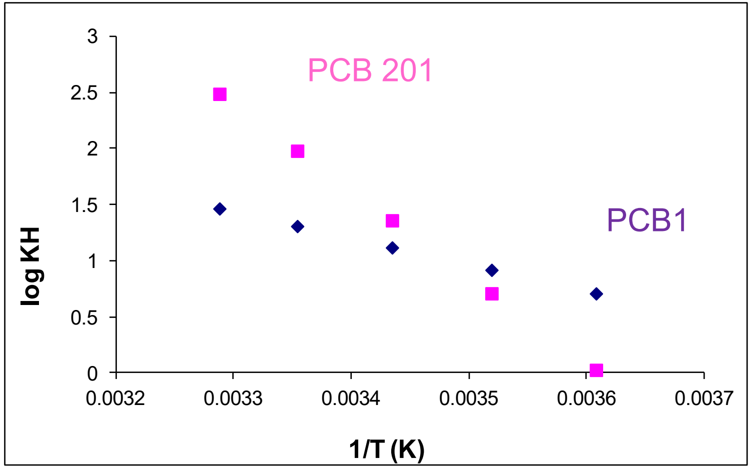
$$\ln\frac{K_{12}(T_2)}{K_{12}(T_1)} = \frac{\Delta_{12}H}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

Here $\Delta_{12}H_i$ is $-\Delta_{wa}H_i$. $-\Delta_{wa}H_i$ (or $\Delta_{Henry}H_i$) is the energy required to move one mole of i dissolved in water to air:

$$-\Delta_{wa}H_i = \Delta_{vap}H_i - \Delta_{wL}H_i$$

Often near zero!





Source: L. Rodenburg

Exercise 6: temperature-dependence of K_H

Evaulating the direction of air-water gas exchange at different temperatures

What is the direction (into water? Out of water?) of the air-water exchange of benzene for a well-mixed, shallow pond located in the center of a big city in each of the following seasons:

a) Typcial summer situation (T=25 ° C)

b) Typcial winter situation (T=5 ° C)

In both cases the concentrations detected in air and water are:

$C_{i,a}$= 0.05 mg/m^3

$C_{i,w}$= 0.4 mg/m^3

Assume that the temperature of water and air are the same.

$K_{i,\ aw}$ (25°C) = 0.22

$\Delta_{12}H$ = 30 kJ/mol

K_H: influence of salinity

Earlier we found: $K_{i,H} = K'_{i,H}\bar{v}_w \approx \frac{p^*_{i,L}}{C^{sat}_{i,w}}$

Since salt does not affect the pure liquid vapor pressure, the dependence of K_H is governed by the salinity effect on the aqueous solubility.

Recall: $C^{sat}_{i,w,salt} = C^{sat}_{i,w} * 10^{-K^s_i[salt]}$

Since $K_H \sim \frac{1}{C^{sat}_{i,w}}$

$$\boxed{K_{i,H,salt} = K_{i,H} * 10^{+K^s_i[salt]}}$$

So the salinity increases K_H by decreasing the solubility of i in water.

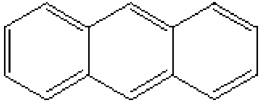
Exercise 7: Salinity-dependence of K_H

Calculate $K_{H,\ seawater}$ (in atm/M) for anthracene at 25 ° C.

Log $p^*_{i,L}$ = -3.01 (Pa)

Log $C^{sat}_{i,w}$ = -6.6 (M)

Salinity of seawater: 0.6 M

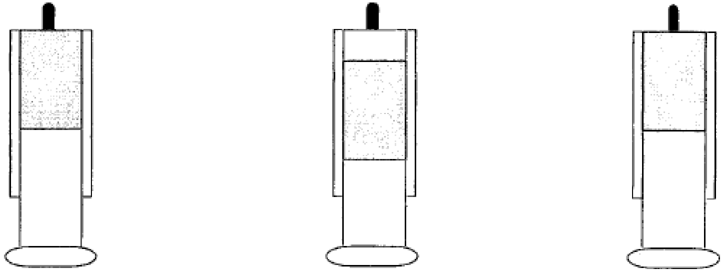


Anthracene

Methods of measuring K_H

Multiple equilibration method

Solute is equilibrated between the air and water in an air-tight syringe. The concentration in the water is analyzed several times after adding different volumes of air.



1. Fill with saturated CF_3I solution; analyze
2. Add 2 mL air to 17 mL water; equilibrate
3. Dispel air and reanalyze
4. Repeat steps 2 and 3 as required.

$$fraction\ of\ CF_3I\ in\ the\ water = \frac{1}{1+\frac{V_a K_H}{V_w RT}}$$

K_H is difficult to measure if the solubility or the vapor pressure or both are low!

Exercise 8: benzene in olive oil

You live in a town where air pollution caused by traffic is quite high. From a recent newspaper article you have learned that the partial pressure of benzene in the air of your town may reach up to 10 ppb on a volume basis. You wonder to what extent the olive oil that you use for your salad, and that you have left in an open bottle on the table on your balcony, is contaminated with this rather toxic compound.

Calculate the maximum concentration of benzene in olive oil, given the following parameters:

T = 25°C

Total pressure = 1 bar

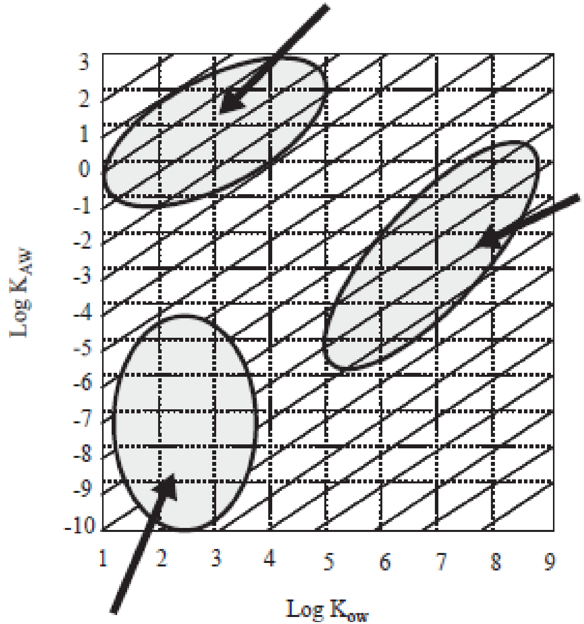
Log K_{ow} (benzene) = 2.17

Log K_{aw} (benzene) = -0.65

Log $K_{a,\text{olive oil}}$ = 1.08 *log K_{ao} +0.22

Relationship between K_{ow} and K_{aw}

The K_{ow} and K_{aw} indicate which compartment an organic will adhere to.



Likely to evaporate

Likely to adsorb to
particles, sediment

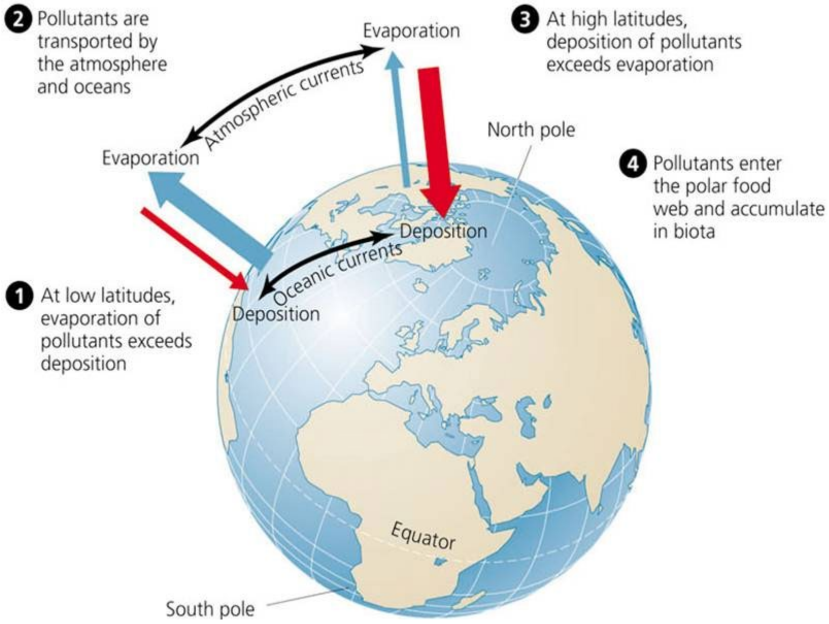
Likely to be dissolved
in water column

Modified from: Van de Meent et al., 1999

Long-range transport of POPs

POPs: persistent organic pollutants:

- Resistant to environmental degradation processes
- Typically low aqueous solubility (mid-range to high K_{ow}) and are semi-volatile (mid-range K_{aw})
- Prone to long-range transport
- Regulated in the Stockholm Convention

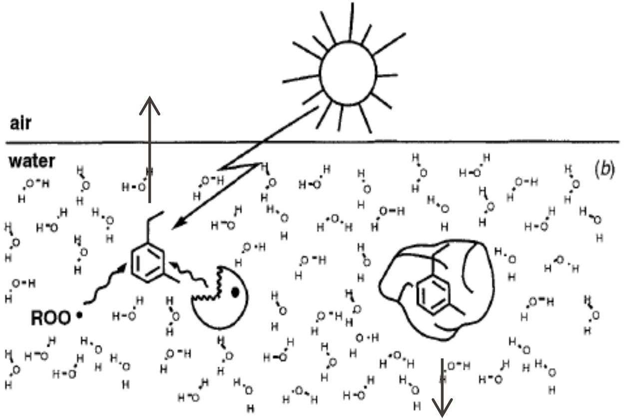


http://web.bryant.edu/~dlm1/sc372/readings/toxicology/toxicology.htm

System 3: Water-solid partitioning (sorption)

Soluble organics can « sorb » onto a solid in different ways:

1) Physical **ad**sorption due to van der Waals or electrostatic interactions
2) Chemisorption due to chemical bonds forming between the organic and the solid (**ad**sorption)
3) Partitioning into the solid (**ab**sorption)

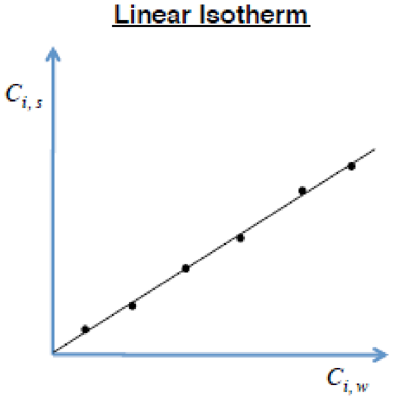


Dissolved species are more accessible to light, to other dissolved chemicals and to microorganisms than sorbed ones. Dissovled species can volatilize, sorbed ones can settle.

Equilibrium sorption isotherms

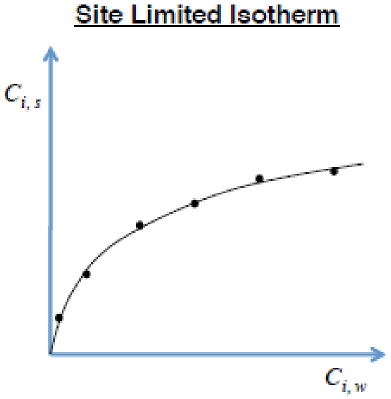
Sorption is described by **sorption isotherms.** Sorption isotherms represent the equilibrium distirubtion (i.e., rate of sorption = rate of desorption) of the dissolved and the adsorbed compound at a range of different concentrations.

$C_{i,w}$: concentration in water (mol i/L water or mass i/L water)
$C_{i,s}$: concentration in or on sorbent (mol i/mass sorbent or mass i/mass sorbent)


Linear Isotherm

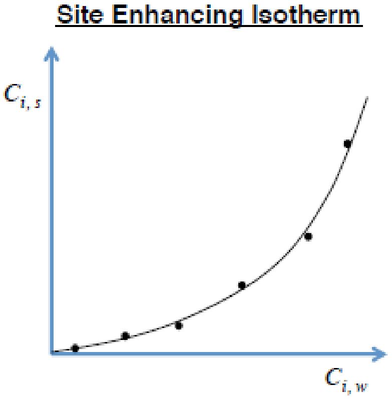
Typically describes **absorption**.

Sorbent is equally favorable throughout the solute concentration range.


Site Limited Isotherm

Typically describes **adsorption**.

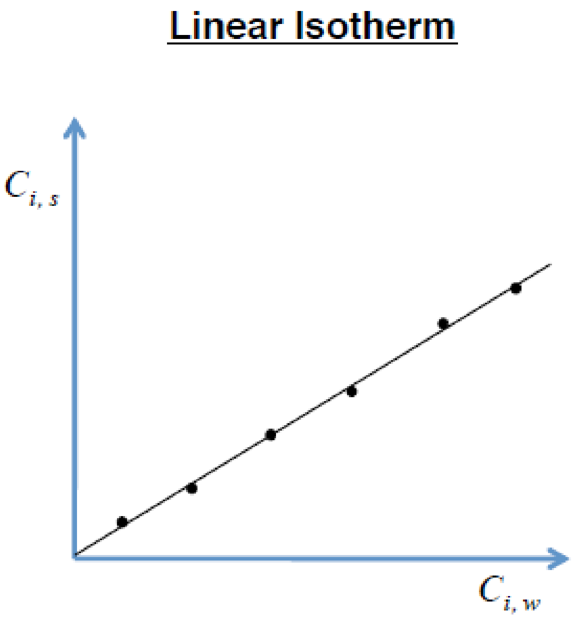
Sorbent is decreasingly favorable as solute concentration is increased.


Site Enhancing Isotherm

Typically describes **adsorption**.

Sorbent is increasingly favorable as solute concentration is increased.

Linear sorption isotherm



The sorbent has an equally favorable affinity throughout the solute concentration range.

Sorption model.

$$K_{i,sw} = \frac{C_{i,s}}{C_{i,w}}$$

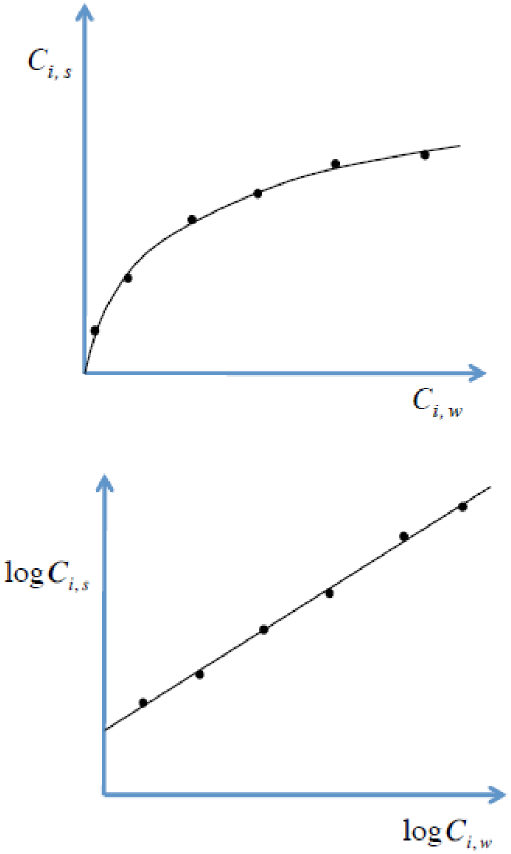
$K_{i,sw}$ is independent of concentration.

This is consistent with partitioning of a dilute solute into a (3-dimensional) bulk sorbent or liquid.

Examples: neutral organic contaminant absorption into soil organic matter, biotic lipid, or diesel fuel.

Freundlich sorption isotherm

Freundlich Isotherm



Sorbent is decreasingly favorable as solute concentration is increased.

Sorption model.

$$K_{i,F} = \frac{C_{i,s}}{C_{i,w}^{n}}$$

$$C_{i,s} = K_{i,F} C_{i,w}^{n}$$

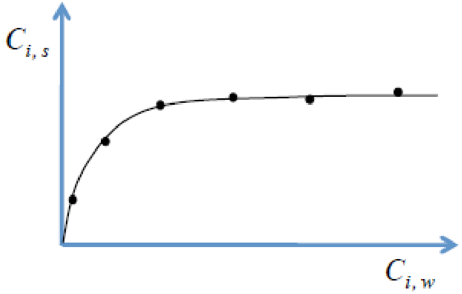
$$\log C_{i,s} = \log K_{i,F} + n \log C_{i,w}$$

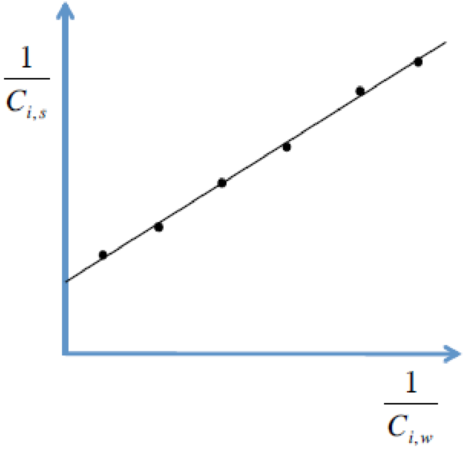
This is consistent with partitioning of a solute onto a (2-dimensional) surface.

Example: neutral organic compound adsorption onto activated carbon.
The units of K_F depend on n: $K_F = C_{i,s}/(C_{i,w}{}^{n})$.
E.g. , if $C_{i,s}$ is in [mol/g] and $C_{i,w}$ in [mol/L], then K_F is in: [mol/g]/([mol/L]^n) = [mol^{1-n} g^{-1} L^n]

Langmuir sorption isotherm

Langmuir isotherm





Sorbent is decreasingly favorable as solute concentration is increased. Additionally, the total number of possible sorption sites is finite ($\Gamma_{\max}$).

Sorption model.

$$C_{i,s} = \frac{\Gamma_{\max} K_{i,L} C_{i,w}}{1 + K_{i,L} C_{i,w}}$$

$$\frac{1}{C_{i,s}} = \left(\frac{1}{\Gamma_{\max} K_{i,L}}\right) \frac{1}{C_{i,w}} + \frac{1}{\Gamma_{\max}}$$

This is consistent with partitioning of a solute onto (2-dimensional) surface. $\Gamma_{\max}$ is often called the “sorption capacity”, and it corresponds to the maximum possible value of $C_{i,s}$. The parameter $K_{i,L}$ is an sometimes called an intrinsic binding constant.

Examples: ion exchange, surface complexation.

The units of K_L are [L/mol] or [L/g] and the units of $\Gamma_{\max}$ are [mol/g] or [g/g]

Derivation of the Lamgmuir sorption isotherm

$C_{i,w}$ = concentration of i in water

S = concentration of vacant sites

$C_{i,s}$ = concentration of filled sorption sites (= concentration of i on solid)

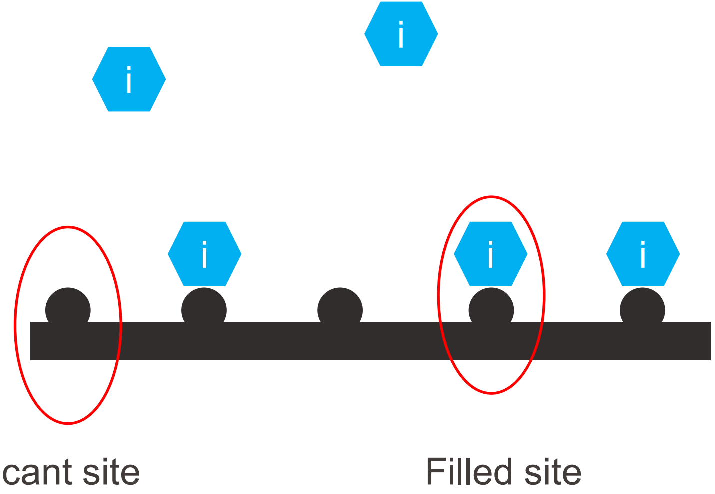
$\Gamma_{\max}$= total number of sites on solid = S + $C_{i,s}$

Vacant sites are in equilibirum with filled sites:

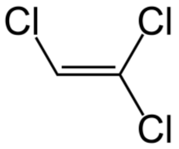
$$S + C_{i,w} \leftrightarrow C_{i,s}$$

$$K_{i,L} = \frac{C_{i,s}}{S \cdot C_{i,w}} = \frac{C_{i,s}}{(\Gamma_{max} - C_{i,s})C_{i,w}}$$

$$C_{is} = \frac{\Gamma_{\max} K_{i,L} C_{i,w}}{1 + K_{i,L} C_{i,w}}$$



Exercise 9: sorption isotherm for TCE

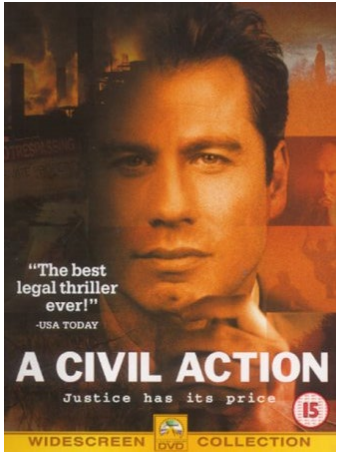


Trichloroethylene (TCE) is a frequent groundwater contaminant. If drinking water is produced from contaminated groundwater, TCE has to be removed. One way to do this is to adsorb it onto activated carbon.

Determine a good isotherm for TCE adsorption to activated carbon.

The following experimental data was found:

$C_{i,wd}$ (µg/L)	$Ci_{,s}$ (µg/g)
23.6	737
6.67	450
3.26	318
0.322	121
0.169	85.2
0.114	75.8



Exercise 10: activated carbon treatment

A town decides to open its groundwater reserves as a new drinking water source. The groundwater is anaerobic and contains 0.1 mM hydrogen sulfide (H_2S) produced through microbial activity. In order to use this groundwater for drinking water, you want to achieve a H_2S concentration of 0.05 mM or lower.

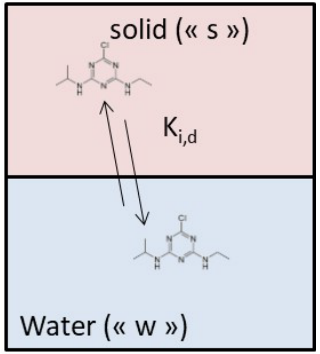
You decide to lower the H_2S concentration by adsorbing it to activated carbon. The sorption isotherm can be described by a Freundlich model with the following parameters:

$K_F = 2.1\ [\text{mmol/g}]/([\text{mmol/L}]^{0.4})$; $n = 0.4$

If you add 0.1 g of activated carbon per L of water, will you reach your goal of at most 0.05 mM H_2S remaining in the water?

The solid-water distribution coefficient K_d

$K_{i,d}$ describes the partitioning between solid and water:



$$\boxed{K_{i,d} = \frac{C_{i,s}}{C_{i,w}}}$$

units: $$\frac{mass\ i \,/\, mass\ sorbent}{mass\ i \,/\, L\ water} = \frac{L\ water}{mass\ sorbent}$$

How does this relate to the different sorption isotherms?

Linear model: $$C_{i,s} = K_{i,sw} C_{i,w} \longrightarrow K_{i,d} = K_{i,sw} = \frac{C_{i,s}}{C_{i,w}}$$

Freundlich model: $$C_{i,s} = K_{i,F} C_{i,w}^{n} \longrightarrow K_{i,d} = K_{i,F} C_{i,w}^{n-1}$$

Langmuir model: $$C_{i,s} = \frac{K_{i,L}\Gamma_{\max} C_{i,w}}{1 + K_{i,L} C_{i,w}} \longrightarrow K_{i,d} = K_{i,L}\Gamma_{\max}$$ (assuming $K_{i,L} *C_{i,w} << 1$)

What is the partitioning coefficient $K_{i,d}$ for the adsorption of TCE onto activated carbon?

Taking the Freundlich model from before: $K_{i,d} = 191.9*C_{i,w}^{-0.5673}$

So for $C_{i,w}$ = 6.67 μg/L → $K_{i,d}$ = 65.4 → $C_{i,s} = K_{i,d}*C_{i,w}$ = 436.2 μg/g

(measured value was 450 μg/g)

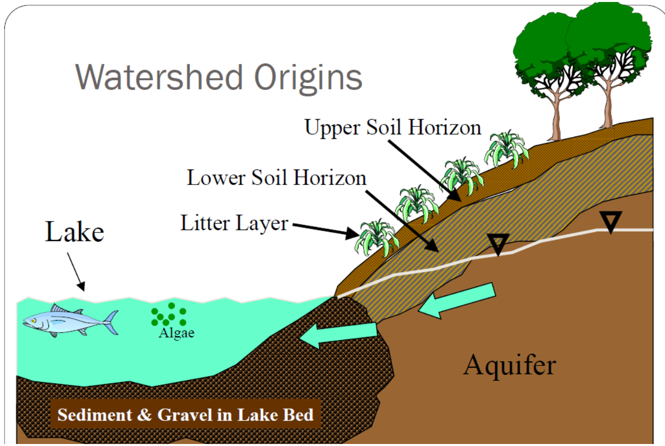
A special case of "solid"-water partitioning: Sorption to organic matter

$K_{i,d}$ lets us describe sorption to particulates, based on some experimental data. But how can we predict without experiments how a compound will absorb onto particulates?

First, we need to recognize that in aquatic environments, hydrophobic organic substances mainly adsorb to the natural organic matter (NOM) in a particulate. What is NOM?

- Particulate organic matter (POM)
- Dissolved organic matter (DOM)
- Dissolved organic carbon (DOC)
- Total organic carbon (TOC)

} Natural organic matter (NOM)

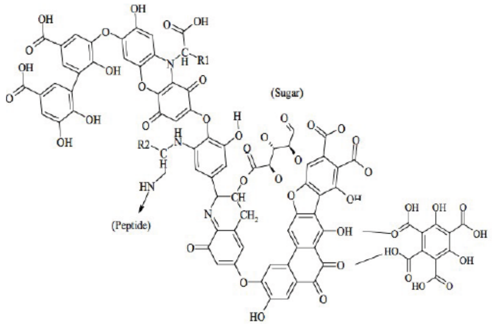


More on NOM

NOM is an assembly of various colloidal breakdown products of living organisms. It includes fractions of lipids, nucleic acids, proteins, cellulose, lignin, cutin, etc. It covers most surfaces in the environment, and acts as a sorbent for organic substances

There is no single chemical formula to describe organic matter, but it can be characterized in terms of:

- Composition (typically 45-55% C, 35-45% O, 3-5% H, 1-4% N, traces of other elements)
- Spectral properties (yellow-brown-black appearance)
- Aromaticity (how many rings)
- Functional groups (phenol, carboxylic acid content, etc.)



One of many possible structures of NOM

(Stevenson and Krastonav, 1982)

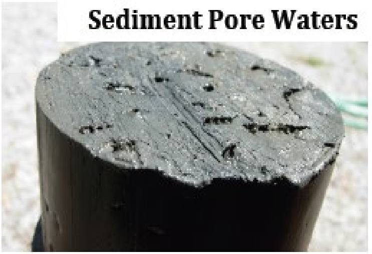
The color of beer stems from dissolved organic carbon

More on NOM

Some roles of NOM in environmental chemistry

- NOM is ubiquitous in water!
- Covers (almost) all surfaces and provides a hydrophobic layer that contaminants can adsorb to
- Complexes metals and adsorbs organic contaminants
- NOM-associated contaminants can be protected from degradation processes
- Shields light and thereby protects contaminants from photolytic degradation
- Reacts with light to form oxidants
- Can interfere with water treatment processes (membrane fouling, disinfection byproducts)

Surface Waters



K_{oc} and f_{oc} to describe organic matter-water partitioning

$K_{i,d}$ depends on the carbon content of organic matter. The weight fraction of organic carbon (f_{oc}) is defined as:

$$\boxed{f_{oc} = \frac{mass_{oc}}{mass_{solid}} \left(\frac{kg\ oc}{kg\ solid}\right)}$$

Assuming that i only sorbes to the organic carbon fraction of the solid, we can re-formulate $K_{i,d}$:

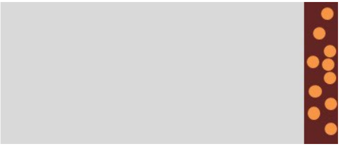
$$C_{i,s} = f_{oc} C_{i,oc} \quad \rightarrow \quad K_{i,d} = \frac{f_{oc} C_{i,oc}}{C_{i,w}}$$

Where $C_{i,oc}$ is the concentration of substance i sorbed to organic carbon (mol i/kg oc).

Weight of solid = 1 kg
No organic carbon

$C_{i,s}$ = 10 mol / kg

Weight of solid = 1 kg,
of which 0.1 kg = organic carbon



$C_{i,s}$ = 10 mol / kg

$C_{i,oc}$ = 100 mol / kg

The organic carbon-water partitioning constant $K_{i,oc}$ then is: $\boxed{K_{i,oc} = \frac{C_{i,oc}}{C_{i,w}} = \frac{K_{i,d}}{f_{oc}}}$

Estimate K_{oc} from K_{ow}

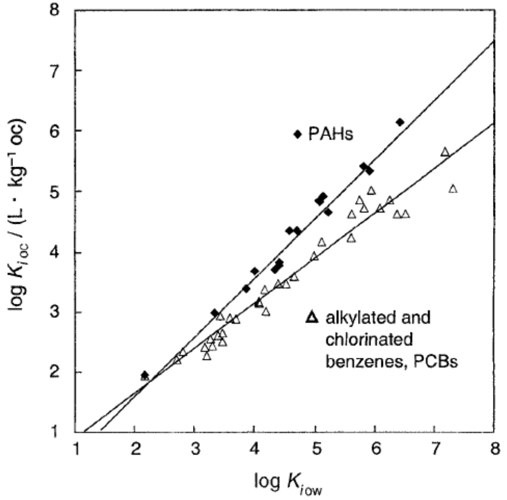
The hydrophobic character of a substance i is described by its K_{ow}. We can thus use K_{ow} to estimate K_{oc}. The relationship has the form:

$$\log K_{oc} = a * \log K_{ow} + b$$

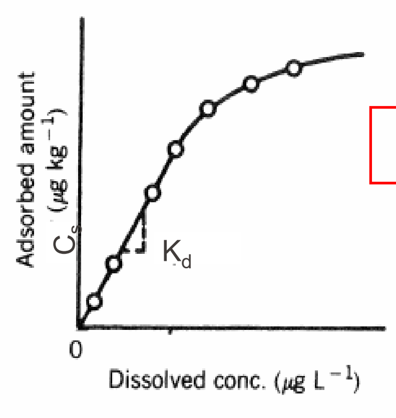
The parameters *a* and *b* depend on the compound class and to a lesser degree on the type of NOM.

Parameters a and b for some compound classes

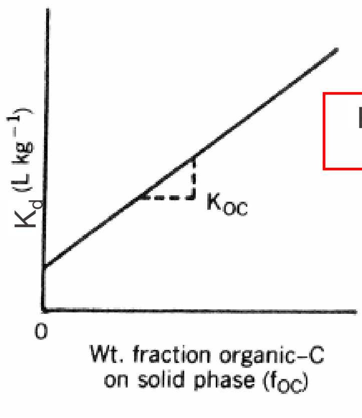
	$\log K_{ioc}{}^{b} = a \cdot \log K_{iow} + b$			
Set of Compounds	a	b	$\log K_{iow}$ range ^{c}	R^2
Alkylated and chlorinated benzenes, PCBs (± apolar)	0.74	0.15	2.2 to 7.3	0.96
PAHs (monopolar)	0.98	–0.32	2.2 to 6.4	0.98
Chlorinated phenols (neutral species; bipolar)	0.89	–0.15	2.2 to 5.3	0.97
C_1- and C_2-halocarbons (apolar, monopolar, and bipolar)	0.57	0.66	1.4 to 2.9	0.68!
Only chloroalkanes (mix)	0.42	0.93		0.59!
Only chloroalkenes (± apolar)	0.96	–0.23		0.97
Only compounds including bromine (mix)	0.50	0.81		0.49!
All phenylureas (bipolar)	0.49	1.05	0.5 to 4.2	0.62!
Only alkylated and halogenated phenylureas, phenyl-methylureas, and phenyl-dimethylurea (bipolar) ^{e}	0.59	0.78	0.8 to 2.9	0.87
Only alkylated and halogenated phenylureas (bipolar) ^{f}	0.62	0.84	0.8 to 2.8	0.98



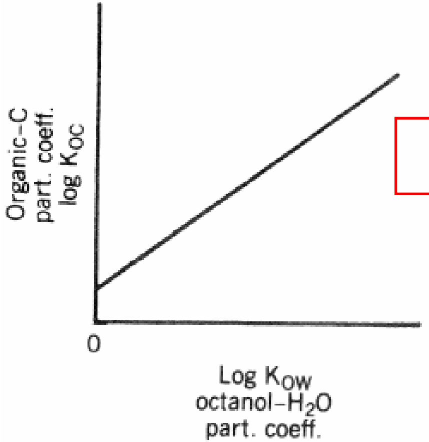
Relation between C_s, K_d, K_{oc} and K_{ow}



Langmuir isotherm



K_d as a f(f_{OC})



K_{OC} as a f(K_{OW})

Distribution of organics in multiphase systems

Now we know how to determine the concentration of a compound i in eqilibrium with two phases: air, liquids or solids. So what fraction of i will be found in each phase? And what is the distribution in a system with more than two phases?

We start with a simple example of i partitioning between two phases (1 and 2), which have volumes V_1 and V_2.

At equilibrium: $K_{i,1,2} = \frac{C_{i,1}}{C_{i,2}}$

Then the fraction of the total amount of i present at equilibrium in phase 1 is simply:

$$f_{i,1} = \frac{mass\ of\ i\ in\ phase\,1}{total\ mass\ of\ i} = \frac{C_{i,1}V_1}{C_{i,1}V_1 + C_{i,2}V_2} = \frac{1}{1+\underbrace{\frac{C_{i,2}}{C_{i,1}}}_{1/K_{i,12}}\underbrace{\frac{V_2}{V_1}}_{1/r_{12}}} = \frac{1}{1+\frac{1}{K_{i,12}r_{12}}}$$

(r_{12}= ratio of volumes)

Analogously for the fraction in phase 2:

$$f_{i,2} = \frac{mass\ of\ i\ in\ phase\,2}{total\ mass\ of\ i} = \frac{1}{1+K_{i,12}r_{12}}$$

Distribution of organics in multiphase systems

And if three phases are present? Then the fraction of the total amount of i present at equilibrium in phase 1 is:

$$f_{i,1} = \frac{mass\ of\ i\ in\ phase\,1}{total\ mass\ of\ i} = \frac{C_{i,1}V_1}{C_{i,1}V_1 + C_{i,2}V_2 + C_{i,3}V_{i,3}} = \frac{1}{1+\frac{C_{i,2}}{C_{i,1}}\frac{V_2}{V_1}+\frac{C_{i,3}}{C_{i,1}}\frac{V_3}{V_1}} = \frac{1}{1+\frac{1}{K_{i,12}r_{12}}+\frac{1}{K_{i,13}r_{13}}}$$

Analogously for the fraction in phases 2 and 3:

$$f_{i,2} = \frac{mass\ of\ i\ in\ phase\,2}{total\ mass\ of\ i} = \frac{1}{1+K_{i,12}r_{12}+\frac{1}{K_{i,23}r_{23}}}$$

$$f_{i,3} = \frac{mass\ of\ i\ in\ phase\,3}{total\ mass\ of\ i} = \frac{1}{1+K_{i,13}r_{13}+K_{i,23}r_{23}}$$

For example, phase 1 = air, phase 2 = water, phase 3 = octanol:

At equilibrium:

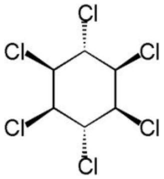
$$K_{i,1,2} = K_{aw} = \frac{C_{i,a}}{C_{i,w}} \qquad K_{i,1,3} = K_{i,ao} = \frac{C_{i,a}}{C_{i,o}} \qquad K_{i,2,3} = \frac{1}{K_{i,ow}} = \frac{C_{i,w}}{C_{i,o}}$$

$$f_{i,1} = f_{i,air} = \frac{1}{1+\frac{1}{K_{i,aw}r_{aw}}+\frac{1}{K_{i,ao}r_{ao}}} \qquad f_{i,2} = f_{i,water} = \frac{1}{1+K_{i,aw}r_{aw}+K_{i,ow}r_{ow}} \qquad f_{i,3} = f_{i,octanol} = \frac{1}{1+K_{i,ao}r_{ao}+\frac{1}{K_{i,ow}r_{ow}}}$$

Exercise 11: contaminant removal by rain

This exercise is an example of a 2-phase problem:

Consider lindane, a volatile pesitcide. When it rains, the lindane will partition into the rain drops and wash out from the atmosphere. What fraction of lindane is washed out of a 5000 m air column by 25 mm/m^2 of rain?



Lindane
log K_H = -2.49
(atm/M)

Exercise 12: contaminant retardation in groundwater

This is another example of a 2-phase problem, though this time the two phases are water and the aquifer:

Again consider lindane (log K_{ow} = 3.78), though this time in an (air tight) aquifer. To what extent will lindane be dissolved in groundwater, and to what extent adsorbed?

Exercise 13: the soup bowl problem

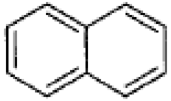
This exercise is an example of a 3 phase problem:

A covered soup bowl contains 1 L of a very diluted, cold soup (25°C), 1L of air and a 1 mL floating bubble of fat. The system also contains 1 mg of naphtalene. Estimate the amount of naphtalene you would ingest if you were to eat only the fat bubble.

In the literature you find the following partition constants:

$K_{i,aw}$=$10^{-1.76}$

$K_{i,ow}$=$10^{3.36}$



i=naphthalene

You can assume that the fat bubble behaves like octanol, so $K_{i,fw} = K_{i,ow}$

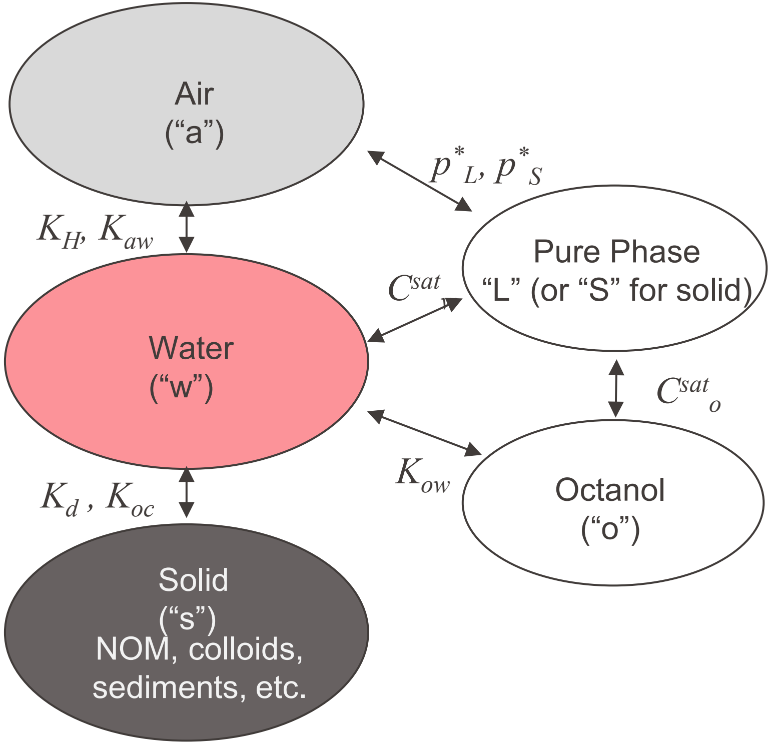
Summary of partition constants

$K_H = P_i/C_w = K_{aw}RT$

$K_{ow} = C_o/C_w$

$K_{aw} = C_a/C_w$

$K_d = C_s/C_w = K_{oc}f_{oc}$



Useful website to find K_{ow}, K_{aw}, K_H, etc. for many different compounds: https://comptox.epa.gov/dashboard/