# Phase equilibrium

# Chemical equilibria – pure phase & water

Let's define K:

$$Y_i \iff Y_{aq,sat} \qquad\qquad K = \frac{\{Y\}_{aq,sat}}{\{Y\}_i}$$

- { }: activity, a unitless thermodynamic property
  - [ ]: molarity;  ( ): eq/L

- For pure phase $Y_i$, activity is defined as

  $\{Y\}_i = 1$ (liquid, solid)

  $\{Y\}_i = p_i$ (gas)   *$p_i$: pressure in atm*

- For a dilute aqueous solution

  $\{Y\}_i \approx [Y]_i$

- So:   $K \approx \dfrac{[Y]_{aq,sat}}{p_i}$   or   $[Y]_{aq,sat}$

  *(gas as pure phase)*      *(liquid or solid as pure phase)*

> **What is a "dilute aqueous solution"?**
> <u>Rule of thumb</u>: Solution can be considered dilute if water molecules make up 99.9% or more of the solution entities

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# What's ideal behavior?

- **An individual molecule's properties (energy distribution, tendency to react, dissolve, vaporize, etc.) are <u>independent</u> of the presence and/or concentration of <u>any</u> other molecules in the phase**
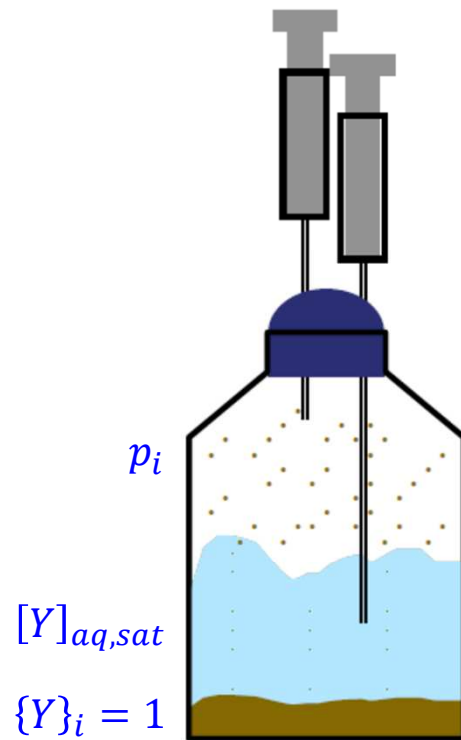
$$\textbf{\textit{Gas phase}}$$
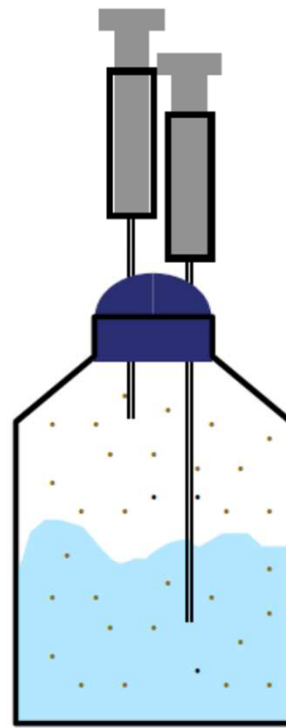
$$Energy = PV = n_t RT = RT \sum_i n_i$$

$$p_i = \frac{n_i RT}{V}; \quad P = \sum_i p_i$$

- **Dilute solution approximation: dissolved component "*i*" behaves (quasi-) ideally**
  - 1$^{st}$ unit of "*i*" added has the same effect as n$^{th}$ unit
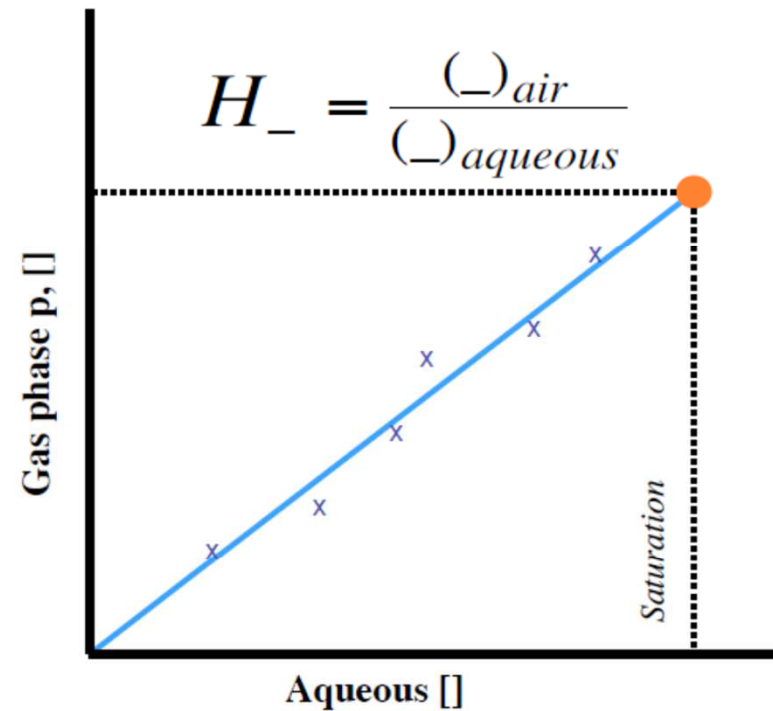  - Effect of adding a unit of "*i*" may not be the same as adding a unit of "*j*"

# Air/water partitioning: Henry's constant



$p_i$

$[Y]_{aq,sat}$

$\{Y\}_i = 1$

Saturation

Calibration curve

$$H_- = \frac{(\_)_{air}}{(\_)_{aqueous}}$$

Gas phase p, []

Aqueous []

Saturation

# Air/water partitioning: Henry's constant

$$H_{\_} = \frac{(\_)_{air}}{(\_)_{aqueous}}$$

- **Linear partitioning because:**
  - Gas phase behaves ideally
  - Dissolution of *i* in water does not affect water's properties (dilute solution, $x_i < \sim 10^{-3}$)

- **Constant is defined using a variety of unit combinations**
  - Mole fraction, atmosphere, molar concentration, mg/L, …
  - H's numerical value depends on units
  - Watch out for "1/H"

$$H_{xy} = \frac{x_g}{x_{aq}} = \frac{mole\ fraction_g}{mole\ fraction_{aq}}$$

$$H_{cc} = \frac{moles/vol_g}{moles/vol_{aq}} = \frac{p_i}{[C_i]_{aq} \times RT}$$

$$H_{pc} = \frac{p_i}{[C_i]_{aq}}, \qquad \frac{l - atm}{mole}$$

# Henry's constants: the different forms

At 1 atm, 25°C,

$$H_{xy} = \frac{x_g}{x_{aq}} = \frac{55.3 p_i}{[C_i]_{aq}}$$

$p_i$ = mole fraction in gas phase

    *gas phase behaves ideally*

    $p_T$ = 1 atm

pure water [ ] is ~55.3 mole/L @ 25°C

    *assume $C_{i,aq}$ << 55.3 mole/L*

$$H_{cc} = \frac{moles/vol_g}{moles/vol_{aq}} = \frac{p_i}{[C_i]_{aq} \times RT} = \frac{p_i}{[C_i]_{aq} \times 24.47}$$

*@ T = 298K & $p_T$ = 1 atm*

*1 mole of gas occupies 24.47 L*

$$H_{pc} = \frac{p_i}{[C_i]_{aq}}, \qquad \frac{l-atm}{mole}$$

$$\boxed{H_{pc} = 0.01807 \, x \, H_{xy} = 24.47 \, x \, H_{cc} \, @ \, 25 \, ℃, \, 1 \, atm}$$

# Aqueous solubility and vapor pressure

| Properties of some organic chemicals of environmental interest | | | | | | |
|---|---|---|---|---|---|---|
| Name | Formula | Mol. Wt. | Melt, C | Boil, C | $-\log(p^{sat})^1$ | $-\log(C^{sat})^2$ |
| methane[@] | $CH_4$ | 16.0 | -182.5 | -164.0 | -2.44 | 2.82 |
| n-butane[@] | $C_4H_{10}$ | 58.1 | -138.4 | -0.4 | -0.39 | 2.98 |
| n-hexane | $C_6H_{14}$ | 86.2 | -95.0 | 69.0 | 0.69 | 3.83 |
| cyclohexane | $C_6H_{12}$ | 84.2 | 6.6 | 80.7 | 0.90 | 3.15 |
| 1-hexene | $C_6H_{12}$ | 84.2 | -139.8 | 63.4 | 0.60 | 3.15 |
| benzene | $C_6H_6$ | 78.1 | 5.5 | 80.1 | 0.90 | 1.64 |
| 1-hexanol | $C_6H_{14}O$ | 102.2 | -46.7 | 158.0 | 2.85 | 0.88 |
| 1-octanol | $C_8H_{18}O$ | 130.2 | -16.7 | 194.4 | | 2.35 |
| toluene | $C_7H_8$ | 92.1 | -95.0 | 110.6 | 1.42 | 2.25 |
| chlorobenzene | $C_6H_5Cl$ | 112.6 | -45.6 | 132.0 | 1.80 | 2.35 |
| 1,4dichlorobenzene | $C_6H_4Cl_2$ | 147.0 | 53.1 | 174.0 | 3.04 | 3.39 |
| bromobenzene | $C_6H_5Br$ | 157.0 | -30.8 | 156.0 | 2.25 | 2.64 |
| dioxin[#] | $C_{12}H_4O_2Cl_4$ | 322.0 | 305 | 421 | 11.6 | 10.3 |
| [@]gas at 25C--$p^{sat}$ refers to pressure needed to obtain pure liquid at 25C | | | | | | |
| [#]2,3,7,8-tetra-chlorodibenzo-p-dioxin | | | | | | |
| [1]vapor pressure @ 25C, atmospheres | | | | | | |
| [2]concentration in saturated aqueous solution, moles/l, 25C | | | | | | |

# Mass partitioning between air & water

**Henry's constant**

$$H_{cc} = \frac{p_i}{C_{i,aq} \times RT} = \frac{C_{i,g}}{C_{i,aq}}$$

**Phase volumes**

$$V_g, \quad V_{aq}$$

**Masses (Moles)**

$$M_{tot}, \quad M_g, \quad M_{aq}$$

$$R_{g/aq} = \frac{M_g}{M_{aq}} = \frac{H_{cc} \times V_g}{V_{aq}}$$

$$M_g = M_{tot} \times \frac{R_{g/aq}}{1 + R_{g/aq}} = M_{tot} \times \frac{H_{cc} \times V_g}{V_{aq} + H_{cc} \times V_g}$$

$$M_{aq} = M_{tot} \times \frac{1}{1 + R_{g/aq}} = M_{tot} \times \frac{V_{aq}}{V_{aq} + H_{cc} \times V_g}$$

# Mass partitioning between air & water

**Q:** A 1.000 L bottle is filled with 500.0 mL water. Then, 42.1 mg 1-hexene (MW: 84.2) is added. After sealing the bottle, it is left at 25°C until equilibrium between air and water. How will the 1-hexene mass partition between air and water in the bottle?

# Additional phase - solid

**Soil**

**Sediment**
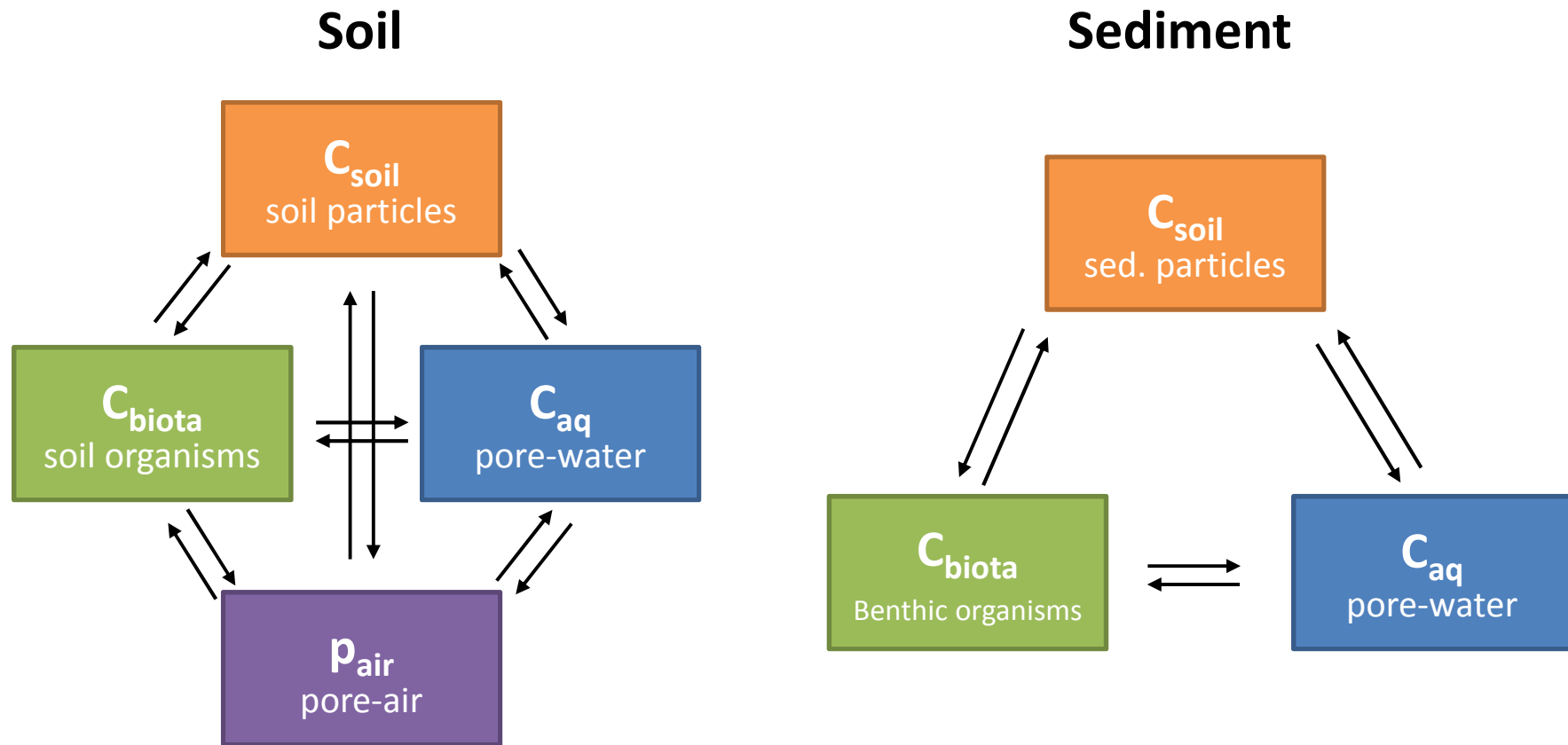


- Need equilibrium between
  - $C_{aq}$ & $C_{soil}$ (or $C_{sed}$)
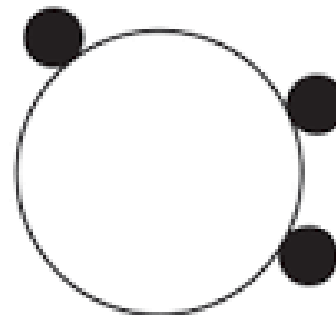  - $C_{aq}$ & $C_{biota}$

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# Mass exchange b/w solid particles & water

- **Sorption**
  - Any accumulation of a substance on/below the surface of solids
  - sorbate vs. sorbent – "sth that is sorbed" vs. "sth that sorbs"
  - adsorption vs. absorption
    - on the surface vs. in the entire volume of the sorbent

absorption          adsorption

# Sorption isotherms

- Isotherm – constant temp. & at thermodynamic equilibrium

- Various models to describe $C_s$ vs. $C_{air}$, $C_s$ vs. $C_{aq}$ sorption isotherm

- Frequently used sorption isotherms for $C_s$ vs. $C_{aq}$

  – **Langmuir isotherm**

$$C_s = \frac{a \cdot b \cdot C_{aq}}{1 + b \cdot C_{aq}}$$

*$C_s$ = concentration in solid at equilibrium [g sorbate/kg solid]*

*$C_{aq}$ = concentration in water at equilibrium [g sorbate/L water]*

*a, b = Langmuir constants*

*a – unit: [g sorbate/kg solid], represents sorption capacity*

*b – unit: [L water/g sorbate], a×b represents sorbate-sorbent affinity*

(Assumptions)

- **Ad**sorption occurs on fixed number of <u>surface</u> sites
- <u>Monolayer</u> coverage, no interaction between adsorbates
- No lateral movement of molecules on the surface

# Sorption isotherms

- – **Freundlich isotherm**

$$C_s = K_F \cdot C_{aq}^{1/n}$$

  $K_F$ = *Freundlich sorption coefficient*

  *[(g sorbate/kg solid)·(L water/g sorbate)$^{-1/n}$]*

  $n$ = *Freundlich exponent (unitless)*

  - • Empirical relationship
  - • Can fit to a case when both adsorption & adsorption occur

- – **For the case of n=1 of Freundlich isotherm, we see linear relationship**

$$C_s = K_p \cdot C_{aq}$$

  $K_p$ = *solid-water partitioning coefficient*

  *[L sorbate/kg solid]*

  - • Some refer the sorption mechanism as "partitioning" if linear isotherm is observed

# Linear sorption isotherm (partitioning)

- Theoretically, linear isotherm is observed when
  - Absorption is the dominant process
    - So, linear isotherm is more likely to be observed for gel-like sorbents than rigid ones
    - Lipid fraction of organisms – gel-like
    - Organic matter in soils & sediments – some gel-like & some rigid fractions

- Can also be observed at low $C_{aq}$ range even when adsorption is dominant
  - Review Langmuir isotherm!

- We will limit our discussion on linear sorption (partitioning)

# Contaminants in organisms - terms

- **Bioaccumulation**
  - Net contaminant accumulation (all sources) in & on an organism
- **Bioconcentration**
  - Net contaminant accumulation (from water) in & on an organism
- **Biomagnification**
  - Contaminant conc. increase from trophic level "n" to "n+1"
- **Bioaccumulation factor (BAF)**
  - $C_{biota}/C_{source}$
- **Bioconcentration factor (BCF)**
  - $C_{biota}/C_{aq}$
- **Biomagnification factor**
  - $C_{biota}{}^{"n+1"}/C_{biota}{}^{"n"}$

# Transport against hydraulic gradient

- Salmons concentrate PCBs (biovectors)
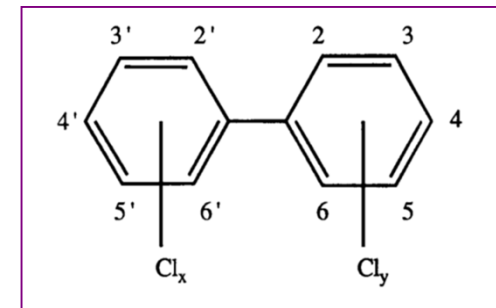


PCB molecular structure

**PCBs in Lake Ontario**

| | microgram PCB per * | | |
|---|---|---|---|
| PCB congener | 52 | 66 | 153 |
| MW | 291.97 | 291.97 | 360.71 |
| dissolved | 6.3E-0.5 | 3.1E-0.5 | 5.0E-0.5 |
| bottom sediment | 25 | 46 | 25 |
| suspended sediment | 15 | 27 | 23 |
| plankton | 2.4 | 1.6 | 2.2 |
| mysids | 3.5 | 15 | 30 |
| amphipods | 22 | 30 | 45 |
| oligochaetes | 6.3 | 8.3 | 7.5 |
| small smelt | 7.6 | 2.7 | 64 |
| large smelt | 18 | 72 | 130 |
| trout/salmon | 62 | 160 | 430 |

*L for dissolved; kg dry wt. for sediments; kg wet wt. for organisms

*Oliver & Nilmi, 1988, ES&T, 22:388-397*

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# Hydrophobic organic compounds (HOCs)

- **Partitioning to biota**
  - Tend to partition to lipids
  - Lipids are fat soluble, naturally occurring molecules
    - Fats, oils, waxes, some vitamins (A, D, E, K), glycerides
    - Have hydrocarbon chains - hydrophobic

- **Partitioning to soils & sediments**
  - HOCs partition much more strongly to the natural organic matter (NOM) fraction of soil than to mineral phases
    - Hydrophobic regions of NOM
    - Only surfaces of minerals are accessible to contaminants
    - NOM typically dominates partitioning down to $f_{oc} \sim 0.001$

$f_{oc}$ = organic carbon fraction in soil or sediment
[g organic carbon/g soil or sediment]

# Octanol water partition coefficient

- ***n*-octanol, C$_8$H$_{17}$OH**
  - Surrogate for natural organic phases
    - Soil/sediment organic matter (SOM), dissolved organic matter (DOM), lipids

  - Octanol-water partition coefficient, K$_{ow}$
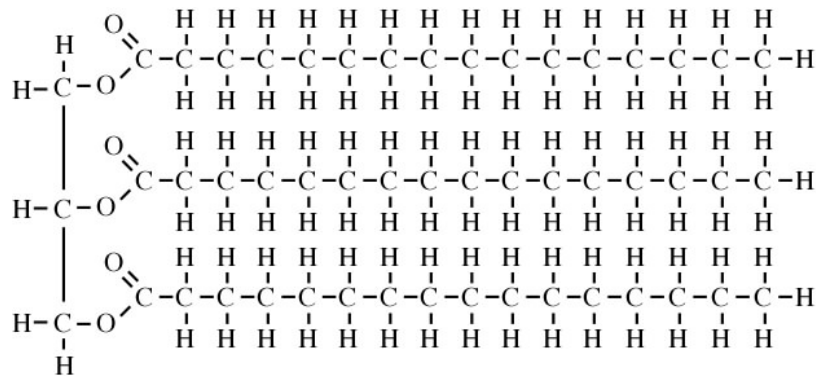
$$K_{ow} = \frac{C_{octanol}}{C_{aq}}$$

*C$_{octanol}$ = concentration in octanol at equilibrium [g sorbate/L octanol]*
*C$_{aq}$ = concentration in water at equilibrium [g sorbate/L water]*
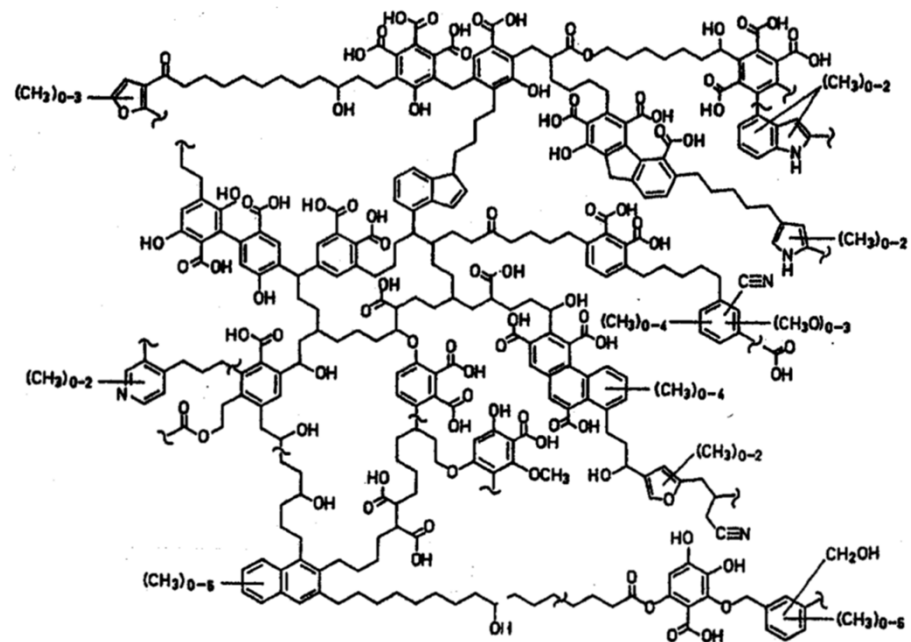
*So, K$_{ow}$ is unitless*



$C_{octanol}$

$C_{aq}$
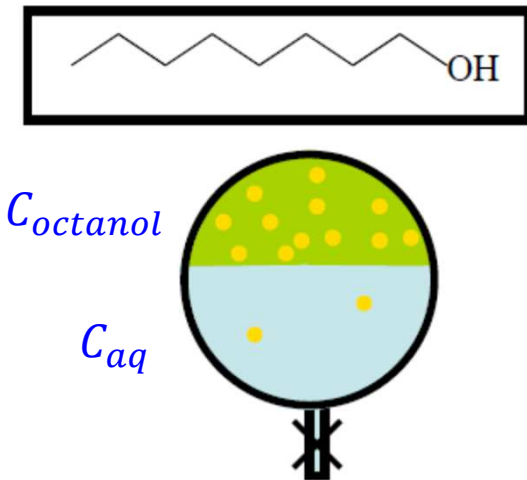
# Lipid & humic substance examples



*fat molecule – example*



*cf) octanol*



*humic substance – example*

# Aq. solubility, vapor pressure, $K_{ow}$

| Compound | Formula | log $K_{ow}$ | -log($p^{sat}$)[1] | -log($C^{sat}$)[2] |
|---|---|---|---|---|
| methane | $CH_4$ | 1.09 | -2.44 | 2.82 |
| n-butane[@] | $C_4H_{10}$ | 2.89 | -0.39 | 2.98 |
| n-hexane | $C_6H_{14}$ | 4.00 | 0.69 | 3.83 |
| cyclohexane | $C_6H_{12}$ | 3.44 | 0.90 | 3.15 |
| 1-hexene | $C_6H_{12}$ | 3.40 | 0.60 | 3.15 |
| benzene | $C_6H_6$ | 2.17 | 0.90 | 1.64 |
| 1-hexanol | $C_6H_{14}O$ | 2.03 | 2.85 | 0.88 |
| 1-octanol | $C_8H_{18}O$ | 2.84 | | 2.35 |
| toluene | $C_7H_8$ | 2.69 | 1.42 | 2.25 |
| chlorobenzene | $C_6H_5Cl$ | 2.78 | 1.80 | 2.35 |
| 1,4 dichlorobenzene | $C_6H_4Cl_2$ | 3.45 | 3.04 | 3.39 |
| bromobenzene | $C_6H_5Br$ | 2.99 | 2.25 | 2.64 |
| dioxin[#] | $C_{12}H_4O_2Cl_4$ | 6.64 | 11.6 | 10.3 |

[@]gas at 25C--$p^{sat}$ refers to pressure needed to obtain pure liquid at 25C

[#]2,3,7,8-tetra-chlorodibenzo-p-dioxin

[1]vapor pressure @ 25C, atmospheres

[2]concentration in saturated aqueous solution, moles/l, 25C

# Using $K_{ow}$ – HOC partitioning to biota

- Bioconcentration factor (BCF) = $C_{biota}/C_{aq}$
  - $C_{biota}$ unit: [g sorbate/kg body weight]
  - BCF not necessarily representative of equilibrium state

- If equilibrium can be assumed, may use octanol as a surrogate for lipid
  - Lipid fraction by weight -- $\alpha$ ($\alpha$=10-30% for humans)
  - For a rough estimate, assume 1 kg lipid = 1 kg octanol

$$BCF \approx \frac{\alpha}{0.826} K_{ow}$$

*0.826 = density of octanol [kg octanol/L octanol]*
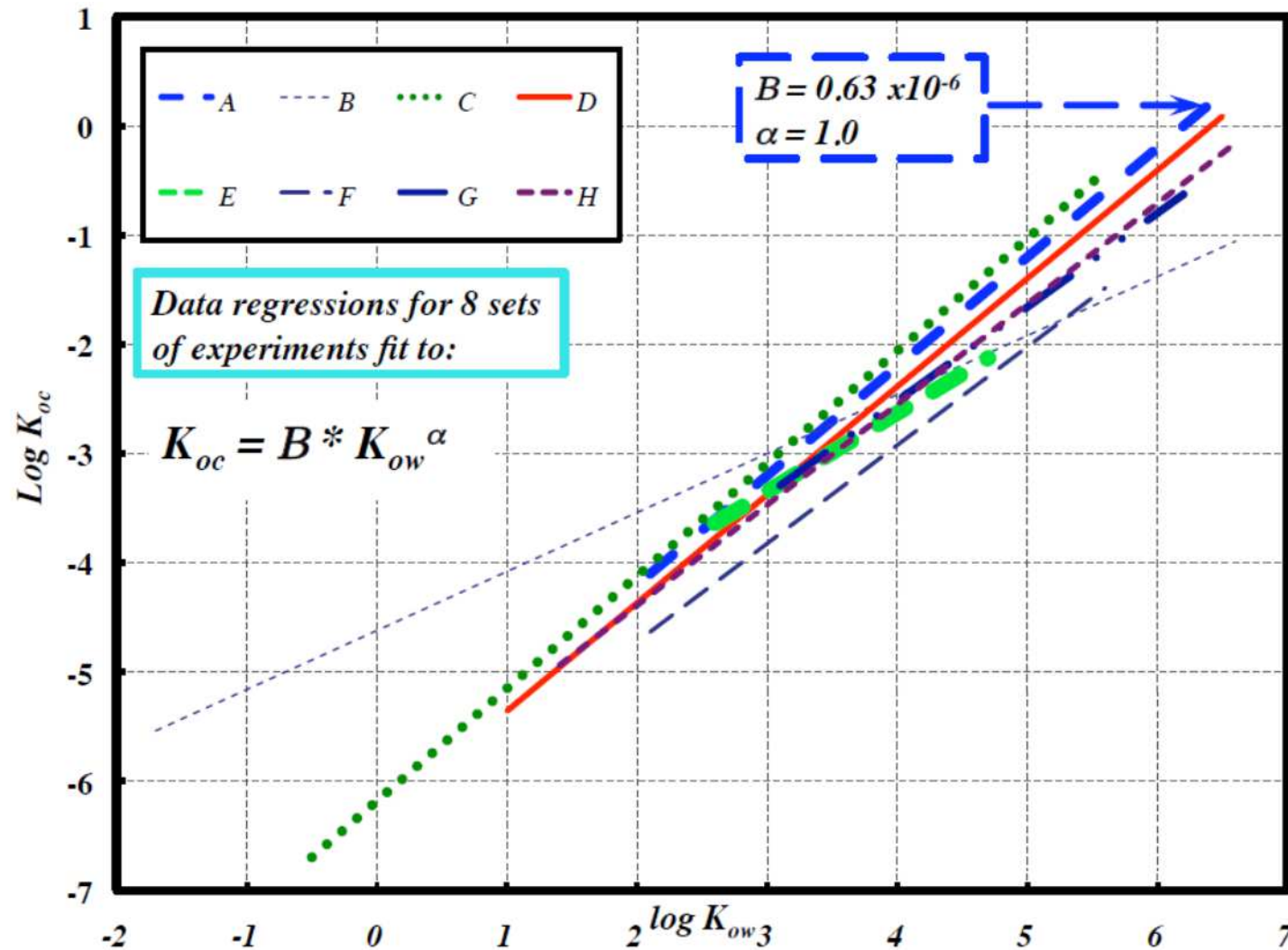*\* Note $K_{ow}$ [L water/L octanol]*

# Using $K_{ow}$ – HOC partitioning to soil/sediment

- As NOM dominates sorption for HOCs,

$$\frac{C_s}{C_{aq}} = K_p = f_{oc} \cdot K_{oc}$$    *$K_{oc}$ = organic carbon-normalized partitioning coefficient*

- Various units of $K_p$ & $K_{oc}$ can be used:
  - volume of water / dry weight of solid
  - $m^3$/g, mL/mg, L/g, L/kg, L/mg, …
  - Numerical value will depend on the units used

- Use $K_{ow}$ to predict $K_{oc}$
  - $K_{ow}$-$K_{oc}$ relationship needed!
  - Note $K_{oc}$ range of ~2 orders of magnitude for a single compound has been reported
  - Use caution when using $K_{oc}$ without experimental determination

# Organic carbon/water partitioning, $K_{oc}$



$$B = 0.63 \times 10^{-6}$$
$$\alpha = 1.0$$

Data regressions for 8 sets of experiments fit to:

$$K_{oc} = B * K_{ow}^{\alpha}$$

Legend: A, B, C, D, E, F, G, H

Here, $K_{oc}$ unit is [m³/g]

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# Organic carbon/water partitioning, $K_{oc}$

$$K_{oc} = \beta \times K_{ow}{}^{\alpha}$$

| Ref. | # of compounds | Range of log $K_{ow}$ | $\beta \times 10^6$ | $\alpha$ | r |
|---|---|---|---|---|---|
| A  Karickhoff, 1983 | 10 | 2.1~6.6 | 0.63 | 1.0 | 1.0 |
| B  Kenaga & Goring, 1980 | 45 | -1.7~6.6 | 24 | 0.54 | 0.93 |
| C  Rao & Davidson, 1980 | 15 | -0.5~5.6 | 0.66 | 1.03 | 0.95 |
| D  Karickhoff, 1981 | 6 | 1.0~6.5 | 0.45 | 0.99 | 0.99 |
| E  Schwarzenbach & Westall, 1981 | 12 | 2.6~4.7 | 3.1 | 0.72 | 0.97 |
| F  Chio et al., 1983 | 12 | 2.1~5.6 | 0.3 | 0.90 | 0.99 |
| G  Mingelgrin & Gerstl, 1983 | 7 | 3.1~6.2 | 1.1 | 0.87 | 0.85 |
| H  Curtis et al., 1986 | 22 | 1.4~6.6 | 0.59 | 0.92 | 0.94 |

($K_{oc}$ in [$m^3$/g])

- Use "A" (Karickhoff, 1983) for this class

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# Phase equilibrium – chemical potential

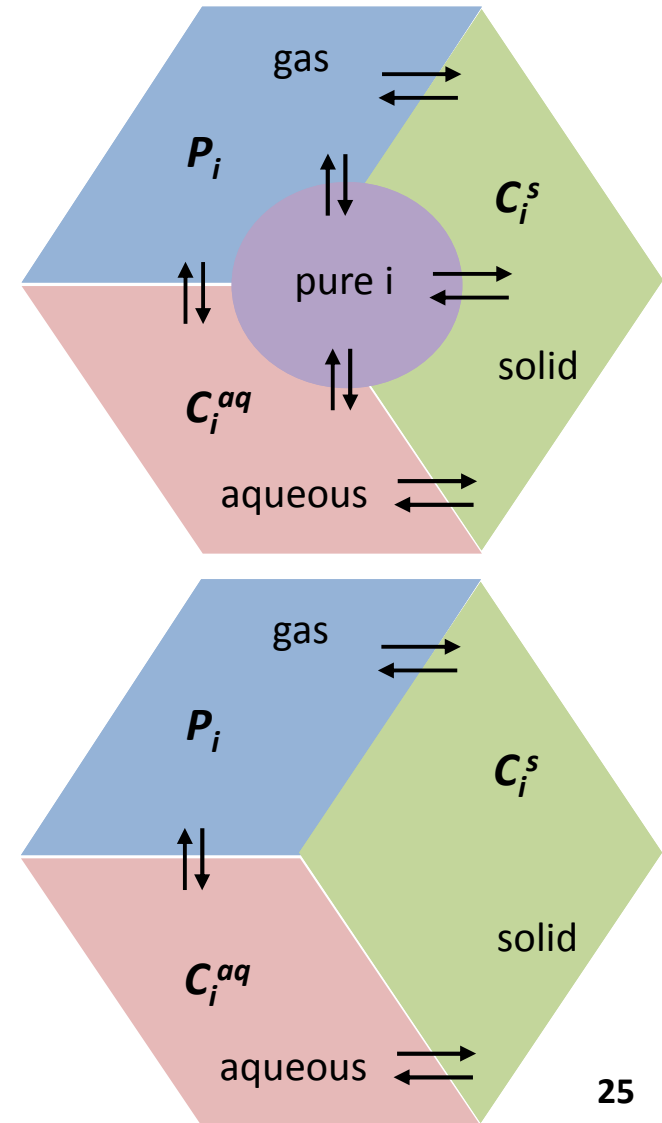**At equilibrium**

$$\mu_i{}^{pure} = \mu_i{}^{gas} = \mu_i{}^{s} = \mu_i{}^{aq}$$

*(If pure phase exists)*

$$\mu_i{}^{eq} = \mu_i{}^{gas} = \mu_i{}^{s} = \mu_i{}^{aq}$$

*(If pure phase does not exist)*

- $\mu$ is the chemical potential; it has units of energy – difficult to measure

- Chemical potential is related to activity

$$\{i\}_{g,s,aq} \propto e^{\mu}$$

- For gas phase, activity equals partial pressure expressed in atm



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# Phase equilibrium - fugacity

Define the **fugacity** of a substance *i* in any phase to be equal to the **partial pressure of *i*** that is in equilibrium with the phase

**At equilibrium**

$$f_i^{pure} = f_i^s = f_i^{aq} = f_i^{gas} = p_i^{sat}$$  *(if pure phase exists)*

$$f_i^s = f_i^{aq} = f_i^{gas} = p_i$$  *(if pure phase does not exist)*

- ***Why use $p_i$?***
  - Pressure is comprehensible & measurable
  - Gas phase behaves ideally – a good reference
    - $p_i \propto \{i\} \propto [i]$

# Phase equilibrium - fugacity

- Advantage of fugacity approach
  - **Predict multi-phase equilibrium partitioning** in a minimally complex fashion


- Fugacity approach is applicable
  - In dilute systems when partitioning is linear among different phases
  - Suited for volatile compounds

# Equilibrium partitioning between phases

- Linear partitioning among phases: review our discussions

    - Henry's law for **gas/water partitioning**:

    $$p_i = H_{pc} \times C_i^{aq} \qquad \text{or} \qquad C_i^{gas} = H_{cc} \times C_i^{aq}$$

    - Linear partitioning among **water and any other phases**:

    $$C_i^s = K_p \times C_i^{aq}$$

    $$C_i^{biota} = BCF \times C_i^{aq}$$

    $$C_i^{oct} = K_{ow} \times C_i^{aq}$$

    $$:$$

# Applying fugacity approach

- **So:** if a system is <u>at equilibrium</u> and <u>partitioning is linear</u>, we can relate the concentration of a compound in any phase to partial pressure, or ***fugacity***

- **Now:** introduce "Z value", the fugacity capacity factor (unit: mole/atm/m$^3$), to relate fugacity to concentration.

- **Then:**

$$C_i{}^j = f_i Z_i{}^j$$

$$Moles_i{}^j = C_i{}^j V^j = f_i Z_i{}^j V^j$$

$$\sum_j Moles_i{}^j = \sum_j C_i{}^j V^j = f_i \sum_j Z_i{}^j V^j \qquad \text{(when } C_i{}^j \text{ are all expressed as moles/volume)}$$

# Z values for different phases

- **Gas phase**

$$p_i V^{gas} = nRT$$

$$\frac{n_i}{V^{gas}} = C_i^{gas} = \frac{p_i}{RT} = \frac{f_i}{RT} \qquad \Rightarrow \qquad Z_i^{gas} = \frac{1}{RT}$$

- **Aqueous phase**

$$p_i = f_i = H_{pc} C_i^{aq}$$

$$C_i^{aq} = \frac{f_i}{H_{pc}} \qquad \Rightarrow \qquad Z_i^{aq} = \frac{1}{H_{pc}}$$

- **Octanol**

$$C_i^{oct} = K_{ow} C_i^{aq} = f_i \times \frac{K_{ow}}{H_{pc}} \qquad \Rightarrow \qquad Z_i^{oct} = \frac{K_{ow}}{H_{pc}}$$

# Z values for different phases

- **Solid phase**

$$C_i^{s*} = K_p C_i^{aq}$$

*Here, $C_i^{s*}$ is per weight basis;*

*$K_p$ has a dimension of (vol. water) / (weight solid)*

$$C_i^{\,s} = \rho_s K_p C_i^{aq} = f_i \times \frac{\rho_s K_p}{H_{pc}} \quad \Rightarrow \quad Z_i^s = \frac{\rho_s K_p}{H_{pc}}$$

*$C_i^s$ should be per volume basis*

- or, we may use:

$$Z_i^{\,s*} = \frac{C_i^{\,s*}}{f_i} = \frac{K_p C_i^{aq}}{f_i} = \frac{K_p}{H_{pc}}$$

*$Z_i^{\,s*}$ has a unit of moles/atm/kg*
*if $C_i^{s*}$ is in moles/kg*

- then,

$$Moles_i^{\,s} = C_i^{\,s*} M^s = f_i Z_i^{\,s*} M^s$$

# Applying fugacity approach

- **Our potential interest: how mass will be distributed among phases.**

- **Need:**
  - Compartment volumes or masses
  - Equilibrium constants (Henry's constant, $K_{ow}$, $K_p$, etc.)

$$M_i^{total} = \sum_j C_i^j V^j = f_i \sum_j Z_i^j V^j = p_i \sum_j Z_i^j V^j$$

  *If $Z_i^{j*}$ is obtained for any solid phase, substitute $Z_i^j V^j$ with $Z_i^{j*} M^j$ for that phase*

  - If we know $\boldsymbol{M_i^{total}}$, we can calculate $f_i$ and then determine $C_i^j$'s and distributions among compartments
  - If we know $\boldsymbol{f}_i$, we can calculate $M_i^{total}$ and then determine $C_i^j$'s and distributions among compartments

# Determine equilibrium partitioning

A
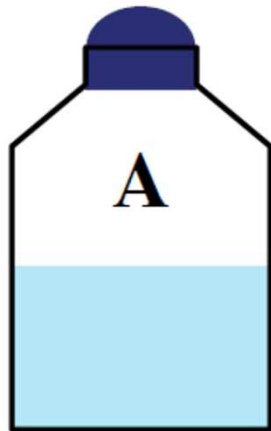
1.000 liter bottles
25C
42.1 mg 1-hexene

B

500 ml air
500 ml water
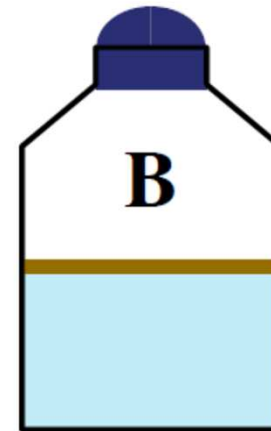
490 ml air
20 ml octanol
490 ml water