Phase equilibrium

Chemical equilibria – pure phase & water

- **Linear phase partitioning – pure phase *i* & water**

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

  - { }: activity, a unitless thermodynamic property
  - For pure phase Y_i, activity is defined as

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

    $\{Y\}_i = p_i$ (gas); p – pressure (in atm)
  - For a dilute aqueous solution

    $\{Y\}_i \approx [Y]_i$; [ ] = molar concentration

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

  - So:

$$K \approx \frac{[Y]_{aq,sat}}{p_i} \quad \text{or} \quad [Y]_{aq,sat}$$

(gas as pure phase)

(liquid or solid as pure phase)

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**

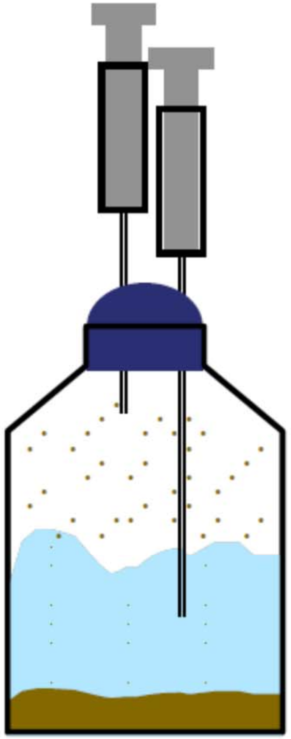
Gas phase

$$Energy = PV = n_t RT = RT \sum_i n_i$$

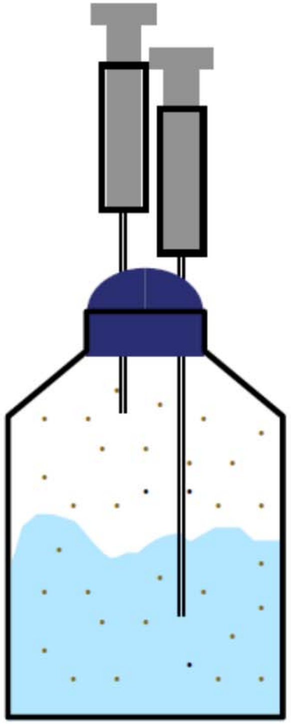
$$p_i = \frac{n_i RT}{V}; \quad P = \sum_i p_i$$

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

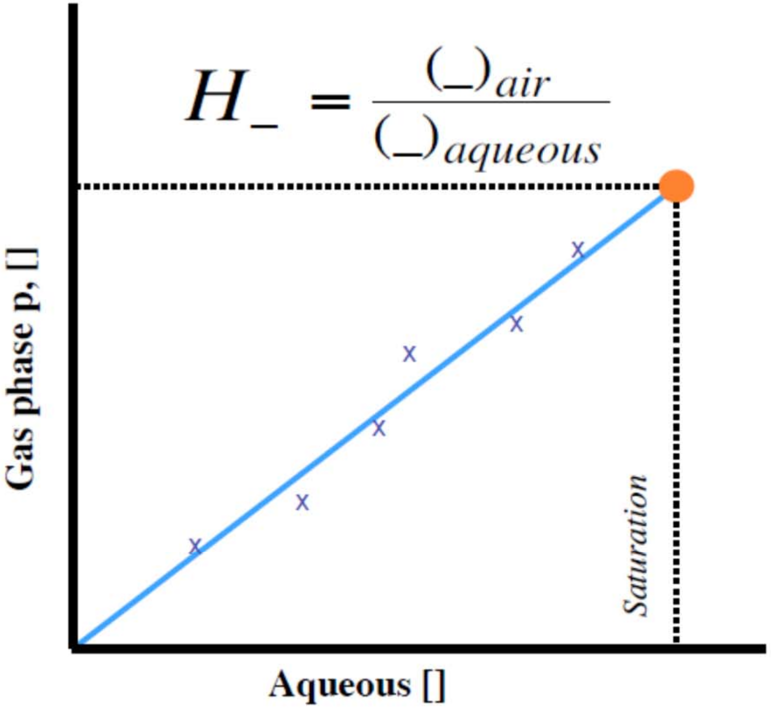
Air/water partitioning: Henry's constant



Saturation



Calibration curve



Air/water partitioning: Henry’s constant

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

- **Constant has been 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”
- **Linear partitioning because:**
  - Gas phase behaves ideally
  - Dissolution of *i* in water does not affect water’s properties (dilute solution, x_i <~10^{-3})

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

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

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

Henry's constants: the different forms

At 1 atm, 25°C,

$$H_{xy} = \frac{x_g}{x_{aq}} = \frac{55.3p_i}{C_{i,aq}}$$

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

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

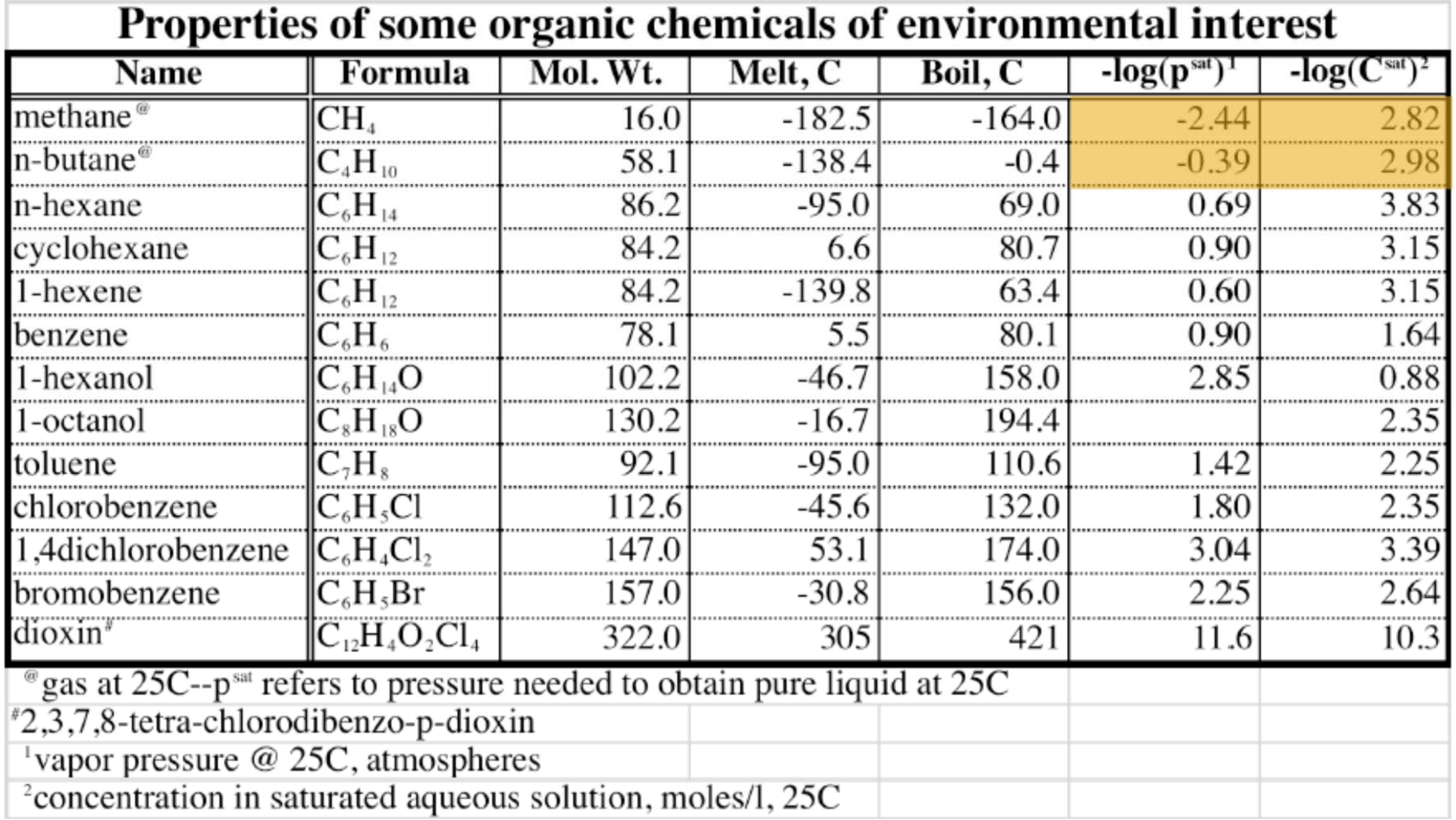
@ T = 298K & p_T = 1 atm

1 mole of gas occupies 24.47 L

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

$$\boxed{H_{pc} = 0.01807 \times H_{xy} = 24.47 \times H_{cc} \text{ @ } 25\,℃}$$

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)

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

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

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

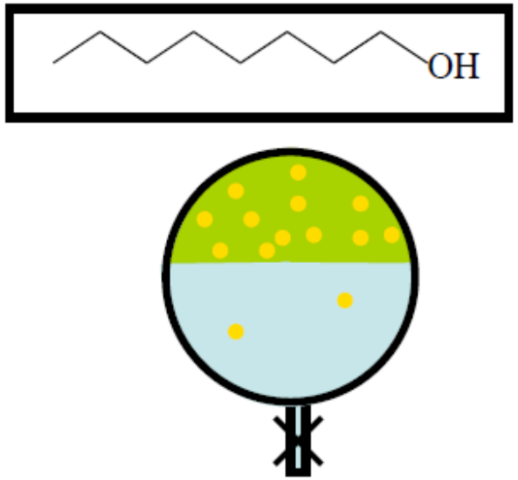
$$M_{aq} = M_{tot} \times \frac{1}{1 + R_{g/aq}} = M_{tot} \times \frac{V_{aq}}{V_{aq} + H_{cc} \times V_g}$$

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?

Octanol water partition coefficient

- ***n*-octanol, $C_8H_{17}OH$**
  - Surrogate for natural organic phases
    - Humics, DOC, lipids
  - Slightly soluble in water, $x_{i,sat} \sim 10^{-4}$
  - MW = 130.2; ρ = 0.826

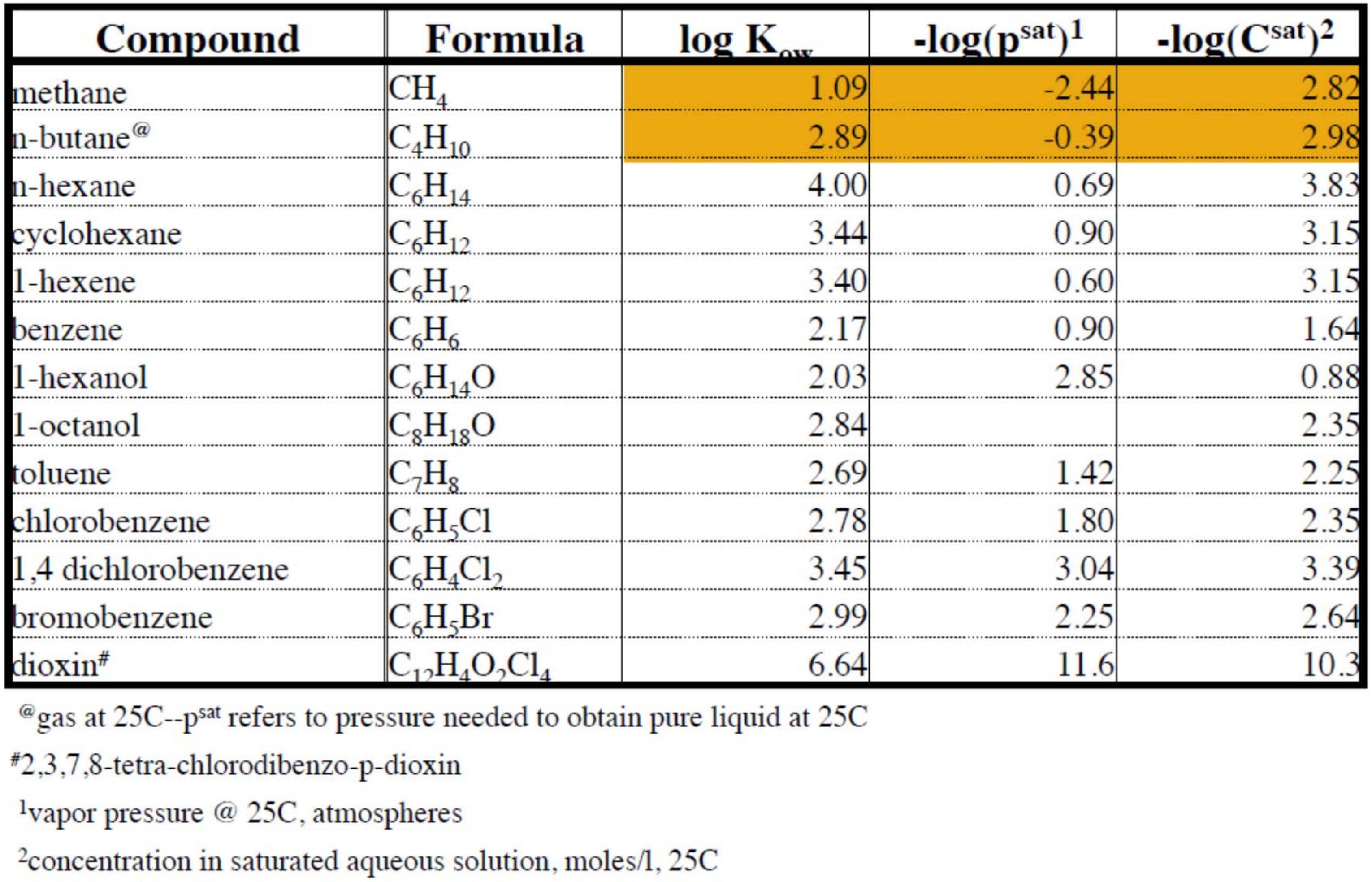


$$K_{ow} = \frac{C_i^{\,oct}}{C_i^{\,aq}} = 0.114\,\frac{x_i^{\,oct}}{x_i^{\,aq}}$$

x_i: mole fraction

C_i: molar concentration

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}

- **Partitioning to biota**
  - Octanol a surrogate for lipids, fats, etc.
    - Humans 10-30% lipids by weight, α
  - Bioconcentration factor (BCF) = C_{biota}/C_{aq}
    - C_{biota}: moles/kg (wet weight)
    - BCF not necessarily representative of equilibrium state
  - As a rough estimate, assume:

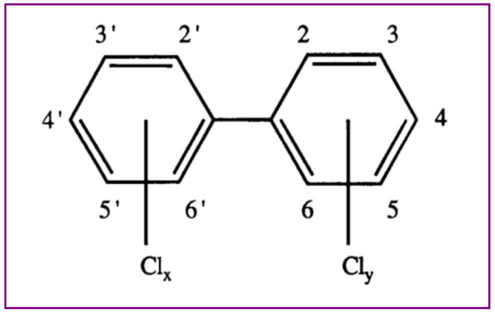
$$K_{biota,aq} = \frac{\alpha}{0.826} K_{ow}$$

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)**
  - $[\ ]_{organism}/[\ ]_{source}$
- **Bioconcentration factor (BCF)**
  - $[\ ]_{organism}/[\ ]_{water}$
- **Biomagnification factor**
  - $[\ ]_{\text{trophic “n+1”}}/[\ ]_{\text{trophic “n”}}$

Transport against hydraulic gradient

- Salmons concentrate PCBs (biovectors)



PCB molecular structure

Bioconcentration of 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

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

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

Hydrophobic contaminants in organisms

- **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
- **Assume lipids are equivalent to octanol**
  - $K_{lipid/water} = K_{ow}$
  - 1 kg lipid = 1 kg octanol
  - 1 liter lipid = 1 liter octanol
- **Uptake/depuration by organisms is a complex combination of processes**
  - Biota may not be in equilibrium with surroundings
  - Depuration: “cleansing”; transfer of contaminant from organism to surroundings

Using K_{ow}

- **Partitioning to soils, sediments**
  - Octanol as a surrogate for natural organic matter (NOM)
  - Neutral, hydrophobic contaminants partition much more strongly to the NOM fraction of soil than to mineral phases
    - Hydrophobic regions of NOM
    - Only mineral surfaces are accessible to contaminants
    - NOM typically dominates partitioning down to $f_{oc} \approx 0.5f_{nom}$ ~ 0.001

Water/sediment partitioning, K_d

$$K_d = f_{oc}K_{oc} = \frac{C_i^{solid}}{C_i^{aq}} \qquad \frac{g\ sorbed/g\ dry\ solid}{g\ aqueous/m^3\ water} = \frac{m^3\ water}{g\ dry\ solid}$$

- **K_{oc} & K_d have strange units, $vol_{aq}/mass_{solid}$**
  - Mass dry solid because:
    - Different soils/sediments have differing densities
    - Sorption experiments use weighed amount of solids
- **Researchers have expressed K_d as:**
  - m^3/g, mL/mg, L/g, L/kg, L/mg
  - Numerical value of K_d will depend on the units used
- **For contaminants, any mass, # units can be used as long as the same units are used for both phases**

Water/sediment partitioning, K_d

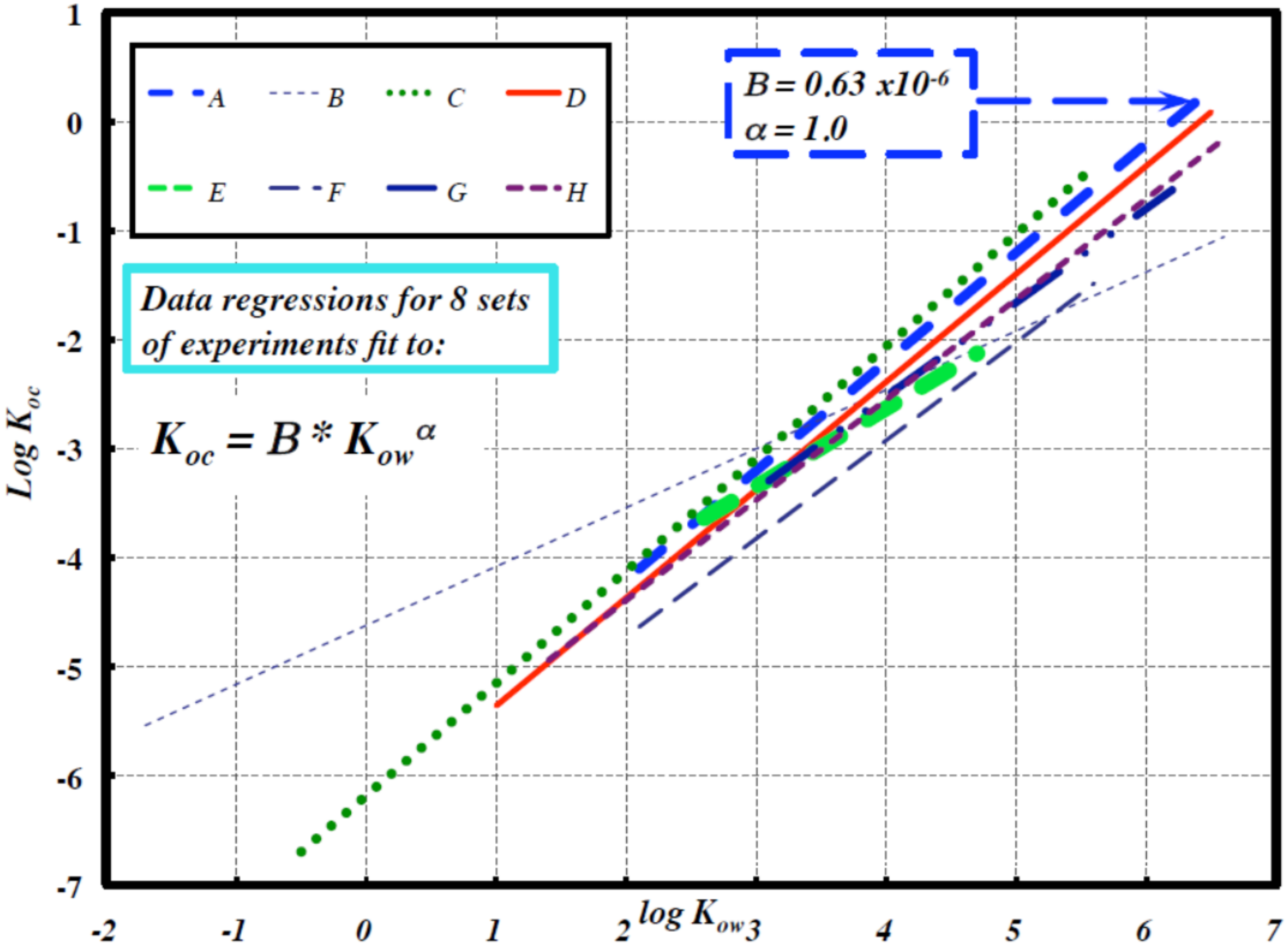
$$K_{oc} = \beta \times {K_{ow}}^{\alpha}$$

Ref.	# of compounds	Range of log K_{ow}	$\beta x 10^6$	α	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

Water/sediment partitioning, K_d



Data regressions for 8 sets of experiments fit to:

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

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

$\alpha = 1.0$

Phase equilibrium - fugacity

At equilibrium

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

(If pure phase exists)

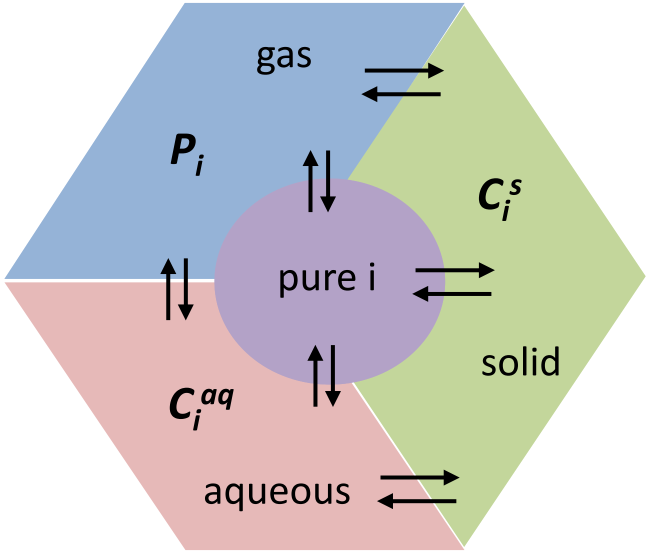
$$\mu_i^{eq} = \mu_i^{gas} = \mu_i^{s} = \mu_i^{aq}$$

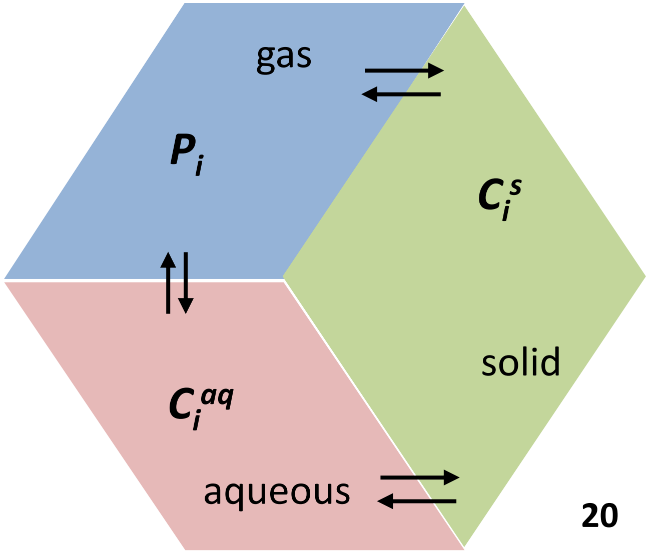
(If pure phase does not exists)

- μ is the chemical potential; it has units of energy – difficult to measure
- Chemical potential is related to activity

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

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





Phase equilibrium - fugacity

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

$$f_i{}^{gas} = f_i{}^{s} = f_i{}^{aq} = p_i \quad (= f_i{}^{pure}), \textit{ if pure phase exists}$$

- ***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
  - For volatile compounds
  - In dilute systems when partitioning is linear among different phases

Equilibrium partitioning between phases

- **Linear partitioning among phases: review our discussions**
  - Henry's law for gas/water partitioning (linear 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:

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

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

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

$$\vdots$$

  - In general,

$$C_i^{j} = K^{jk} \times C_i^{k}\ , \quad C_i^{k} = K^{kj} \times C_i^{j} = \left(1/K^{kj}\right) \times C_i^{j}$$

$$C_i^{j} = K^{jk} \times K^{kl} \times C_i^{l} = K^{jl} \times C_i^{l}$$

Applying fugacity approach

- **So:** if a system is at equilibrium and partitioning is linear, 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:**

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

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

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

(when $C_i{}^j$ are all expressed as moles/volume)

Z values for different phases

- **Gas phase**

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

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

- **Aqueous phase**

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

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

- **Octanol**

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

Z values for different phases

- **Solid phase**

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

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

K_d has a dimension of (vol. water) / (weight solid)

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

C_i^s is per volume basis

\- or, we may use:

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

$Z_i{}^{s*}$ has a unit of moles/atm/kg

\- then,

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

Applying fugacity approach

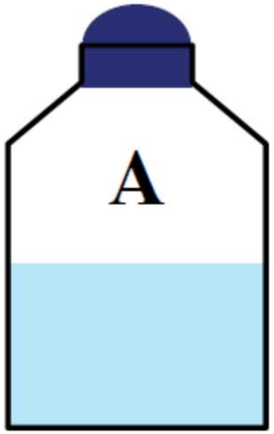
- **Our potential interest: how mass will be distributed among phases.**
- **Need:**
  - Compartment volumes or masses
  - Equilibrium constants (Henry's constant, K_{ow}, K_{oc}, etc.)

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

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

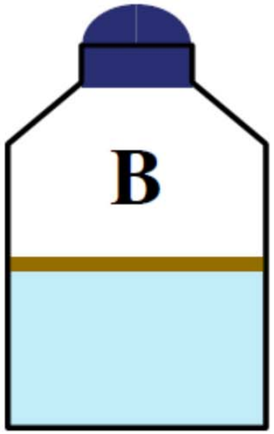
  - If we know $\boldsymbol{M_i^{total}}$, we can calculate f_i and then determine C_i^js and distributions among compartments
  - If we know $\boldsymbol{f}_i$, we can calculate M_i^{total} and then determine C_i^js and distributions among compartments

Determine equilibrium partitioning



500 ml air
500 ml water

1.000 liter bottles
25C
42.1 mg 1-hexene



490 ml air
20 ml octanol
490 ml water