Phase equilibrium I:
Air/water partitioning

Chemical equilibria – pure phase & water

Let's define H for chemical i:

$$i_{pure} \iff i_{aq,sat} \qquad H = \frac{\{i\}_{aq,sat}}{\{i\}_{pure}}$$

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

- For pure phase of chemical i, activity is defined as
  $\{i\}_{pure} = 1$ (liquid, solid)
  $\{i\}_{pure} = p_i$ (gas; p_i is pressure in atm)

- For a dilute aqueous solution
  $\{i\}_{aq} \approx [i]_{aq}$

- So: $\quad H \approx \dfrac{[i]_{aq,sat}}{p_i} \qquad$ or $\qquad [i]_{aq,sat}$

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

What's ideal behavior?

Individual molecule's properties (energy distribution, tendency to react, dissolve, vaporize, etc.) are **independent** of the presence and/or concentration of **any** other molecules in the phase
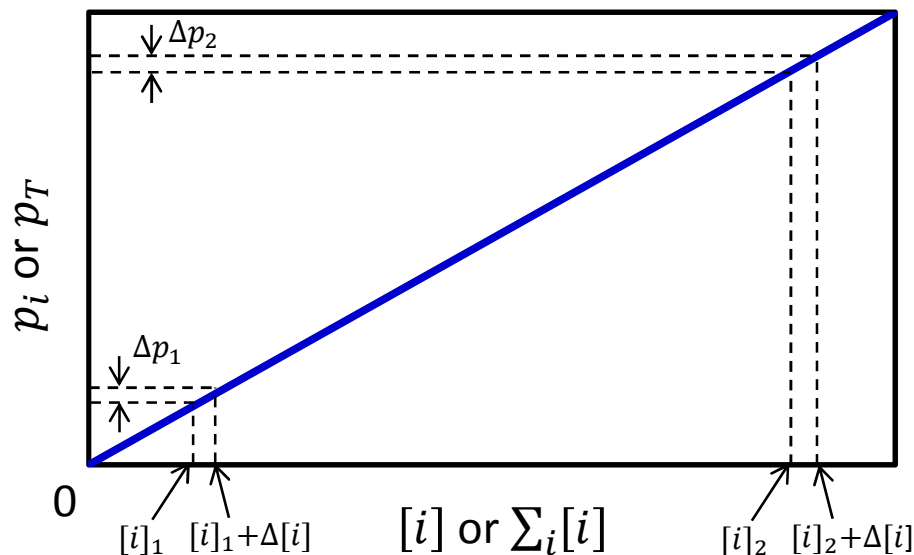
Do gas phase molecules behave ideally?

Ideal gas law:

$$Energy\ (E_T) = p_T V = n_T RT = RT \sum_i n_i$$

$$p_T = \frac{E_T}{V} = \frac{n_T}{V} RT = RT \sum_i \frac{n_i}{V} = RT \sum_i [i] = \sum_i p_i$$

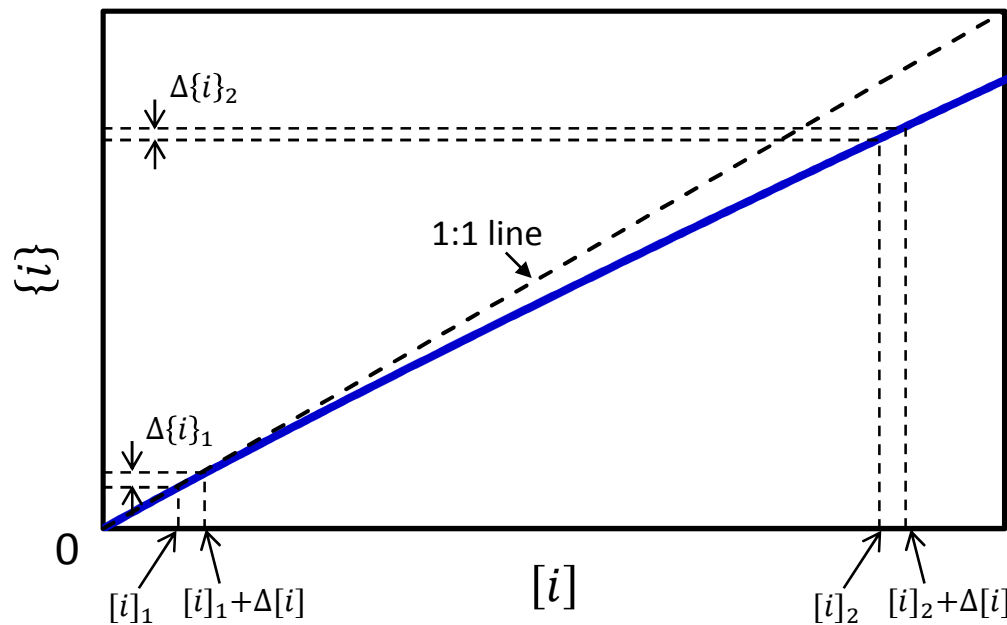If you start adding gas molecules to a void space, what will happen?

$\Delta p_1 = \Delta p_2$ *holds for any value of* $[i]_1$ *&* $[i]_2$

Do molecules dissolved in water behave ideally?

Note chemical potential $(\mu_i) \propto \ln \{i\}$ *for any given substance i in any phase*
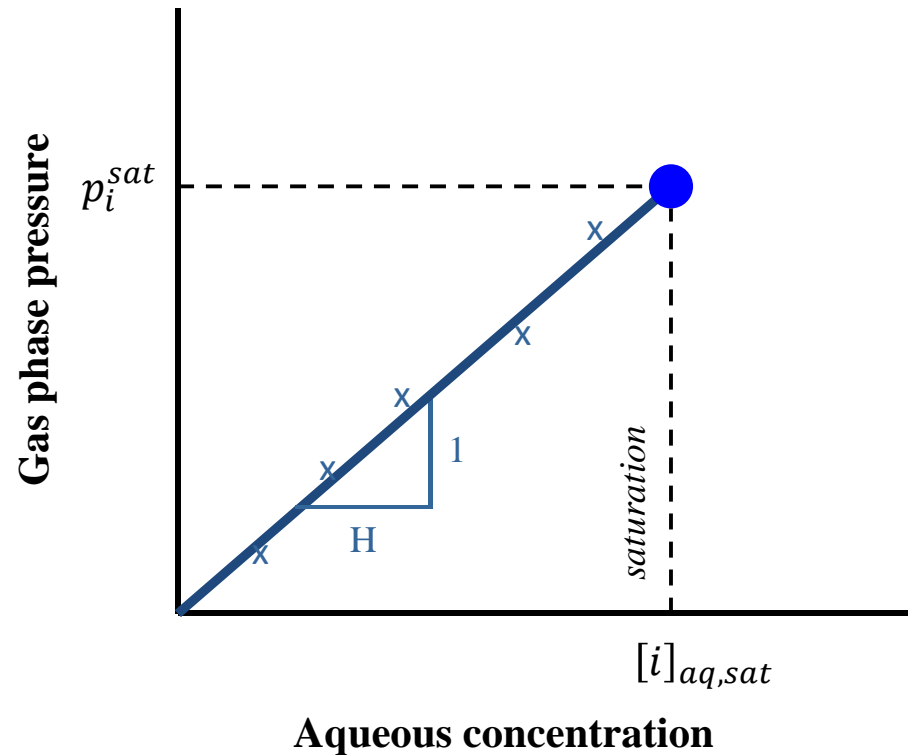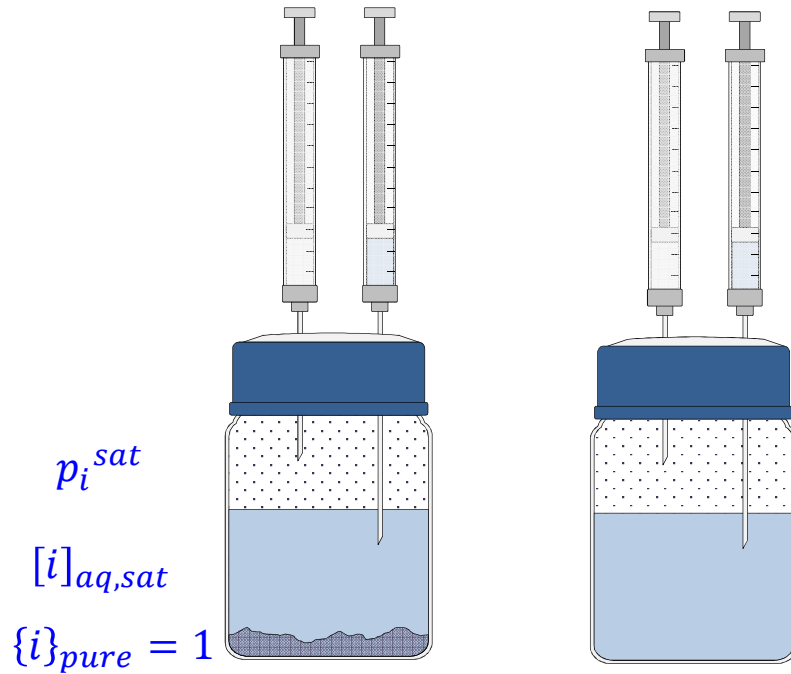
$\{i\}_{aq} \approx [i]_{aq}$ in dilute solutions, but $\{i\}_{aq} = \gamma_i [i]_{aq}$ in general

$\Delta\{i\}_1 \approx \Delta\{i\}_2$ *holds for dilute solutions; does not hold for concentrated solutions*

* This figure is drawn for A^+ or B^- in A^+B^- solution in pure water; $[i]$ range of 0-0.02 M is used; Güntelberg equation is used to calculate { } from [ ]

Air/water partitioning: Henry's law

p_i^{sat}

$[i]_{aq,sat}$

$\{i\}_{pure} = 1$

Gas phase pressure

p_i^{sat}

saturation

$[i]_{aq,sat}$

Aqueous concentration

* *Note we have* $H \approx \frac{[i]_{aq,sat}}{p_i}$

- **Linear partitioning because:**
  - Gas phase behaves ideally
  - Dissolved phase behaves ideally as long as dilute solution assumption is valid

Henry's constant

$$H_{-} = \frac{(\underline{\quad})_{air}}{(\underline{\quad})_{aq}}$$

- **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 $(\underline{\quad})_{aq}/(\underline{\quad})_{air}$

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

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

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

Henry's constants: unit conversions

$$H_{pc} = \frac{p_i}{[C_i]_{aq}}$$

because gas behaves ideally

$$\boldsymbol{H_{xy}} = \frac{x_i{}^g}{x_i{}^{aq}} = \frac{p_i/p_T}{[i]_{aq}/\sum_i [i]_{aq}} = \frac{p_i/p_T}{[i]_{aq}/[H_2O]_{aq}} = \frac{[\boldsymbol{H_2O}]_{\boldsymbol{aq}}}{\boldsymbol{p_T}} \times \boldsymbol{H_{pc}}$$

$[H_2O]_{aq} = 55.3\ M\ @\ 25\ ^oC$

$$p_i V = n_i RT$$

$$\boldsymbol{H_{cc}} = \frac{[i]_g}{[i]_{aq}} = \frac{(n_i/vol)_g}{[i]_{aq}} = \frac{p_i/RT}{[i]_{aq}} = \frac{\boldsymbol{1}}{\boldsymbol{RT}} \times \boldsymbol{H_{pc}}$$

R = ideal gas constant = 0.0821 L-atm/K-mol

@ 1 atm, 25°C, $H_{pc} = 0.01807 \times H_{xy} = 24.47 \times H_{cc}$

Vapor pressure & aqueous solubility

For selected organic chemicals of significant environ. interest (@ 25 ^{o}C, 1 atm)

Name	Formula	MW	Melting pt. (^{o}C)	Boiling pt. (^{o}C)	$-\log_{10}(p^{sat})$[1]	$-\log_{10}(C^{sat})$[1]
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
1,4-dichlorobenzene	$C_6H_4Cl_2$	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

[1] p^{sat} in atm; for chemicals in gas phase @ 25 ^{o}C, p^{sat} refers to p needed to obtain pure liquid @ 25 ^{o}C

[2] C^{sat} in mol/L   * 2,3,7,8-tetrachlorodibenzo-p-dioxin

p^{sat} = vapor pressure = gas pressure in equilibrium with the pure phase
    * if p^{sat} > 1 atm, the chemical exists in gas phase at 1 atm
C^{sat} = aqueous solubility = aqueous conc. in equilibrium with the pure phase

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Mass partitioning between air & water

Henry's constant   *Phase volumes*   *Masses (Moles)*

$$H_{cc} = \frac{[i]_g}{[i]_{aq}}$$

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

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

$$(M_T = M_g + M_{aq})$$

define
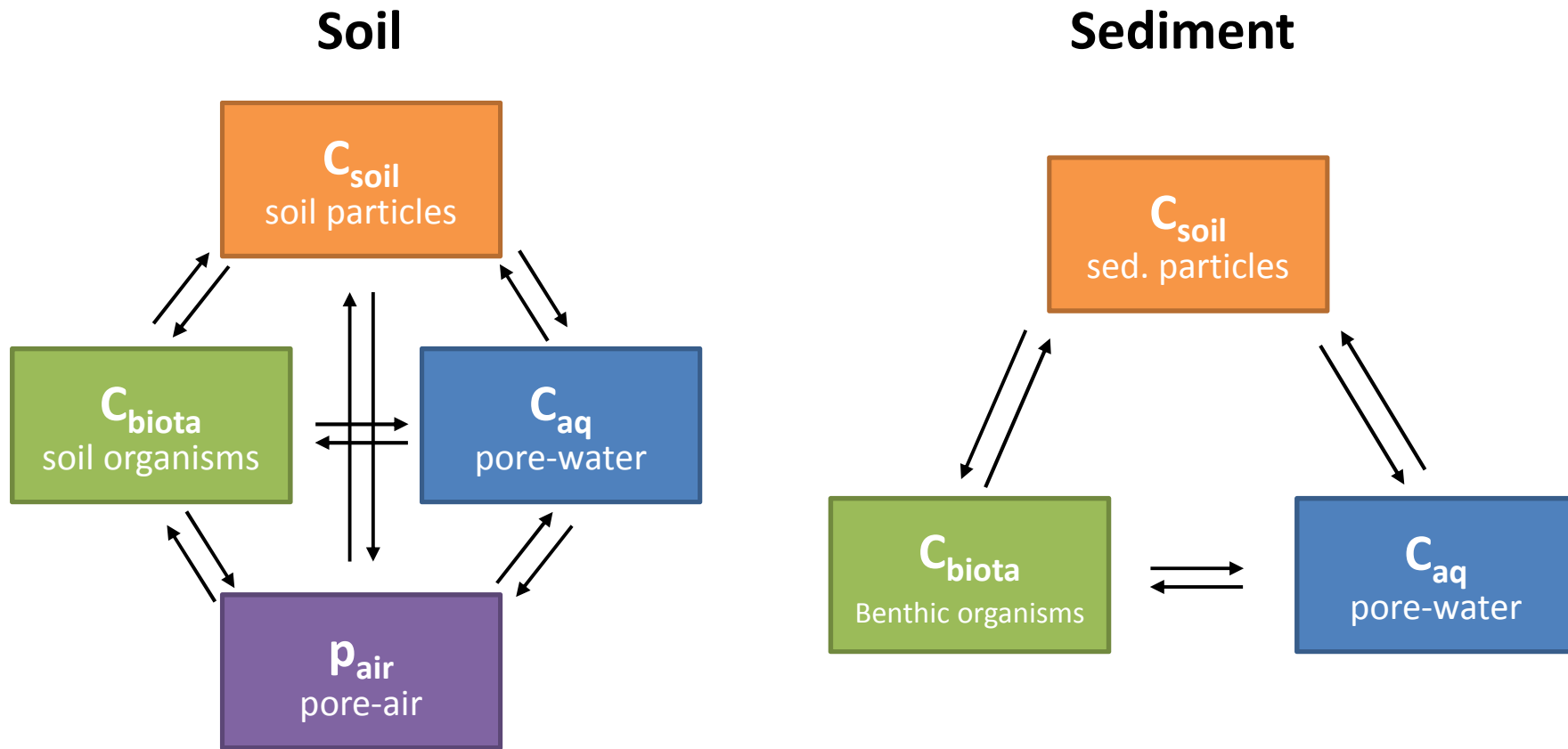
$$R_{g/aq} = \frac{M_g}{M_{aq}} = \frac{[i]_g \times V_g}{[i]_{aq} \times V_{aq}} = \frac{H_{cc} \times V_g}{V_{aq}}$$

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

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

Phase equilibrium II:
# Solid/water distribution

Additional phase - solid

Soil

Sediment

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

2

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

solid/water interface

absorption   **ad**sorption
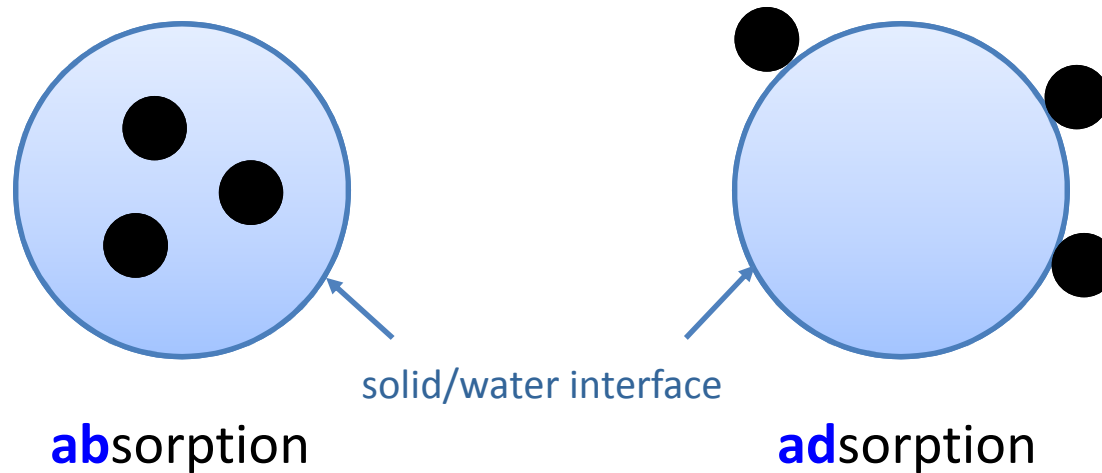
Sorption isotherms

- Isotherm – constant temp. & at thermodynamic equilibrium
- Various models to describe C_s vs. C_{air}, C_s vs. C_{aq} sorption isotherm
- Most frequently used sorption isotherms for C_s vs. C_{aq}
  - **Langmuir isotherm**
  - **Freundlich isotherm**

Langmuir isotherm

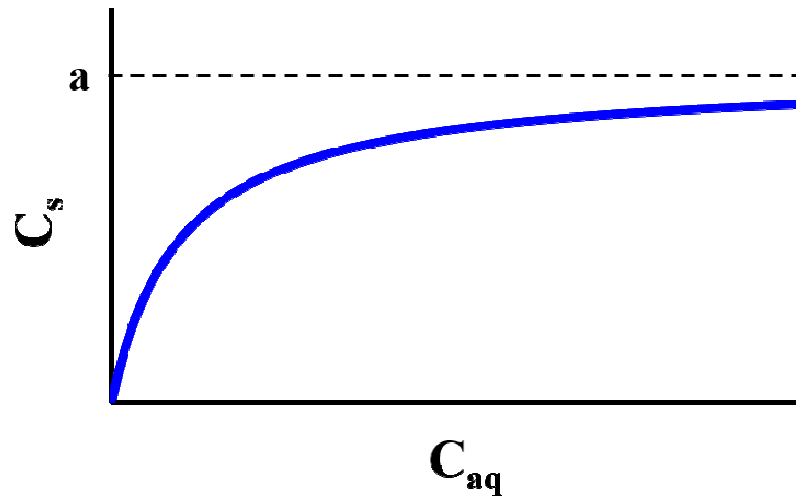**Assumptions**

- **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

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

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

[Langmuir constants]
  a represents sorption capacity
    [g sorbate/kg solid]
  *b represents the sorbate affinity **to a sorption site** of the sorbent [L water/g sorbate]*
  a×b represents the slope at $C_{aq} \rightarrow 0$

5

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 with greater complexity
  - ex) when multiple adsorption sites with different Langmuir constants co-exist in a sorbent; or when both adsorption & absorption occur
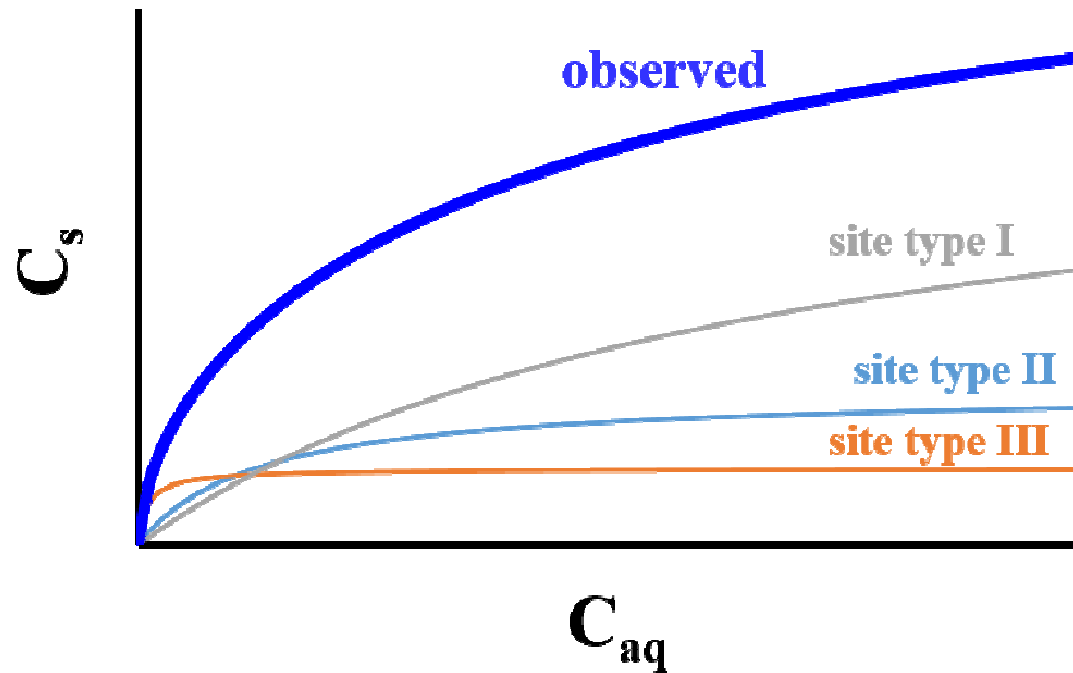
- **For the case of n=1 of Freundlich isotherm, we see linear relationship**

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

K_p = solid-water partition coefficient [L sorbate/kg solid]

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

6

Multiple Langmuir sites, Freundlich overall

observed
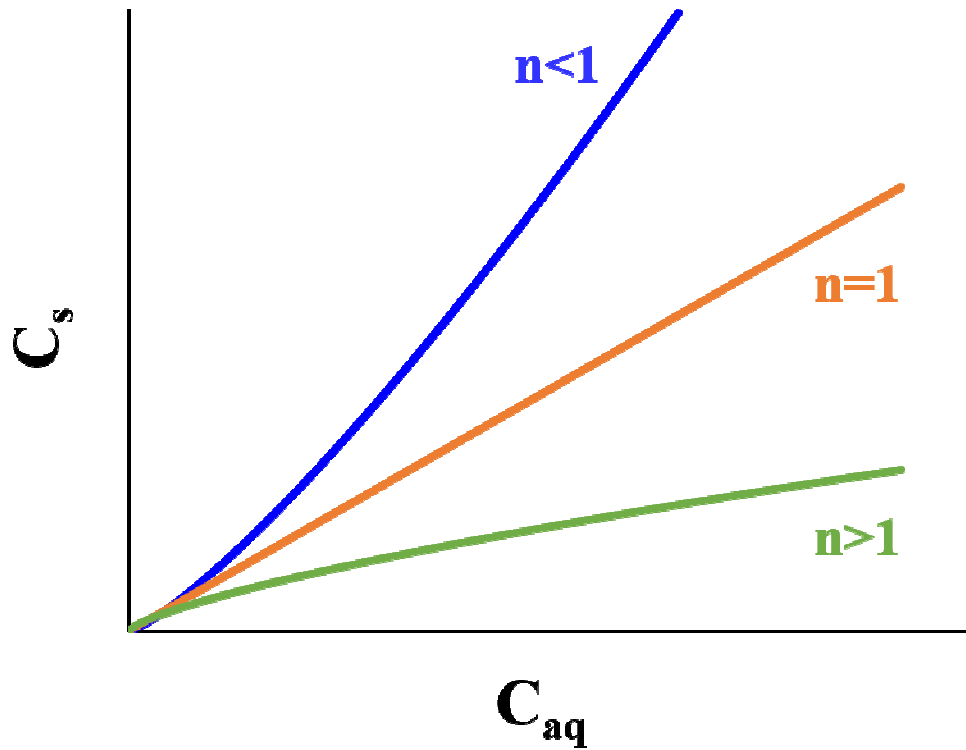
site type I

site type II

site type III

C_s

C_{aq}

Various types of sorption sites in a heterogeneous sorbent, all described by Langmuir but with different a's & b's

The sorption isotherm of the sorbent, which is the summed result of all types, may be represented by Freundlich (linear relationship b/w $\ln C_s$ & $\ln C_{aq}$)

observed

$\ln C_s$

$\ln C_{aq}$

7
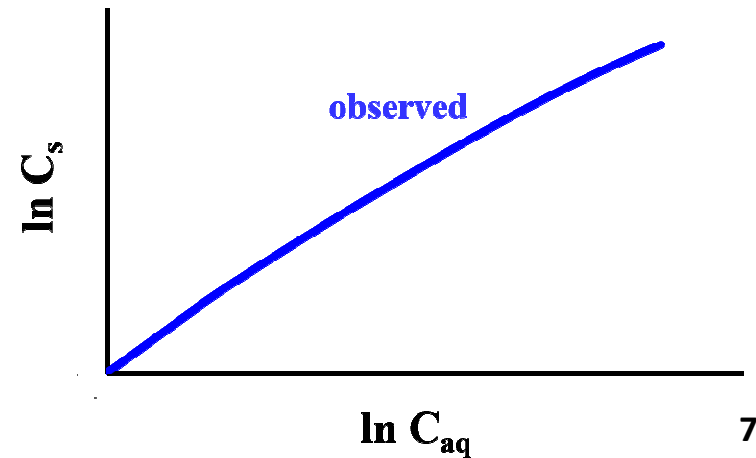
Freundlich isotherm: shapes

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

When is n<1 possible?
If *sorbate-sorbate interaction is stronger than sorbate-sorbent interaction*
→ *for a weak sorbent*

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

#1

- Salmons concentrate PCBs (biovectors)

#2

PCB molecular structure
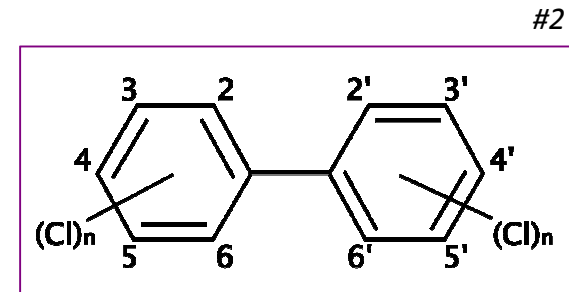
Bioconcentration of PCBs in Lake Ontario #3

PCB congener	microgram PCB per *		
	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

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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, $C_8H_{17}OH$**

  - Surrogate for natural organic phases
    - Soil/sediment organic matter (SOM), dissolved organic matter (DOM), lipids

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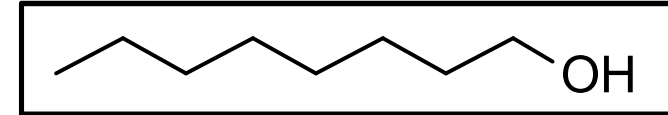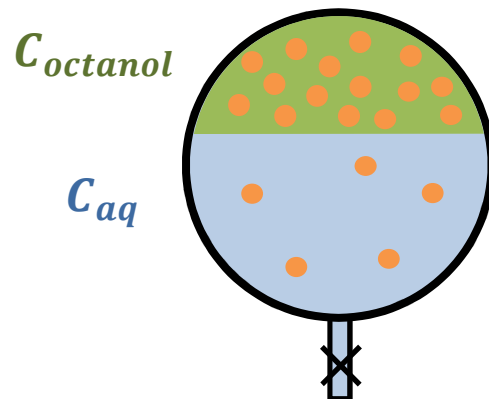
$$K_{ow} = \frac{C_{octanol}}{C_{aq}}$$

$C_{octanol}$ = concentration in octanol at equilibrium [g sorbate/L octanol]

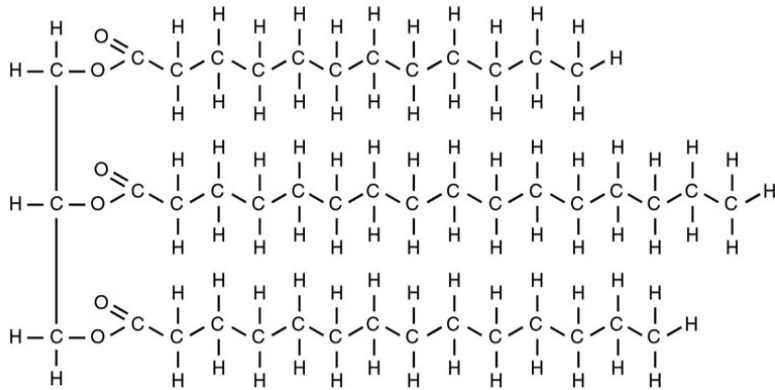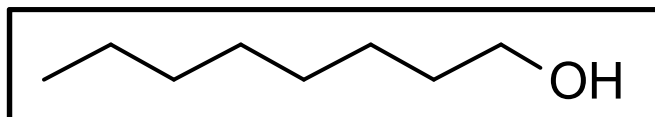*C_{aq} = concentration in water at equilibrium [g sorbate/L water]*

So, K_{ow} is unitless

$C_{octanol}$

C_{aq}

Lipid & humic substance examples

#4

fat molecule – example

#5

humic substance – example

cf) octanol

OH

14
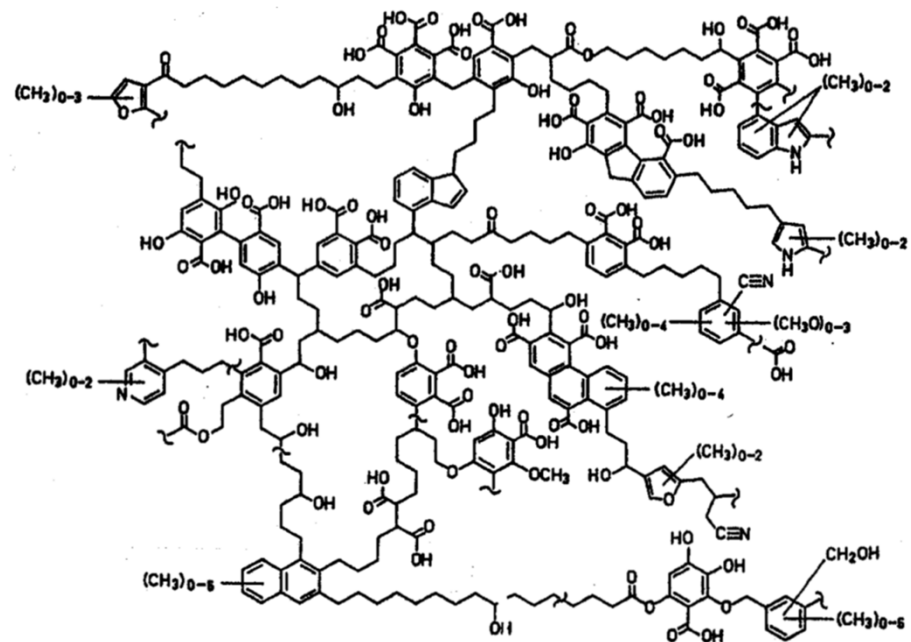
Vapor pressure, aq. solubility, & K_{ow}

Name	Formula	$\log_{10}K_{ow}$	$-\log_{10}(p^{sat})$	$-\log_{10}(C^{sat})$
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

[1] p^{sat} in atm; for chemicals in gas phase @ 25 °C, p^{sat} refers to p needed to obtain pure liquid @ 25 °C

[2] C^{sat} in mol/L

* 2,3,7,8-tetrachlorodibenzo-*p*-dioxin

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 -- α (α=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} has a unit of [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 partition 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}

$$K_{oc} = \beta \times K_{ow}{}^{\alpha} \qquad \text{or} \qquad logK_{oc} = log\beta + \alpha \cdot logK_{ow}$$

(K_{oc} in [L/kg])

Reference	# of compounds	Range of log K_{ow}	β	α	r[1]
Karickhoff et al., 1979	10	2.1~6.6	0.63	1.0	1.0
Kenaga & Goring, 1980	45	-1.7~6.6	24	0.54	0.93
Rao & Davidson, 1980	15	-0.5~5.6	0.66	1.03	0.95
Karickhoff, 1981	6	1.0~6.5	0.45	0.99	0.99
Schwarzenbach & Westall, 1981	12	2.6~4.7	3.1	0.72	0.97
Chio et al., 1983	12	2.1~5.6	0.3	0.90	0.99
Mingelgrin & Gerstl, 1983	7	3.1~6.2	1.1	0.87	0.85
Curtis et al., 1986	22	1.4~6.6	0.59	0.92	0.94

[1] coefficient of correlation

* Use "Karickhoff et al., 1979" for this class

References

#1) http://www.oceanlight.com/lightbox.php?x=brown_bear_catching_salmon__bear_behavior__bear__ mammal__animal

#2) https://en.wikipedia.org/wiki/Polychlorinated_biphenyl

#3) Oliver, B. G., Nilmi, A. J. (1988) Trophodynamic analysis of polychlorinated biphenyl congeners and other chlorinated hydrocarbons in the Lake Ontario ecosystem. Environmental Science & Technology, 22, 388-397.

#4) https://opentextbc.ca/anatomyandphysiology/chapter/24-4-lipid-metabolism

#5) Schulten, H. -R., Schnitzer, M. (1993) A state of the art structural concept of humic substances. Naturwissenschaften, 80, 29-30.

Phase equilibrium III:
Multi-phase equilibrium

Chemical potential

At equilibrium

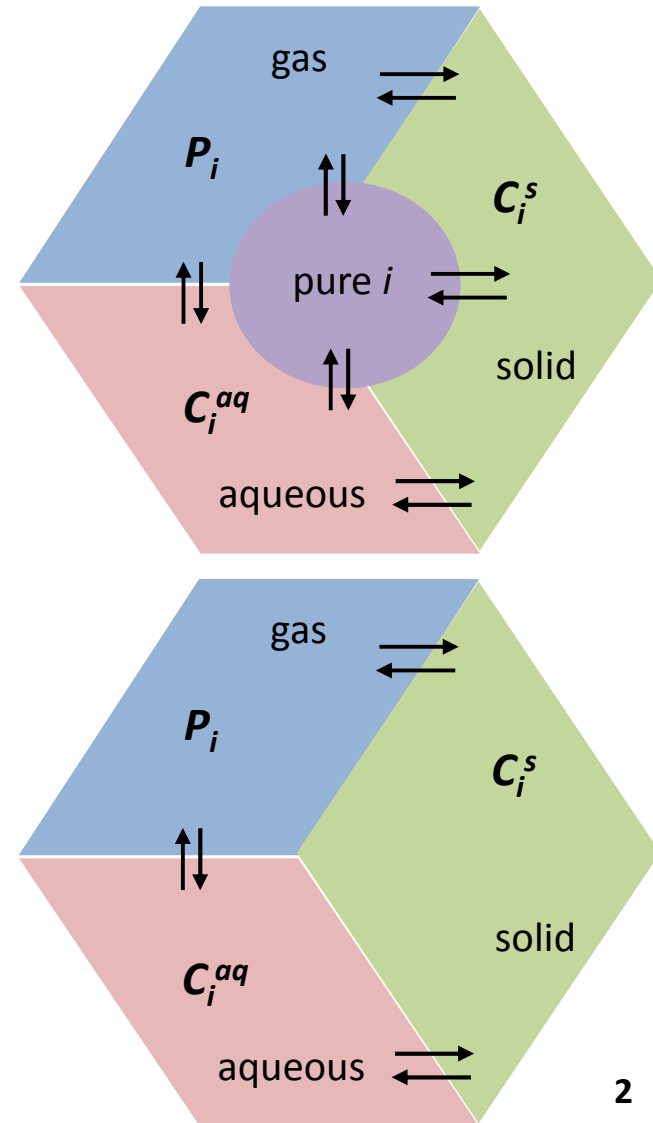$$\mu_i^{pure} = \mu_i^{gas} = \mu_i^{s} = \mu_i^{aq}$$

(If pure phase exists)

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

(If pure phase does not exist)

- μ is the <u>chemical potential</u>; it has an unit of energy – difficult to measure

- **Chemical potential is related to activity**

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

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

2

Fugacity – definition

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

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

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

in other words, $\boldsymbol{f_i^j = f_i = p_i}$ *for any phase* j

- ***Why use p_i?***
  - Pressure is comprehensible & measurable
  - Gas phase behaves ideally – a good reference
    - $p_i \propto \{i\}$ for any substance at any reasonable p_i

Fugacity approach…

- **Enables predicting multi-phase equilibrium partitioning in a minimally complex fashion**

- Is applicable **in dilute systems when partitioning is linear among different phases**; suited for volatile compounds

Equilibrium partitioning review

- **Gas/water partitioning: Henry's law**

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

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

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

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

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

$$\vdots$$

Here, * is used for concentrations given in per mass basis; otherwise concentrations are in per volume basis

Therefore we find:
$$C_i^{gas} = \boldsymbol{p_i} \times H_{cc}/H_{pc}$$
$$C_i^{aq} = \boldsymbol{p_i} \times 1/H_{pc}$$
$$C_i^{oct} = \boldsymbol{p_i} \times K_{ow}/H_{pc}$$
$$C_i^{biota*} = \boldsymbol{p_i} \times BCF/H_{pc}$$
$$C_i^{s*} = \boldsymbol{p_i} \times K_p/H_{pc}$$
$$\vdots$$

Applying fugacity approach

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

- **Now:** introduce ***Z value*** (<u>fugacity capacity factor</u>) to relate fugacity to concentration

- **Then:**

$$C_i^j = f_i Z_i^j$$

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

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

> *We find **Z** is in unit of e.g., [mol/m³-atm]*

Z values for different phases

Recall

$$C_i^{gas} = \boxed{p_i} \times \boxed{H_{cc}/H_{pc}} \qquad \Rightarrow \qquad Z_i^{gas} = \frac{H_{cc}}{H_{pc}} = \frac{1}{RT}$$

$$C_i^{aq} = \boxed{p_i} \times \boxed{1/H_{pc}} \qquad \Rightarrow \qquad Z_i^{aq} = \frac{1}{H_{pc}}$$

$$C_i^{oct} = \boxed{p_i} \times \boxed{K_{ow}/H_{pc}} \qquad \Rightarrow \qquad Z_i^{oct} = \frac{K_{ow}}{H_{pc}}$$

Z values for solid phase – caution needed!

Note that concentrations in solid phase are typically expressed in $moles_{compound}/mass_{solid}$ or $mass_{compound}/mass_{solid}$

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

C_i^{s*} per mass of solid (e.g., mol/kg)

K_p has a dimension of [(volume_water)/(mass_solid)] (e.g., m³/kg)

- to use per volume basis unit for concentrations in solid phase:

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

C_i^s per volume of solid (e.g., mol/m³)

ρ_s = solid density (e.g., kg/m³)

- alternatively, we may define **Z*** for solids:

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

Z_i^{s*} has a unit of e.g., mol/kg-atm

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

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.)

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

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

Phase equilibrium IV:
Exercise

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? If needed, use the following table.

Name	Formula	MW	Melting pt. (^{0}C)	Boiling pt. (^{0}C)	$-\log_{10}(p^{sat})^1$	$-\log_{10}(C^{sat})^1$
⋮	⋮	⋮	⋮	⋮	⋮	⋮
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] p^{sat} = vapor pressure @ 25 ^{0}C, in atm
[2] C^{sat} = aqueous solubility @ 25 ^{0}C, in mol/L

Mass partitioning between air & water

From our discussion, we understand:

$$H_{pc} = \frac{p^{sat}}{C^{sat}}$$

$$= \frac{10^{-0.60} \, atm}{10^{-3.15} \, mol/L} = 10^{2.55} \, L - atm/mol$$

$$H_{cc} = \frac{H_{pc}}{RT} = \frac{10^{2.55} \, L - atm/mol}{24.47 \, L - atm/mol} = 14.5$$

Recall that we have derived:

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

$$= \frac{14.5 \times 500 \, mL}{500 \, mL} = 14.5$$

3

$$M_g = M_T \times \frac{R_{g/aq}}{1 + R_{g/aq}}$$

$$= 42.1 \, mg \times \frac{14.5}{1 + 14.5} = \boldsymbol{39.4 \, mg}$$

$$M_{aq} = M_T \times \frac{1}{1 + R_{g/aq}}$$

$$= 42.1 \, mg \times \frac{1}{1 + 14.5} = \boldsymbol{2.7 \, mg}$$

Fugacity approach

Q: Let's work on a similar system as that for the previous example, but add an additional phase. A 1.000 L bottle is filled with 500.0 mL water and 20.0 mL octanol. How will 42.1 mg of 1-hexene added to the bottle partition among air, water, and octanol? Use the fugacity approach to answer. Calculate the 1-hexene fugacity (in atm) in the bottle.

     * 1-hexene $\log_{10}K_{ow}$ = 3.40

Fugacity approach

$$H_{pc} = 10^{2.55} \, L - atm/mol$$

$$K_{ow} = 10^{3.40}$$

Calculate Z values:

$$Z_{air} = \frac{1}{RT} = \frac{1}{(0.0821 \, L - atm/mol - K) \times 298 \, K}$$

$$= 0.0409 \, mol/L - atm$$

* for any substance @ 25 ⁰C & 1 atm, Z_{air} = 0.0409 mol/L-atm

$$Z_{water} = \frac{1}{H_{pc}} = \frac{1}{10^{2.55} \, L - atm/mol} = 2.82 \times 10^{-3} \, mol/L - atm$$

$$Z_{oct} = \frac{K_{ow}}{H_{pc}} = \frac{10^{3.40}}{10^{2.55} \, L - atm/mol} = 7.08 \, mol/L - atm$$

Now, construct a table as follows:

Phase (j)	Volume (V^j in L)	Z^j (mol/L-atm)	$Z^j \times V^j$ (mol/atm)	$Z^j \times V^j / \sum_j (Z^j \times V^j)$	mass (mg)
Air	0.480	0.0409	0.0196	0.120	**5.05**
Water	0.500	0.00282	0.00141	0.009	**0.36**
Octanol	0.020	7.08	0.142	0.871	**36.67**
Total			0.163	1.000	42.1

Recall $\quad Moles^{total} = f \sum_j (Z^j V^j)$

$$f = \frac{Moles^{total}}{\sum_j (Z^j V^j)} = \frac{(42.1 \; mg)/(84.2 \times 10^3 \; mg/mol)}{0.163 \; mol/atm}$$

$$= \mathbf{3.07 \times 10^{-3} \; atm}$$

Fugacity approach – treating a solid phase

Q: Let's keep working on a 1.000 L bottle filled with multiple phases. Now, suppose 500.0 mL water and 100.0 g sediment is added to the bottle, leaving 450.0 mL as headspace. The sediment has an organic carbon content (f_{oc}) of 0.05, and it can be safely assumed that 1-hexene sorbed only to the organic fraction of sediment. How will 42.1 mg of 1-hexene added to the bottle partition among air, water, and sediment? Use the fugacity approach to answer. Calculate the 1-hexene fugacity (in atm) in the bottle.

Use the following K_{oc}-K_{ow} relationship:

$$K_{oc} = 0.63 K_{ow}$$

Karickhoff et al. (1979); K_{oc} in L/kg

Fugacity approach – treating a solid phase

First, we need to obtain the sediment-water partition coefficient, K_p:

$$K_{oc} \ (in \ L/kg) = 0.63 K_{ow} = 0.63 \times 10^{3.40}$$

$$= 1580 \ L/kg$$

$$K_p = f_{oc} K_{oc} = 0.05 \times 1580 \ L/kg$$

$$= 79.0 \ L/kg$$

Now, let's get $Z_{sed}{}^*$:

$$Z_{sed}{}^* = \frac{K_p}{H_{pc}} = \frac{79.0 \ L/kg}{10^{2.55} \ L-atm/mol} = 0.223 \ mol/kg - atm$$

We already know Z values for air and water:

$$Z_{air} = 0.0409 \ mol/L - atm, \qquad Z_{water} = 2.82 \times 10^{-3} \ mol/L - atm$$

The remaining procedure is the same as that for the previous question.

Phase (*j*)	Volume or mass (V^j in L; M^j in kg)	Z^j or Z^{j*} (mol/L-atm)	$Z^j \times V^j$ or $Z^{j*} \times M^j$ (mol/atm)	$Z^j \times V^j / \sum_j (Z^j \times V^j)$	mass (mg)
Air	0.450	0.0409	0.0184	0.437	**18.4**
Water	0.500	0.00282	0.00141	0.033	**1.4**
Sediment	0.100	0.223	0.0223	0.530	**22.3**
Total			0.0421	1.000	42.1

$$f = \frac{Moles^{total}}{\sum_j (Z^j V^j)} = \frac{(42.1\ mg)/(84.2 \times 10^3\ mg/mol)}{0.0421\ mol/atm}$$

$$= \mathbf{1.19 \times 10^{-2}\ atm}$$