# Phase equilibrium I & II

### I. Air/water partitioning

- "Ideal" behavior
- Henry's law
- Mass partitioning between air & water

#### **II. Solid/water distribution**

- Sorption
- Sorption isotherms
- Octanol-water partition coefficient, K<sub>ow</sub>

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
- $\begin{array}{l} \ \mbox{For pure phase of chemical } i, \mbox{ activity is defined as} \\ \{i\}_{pure} = 1 \quad (\mbox{liquid, solid}) \\ \{i\}_{pure} = p_i \quad (\mbox{gas}; p_i \mbox{ is pressure in atm}) \end{array}$
- For a dilute aqueous solution

$$\{i\}_{aq}\approx [i]_{aq}$$

- So: 
$$H \approx \frac{[i]_{aq,sat}}{p_i}$$
 or  $[i]_{aq,sat}$ 
(gas as pure phase) (liquid or solid as pure phase)

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

### 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?



### 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



\* This figure is drawn for A<sup>+</sup> or B<sup>-</sup> in A<sup>+</sup>B<sup>-</sup> 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



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

### Henry's constant

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

# • 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  $(\_)_{aq}/(\_)_{air}$

$$H_{xy} = \frac{x_g}{x_{aq}} = \frac{mole \ fraction_g}{mole \ fraction_{aq}}$$
$$H_{cc} = \frac{moles/vol_g}{moles/vol_{aq}} = \frac{p_i}{[i]_{aq} \times RT}$$
$$H_{pc} = \frac{p_i}{[i]_{aq}}, \qquad \frac{l-atm}{mole}$$

### Henry's constants: unit conversions

$$H_{pc} = \frac{p_i}{[C_i]_{aq}}$$
 because gas behaves ideally  

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

$$[H_2O]_{aq} = 55.3 M @ 25 °C$$

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

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

Name	Formula	MW	Melting pt. (°C)	Boiling pt. (°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	$C_{4}H_{10}$	58.1	-138.4	-0.4	-0.39	2.98
n-hexane	C <sub>6</sub> H <sub>14</sub>	86.2	-95.0	69.0	0.69	3.83
cyclohexane	C <sub>6</sub> H <sub>12</sub>	84.2	6.6	80.7	0.90	3.15
1-hexene	C <sub>6</sub> H <sub>12</sub>	84.2	-139.8	63.4	0.60	3.15
benzene	C <sub>6</sub> H <sub>6</sub>	78.1	5.5	80.1	0.90	1.64
1-hexanol	C <sub>6</sub> H <sub>14</sub> O	102.2	-46.7	158.0	2.85	0.88
1-octanol	C <sub>8</sub> H <sub>18</sub> O	130.2	-16.7	194.4		2.35
toluene	C <sub>7</sub> H <sub>8</sub>	92.1	-95.0	110.6	1.42	2.25
chlorobenzene	C <sub>6</sub> H <sub>5</sub> Cl	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 <sub>6</sub> H <sub>5</sub> Br	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

#### For selected organic chemicals of significant environ. interest (@ 25 °C, 1 atm)

<sup>1</sup> p<sup>sat</sup> in atm; for chemicals in gas phase @ 25 °C, p<sup>sat</sup> refers to p needed to obtain pure liquid @ 25 °C <sup>2</sup> C<sup>sat</sup> in mol/L \* 2.2.7.8 totrachlorodibanzo n diaxin

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

p<sup>sat</sup> = vapor pressure = gas pressure in equilibrium with the pure phase

\* if p<sup>sat</sup> > 1 atm, the chemical exists in gas phase at 1 atm

C<sup>sat</sup> = aqueous solubility = aqueous conc. in equilibrium with the pure phase

### Mass partitioning between air & water

Henry's constantPhase volumesMasses (Moles) $H_{cc} = \frac{[i]_g}{[i]_{aq}}$  $V_g, V_{aq}$  $M_g, M_{aq}$  $(M_T = M_g + M_{aq})$  $(M_T = M_g + M_{aq})$ 

define

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

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

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

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Phase equilibrium II: Solid/water distribution

# Additional phase - solid



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

### 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"
- <u>adsorption vs.</u> <u>absorption</u>
  - on the surface vs. in the entire volume of the sorbent



# **Sorption isotherms**

- Isotherm constant temp. & at thermodynamic equilibrium
- Various models to describe C<sub>s</sub> vs. C<sub>air</sub>, C<sub>s</sub> vs. C<sub>aq</sub> sorption isotherm
- Most frequently used sorption isotherms for C<sub>s</sub> vs. C<sub>aq</sub>
  - Langmuir isotherm
  - Freundlich isotherm

# Langmuir isotherm

#### Assumptions

- <u>Ad</u>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<sub>s</sub> = concentration in solid at equilibrium [g adsorbate/kg solid] C<sub>aq</sub> = concentration in water at equilibrium [g adsorbate/L water] a, b = Langmuir constants



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

# Langmuir isotherm – derivation



- Assume this reaction has a constant standard free energy change for all adsorption sites,  $\Delta G^0_{ads}$
- Recall:  $\Delta_r G^0 = -RTln(K)$

$$K_{ads} = \frac{SA}{S_V C_{aq}} = exp(-\Delta G_{ads}^0/RT)$$

- $S_V$  = surface concentration of vacant adsorption sites at equilibrium [mol sites/m<sup>2</sup> solid]
- SA = surface concentration of adsorption sites occupied with adsorbate at equilibrium [mol sites/m<sup>2</sup> solid]

Surface concentration of all adsorption sites,  $S_T$  [mol sites/m<sup>2</sup> solid]

$$S_T = S_V + SA = \frac{SA}{K_{ads}C_{aq}} + SA$$

Solving for *SA*:

$$SA = \frac{S_T}{1 + 1/(K_{ads}C_{aq})} = \frac{K_{ads}C_{aq}S_T}{1 + K_{ads}C_{aq}}$$

Concentration in solid at equilibrium,  $C_s$  [g adsorbate/kg solid]

$$C_s = SA \cdot A_s \cdot MW$$

A<sub>s</sub> = specific surface area of solid [m<sup>2</sup> solid/kg solid] MW = molecular weight of adsorbate [g adsorbate/mol adsorbate]

$$C_{s} = \frac{K_{ads}C_{aq}S_{T}A_{s}MW}{1 + K_{ads}C_{aq}}$$
$$= \frac{C_{s,max}K_{ads}C_{aq}}{1 + K_{ads}C_{aq}}$$

By comparison with slide#16 we confirm:

- $a = C_{s,max}$  represents sorption capacity [g adsorbate/kg solid]
- b = K<sub>ads</sub> represents the sorbate affinity to an adsorption site
   of the sorbent [L water/g adsorbate]

# BET (Brunauer-Emmett-Teller) isotherm

- Theoretically derived assuming multi-layer adsorption
- Assume the Langmuir isotherm applies to the first layer
  - With standard free energy change of  $\Delta G_{ads}^0$
- The Langmuir isotherm applies to the 2<sup>nd</sup>, 3<sup>rd</sup>, 4<sup>th</sup>, ... layers as well, but now the free energy change is different
  - Standard free energy of precipitation,  $\Delta G_{prec}^{0}$



Langmuir isotherm: 
$$\frac{C_s}{C_{s,max}} = \frac{K_{ads}C_{aq}}{1 + K_{ads}C_{aq}}$$

BET isotherm:  

$$\frac{C_s}{C_{s,max}} = \frac{B \cdot C_{aq}}{(C_{aq,sat} - C_{aq}) [1 + (B - 1) (C_{aq} / C_{aq,sat})]}$$



where 
$$B = \frac{K_{1,ads}}{K_{2,ads}} = \frac{exp(-\Delta G_{ads}^0)}{exp(-\Delta G_{prec}^0)}$$

C<sub>s,max</sub>= maximum concentration in solid when only monolayer adsorption is possible [g adsorbent/kg solid] C<sub>aq,sat</sub> = saturated concentration in water [g adsorate/L water]

# **Freundlich isotherm**

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

K<sub>F</sub> = Freundlich sorption coefficient
 [(g sorbate/kg solid)·(L water/g sorbate)<sup>-1/n</sup>]
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

### Multiple Langmuir sites, Freundlich overall



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  $\ln C_s \& \ln C_{aq}$ )



### Freundlich isotherm: shapes

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



#### When is n<1 possible? If <u>sorbate-sorbate</u> interaction is stronger than <u>sorbate-sorbent</u> 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<sub>aq</sub> 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<sub>biota</sub>/C<sub>source</sub>
- Bioconcentration factor (BCF)

 $- C_{biota}/C_{aq}$ 

• Biomagnification factor

$$- C_{biota}$$
"<sup>n+1</sup>"/ $C_{biota}$ "<sup>n</sup>

# Transport against hydraulic gradient



• Salmons concentrate PCBs (biovectors)

#### **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	



#### PCB molecular structure

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

# 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  $f_{oc} \simeq 0.001$

f<sub>oc</sub> = organic carbon fraction in soil or sediment [g organic carbon/g soil or sediment]

# **Octanol water partition coefficient**

- *n*-octanol, C<sub>8</sub>H<sub>17</sub>OH
  - Surrogate for natural organic phases
    - Soil/sediment organic matter (SOM), dissolved organic matter (DOM), lipids



Octanol-water partition coefficient, K<sub>ow</sub>

$$K_{ow} = \frac{C_{octanol}}{C_{aa}}$$

 $V_{V} = \frac{C_{aq}}{C_{aq}}$   $C_{octanol} = con$ 



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

So, <u>K<sub>ow</sub> is unitless</u>

# Lipid & humic substance examples



*humic substance – example* 

cf) octanol



# Vapor pressure, aq. solubility, & K<sub>ow</sub>

Name	Formula	$log_{10}K_{ow}$	-log <sub>10</sub> (p <sup>sat</sup> )	-log <sub>10</sub> (C <sup>sat</sup> )
methane	$CH_4$	1.09	-2.44	2.82
n-butane	$C_4H_{10}$	2.89	-0.39	2.98
n-hexane	$C_{6}H_{14}$	4.00	0.69	3.83
cyclohexane	C <sub>6</sub> H <sub>12</sub>	3.44	0.90	3.15
1-hexene	C <sub>6</sub> H <sub>12</sub>	3.40	0.60	3.15
benzene	$C_6H_6$	2.17	0.90	1.64
1-hexanol	C <sub>6</sub> H <sub>14</sub> O	2.03	2.85	0.88
1-octanol	C <sub>8</sub> H <sub>18</sub> O	2.84		2.35
toluene	C <sub>7</sub> H <sub>8</sub>	2.69	1.42	2.25
chlorobenzene	C <sub>6</sub> H <sub>5</sub> Cl	2.78	1.80	2.35
1,4-dichlorobenzene	$C_6H_4Cl_2$	3.45	3.04	3.39
bromobenzene	C <sub>6</sub> H <sub>5</sub> Br	2.99	2.25	2.64
dioxin*	$C_{12}H_4O_2Cl_4$	6.64	11.6	10.3

<sup>1</sup> p<sup>sat</sup> in atm; for chemicals in gas phase @ 25 °C, p<sup>sat</sup> refers to p needed to obtain pure liquid @ 25 °C

# Using Kow: HOC partitioning to biota

- Bioconcentration factor (BCF) =  $C_{biota}/C_{aq}$ 
  - C<sub>biota</sub> 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<sub>ow</sub> has a unit of [L water/L octanol]

# Using K<sub>ow</sub>: HOC partitioning to soil/sediment

• As NOM dominates sorption for HOCs,

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

- Various units of K<sub>p</sub> & K<sub>oc</sub> can be used:
  - volume of water / dry weight of solid
  - m<sup>3</sup>/g, mL/mg, L/g, L/kg, L/mg, ...
  - Numerical value will depend on the units used
- Use K<sub>ow</sub> to predict K<sub>oc</sub>
  - $K_{ow}$ - $K_{oc}$  relationship needed!
  - Note K<sub>oc</sub> range of ~2 orders of magnitude for a single compound has been reported
  - Use caution when using K<sub>oc</sub> without experimental determination

# Organic carbon/water partitioning, K<sub>oc</sub>

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

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

Reference	# of compounds	Range of log K <sub>ow</sub>	β	α	r <sup>1</sup>
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

<sup>1</sup> coefficient of correlation

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