

## Lesson 1:

### Charge balance: (electro neutrality equation)

$$\sum_i^n z[C_i^{z+}] = \sum_i^n z[C_i^{z-}]$$

\*Charge balance is written in terms of Molar concentrations

### Mass balance:

$$TOTSO_4 = 10^{-3} = [H_2SO_4] + [HSO_4^-] + [SO_4^{2-}]$$

Standard T = 25 C, 298.15 K

Standard concentration is 1 M

Standard pressure is 1 atm

$$R = 8.31 \text{ J/mol-K} = 0.082 \text{ L-atm/mol-K} = 0.001986 \text{ kcal/mol-K}$$

$$\Delta G^\circ = \sum \nu \Delta G^\circ_{f \text{ products}} - \sum \nu \Delta G^\circ_{f \text{ reactants}}$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G^\circ = -RT \ln K$$

$$K = \exp(-\Delta G^\circ / (R \cdot T))$$

Q = K at equilibrium

Q/K < 1, ΔG negative, reaction forward

Q/K > 1, ΔG positive, reaction reverse

Q/K = 1, ΔG = 0, at equilibrium

Molecular weight = sum of atomic weights for a molecule, g/mol

$$\text{Density water} = 1 \frac{g}{ml} = 1 \frac{kg}{l} = 0.9982 \frac{g}{ml}$$

$$\text{Ppm} = \frac{mg \text{ solute}}{L \text{ water}} = \frac{mg \text{ solute}}{kg \text{ water}}$$

$$\text{Ppm} = \frac{\mu g \text{ solute}}{L \text{ water}}$$

### **\*\* Normality to Molarity:**

If you know the Molarity of an acid or base solution, you can easily convert it to Normality by multiplying Molarity by the number of hydrogen (or hydroxide) ions in the acid (or base). For example, a 2 M H<sub>2</sub>SO<sub>4</sub> solution will have a Normality of 4N (2 M x 2 hydrogen ions)

\*CO<sub>2</sub>(aq) is also referred to as H<sub>2</sub>CO<sub>3</sub>\*(aq),

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## Lesson 2:

**STRONG ACID:** Complete dissociation at environmental pH (5-9)

(HCl, HNO<sub>3</sub>, HNO<sub>2</sub>, HBr, H<sub>2</sub>SO<sub>4</sub>)

**STRONG BASE:** Complete dissociation (NaOH, KOH)

1. The equilibrium equations are in terms of activity. To account for ionic strength, you need to use the concentration-based equilibrium constant <sup>c</sup>K.
2. Mass balances are in terms of concentrations, not activity.
3. Charge balances are in terms of concentrations, not activity.

\*Special point: Where {HA} = {A<sup>-</sup>} (derivation of the Henderson-Hasselbach equation)

- Henderson-Hasselbach equation:

$$PH = PK_a + \log \frac{\{A^-\}}{\{HA\}}$$

**Remember:** K<sub>a</sub> tells us the pH where {HA} = {A<sup>-</sup>}

K<sub>a</sub> indicates the strength of the acid or base

STRONG ACID: Complete dissociation at environmental pH (5-9)

(HCl, HNO<sub>3</sub>, HNO<sub>2</sub>, HBr, H<sub>2</sub>SO<sub>4</sub>)

WEAK ACID: Partial dissociation

STRONG BASE: Complete dissociation (NaOH, KOH)

**Ionization fraction  $\alpha$**  = fraction of total species present as a certain species

For a monoprotic acid:

$$\alpha_1 = \frac{K_a}{[H^+] + K_a} = \frac{[A^-]}{Tot A}$$

$$\alpha_0 = \frac{[H^+]}{[H^+] + K_a} = \frac{[HA]}{Tot A}$$

$$\alpha_0 + \alpha_1 = 1$$

For a diprotic acid:

$$\alpha_0 = \frac{[H^+]^2}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

$$\alpha_1 = \frac{K_{a1}[H^+]}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

$$\alpha_2 = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

$$\alpha_0 + \alpha_1 + \alpha_2 = 1$$

### Properties of $\alpha$

$\alpha_0 = 1, \alpha_1 = 0$  when  $[HA] \gg [A^-]$

$\alpha_0 = \alpha_1 = 0.5$  when  $[HA] = [A^-]$

$\alpha_0 = 0, \alpha_1 = 1$  when  $[HA] \ll [A^-]$

**Buffer Capacity:**

$\beta$  = moles/liter of strong acid or strong base added to a solution to cause a unit change in pH

$$\beta = \frac{\Delta C_B}{\Delta \text{pH}} = - \frac{\Delta C_A}{\Delta \text{pH}}$$

$$\beta = \frac{dC_B}{d\text{pH}} = - \frac{dC_A}{d\text{pH}}$$

Maximum buffer capacity,  $\beta_{\text{max}}$ , occurs when  $\text{pH} = \text{pK}_a$

Here,  $a_0 = a_1 = 0.5$

$$\beta_{\text{HA}} = 2.3(0.5)(0.5)C_{\text{T,A}} = 0.575C_{\text{T,A}}$$

The ionization fractions =  $f(\text{pH}, K_a)$ , and  $K_a$  is influenced by ionic strength

If we must account for ionic strength effects, use  ${}^cK_a$  instead of  $K_a$  in a.

Derive  ${}^cK_a$

When a conjugate base of a weak acid,  $A^-$ , is added as a salt to solution ( $\text{NaA}$ ), the salt will completely dissociate to  $\text{Na}^+$  and  $A^-$ . Some  $A^-$  will then acquire an  $\text{H}^+$  from water and form some  $\text{HA}$ .

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### Lesson 3

$$K_H = \frac{C(aq)}{C(g)} = \frac{M}{atm}$$

$$K_H = \frac{H}{RT} =$$

Closed system
<p>If TOTCO<sub>3</sub> is added as H<sub>2</sub>CO<sub>3</sub>*</p> <p>Assume: PH is acidic [H<sup>+</sup>] &gt;&gt; [OH<sup>-</sup>]</p> <p>Cb: [H<sup>+</sup>] = [OH<sup>-</sup>] + [HCO<sup>-</sup>] + 2[CO<sub>3</sub><sup>2-</sup>]</p>
<p>If TOTCO<sub>3</sub> is added as NaHCO<sub>3</sub></p> <p>Cb: [Na<sup>+</sup>] + [H<sup>+</sup>] = [OH<sup>-</sup>] + [HCO<sup>-</sup>] + 2[CO<sub>3</sub><sup>2-</sup>]</p> <p>TOT-Na = TOT-CO<sub>3</sub></p>
<p>If TOTCO<sub>3</sub> is added as Na<sub>2</sub>CO<sub>3</sub></p> <p>Cb: [Na<sup>+</sup>] + [H<sup>+</sup>] = [OH<sup>-</sup>] + [HCO<sup>-</sup>] + 2[CO<sub>3</sub><sup>2-</sup>]</p> <p>TOT-Na = 2 * TOT-CO<sub>3</sub></p>

Closed system	Open system
<p>If TOTCO<sub>3</sub> is added as H<sub>2</sub>CO<sub>3</sub>*</p> <p>Assume: PH is acidic [H<sup>+</sup>] &gt;&gt; [OH<sup>-</sup>]</p> <p>Cb: [H<sup>+</sup>] = [OH<sup>-</sup>] + [HCO<sup>-</sup>] + 2[CO<sub>3</sub><sup>2-</sup>]</p>	<p><math>K_H = \frac{[HCO_3^*]}{P_{CO_2}}</math></p> <p>[H<sub>2</sub>CO<sub>3</sub>*] remains constant! =&gt; P<sub>c</sub> = 5 for all pH values.</p> <p>H<sub>2</sub>CO<sub>3</sub>* behaves as a weak acid. Therefore, pure water open to the atmosphere will be slightly acidic.</p> <p>pC = 11.3 – pH</p> <p>PC = 12.6 - pH</p> <p>Cb: [H<sup>+</sup>] = [OH<sup>-</sup>] + [HCO<sup>-</sup>] + 2[CO<sub>3</sub><sup>2-</sup>]</p> <p>PH = 5.5 rainwater</p>
in a closed system, TOTCO <sub>3</sub> is constant	TOTCO <sub>3</sub> increases at higher pH

**TOTCO<sub>3</sub> increases at higher pH.** (in a closed system, TOTCO<sub>3</sub> is constant)

**Alkalinity** = Measure of the capacity of water to neutralize strong acid addition.

$$\text{Alk} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

$$\text{Alk} = (\alpha_1 + 2\alpha_2) * \text{TOT} - \text{CO}_3 + [\text{OH}^-] - [\text{H}^+]$$

Strong bases and weak bases / weak acids are responsible for alkalinity. They accept H<sup>+</sup> as the H<sup>+</sup> ions are added (as a strong acid). The titration procedure adds a strong acid until the pH reaches a defined endpoint.

**Operational definition:** Total alkalinity is the equiv/liter or moles/liter of a strong acid added to a solution until pH=4.5. Usually, a color indicator is added to the solution

**Methyl orange:** pH > ~4.5, yellow color  
pH < ~4.5, orange color

Moles of H<sup>+</sup> added from acid until PH 4.5

$$\frac{\text{Moles of added H}^+}{(\text{volume})\text{L sample}} = \text{Alk} = M$$

Usually, the major species contributing to alkalinity are carbonate species and OH<sup>-</sup>. Why? Because waters are usually exposed to CO<sub>2(g)</sub> and have some carbonate buffer.

Carbonate and bicarbonate contribute to alkalinity by accepting H<sup>+</sup> during strong acid addition.

A simplified equation for total alkalinity of the carbonate system is:

$$\text{ALK} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

Use this equation when alkalinity is due to the carbonate system alone. (*most of the time this is true for natural waters*)

$$\text{ALK} = C_B - C_A$$

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## Lesson 4:

Coordination number = total possible number of attachments per species

Ion-pair: A cation and an anion operating as a unit without a true bond and with one or two water molecules in between.

Somewhat common for calcium and magnesium cations

### Naming complexes:

Ligand – Ligand – Ligand – metal – ion (metal oxidation #)

#      name    suffix    name    suffix

Ligand names: aquo  $\text{H}_2\text{O}$ , ammine  $\text{NH}_3$ , carbonate ( $\text{CO}_3$ ), phosphate ( $\text{PO}_4$ )...

Ligand suffix: “o” if negative carbonato, phosphato, ...

“ate” if positive

(note: if more than one ligand, place them in alphabetical order)

Metal name: Use the Latin name for some, otherwise just the element name

Ion suffix: “ate” if negative

**Multidentate ligands** are also known as chelating agents

Chelating agent + central metal ion = Chelate

For chelates, the more ligands per complex, the more stable the complex

ethylenediamine < **di**ethylenediamine < **tri**ethylenediamine

**Metal cations act as an acid.** The release of  $\text{H}^+$  from a water ligand or the consumption of a hydroxide ligand will both result in lowering the pH.

For example: The addition of  $\text{Fe}^{3+}$  cations to water will lower the pH.

10 mg  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  into 100 ml should give a pH of 5.0.

50 mg  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  into 100 ml should give a pH of 2.6.

\* Metal cations have a buffer capacity

3. Alkali metals (group 1) form very weak, usually negligible complexes.  $\text{Na}^+$ ,  $\text{K}^+$

4. Alkaline earth metals (group 2) usually prefer ligands with O:  $\text{OH}$ ,  $\text{CO}_3$ ,  $\text{BO}_4$

5. Transition metals do enjoy  $\text{OH}$  ligands but also prefer those containing S, P, and N such as  $\text{S}^{2-}$ ,  $\text{PO}_4$ ,  $\text{NH}_3$ .

6. The stability is usually proportional to the charge of the central metal ion

Stronger complex, larger b as metal charge increases:

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<u>Complexes with EDTA</u>	<u>log b</u>
Na <sup>+</sup>	2.5
Ba <sup>2+</sup>	9.6
Fe <sup>3+</sup>	

27.7

7. Ligands have different strengths

Form strong complexes: PO<sub>4</sub><sup>3-</sup>, OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>

Form weak complexes: ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>

8. For chelates, the more ligands per complex, the more stable the complex  
ethylenediamine < **di**ethylenediamine < **tri**ethylenediamine

**Metal cations have a buffer capacity**

The acidity of the metal cation (or, how low the solution pH it creates) increases with increasing charge of the central metal ion.

**Stability constant**

The bigger formation constant = the more stable complex.

The stability is usually proportional to the charge of the central metal ion

Stronger complex, larger B as metal charge increases

**Ligands have different strengths**

Form strong complexes: PO<sub>4</sub><sup>3-</sup>, OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>

Form weak complexes: ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>

**Differences between freshwater and seawater and their effect on metal complexes**

1. Ionic strength: freshwater < 10<sup>-4</sup> M

Seawater ~ 0.5 M

2. Activity coefficients: freshwater < 1

Seawater << 1

3. stability constants: decrease up to 1 order of magnitude for seawater

4. Same mass balances and charge balance equations, but TOTX values are larger for seawater (due to higher concentrations of salts).

5. Metal-ligand complexes: minor in freshwater

significant in seawater

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### **Three fractions of humic substances:**

Humins: Solid organic matter, removed from water by filtering.

Humic acid: Dissolved organic matter at neutral and basic pH. Acidify the water, and humic acids precipitate and can be filtered.

Fulvic acid: Dissolved organic matter that remains dissolved at all pH values

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## **Lesson 5:**

**Saturation:** equilibrium point, point where solution holds maximum amount of [Me] and [L].

### **Ion Activity Product: IAP**

Compute the Saturation Index:

$$SI = \frac{IAP}{K_{sp}} = \frac{Q}{K_{sp}}$$

If  $SI > 1$ , solution is supersaturated and solid will precipitate

If  $SI = 1$ , solution is saturated and a little solid will (should) precipitate

If  $SI < 1$ , solution is undersaturated and solid will not precipitate

**Solubility** = moles / liter of solid that dissolves at equilibrium =  $s$

High solubility	$s > \sim 0.01 \text{ M}$
Slightly soluble	$0.0001 < s < 0.01 \text{ M}$
Insoluble	$s < 0.0001 \text{ M}$

For the same reaction stoichiometry, a smaller  $K_{sp}$  gives a lower solubility

### **The common ion effect:**

The ion is already present, so not as much of the solid needs to dissolve to reach the equilibrium state this will decrease the solubility of the solid possessing that ion.

### **The effect of ligand protonation**

If ligand is a weak acid, the ligand can protonate (depending on solution pH). The unprotonated ligand concentration decreases in solution (some got protonated). The solid dissolves more to replenish the unprotonated ligand concentration.

Ligands that can become protonated during  
pH changes: any weak acid,  $\text{OH}^-$ ...



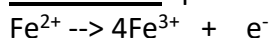
### **The effect of the formation of soluble metal complexes**

Dissolved metals can form complexes with ligands (Lesson 4) (depending on solution pH and / or ligand concentration). The uncomplexed metal (free metal) concentration then decreases as some metal forms complexes. The solid dissolves more to replenish the free metal concentration.

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## **Lesson 6**

**Reductant:** species that donates  $e^-$  to another species

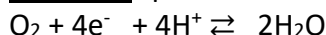


Iron (II) is a reductant because it donates an electron

Iron (II) becomes oxidized to iron (III) after the electron transfer

This half-reaction is an oxidation half reaction because the iron species is getting oxidized

**Oxidant:** species that accepts  $e^-$  from another species



Oxygen is an oxidant because it accepts an electron

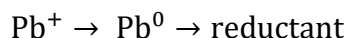
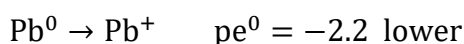
Oxygen becomes reduced to water after the electron transfer

This half-reaction is a reduction half reaction because the oxygen is getting reduced.

Balancing:

- 1- Species other than  $\text{H}^+$ ,  $\text{OH}^-$ , and  $\text{H}_2\text{O}$
- 2- Balancing the oxygen using  $\text{H}_2\text{O}$
- 3- Balancing the hydrogen with  $\text{H}^+$
- 4- Balancing the charge with electrons
- 5- If we have  $\text{H}^+$ , dissociate of  $\text{H}_2\text{O}$  to eliminate  $\text{H}^+$ .

→ Compare two half-reactions: The one with the higher  $\text{pe}^0$  is the oxidant The one with the lower  $\text{pe}^0$  is the reductant (at standard conditions)



NEVER ADD  $\text{pe}^0$  VALVES

**When we want to compare two half reaction according to their  $\text{pe}$  their  $n$  should be equal.**

**$\text{pe}$  is only only only for half reactions.**

$$\Delta G^0 = -nFE^0 \quad \text{where: } n = \text{number of electrons transferred}$$

$$F = \text{Faraday's constant} = 96,500 \text{ C/mol } e^-.$$

$E$  = electrochemical potential in Volts (or mV).

$$\rightarrow \Delta G = -n F E = \text{mol } e^- \times C / \text{mol } e^- \times V = CV = J$$

$$F = 96500 \text{ C/mol.}e^-$$

→ If values with these units are used, J needs to be converted to kJ.

Implication: A reaction is at equilibrium when  $\Delta G = 0$  and  $E = 0$

A reaction is proceeding forward when  $\Delta G < 0$  and  $E > 0$

A reaction is proceeding in the reverse direction when  $\Delta G > 0$  and  $E < 0$

high dissolved oxygen = "oxidizing" = high  $E$  or  $pe$  = ORP  $E > 0$

→ low dissolved oxygen = "reducing" = low  $E$  or  $pe$  = ORP  $E < 0$

→ *Best way to think of this whole thing is, if oxygen is present, it will chemically oxidize most of the reduced species to the oxidized form, creating oxidizing conditions of higher Eh.*

→ Things at the top of the chart are really good reducers and things at the bottom of the chart are really good oxidizer.

→ What is the largest  $E$  that we can calculate we go to the largest  $G$  that we can calculate. The most possible favorite thing would be to pick the best reducer as the reducer and the worst reducer as the oxidizer.

→ Smaller  $K_{sp}$  gives lower solubility

→ Ligands can increase solubility by forming complex.

→ Assume no complexes of  $Ag^+$  with  $OH^-$  form, and that no other silver solid is present.

→ Electrodes measure reduction potential, or redox potential, or oxidation-reduction potential (ORP) with respect to a reference material ( $Ag/AgCl$ , or  $Pt$ )

→ At equilibrium,  $\Delta G = 0$ ,  $\Delta E = 0$ ,  $\Delta pe = 0$ .

Therefore,  $pe_{ox} = pe_{red} = \text{measured } pe$  Also  $E_{ox} = E_{red} = \text{measured } E$  for two half-reactions. Just like pH! We measure one pH value for an entire solution.

→ Best way to think of this whole thing is, if oxygen is present, it will chemically oxidize most of the reduced species to the oxidized form, creating oxidizing conditions of higher Eh.

→ high dissolved oxygen = "oxidizing" = high  $E$  or  $pe$   $E > 0$

→ low dissolved oxygen = "reducing" = low  $E$  or  $pe$   $E < 0$

→ Things at the top of the chart are really good reducers and things at the bottom of the chart are really good oxidizer.

→ What is the largest  $E$  that we can calculate? we go to the largest  $G$  that we can calculate. The most possible favorite thing would be to pick the best reducer as the reducer and the worst reducer as the oxidizer.

→ However, changing  $n$  will change  $\Delta G = -nFE$ .

→ Also, in the whole reaction,  $E$  is independent of stoichiometry.

→ Harcheghadr e bozorgtar behtar reduce mishe

$$\rightarrow p_{e0} = \frac{1}{n} \log k$$

→ *lower  $pe \Rightarrow$  better reductant*

→ Rules for using  $pe^0$  similar to  $E^0$  but can only use for half reactions

→  $Ox + ne \rightarrow red$

Overall: We have four ways to describe redox equilibrium! The most important ways will be E or pe (combined with Nernst equation to account for non- standard conditions).

$$\Delta G = -nFE \quad \Delta G^0 = -nFE^0$$

$$E = E^0 - 2.303RT/nF \log Q \quad \text{nernst}$$

$$Pe^0 = 1/n \log K$$

$$pe = -\log\{e-\}$$

$$pe = pe^0 - 1/n \log Q \quad \text{nernst}$$

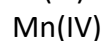
$$pe = E F/2.303RT \quad pe^0 = E^0 F/2.303 RT$$

$$pe = -\Delta G/2.303nRT \quad pe^0 = -\Delta G^0/2.303nRT$$

- Electrodes measure reduction potential, or redox potential, or oxidation-reduction potential (ORP) with respect to a reference material (Ag/AgCl, or Pt)
- pe of solution characterizes tendency of solution to favor oxidized or reduced species
- $pe_o$  characterizes inherent tendency of species forming a redox pair to be oxidized or reduced
- the speciation of a given redox couple depends on its chemistry (as embedded in  $e_o$  or  $p_{e_o}$ ) and on the redox status of the solution (pe).

Oxidized species

reduced species



## Lesson 7:

**Sorption** can be viewed, in its simplest terms, as a partitioning between the aqueous and sorbed phases: Partitioning coefficient:  $K$ ,  $K_p$ ,  $K_d$

$K_d = C_{sorb} / C_{aq} \rightarrow$  works for very low  $C_{sorb} = 10 \mu M$

$$R = \frac{V_{gw}}{V_{cont}}$$

$$R = 1 + \rho_b K_d / q$$

$\rho_b$  = bulk density of soil

$q$  = porosity

$$C_{sorb} = \frac{(C_{aq(before)} - C_{aq(after)})}{\text{mass of sorbent}}$$

\*As  $K_d$  increase, we have lots of sorption,  $R$  increase

Lungmuir:

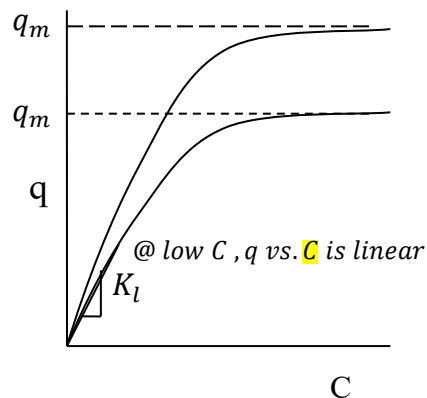
$$q = \frac{q_m K_L C}{1 + K_L C}$$

$\uparrow$                        $\uparrow$   
 $C_{sorb}$                        $\text{maximm } C_{sorb}$

$$\frac{\text{moles sorbate}}{\text{g sorbent}}$$

$K_L$  = equil. partitioning coefficient

$$C = C_{aq}$$



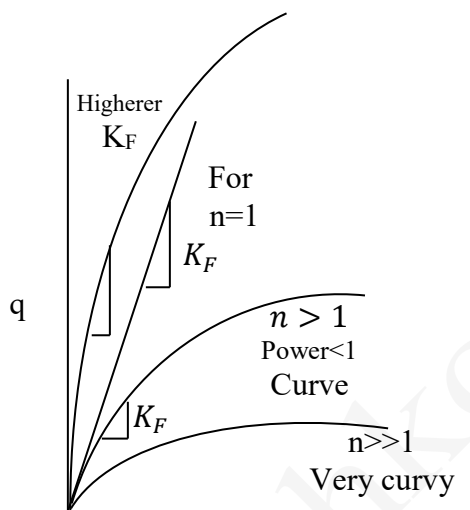
**Fruendlich:**

“Surface heterogeneity”  
Different types of sites, no  $q_m$

This ok:

$$\underset{C_{sorb}}{\overset{q}{\uparrow}} = \underset{\substack{\uparrow \\ \text{partitioning} \\ \text{Coef}}}{K_F} \underset{C_{aq}}{\overset{C^{\frac{1}{n}}}{\uparrow}}$$

(note:  $q = K_F C^n$ )



$n$ =coefficient linearity

higher  $K_F$  = greater sorption

$$n = 1, \quad q = K_F C^{\frac{1}{1}} = K_F C \text{ line}$$

Lesson 8:

Carbon atoms

- sorption ability
- Usually lower solubility
- Slower reaction rates
- Have some nonpolar groups (or entirely nonpolar)

Isomers = same formula but different compound structure

Class of Compound	Functional Group	General Formula	Example
halide (halocarbon)	$\text{—F}$ (fluoro-) $\text{—Cl}$ (chloro-) $\text{—Br}$ (bromo-) $\text{—I}$ (iodo-)	$R\text{—}X$ ( $X$ represents any halogen)	$\text{CH}_3\text{CHClCH}_3$ 2-chloropropane
alcohol	$\text{—OH}$	$R\text{—OH}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ 1-propanol
ether	$\text{—O—}$	$R\text{—O—}R'$	$\text{CH}_3\text{OCH}_2\text{CH}_3$ methyl ethyl ether
aldehyde	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—H} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ R\text{—C—H} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{C—H} \end{array}$ propanal
ketone	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ R\text{—C—}R' \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CCH}_2\text{CH}_2\text{CH}_3 \end{array}$ 2-pentanone
organic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—OH} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ R\text{—C—OH} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{C—OH} \end{array}$ propanoic acid
ester	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—O—} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ R\text{—C—O—}R' \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{COCH}_3 \end{array}$ methyl propanoate
amine	$\begin{array}{c}   \\ \text{—N—} \end{array}$	$\begin{array}{c} R' \\   \\ R\text{—N—}R'' \end{array}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ 1-propanamine
amide	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—NH} \\   \end{array}$	$\begin{array}{c} \text{O} \quad R' \\ \parallel \quad   \\ R\text{—C—NH} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{C—NH}_2 \end{array}$ propanamide

**Note:**  $R$  represents a bonded atom or group of atoms.

Organics partition to different compartments more readily than inorganics. The carbon nature makes a compound more volatile and more sorptive (to organic soil matter, at least) and possibly have its own nonaqueous phase liquid or even solid.

**Parameters and their units:**

Parameter	unit
Ionic strength	M
$K_H$	$\frac{[C_{aq}]}{P_g} \frac{M}{atm}$
H Henry's constant	$\frac{[C_{aq}]}{[C_g]} = (\text{moles / liter solution})/(\text{moles/liter air})$
$K, K_p, K_d$	
$Q=C_{sorb}$	$C_{sorb} = \frac{(C_{aq(before)} - C_{aq(after)})}{\text{mass of sorbent}} = \frac{\text{mmoles sorbate}}{\text{gr of sorbent}}$

**Assumptions can be maid:**

- The sulfuric acid completely dissociates to the  $H^+$  and sulfate.
- An ideal solution.  $\gamma = 1$
- The solution will be acidic or basic.
- For weak diprotic acid systems: If the species are added as  $H_2A$ , the  $A^{2-}$  species is likely negligible in the charge balance and mass balance.
- For weak diprotic acid systems: If the species are added as  $Na_2A$ , the  $H_2A$  species is likely negligible in the mass balance.
- For a weak monoprotic acid added to solution as  $NaA$  and for a weak diprotic acid solution added as  $NaHA$  or  $Na_2A$ , it is a very good idea to revise the charge balance by (i) first equating the mass balance for TOTNa and the mass balance for TOTA, then (ii) substitute this equation into the charge balance, and finally (iii) eliminating common terms. This equation can be further simplified using assumptions above.

**Complexation: General assumptions for these problems:**

- Assume only mononuclear species form (unless you really want polynuclear species)
- Assume no loss to volatilization or precipitation (this calculation method cannot work for volatilization or precipitation)
- We can make an additional assumption:  $TOT-Cl = [Cl^-]$  is constant.

**K table:**

Type of K	How it presents in table	Formula
<b>K</b>	$K \gg 1$ reaction forward $K \ll 1$ reaction backward K is written in terms of <u>activity</u>	$aA + bB \rightarrow cC + dD$ $K = \frac{\{C\}^c + \{D\}^d}{\{A\}^a + \{B\}^b}$
<b>K<sub>a</sub></b>	Acid-dissociation constant $HA \rightleftharpoons H^+ + A^-$ $pK_a = -\log K_a$ As $K_a \uparrow$ , $pK_a \downarrow$ , and the acid is “stronger” As $K_a \downarrow$ , $pK_a \uparrow$ , and the acid is “weaker” <div style="text-align: right; margin-right: 50px;">Pka</div> Strong acid $\leq 2$ Weak acid 2-12 Strong base $\geq 2$	
<b>K<sub>H</sub></b>		$K_H = \frac{C(aq)}{C(g)} = \frac{M}{atm}$
<b>K</b>	formation constant = stability constant <b>Log K</b> General assumptions for these problems: Assume only mononuclear species form (unless you really want polynuclear species) Assume no loss to volatilization or precipitation (this calculation method cannot work for volatilization or precipitation)	
<b>K<sub>sp</sub></b> <b>K<sub>s0</sub></b> <b>K, K<sub>p</sub>, K<sub>d</sub></b>	<b>Solid(s) <math>\rightleftharpoons</math> Metal + Ligand</b> Like any equilibrium constant, $K_{sp}$ is written in terms of <u>activity</u> <b><math>pK_{sp} = -\log K_{sp}</math></b> $K_d = C_{sorb} / C_{aq} \rightarrow$ works for very low $C_{sorb} = 10 \mu M$	$K_{sp} = \{A^{y+}\}^z \{B^{z-}\}^y$
<b>K<sub>L</sub></b>	Langmuir, equilibrium partitioning coefficient	
<b>K<sub>F</sub></b>	Freundlich partitioning coefficient Surface heterogeneity, different types of sites Higher $K_F$ = greater sorption	