Basic Chemistry Concepts II

Chemical equilibrium: acid-base equilibria

- Ionization of water: $H_2O + H_2O = H_3O^+ + OH^-$

$$K = \frac{\{OH^-\}\{H_3O^+\}}{\{H_2O\}^2}$$

$$\{H_2O\} = \gamma_{H_2O} \cdot [H_2O], \quad \gamma_{H_2O} \approx 1, \quad [H_2O] = 55.6\,M$$

- Dissociation constant of water, K_w

$$K_w = K \cdot \{H_2O\}^2 = \{OH^-\}\{H_3O^+\}$$

Chemical equilibrium: acid-base equilibria

$K_w = \{OH^-\}\{H_3O^+\}$ or $K_w = \{OH^-\}\{H^+\}$

$pK_w = 14 \quad \text{(at 25°C)}$

$pH < 7 \longrightarrow \{H^+\} > \{OH^-\}, \quad \text{acidic}$

$pH > 7 \longrightarrow \{H^+\} < \{OH^-\}, \quad \text{basic}$

Acid dissociation constant

$$HA = H^{+} + A^{-}$$

- Acid dissociation constant, K_a

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

- Strong acid = strong tendency to dissociate = high K_a = low pK_a
- Weak acid = only a small fraction dissociates = low K_a = high pK_a

Acid dissociation constant

Acid	**Reaction**	**pK_a**	
Hydrochloric acid	$HCl = H^+ + Cl^-$	≈-3	**Strong**
Nitric acid	$HNO_3 = H^+ + NO_3^-$	-1	
Sulfuric acid	$H_2SO_4 = H^+ + HSO_4^-$	≈-3	
Bisulfate	$HSO_4^- = H^+ + SO_4^{2-}$	1.9	
Acetic acid	$CH_3COOH = H^+ + CH_3COO^-$	4.75	**Weak**
Carbonic acid	$H_2CO_3{}^* = H^+ + HCO_3^-$ $HCO_3^- = H^+ + CO_3^{2-}$	6.35 10.33	
Phosphoric acid	$H_3PO_4 = H^+ + H_2PO_4^-$ $H_2PO_4^-\ \ H^+ + HPO_4^{2-}$- $HPO_4^{2-} = H^+ + PO_4^{3-}$	2.12 7.20 12.32	

Acid dissociation constant

Q: A solution of HOCl is prepared in water by adding 15 mg HOCl to a volumetric flask, and adding water to the 1.0 L mark. The final pH is measured to be 7.0. What are the concentrations of HOCl and OCl^-?

(T = 25˚C)

Chemical equilibrium: gas dissolution

- Henry's Law: partial pressure of a chemical in the gas phase is linearly proportional to the concentration of the chemical in the aqueous phase

$$P_{gas} = kC^*$$

where P_{gas} = partial pressure in the gas phase

C^* = concentration in the water

k = constant

Caveat!

- The equilibrium/solubility product constants do not tell anything about the reaction rate!
- Differentiate equilibrium and kinetics

Reaction kinetics

- Reaction kinetics: study of the speed at which reactions proceed

$a\text{A} + b\text{B} \rightarrow c\text{C}$

$$r_A = \frac{d[A]}{dt} = -k[A]^{\alpha}[B]^{\beta}$$

r_A = reaction rate w.r.t. chemical A [conc./time]

k = reaction rate constant

$\alpha + \beta$ = reaction order

Reaction kinetics

Reaction order	**Rate expression**	**Units on *k***
Zero	$r_A = -k$	$(\text{conc.})(\text{time})^{-1}$
First	$r_A = -k[\text{A}]$	$(\text{time})^{-1}$
Second	$r_A = -k[\text{A}]^2$	$(\text{conc.})^{-1}(\text{time})^{-1}$
Second	$r_A = -k[\text{A}][\text{B}]$	$(\text{conc.})^{-1}(\text{time})^{-1}$

- Half-life ($t_{1/2}$): time required for the concentration to reach ½ of its initial conc.

Concentration units in water

- Weight percent, *P*

$$P = \frac{W}{W + W_0} \times 100\%$$

W = mass of substance (g)
W_0 = mass of solute (g)

- ppm, ppb, ppt
- Molarity, *M*
- Normality, *N* (acid-base reaction)

$$N = nM$$

n = no. of protons transferred

Carbonate system

- Buffer: a solution that resists large changes in pH
- A solution of weak acid and its salt is a buffer
- Atmospheric CO_2 produces a natural buffer:

$$CO_2\ (g) + H_2O = H_2CO_3{}^* = H^+ + HCO_3{}^- = 2H^+ + CO_3{}^{2-}$$

H_2CO_3* = sum of true H_2CO_3(aq) and $CO_2(aq)$

Carbonate system

Acid dissociation:

$$H_2CO_3{}^* = H^+ + HCO_3{}^- , \quad K_{a1} = 10^{-6.35} \quad \text{(at 25°C)}$$

$$HCO_3{}^- = H^+ + CO_3{}^{2-} , \quad K_{a2} = 10^{-10.33} \quad \text{(at 25°C)}$$

Define C_T as:

$$C_T = [H_2CO_3{}^*] + [HCO_3{}^-] + \left[CO_3{}^{2-}\right]$$

Carbonate system

Then:

$$[H_2CO_3{}^*] = C_T \cdot \left(1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}K_{a2}}{[H^+]^2}\right)^{-1}$$

$$[HCO_3{}^-] = \frac{K_{a1}}{[H^+]} \cdot [H_2CO_3{}^*]$$

$$[CO_3{}^{2-}] = \frac{K_{a1}K_{a2}}{[H^+]^2} \cdot [H_2CO_3{}^*]$$

- If C_T is known, we can obtain the concentration of each species at a certain pH

Carbonate system

Now, think of

$$K_{a1} = \frac{[H^+][HCO_3{}^-]}{[H_2CO_3{}^*]}$$

$$pH - pK_{a1} = log\,\frac{[HCO_3{}^-]}{[H_2CO_3{}^*]}$$

If pH < pK_{a1}, $[H_2CO_3*] > [HCO_3^-]$

(If pH – pK_{a1} = -2, $[H_2CO_3*] = 100[HCO_3^-]$)

If pH > pK_{a1}, $[H_2CO_3*] < [HCO_3^-]$

(If pH – pK_{a1} = 2, $[HCO_3^-] = 100\ [H_2CO_3*]$)

Carbonate system

This applies to HCO_3^- - CO_3^{2-} relationship as well:

If $pH < pK_{a2}$, $[HCO_3^-] > [CO_3^{2-}]$

If $pH > pK_{a2}$, $[HCO_3^-] < [CO_3^{2-}]$

Actually this principle applies to any acids:

If $pH < pK_a$, <u>associated (protonated) form dominates</u>

If $pH > pK_a$, <u>dissociated (deprotonated) form dominates</u>

Carbonate system

1. Closed system: C_T is constant

Solving for pH < pK_{a1} region as an example

At this pH range, H_2CO_3* dominant:

$$C_T \approx [H_2CO_3{}^*] \Rightarrow log[H_2CO_3{}^*] \approx logC_T$$

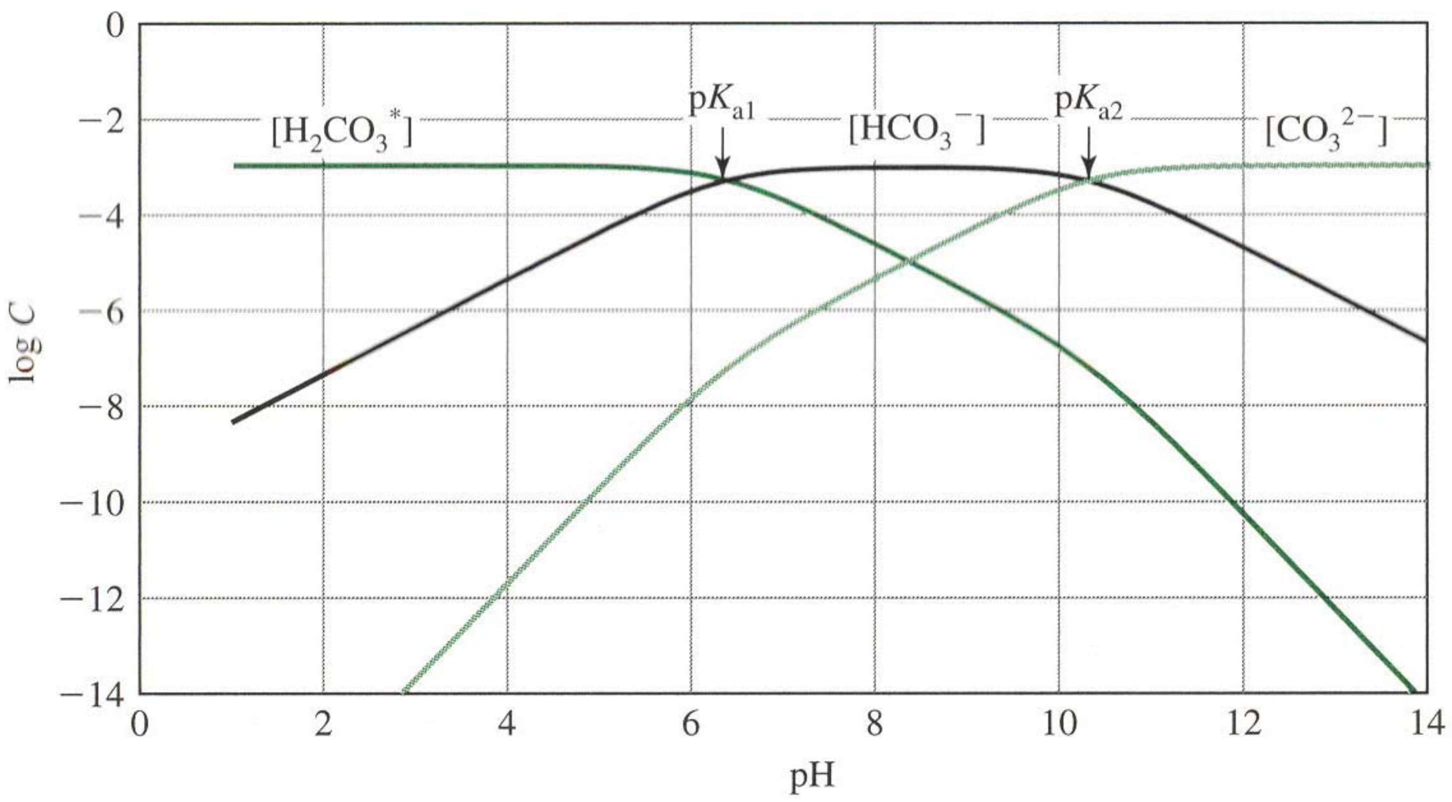
$$[HCO_3{}^-] = \frac{K_{a1}}{[H^+]} \cdot [H_2CO_3{}^*] \Rightarrow log[HCO_3{}^-] = logC_T - pK_{a1} + pH$$

$$[CO_3{}^{2-}] = \frac{K_{a1}K_{a2}}{[H^+]^2} \cdot [H_2CO_3{}^*] \Rightarrow log\left[CO_3{}^{2-}\right] = logC_T - pK_{a1} - pK_{a2} + 2pH$$

Carbonate system

1. Closed system

$C_T = 10^{-3}$ M



Davis & Masten (2014)

Carbonate system

2. Open system: constant $[H_2CO_3{}^*]$

$$[H_2CO_3{}^*] = K_H P_{CO_2} = (10^{-1.47}\ M/atm)(10^{-3.53}\ atm)$$

$$= 10^{-5.00}\ M \quad \text{(at 25°C), ambient air}$$

$$[HCO_3{}^-] = \frac{K_{a1}}{[H^+]} \cdot [H_2CO_3{}^*] \quad \Rightarrow \quad log[HCO_3{}^-] = log\left(K_H P_{CO_2}\right) - pK_{a1} + pH$$

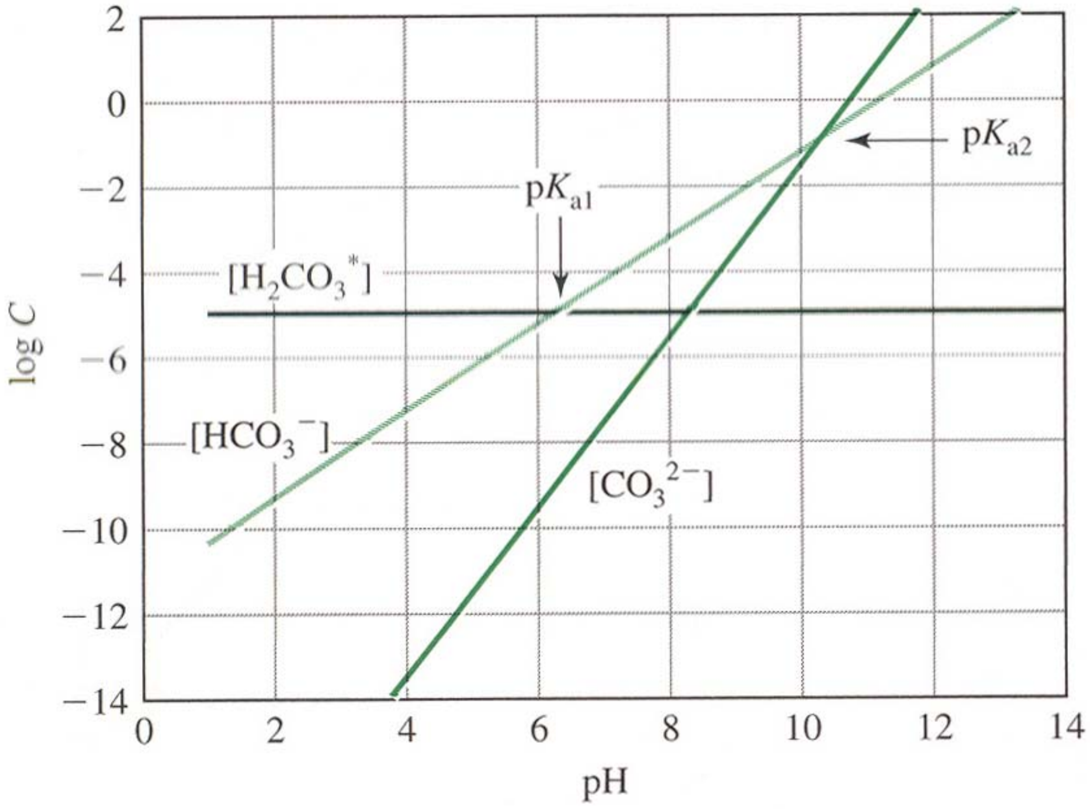
$$= -11.35 + pH$$

$$\left[CO_3{}^{2-}\right] = \frac{K_{a1}K_{a2}}{[H^+]^2} \cdot [H_2CO_3{}^*]$$

$$\Rightarrow \quad log\left[CO_3{}^{2-}\right] = log\left(K_H P_{CO_2}\right) - pK_{a1} - pK_{a2} + pH = -21.68 + 2pH$$

Carbonate system

2. Open system



Davis & Masten (2014)

Alkalinity

- Alkalinity: sum of all titratable bases to a pH of approximately 4.5

$$Alkalinity = [HCO_3{}^-] + 2[CO_3{}^{2-}] + \cdots + [OH^-] - [H^+]$$

Include $B(OH)_4$, $PO_4{}^{3-}$, $HPO_4{}^{2-}$, $SiO(OH)_3$, etc. if significant

$$Carbonate\ alkalinity = [HCO_3{}^-] + 2[CO_3{}^{2-}]$$

(bicarbonate and carbonate are major contributors of alkalinity in natural waters)

Alkalinity

- Unit of alkalinity
  - Using molarity for each species, we get “eq/L”
  - “eq”: equivalent, moles of H^+ ion in an acid-base solution or electrons in a redox reaction
  - More common unit is “mg/L as $CaCO_3$”
  - Unit conversion: 1 meq/L = 10^{-3} eq/L = 50 mg/L as $CaCO_3$

Reading assignment

- Textbook Ch2 p. 51-75

Acid dissociation

Slide#6 solution)

MW of HOCl = 52.46 g/mole

Unit conversion - mg/L to molarity:

$$\frac{15\ mg\ HOCl}{1\ L\ water} \times \frac{1}{52.46\ g\ HOCl/mole\ HOCl} \times 10^{-3}\ g/mg = 2.86 \times 10^{-4}\ M$$

$HOCl = H^+ + OCl^-$, $pK_a = 7.54$

weak acid → only a fraction dissociates

$$K_a = 10^{-7.54} = \frac{[H^+][OCl^-]}{[HOCl]} = \frac{10^{-7} \cdot [OCl^-]}{[HOCl]}$$

$$[HOCl] = 3.47[OCl^-]$$

$$[HOCl] + [OCl^-] = 4.47[OCl^-] = 2.86 \times 10^{-4}\ M$$

$[OCl^-] = 0.64 \times 10^{-4}$ M

$[HOCl] = 2.22 \times 10^{-4}$ M