Basic Chemistry Concepts II

Today's lecture

- More on equilibrium chemistry
- Reaction kinetics
- Concentration units in water
- Carbonate system

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

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

$$pK_w = 14 \qquad \text{(at 25°C)}$$

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

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

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**	**pKa**
Hydrochloric acid	$HCl = H^+ + Cl^-$	≈-3
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
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

Strong (Hydrochloric acid, Nitric acid, Sulfuric acid, Bisulfate)

Weak (Acetic acid, Carbonic acid, Phosphoric acid)

Acid dissociation constant

Q: If 100 mg of H_2SO_4 (MW=98) is added to water, bringing the final volume to 1.0 L, what is the final pH?

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

Reaction kinetics

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

$aA + bB \rightarrow cC$

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

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	$r_A = -k$	(conc.)(time)$^{-1}$
First	$r_A = -k[A]$	(time)$^{-1}$
Second	$r_A = -k[A]^2$	(conc.)$^{-1}$(time)$^{-1}$
Second	$r_A = -k[A][B]$	(conc.)$^{-1}$(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

Concentration units in water

Q: Commercial H_2SO_4 is often purchased as a 93 wt% solution. Find the concentration of this solutions in units of mg/L, molarity, and normality.

(H_2SO_4 specific gravity = 1.839, T=15˚C)

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:

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

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

Carbonate system

Acid dissociation:

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

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

1. Closed system: constant C_T

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

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

Carbonate system

1. Closed system

$$pH < pK_{a1}: \quad log[H_2CO_3*] \approx log\,C_T$$

$$pH = pK_{a1}: \quad log[H_2CO_3*] \approx log(0.5C_T)$$

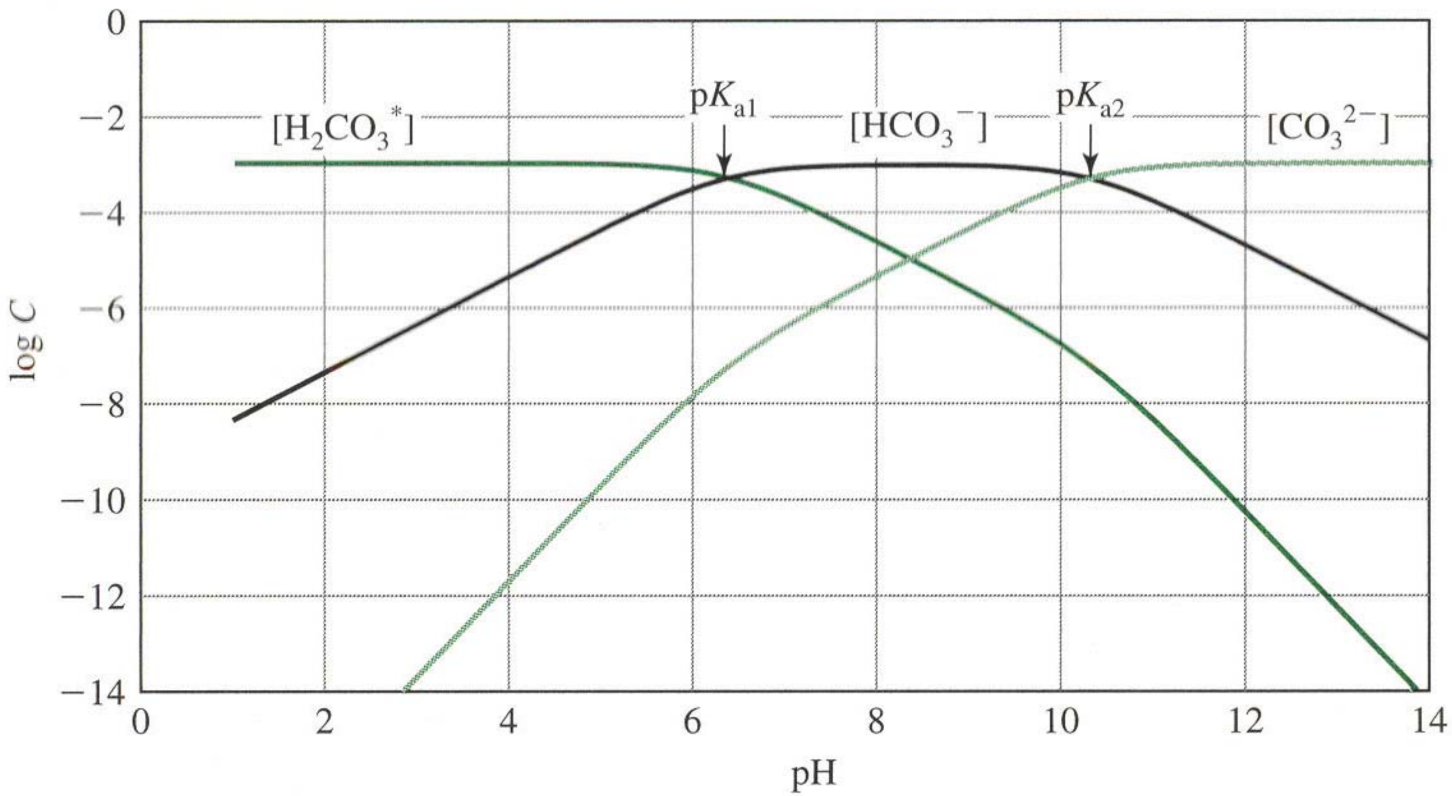
$$pK_{a1} < pH < pK_{a2}: \quad log[H_2CO_3*] \approx pK_{a1} + log\,C_T - pH$$

$$pH = pK_{a2}: \quad log[H_2CO_3*] \approx pK_{a1} + log(0.5C_T) - pH$$

$$pH > pK_{a2}: \quad log[H_2CO_3*] \approx pK_{a1} + pK_{a2} + log\,C_T - 2pH$$

Carbonate system

1. Closed system



Carbonate system

2. Open system: constant [H_2CO_3*]

$$\left[H_2CO_3*\right] = K_H P_{CO_2} = \left(10^{-1.47}\ M \cdot atm^{-1}\right)\left(10^{-3.53}\ atm\right)$$

$$= 10^{-5.0}\ M \qquad \text{(at 25°C), ambient air}$$

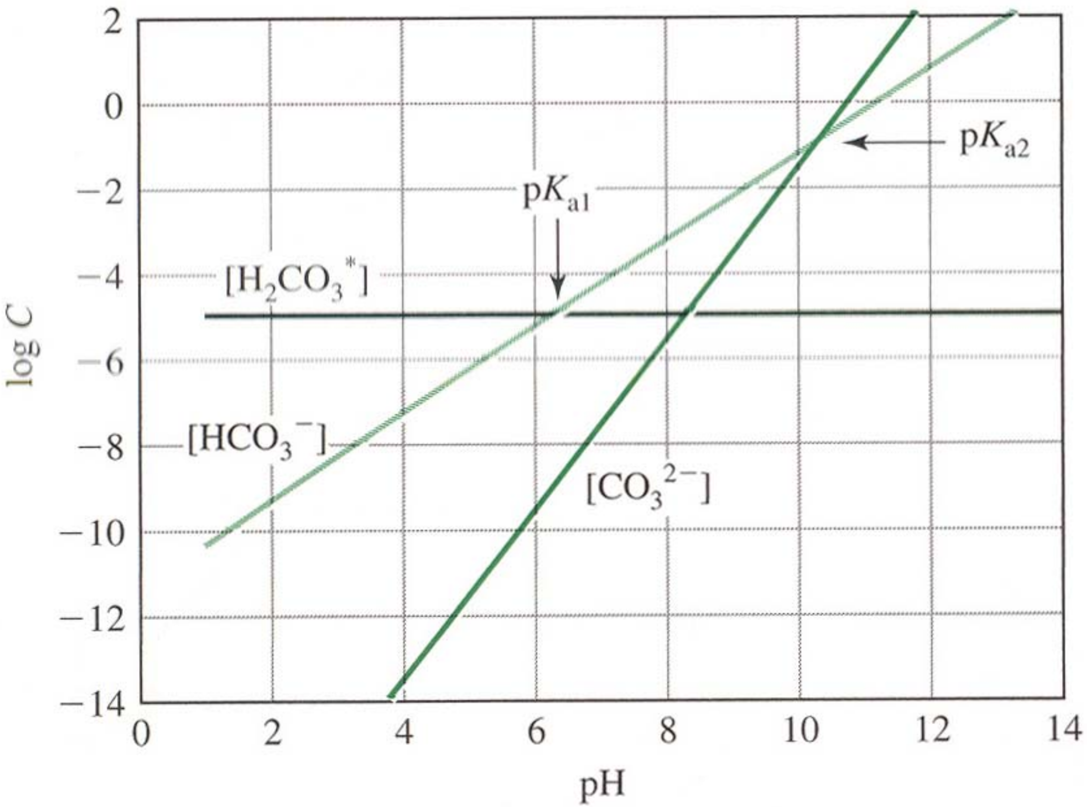
$$log\left[HCO_3^{\ -}\right] = -pK_{a1} + log\left(K_H P_{CO_2}\right) + pH = -11.35 + pH$$

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

$$= -21.68 + 2pH$$

Carbonate system

2. Open system



Alkalinity

- Alkalinity: sum of all titratable bases to a pH of approximately 4.5 (in *N*)

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

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

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

Reading assignment

- Textbook Ch2 p. 52-75