

VC210 Recitation Class 8

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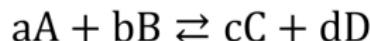
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① Chemical Equilibrium

② Acid & Base

③ Aqueous equilibria

Equilibrium Constant



$$K = \frac{(a_C)^c \cdot (a_D)^d}{(a_A)^a \cdot (a_B)^b}$$

$$K = \frac{(a_C)^c \cdot (a_D)^d}{(a_A)^a \cdot (a_B)^b} \Rightarrow \boxed{\begin{array}{l} K_c = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b} \\ K_P = \frac{(P_C)^c \cdot (P_D)^d}{(P_A)^a \cdot (P_B)^b} \end{array}}$$

◆ The relation between K_c & K_P

$$K_P = (RT)^{\Delta n} \cdot K_c, \text{ (where } \Delta n = \Sigma n_{prod} - \Sigma n_{reac})$$

Kinetic View of K

Forward: $Rate_f = k_f \cdot [A]^a[B]^b$

Backward: $Rate_b = k_b \cdot [C]^c[D]^d$

At equilibrium:

$$Rate_f = Rate_b$$

$$K = \frac{k_f}{k_b} = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$$

Thermodynamic view

$$\Delta G_r = \Delta G_r^\circ + RT \cdot \ln \frac{(a_C)^c \cdot (a_D)^d}{(a_A)^a \cdot (a_B)^b}$$

Denote $Q = \frac{(a_C)^c \cdot (a_D)^d}{(a_A)^a \cdot (a_B)^b} = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$

So $\Delta G_r = \Delta G_r^\circ + RT \cdot \ln Q$

At eq. $\Delta G_r = 0; K = Q$

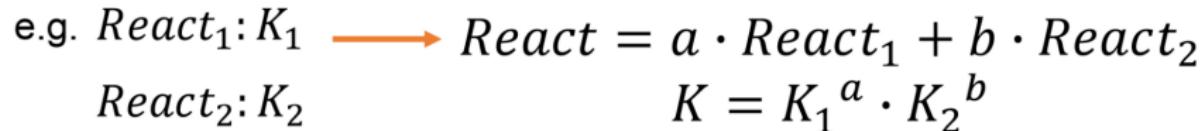
Therefore $-\Delta G_r^\circ = RT \cdot \ln K$

$$\Delta G_r = -RT \cdot \ln K + RT \cdot \ln Q$$

$Q < K: \Delta G_r < 0$, Forward $Q = K: \Delta G_r = 0$, Equilibrium $Q > K: \Delta G_r > 0$, Backward
--

Calculation of K

① Combination reaction



② ICE Table

	Matter 1	Matter 2	Matter 3	...
Initial				
Change				
Equilibrium				



Substitute into the formula of K ,
and solve for the answer

Le Chatelier's Principle

- Disturbed equilibrium re-approaches equilibrium

① Add/remove reactants/products:

- a) Add reactants/remove products: forward reaction
- b) Add products/remove reactants: backward reaction
- Adding/remove solids/liquid doesn't change equilibrium

② For reactions include gases:

- a) Increase pressure:
 - i) If it changes the concentration of components to the direction that decreases pressure
 - ii) If it doesn't change the concentration of components equilibrium won't change
- b) Decrease pressure: similar

Le Chatelier's Principle

For reactions include heat change:

$$\ln \frac{K_{T_2}}{K_{T_1}} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (1)$$

1 Chemical Equilibrium

2 Acid & Base

3 Aqueous equilibria

Acid & Base Theories

1. Arrhenius

- ① Acid produces H^+ in water
- ② Base produces OH^- in water

Only considers one solvent; not all base reactions produce OH^- ; the key process in an acid and base reaction is a proton (H^+) transfer

2. Lowry & Bronsted

- ① Acid is a proton(H^+) donor
- ② Base is a proton(H^+) acceptor

Strong acid/base: completely deprotonated/protonated in solution

Weak acid/base: partially deprotonated/protonated

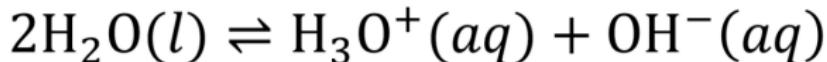
Acid & Base Theories

3. Lewis

- ① Acid accepts electron pair
- ② Base donates electron pair

- **Amphoteric:** a molecule or ion that can react both as an acid as well as a base.
E.g. $\text{Al}(\text{OH})_3$, Al_2O_3
- **Amphiprotic:** a molecule can act both as a proton donor and as a proton acceptor.

Water and pH



- Recall the equilibrium constant:

$$K_W = [\text{H}_3\text{O}^+][\text{OH}^-]$$

- At 25°C, in pure water

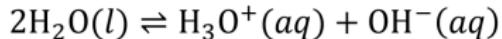
$$[\text{H}_3\text{O}^+] = 1 \times 10^{-7}; [\text{OH}^-] = 1 \times 10^{-7}$$

$$K_W = 1 \times 10^{-14}$$

- Remember that K_W is only related to T

- So at certain temperature, the product of $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ in a solution is constant.

pH



- Recall the equilibrium constant:

$$K_W = [\text{H}_3\text{O}^+][\text{OH}^-]$$

- At 25°C, in pure water

$$[\text{H}_3\text{O}^+] = 1 \times 10^{-7}; [\text{OH}^-] = 1 \times 10^{-7}$$

$$K_W = 1 \times 10^{-14}$$

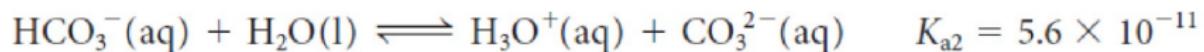
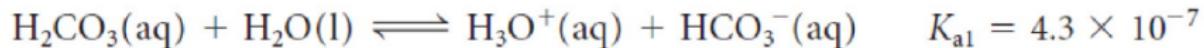
- Remember that K_W is only related to T

- So at certain temperature, the product of $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ in a solution is constant.

Exercise

Determine the pH of a solution that is 0.00528 M HCl and 0.0280 M HClO_2 . The K_a of HClO_2 is 1.1×10^{-2} .

Polyprotic Acid



$$K_{a1} \gg K_{a2} \gg K_{a3} \gg \dots$$

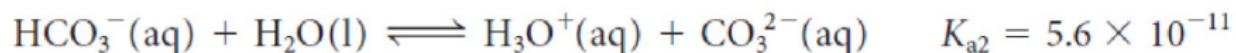
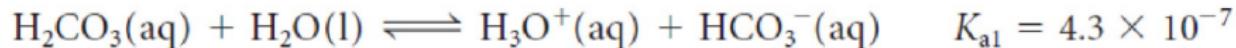
Reversibly,

$$K_{b1} = \frac{K_W}{K_{a1}} \ll K_{b2} = \frac{K_W}{K_{a2}} \ll K_{b3} = \frac{K_W}{K_{a3}} \ll \dots$$

Tricks:

- Estimate the pH of a polyprotic acid for which all deprotonations are weak by using only the first deprotonation equilibrium and assuming that further deprotonation is insignificant.

Composition



$$\text{Let } M = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

(M is constant) Why?

$$\text{Let } X_0 = \frac{[\text{H}_2\text{CO}_3]}{M}, X_1 = \frac{[\text{HCO}_3^-]}{M}, X_2 = \frac{[\text{CO}_3^{2-}]}{M}$$

Then we have:

$$\begin{cases} K_{a1}X_0 = [\text{H}_3\text{O}^+]X_1 \\ K_{a2}X_1 = [\text{H}_3\text{O}^+]X_2 \\ X_0 + X_1 + X_2 = 1 \end{cases} \quad \text{Solve it.}$$

Composition

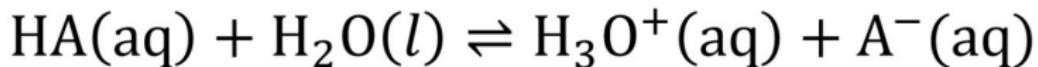
$$X_0 = \frac{[\text{H}_3\text{O}^+]^2}{[\text{H}_3\text{O}^+]^2 + [\text{H}_3\text{O}^+]k_{a1} + k_{a1}k_{a2}}$$

$$X_1 = \frac{[\text{H}_3\text{O}^+]k_{a1}}{[\text{H}_3\text{O}^+]^2 + [\text{H}_3\text{O}^+]k_{a1} + k_{a1}k_{a2}}$$

$$X_0 = \frac{k_{a1}k_{a2}}{[\text{H}_3\text{O}^+]^2 + [\text{H}_3\text{O}^+]k_{a1} + k_{a1}k_{a2}}$$



Dilute Weak Acid



- ① Charge balance: $[\text{H}_3\text{O}^+] = [\text{A}^-] + [\text{OH}^-]$
- ② Matter balance: $[\text{HA}]_{\text{initial}} = [\text{HA}] + [\text{A}^-]$
- ③ $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$
- ④ $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$

$$K_a = \frac{[\text{H}_3\text{O}^+] \left([\text{H}_3\text{O}^+] - \frac{K_w}{[\text{H}_3\text{O}^+]} \right)}{[\text{HA}]_{\text{initial}} - [\text{H}_3\text{O}^+] + \frac{K_w}{[\text{H}_3\text{O}^+]}}$$



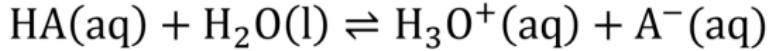
Exercise

If enough of a monoprotic acid is dissolved in water to produce a 0.0174 M solution with a pH of 6.68, what is the equilibrium constant K_a for the acid?

- 1 Chemical Equilibrium
- 2 Acid & Base
- 3 Aqueous equilibria

Buffer

- Function: maintain small change in pH when small amounts of strong acids or bases are added.
- Composition: weak acid+conjugate base or a weak base+conjugate acid.
- Best working range (experimental): $\text{pH} = \text{p}K_a \pm 1$ (conjugated acid=base in concentration)



pH Calculation

- Henderson-Hasselbalch (approximation)

$$pH = pK_a + \log \frac{[Base]_{(initial)}}{[Acid]_{(initial)}}$$

$$pOH = pK_b + \log \frac{[Acid]_{(initial)}}{[Base]_{(initial)}}$$

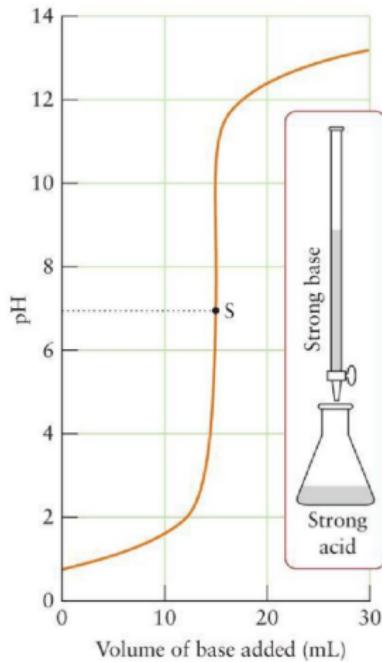
- Use ICE table to solve questions

- Strong acid reacts completely with a weak base
- Strong base reacts completely with a weak acid

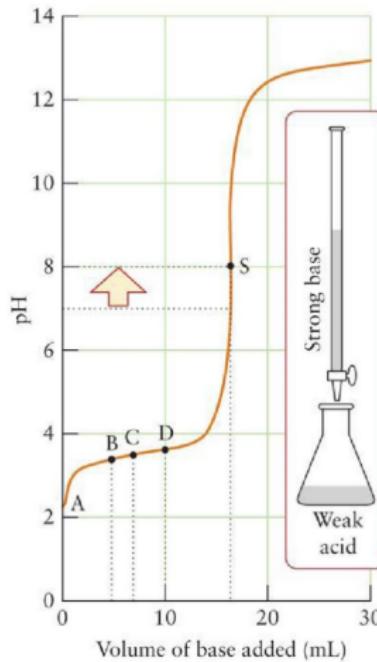


Titration

1. Strong → Strong

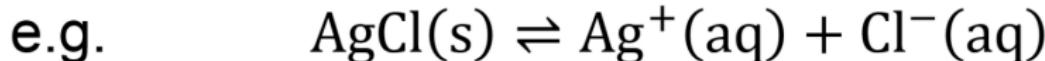


2. Strong → Weak



Solubility Equilibria

- Solubility Product (K_{SP})



$$K_{SP} = [\text{Ag}^+][\text{Cl}^-]$$

- Common-ion effect

- Based on Le Chatelier's principle
- Precipitate unwanted ions by adding common ions
- E.g. By adding Cl^-

→ equilibrium will shift to the left

→ Ag^+ will precipitate

Solubility Equilibria

- Order of precipitation
 - Compare the solubility of the precipitant
 - The one with smaller K_{SP} will precipitate first

Exercise

Calculate the solubility of $\text{CaSO}_4(\text{s})$ in 0.300 M $\text{Na}_2\text{SO}_4(\text{aq})$ at 25°C.
The K_{sp} of CaSO_4 is 4.93×10^{-5} .

Complex Ion

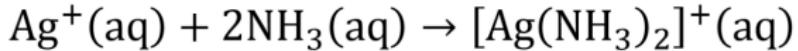
- Lewis acids and Lewis bases form coordinate covalent bonds → coordination complex
- E.g. $\text{Ag}^+(\text{aq}) + 2\text{NH}_3(\text{aq}) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(\text{aq})$
- Formation constant:

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$

K_f is often quite large, so the formation equilibrium is sometimes regarded as a one-way reaction “ \rightarrow ”

Exercise

Based on the equation



where $K_f = 2.00 \times 10^7$, determine the concentration of $\text{NH}_3(\text{aq})$ needed to dissolve 0.164 mol of AgCl(s) in 100.0 mL of solution. (The K_{SP} of AgCl is 1.77×10^{-10})

End

Q&A