VC210 Final Review

Acid& Base &Solution

Electrochemistry

Acid & Base & Solution

Definition of Acid & Base

Brønsted–Lowry Acids and Bases
An **acid** is a proton donor
A **base** is a proton acceptor

Lewis Acids and Bases
A **Lewis acid** is an electron pair acceptor.
A **Lewis base** is an electron pair donor.

In these 2 definition, an **acid does not necessarily contain $\boldsymbol{H^+}$ and a base does not necessarily contain $\boldsymbol{OH^-}$**

Definition of Acid & Base

Complete this Brønsted-Lowry reaction, placing each product by its appropriate label.

$$HCO_3^- + HCN \rightleftharpoons \boxed{H_2CO_3} + \boxed{CN^-}$$

H_2CO_3	+	CN^-
acid		base

Identify the Lewis acid and Lewis base in each of the following reactions.

$$Cl^- + AlCl_3 \longrightarrow AlCl_4^-$$

Cl^-	+	$AlCl_3$	$\longrightarrow$	$AlCl_4^-$
Lewis base		Lewis acid		

Lewis acid

Lewis base

The pH Scale

- $\mathrm{pH} = -\log\,[\mathrm{H_3O^+}]$
- $[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}}\,\mathrm{mol{\cdot}L^{-1}}$
- $\mathrm{pOH} = -\log\,[\mathrm{OH^-}]$
- $\overbrace{-\log\,[\mathrm{H_3O^+}]}^{\mathrm{pH}} + \overbrace{(-\log\,[\mathrm{OH^-}])}^{\mathrm{pOH}} = \overbrace{-\log K_w}^{\mathrm{p}K_w}$

- Because $\mathrm{p}K_w = 14.00$ at 25 °C, at that temperature

$$\mathrm{pH} + \mathrm{pOH} = 14.00$$

Conjugate

- **The Conjugate Seesaw**

$$\text{Acid} \xrightarrow{\text{donates } H^+} \text{conjugate base} \qquad \text{Base} \xrightarrow{\text{accepts } H^+} \text{conjugate acid}$$

- The stronger the acid, the weaker is its conjugate base
- The stronger the base, the weaker is its conjugate acid
- $K_a \times K_b = K_w$
- $pK_a + pK_b = pK_w$

Give the conjugate base for each compound below.

Acid	Conjugate Base
H_3PO_4	$H_2PO_4^-$
HPO_4^{2-}	PO_4^{3-}
NH_4^+	NH_3

Polyprotic Acids and Bases

- **Solutions of Salts of Polyprotic Acids**
- $$HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq) \quad K_{a2} = 7.1 \times 10^{-15}; pK_{a2} = 14.15$$
  $$HS^-(aq) + H_2O(l) \rightleftharpoons H_2S(aq) + OH^-(aq) \quad K_{b1} = K_w/K_{a1} = 7.7 \times 10^{-8}; pK_{b1} = 7.11$$
- $$pH = \tfrac{1}{2}(pK_{a1} + pK_{a2})$$
- Must check (where S is the initial concentration of the salt)

$$S \gg K_w/K_{a2} \text{ and } S \gg K_{a1}$$

Very Dilute Solutions

- **Very dilute: concentration is less than $\mathbf{10^{-6}}$**
- **Charge balance:** $[H_3O^+] = [Cl^-] + [OH^-]$
- **Material balance:** $[Cl^-] = [HCl]_{initial}$ $\quad [OH^-] = [H_3O^+] - [HCl]_{initial}$

$$K_w = [H_3O^+]\overbrace{([H_3O^+] - [HCl]_{initial})}^{[OH^-]}$$
$$= [H_3O^+]^2 - [HCl]_{initial}[H_3O^+]$$

$$[H_3O^+]^2 - [HCl]_{initial}[H_3O^+] - K_w = 0$$

- **Very Dilute Solutions of Weak Acids**
- $$K_a = \frac{[H_3O^+]\left([H_3O^+] - \frac{K_w}{[H_3O^+]}\right)}{[HA]_{initial} - [H_3O^+] + \frac{K_w}{[H_3O^+]}}$$
- $[H_3O^+]^3 + K_a[H_3O^+]^2 - (K_w + K_a[HA]_{initial})[H_3O^+] - K_aK_w = 0$

Derivation process of the formula

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \quad K_a$$

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \quad K_w = [H_3O^+][OH^-]$$

Charge balance: $[H_3O^+] = [A^-] + [OH^-]$

$$\Rightarrow [A^-] = [H_3O^+] - [OH^-] = [H_3O^+] - \frac{K_w}{[H_3O^+]}$$

Material balance: $[HA]_{initial} = [HA] + [A^-]$

$$\Rightarrow [HA] = [HA]_{initial} - \left([H_3O^+] - \frac{K_w}{[H_3O^+]}\right)$$

$$K_a = \frac{[H_3O^+]\cdot[HA]}{[HA]} = \sim$$

Buffers

- **Buffer capacity** is the maximum amount of acid or base that can be added before the buffer loses its ability to resist large changes in pH.

- A buffer is found experimentally to have a high capacity for stabilizing against the addition of acid when the amount of weak base present is at least 10% of the amount of weak acid.

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{base}]}{10[\text{base}]} = \mathrm{p}K_a + \overbrace{\log\frac{1}{10}}^{-1} = \mathrm{p}K_a - 1$$

Solubility Equilibria

- **Complex Ion Formation**
- $$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = [Ag^+][Cl^-] \qquad (\mathbf{A})$$

$$Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \qquad K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} \qquad (\mathbf{B})$$

$$AgCl(s) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq) \qquad K = K_{sp} \times K_f$$

- The solubility of a salt increases if the salt can form a complex ion with other species in the solution.

Electrochemistry

Oxidation & Reduction

- **Oxidation Reaction: Electrons are removed**
- **Reduction Reaction: Electrons are taken**

$$Zn(s) + 2\,Ag^{+}(aq) \rightarrow Zn^{2+}(aq) + 2\,Ag(s)$$

$Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^{-}$ **oxidation half-reaction.**

$2\,Ag^{+}(aq) + 2\,e^{-} \rightarrow 2\,Ag(s)$ **reduction half-reaction.**

Balancing redox reactions

Conservation of atom, charge

Surrounding/ pH:

acidic solution:$\boldsymbol{OH^-}$ would not appear in the reaction

basic solution: $\boldsymbol{H^+}$ would not appear in the reaction

- Valence up, reductant, oxidized
- Valence down, oxidant, reduced
- In some reactions, more than one reductant/ oxidant may exist.

Galvanic cell

- **Galvanic cells are spontaneous reactions generating current**

Anode: Oxidation reaction occurs

Cathode: Reduction reaction occurs

- **Notation:**

Anode electrode | anode electrolyte || cathode electrolyte | cathode electrode

$\boxed{Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)}$

- **Generally, the material of anode is more active than cathode**

- **Anode/ Cathode are not necessarily the reactant for the Redox reaction.**

Galvanic Cell

- Standard reaction Gibbs free energy
- $\Delta G^o = -nFE^o_{cell}$
- $F = 9.6485 \times 10^4 C \cdot mol^{-1}$

The value of E is the same regardless of how we write the equation

eg. Multiple the same constant with each side of the equation

Do not confuse it with the Hess’s law

- $E^o_{cell} = E^o_{right} - E^o_{left}$

Galvanic Cell

Standard Hydrogen Electrode (SHE):

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \quad E^\circ = 0.0\ V$$

- **Nernst Equation:**

$$E_{cell} = E^o_{cell} - \frac{RT}{nF} lnQ$$

- **At 298.15K, RT/F=0.025693 V**
- Can be applied to predict a cell's potential by concentration &temperature, and vice versa

Some applications:

Electrolytic Cells

Purification & Preservation of Metal

Corrosion

……

You don’t have to recite everything in the book

However, you’d better have a rough impression on these application, so that you can solve such problems faster

Calculation:

- Figure out the scenario of the problem(Polytopic. Very diluted, Buffer···) and use corresponding formula.
- Nearly all kinds of questions are covered in the final review materials on canvas. You are suggested to finish them by yourselves, and praise WYS after get A+

Some other suggestions:

- Significant Figure!!!
- Make sure you comprehend every concept correctly
  (e.g. Enthalpy of formation/ Enthalpy of combustion in MID 2)
- Review the problems on sapling learning. Try to solve those typical problems without hint.
- If you make preparation seriously, the exam would be easy; if you don't prepare, the exam would be incredibly hard.

Thank you