10610CHEM311000-Analytical Chemistry (I)

分析化學一

Second Midterm Examination

Date: 07-12-2017, 10:10 am to 12:10 pm

Answer **all 10 questions** (total 105%). You have **2** hours to finish this paper.

1. (a) What is a buffer solution, and what are its properties? **[3%]**

(b) Define buffer capacity? **[3%]**

(c) Which has the greater buffer capacity: (i) a mixture containing 0.1 mol of NH_3 and 0.2 mol of NH_4Cl or (ii) a mixture containing 0.05 mol of NH_3 and 0.1 mol of NH_4Cl? Please explain. Acid dissociation constant K_a for NH_4^+ = 5.70 x 10^{-10}. **[4%]**

Ans:

9-22. A *buffer solution* resists changes in pH with dilution or with addition of acids or bases. A buffer is composed of a mixture of a weak acid and its conjugate base.

9-23. *Buffer capacity* of a solution is defined as the number of moles of a strong acid (or a strong base) that causes 1.00 L of a buffer to undergo a 1.00-unit change in pH.

9-24.

(a) $pH = pK_a + \log\dfrac{[NH_3]}{[NH_4^+]}$ $= -\log(5.7 \text{ ? } 10^{-10}) + \log\dfrac{(0.100M)}{(0.200M)} = 8.943$

(b) $pH = pK_a + \log\dfrac{[NH_3]}{[NH_4^+]}$ $= -\log(5.7 \text{ ? } 10^{-10}) + \log\dfrac{(0.050M)}{(0.100M)} = 8.943$

Although the two solutions have identical pH values, the solution in (a) has the greatest buffer capacity, because it has the higher concentration of weak acid and its conjugate base.

2. What mass of sodium formate must be added to 500.0 mL of 1.0 M formic acid to produce a buffer solution that has a pH of 3.50? (formic acid pK$_a$ = 3.74, molecular weight of sodium formate = 67.997g/mol) **[10%]**

Ans

9-27.

$$pH = 3.50 = pK_a + \log\frac{[HCOO^-]}{[HCOOH]} = -\log(1.8 \times 10^{-4}) + \log\frac{[HCOO^-]}{[HCOOH]}$$

$$3.50 = 3.74 + \log\frac{[HCOO^-]}{[HCOOH]} \qquad \frac{[HCOO^-]}{[HCOOH]} = 10^{-0.24} = 0.575$$

$$500 \text{ mL} \times 1.00 \frac{\text{mmol HCOOH}}{\text{mL}} = 500 \text{ mmol}$$

So amount of HCOO⁻ needed = 0.575 × 500 mmol = 287.5 mmol

287.5 mmol × 10⁻³ mol/mmol = 0.2875 mol HCOO⁻

Mass HCOONa = 0.2875 mol × 67.997 g/mol = 19.6 g

3. (a) Explain why the activity coefficient for a neutral molecule is usually 1. **[5%]**

(b) Calculate the ionic strength of a solution that is 0.30 M in $FeCl_3$ and 0.20 M in $FeCl_2$. **[5%]**
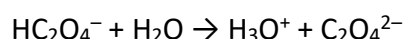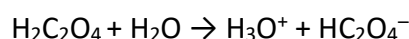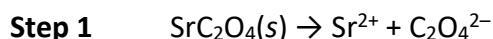
Ans

10-6. There is no ionic atmosphere surrounding a neutral molecule and so its activity is does not change with increasing ionic strength.   Hence, its activity coefficient is essentially unity and its activity is equal to its concentration.

10-9.   **(c)** $\mu = \frac{1}{2}[0.30 \times 3^2 + 0.90 \times 1^2 + 0.20 \times 2^2 + 0.40 \times 1^2] = 2.4$

4. Calculate the molar solubility of SrC_2O_4 in a solution that has a fixed H_3O^+ concentration of 1.0×10^{-6} M. Solubility product of SrC_2O_4 $K_{sp} = 5 \times 10^{-8}$, Dissociation constant for oxalic acid $H_2C_2O_4$, $K_1 = 5.6 \times 10^{-2}$, $K_2 = 2.42 \times 10^{-5}$. **[15%]**

Ans:

11-7. Following the systematic procedure, using part (a)

Step 1 $SrC_2O_4(s) \rightarrow Sr^{2+} + C_2O_4^{2-}$

$H_2C_2O_4 + H_2O \rightarrow H_3O^+ + HC_2O_4^-$

$HC_2O_4^- + H_2O \rightarrow H_3O^+ + C_2O_4^{2-}$

Step 2 $S = $ solubility $= [Sr^{2+}] = [C_2O_4^{2-}] + [HC_2O_4^-] + [H_2C_2O_4]$

Step 3 $[Sr^{2+}][C_2O_4^{2-}] = K_{sp} = 5 \times 10^{-8}$ $\hspace{2cm}$ (1)

$$\frac{[H_3O^+][HC_2O_4^-]}{[H_2C_2O_4]} = K_1 = 5.6 \times 10^{-2} \hspace{2cm} (2)$$

$$\frac{[H_3O^+][C_2O_4^-]}{[HC_2O_4^-]} = K_2 = 2.42 \times 10^{-5} \hspace{2cm} (3)$$

Step 4 $[Sr^{2+}] = [C_2O_4^{2-}] + [HC_2O_4^-] + [H_2C_2O_4]$ $\hspace{1.5cm}$ (4)

$[H_3O^+] = 1.0 \times 10^{-6}$ M

Step 5 No charge balance because an unknown buffer is maintaining the pH.

Step 6 Unknowns are $[Sr^{2+}]$, $[C_2O_4^{2-}]$, $[HC_2O_4^-]$, $[H_2C_2O_4]$

Step 7 No approximations needed, because we have 4 equations and 4 unkowns.

Step 8 Substituting $[H_3O^+] = 1.0 \times 10^{-6}$ M into equation (3) and rearranging gives

$$[HC_2O_4^-] = \frac{1 \times 10^{-6}[C_2O_4^-]}{5.42 \times 10^{-5}} = 1.845 \times 10^{-2}[C_2O_4^-]$$

Substituting this relationship and $[H_3O^+] = 1.0 \times 10^{-6}$ M into equation (2) and rearranging gives

$$[H_2C_2O_4] = \frac{1 \times 10^{-6} \times 1.845 \times 10^{-2}[C_2O_4^-]}{5.6 \times 10^{-2}} = 3.295 \times 10^{-7}[C_2O_4^-]$$

Substituting these last two relationships in to equation (4) gives

$[Sr^{2+}] = [C_2O_4^{2-}] + 1.845 \times 10^{-2}[C_2O_4^{2-}] + 3.295 \times 10^{-7}[C_2O_4^{2-}] = 1.0185[C_2O_4^{2-}]$

Substituting this last relationship into equation (1) gives

$$K_{sp} = \frac{[Sr^{2+}][Sr^{2+}]}{1.0185} = 5 \times 10^{-8}$$

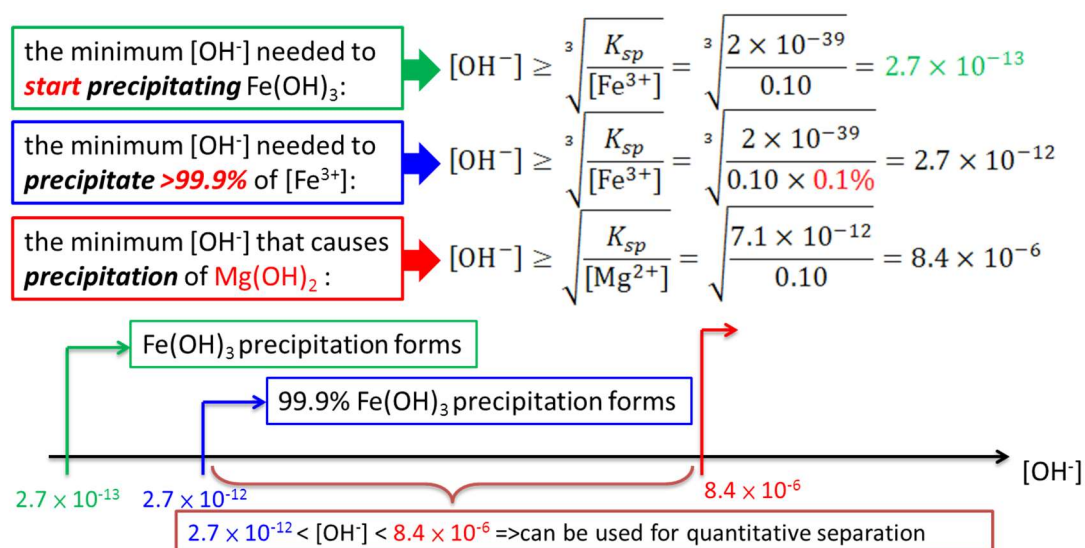$[Sr^{2+}] = (5 \times 10^{-8} \times 1.0185)^{1/2} = 2.26 \times 10^{-4}$

$S = [Sr^{2+}] = 2.3 \times 10^{-4}$ M

5. Can Fe^{3+} and Mg^{2+} be separated quantitatively (more than 99.9% form precipitate) as hydroxides from a solution that is 0.10 M in each cation? If the separation is possible, what **range** of [OH-] is required? (K_{sp} of $Fe(OH)_3$= 2 × 10^{-39}; K_{sp} of $Mg(OH)_2$= 7.1 × 10^{-12}). **[10%]**

Ans:

quantitative precipitation => more than 99.9% form precipitate => less than 0.1% left as aqueous ions

the minimum [OH-] needed to ***start precipitating*** $Fe(OH)_3$:	$[OH^-] \geq \sqrt[3]{\dfrac{K_{sp}}{[Fe^{3+}]}} = \sqrt[3]{\dfrac{2 \times 10^{-39}}{0.10}} = 2.7 \times 10^{-13}$
the minimum [OH-] needed to ***precipitate >99.9%*** of [Fe^{3+}]:	$[OH^-] \geq \sqrt[3]{\dfrac{K_{sp}}{[Fe^{3+}]}} = \sqrt[3]{\dfrac{2 \times 10^{-39}}{0.10 \times 0.1\%}} = 2.7 \times 10^{-12}$
the minimum [OH-] that causes ***precipitation*** of $Mg(OH)_2$:	$[OH^-] \geq \sqrt{\dfrac{K_{sp}}{[Mg^{2+}]}} = \sqrt{\dfrac{7.1 \times 10^{-12}}{0.10}} = 8.4 \times 10^{-6}$

$Fe(OH)_3$ precipitation forms

99.9% $Fe(OH)_3$ precipitation forms

[OH-]

2.7 x 10^{-13} 2.7 x 10^{-12} 8.4 x 10^{-6}

2.7 x 10^{-12} < [OH-] < 8.4 x 10^{-6} =>can be used for quantitative separation

Or refer to the Skoog text book page 268.

6. A 0.872 g sample of a mixture consisting solely of sodium bromide and potassium bromide yields 1.505 g of silver bromide after silver precipitation. What are the percentage of two salts in the sample? Molecular weight of NaBr = 102.894 g/mol, KBr = 119.002 g/mol, AgBr = 187.772 g/mol. **[10%]**

Ans:

12-27. $\mathcal{M}_{NaBr} = 102.894$ g/mol $\mathcal{M}_{KBr} = 119.002$ g/mol $\mathcal{M}_{AgBr} = 187.772$ g/mol

0.8720 g sample $= x$ g NaBr$+ y$ g KBr

g AgBr from NaBr $= x$ g NaBr ? $\dfrac{1 \text{ mol NaBr}}{102.894 \text{ g}}$? $\dfrac{1 \text{ mol AgBr}}{1 \text{ mol NaBr}}$? $\dfrac{187.772 \text{ g AgBr}}{1 \text{ mole}}$ $= 1.823\ x$ g AgBr

g AgBr from KBr $= y$ g KBr ? $\dfrac{1 \text{ mol KBr}}{119.002 \text{ g}}$? $\dfrac{1 \text{ mol AgBr}}{1 \text{ mol KBr}}$? $\dfrac{187.772 \text{ g AgBr}}{1 \text{ mol}}$ $=1.578\ y$ g AgBr

1.505 g AgBr $= 1.823$ (x g NaBr) $+ 1.578$ (y g KBr)

So, we have 2equations and 2 unknowns,

$x + y = 0.8720$

$1.823x + 1.578y = 1.505.$

x = 0.342,   y = 0.530

%KBr = (0.342/0.872) * 100% =39.6%

%NaBr = 60.4%

7. There are four types of coprecipitation: surface adsorption, mixed-crystal formation, occlusion and mechanical entrapment that can cause contamination during gravimetric analysis. Please explain these four coprecipitation processes and how to remove the contaminant. **[10%]**

Ans:

You can refer to the Skoog Text book page 286-289 or the following

Coprecipitation

Coprecipitation is a process in which the **normally soluble** compounds **are carried out of solution** by a precipitate.
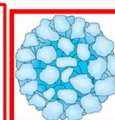
Four types of coprecipitation
1. surface adsorption
2. mixed-crystal formation
3. occlusion (吸納)
4. mechanical entrapment

Surface adsorption is the major source of *contamination* in coagulation colloids but of no significance in crystalline precipitates=> the purity can be improved by digestion, *i.e.* re-crystallization. [Example] Coagulated $AgCl_{(s)}$ is usually contaminated by $AgNO_3$ due to coprecipitation.

[Think] How to remove contaminations from coprecipitation?

Ans:
1. washing with a solution containing a volatile electrolyte
2. re-precipitation

In **mixed-crystal formation**, a contaminant ion replaces an ion in the lattice of a crystal
=> This requires: (a) same ionic charge, (b) similar ion size, < 5% difference, (c) same crystal class. [Example] $BaSO_4$ and $PbSO_4$
=> Hard to avoid! use different precipitation reagent that does not contain contaminant ions.

In **occlusion**, a compound is trapped within a pocket formed due to **rapid crystal growth**. The amount in contaminant is greatest in the part of a crystal that form first=> **Why?**

[Think] How to avoid **occlusion** and **mechanical entrapment** ?

Ans:
1. slow precipitation
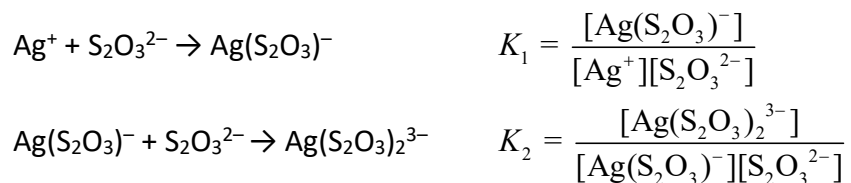2. digestion at high temperature

Mechanical entrapment occurs when crystals lie close together during growth=> solution is trapped in a tiny pocket.

Coprecipitation errors can be either positive or negative!

8. (a) Write chemical equations and equilibrium constant expressions for the stepwise formation of $Ag(S_2O_3)_2^{3-}$. **[5%]**

(b) Explain how stepwise and overall formation constants are related. **[5%]**

Ans:

17-1. **(a)**

$$Ag^+ + S_2O_3^{2-} \rightarrow Ag(S_2O_3)^- \qquad K_1 = \frac{[Ag(S_2O_3)^-]}{[Ag^+][S_2O_3^{2-}]}$$

$$Ag(S_2O_3)^- + S_2O_3^{2-} \rightarrow Ag(S_2O_3)_2^{3-} \qquad K_2 = \frac{[Ag(S_2O_3)_2^{3-}]}{[Ag(S_2O_3)^-][S_2O_3^{2-}]}$$

17-2. The overall formation constant β_n is equal to the product of the individual stepwise constants. Thus, the overall constant for formation of $Ag(S_2O_3)_2^{3-}$ in Problem 17-1 (a) is

$$\beta_2 = K_1K_2 = \frac{[Ag(S_2O_3)_2^{3-}]}{[Ag^+][S_2O_3^{2-}]^2}$$

9. Write equations in terms of the acid dissociation constant (K_a) and [H$^+$] for the alpha value (α_1) of acetic acid (HOAc). **[10%]**

17-3. **(a)** Acetate (OAc$^-$)

HOAc → OAc$^-$ + H$^+$ $\qquad K_a = \dfrac{[\text{OAc}^-][\text{H}^+]}{[\text{HOAc}]}$

c_T = [HOAc] + [OAc$^-$]

$$= \frac{[\text{OAc}^-][\text{H}^+]}{K_a} + [\text{OAc}^-] = [\text{OAc}^-]\left\{\frac{[\text{H}^+]}{K_a} + 1\right\} = [\text{OAc}^-]\left\{\frac{[\text{H}^+] + K_a}{K_a}\right\}$$

$$\alpha_1 = \frac{[\text{OAc}^-]}{c_T} = \frac{K_a}{[\text{H}^+] + K_a}$$

10. (a) Propose an EDTA complexometric method for the determination of the individual components in a solution containing In^{3+}, Zn^{2+} and Mg^{2+}. **[5%]**

(b) Why is a small amount of MgY^{2-} (Y = EDTA) often added to a water specimen that is to be titrated for hardness (e.g. Ca^{2+})? **[5%]**

Ans:

17-4. First, titrate an aliquot that has been brought to a pH of about 1.5. Only the indium is complexed under these conditions. Then, Buffer a second aliquot to a pH of about 4 and titrate the zinc. Finally, Titrate the Magnesium in an aliquot of the sample that has been buffered to a pH of about 10.

17-5. The MgY^{2-} is added to assure a sufficient analytical concentration of Mg^{2+} **to provide a sharp end point** with Eriochrome Black T indicator.

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