

11010CHEM311000-Analytical Chemistry (I) 分析化學一

Second Midterm Examination

Date: 14-12-2021, 10:10 am to 12:30 pm

Answer all 10 questions (total 100%). You have 2 hours and 20 minutes to finish this paper.

1. What mass of sodium formate (MW = 67.99 g/mol) must be added to 500 mL of 1.00 M formic acid (MW = 46.03 g/mol, and $K_a = 1.8 \times 10^{-4}$) to produce a buffer solution that has a pH of 3.50? [10 %]

ANS:

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

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

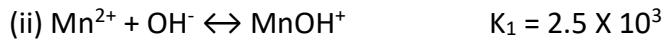
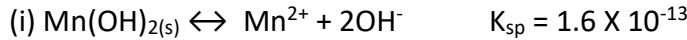
$$500 \text{ mL} \times 1.00 \frac{\text{mmol HCOOH}}{\text{mL}} = 500 \text{ mmol}$$

$$\text{So amount of } HCOO^- \text{ needed} = 0.575 \times 500 \text{ mmol} = 287.5 \text{ mmol}$$

$$287.5 \text{ mmol} \times 10^{-3} \text{ mol/mmol} = 0.2875 \text{ mol } HCOO^-$$

$$\text{Mass HCOONa} = 0.2875 \text{ mol} \times 67.99 \text{ g/mol} = \underline{\underline{19.54 \text{ g}}}$$

2. Find the activity of OH^- in 0.10 M NaClO_4 saturated with $\text{Mn}(\text{OH})_2$. At 0.10 M ionic strength, the activity coefficient for $\gamma_{\text{Mn}^{2+}} = 0.405$, $\gamma_{\text{MnOH}^+} = 0.80$, and $\gamma_{\text{OH}^-} = 0.76$, respectively. Consider just the following chemistry: [15 %]



ANS:

$$\text{Charge balance: } 2[\text{Mn}^{2+}] + [\text{MnOH}^+] + [\text{H}^+] = [\text{OH}^-]$$

$$\text{Mass balance: } [\text{OH}^-] + [\text{MnOH}^+] = 2\{[\text{Mn}^{2+}] + [\text{MnOH}^+]\} + [\text{H}^+]$$



Species containing OH^- Species containing Mn^{2+}

(Mass balance gives the same result as charge balance)

Equilibrium constant expression in terms of activity

$$K_{sp} = [\text{Mn}^{2+}] \gamma_{\text{Mn}^{2+}} [\text{OH}^-]^2 \gamma_{\text{OH}^-}$$

$$K_1 = \frac{[\text{MnOH}^+] \gamma_{\text{MnOH}^+}}{[\text{Mn}^{2+}] \gamma_{\text{Mn}^{2+}} [\text{OH}^-] \gamma_{\text{OH}^-}}$$

$$K_w = [\text{H}^+] \gamma_{\text{H}^+} [\text{OH}^-] \gamma_{\text{OH}^-}$$

$$\text{From } K_1, \text{ we write } [\text{MnOH}^+] = \left(\frac{K_1}{\gamma_{\text{MnOH}^+}} \right) ([\text{Mn}^{2+}] \gamma_{\text{Mn}^{2+}} [\text{OH}^-] \gamma_{\text{OH}^-})$$

Substitute for $[\text{MnOH}^+]$ in the charge balance:

$$2[\text{Mn}^{2+}] + \left(\frac{K_1}{\gamma_{\text{MnOH}^+}} \right) ([\text{Mn}^{2+}] \gamma_{\text{Mn}^{2+}} [\text{OH}^-] \gamma_{\text{OH}^-}) + [\text{H}^+] = [\text{OH}^-] \quad (\text{A})$$

In a basic solution, neglect $[\text{H}^+]$ in comparison $[\text{OH}^-]$ and solve the equation (A) for $[\text{Mn}^{2+}]$

$$[\text{Mn}^{2+}] = \frac{[\text{OH}^-]}{2 + \left(\frac{K_1 \gamma_{\text{Mn}^{2+}}}{\gamma_{\text{MnOH}^{2+}}} \right) [\text{OH}^-] \gamma_{\text{OH}^-}} \quad (\text{B})$$

Substitute (B) into K_{sp} :

$$K_{sp} = \frac{[\text{OH}^-]^3 \gamma_{\text{Mn}^{2+}} \gamma_{\text{OH}^-}^2}{2 + \left(\frac{K_1 \gamma_{\text{Mn}^{2+}}}{\gamma_{\text{MnOH}^{2+}}} \right) [\text{OH}^-] \gamma_{\text{OH}^-}} \quad (\text{C})$$

Solve equation (C), the value of $[\text{OH}^-] = \underline{1.13 \times 10^{-4} \text{ M}}$

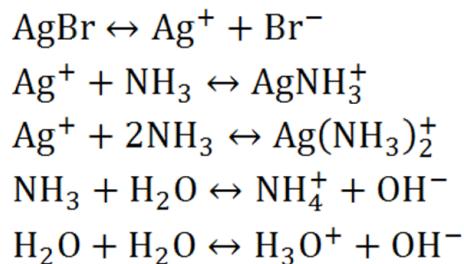
The activity = $[\text{OH}^-] \times 0.76 = \underline{8.59 \times 10^{-5}}$

3. (a) Write **mass balance expressions** (as many as possible) for the system formed when a 0.010 M NH₃ solution is saturated with AgBr. [5 %]

(b) Write a **charge balance equation** for a saturated solution of CdCO₃. [5 %]

ANS:

(a) You can refer to the Skoog text book, page 252 or the following

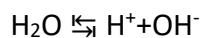
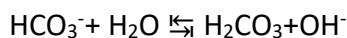
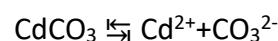


All **Ag containing species** comes from **AgBr** and the **ratio is 1:1**
=> [Br⁻] = [Ag⁺] + [AgNH₃⁺] + [Ag(NH₃)₂⁺]

All **N containing species** comes from **NH₃** (0.010 M)
=> 0.010 M = [NH₃] + [NH₄⁺] + [AgNH₃⁺] + 2[Ag(NH₃)₂⁺]

OH⁻ comes from **the last two equilibria**
=> [OH⁻] = [NH₄⁺] + [H₃O⁺]

(b) The equilibria are



Again, the charge concentration for the singly charged species (H⁺, OH⁻, HCO₃⁻) will be equal to the concentrations of the species. But for Cd²⁺ and CO₃²⁻ the charge concentration will be twice their concentrations. We must again equate the positive and negative charge concentrations.

$$2[\text{Cd}^{2+}] + [\text{H}^+] = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-]$$

4. Silver ion is being considered for separating I^- from SCN^- in a solution that is 0.040 M in KI and 0.080 M in NaSCN. (K_{sp} for AgI = 8.3×10^{-17} ; AgSCN = 1.1×10^{-12})

- (i) What Ag^+ concentration is needed to lower the I^- concentration to 1.0×10^{-6} M? [2.5 %]
- (ii) What is the Ag^+ concentration of the solution when AgSCN begins to precipitate? [2.5 %]
- (iii) What is the ratio of SCN^- to I^- when AgSCN begins to precipitate? [2.5 %]
- (iv) What is the ratio of SCN^- to I^- when the Ag^+ concentration is 1.0×10^{-3} M? [2.5 %]

ANS:

- (i) $[Ag^+] = K_{sp}/[I^-] = 8.3 \times 10^{-17}/(1.0 \times 10^{-6}) = \underline{\underline{8.3 \times 10^{-11} M}}$
- (ii) $[Ag^+] = K_{sp}/[SCN^-] = 1.1 \times 10^{-12}/(0.080) = 1.375 \times 10^{-11} M \approx \underline{\underline{1.4 \times 10^{-11} M}}$
- (iii) $[I^-]$ when $[Ag^+] = 1.375 \times 10^{-11} M$
 $[I^-] = 8.3 \times 10^{-17}/(1.375 \times 10^{-11}) = 6.0 \times 10^{-6} M$
 $[SCN^-]/[I^-] = 0.080/(6.0 \times 10^{-6}) = \underline{\underline{1.3 \times 10^4}}$
- (iv) $[I^-] = 8.3 \times 10^{-17}/(1.0 \times 10^{-3}) = 8.3 \times 10^{-14} M$
 $[SCN^-] = 1.1 \times 10^{-12}/(1.0 \times 10^{-3}) = 1.1 \times 10^{-9} M$
 $[SCN^-]/[I^-] = 1.1 \times 10^{-9}/(8.3 \times 10^{-14}) = \underline{\underline{1.3 \times 10^4}}$

Note that this ratio is independent of $[Ag^+]$ as long as some $AgSCN_{(s)}$ is present.

5. Is it possible to precipitate 99.0% of 0.010 M Ce³⁺ by adding oxalate (C₂O₄²⁻) without precipitating 0.010 M Ca²⁺? CaC₂O₄ K_{sp} = 1.3 X 10⁻⁸, Ce₂(C₂O₄)₃ K_{sp} = 5.9 X 10⁻³⁰. [10 %]

ANS:

We want to reduce [Ce³⁺] to 1.0% of 0.010 M = 0.00010 M. The concentration of oxalate in equilibrium with 0.00010 M Ce³⁺ is computed as follows:

$$[\text{Ce}^{3+}]^2[\text{C}_2\text{O}_4^{2-}]^3 = K_{\text{sp}} = 5.9 \times 10^{-30}$$

$$(0.00010)^2[\text{C}_2\text{O}_4^{2-}]^3 = 5.9 \times 10^{-30}$$

$$[\text{C}_2\text{O}_4^{2-}] = \sqrt[3]{\frac{5.9 \times 10^{-30}}{(0.00010)^2}} = \underline{\underline{8.4 \times 10^{-8} \text{ M}}}$$

To see if 8.4 X 10⁻⁸ M C₂O₄²⁻ will precipitate 0.010 M Ca²⁺, evaluate Q for CaC₂O₄.

$$Q = [\text{Ca}^{2+}]^2[\text{C}_2\text{O}_4^{2-}] = (0.010)(8.4 \times 10^{-8}) = 8.4 \times 10^{-10}$$

Because Q < K_{sp} for CaC₂O₄ (K_{sp} = 1.3 X 10⁻⁸), Ca²⁺ will not precipitate.

6. In her PhD research (*Radioactive Substances*, 1903), Marie Curie measured the atomic mass of the element radium, which she discovered. She knew that radium is in the same family as barium, so the formula of radium chloride is RaCl_2 . When 0.09192 g of pure RaCl_2 was dissolved and treated with excess AgNO_3 , 0.08890 g of AgCl precipitated. MW for $\text{AgCl} = 143.21$ and $\text{Cl} = 35.453$.

- (a) How many moles of Cl^- were in the RaCl_2 ? [5 %]
- (b) From the measurement, find the atomic mass of Ra. [5 %]

ANS:

(a) AgCl precipitate weighing 0.08890 g contains $0.08890/143.21(\text{AgCl}) = 6.202 \times 10^{-4}$ mol AgCl . Because 1 mol of AgCl contains 1 mol of Cl^- , there must have been 6.202×10^{-4} mol Cl^- in the RaCl_2 .

(b) For 2 mol of Cl^- , there must be 1 mol of Ra, so mol Ra = $6.202 \times 10^{-4}/2 = 3.101 \times 10^{-4}$ mol.

Let the MW of RaCl_2 be x. We found that 0.09192 g RaCl_2 contains 3.101×10^{-4} mol RaCl_2 .

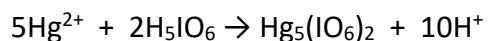
Therefore, $3.101 \times 10^{-4} = 0.09192/x$

$$x = 296.3 \text{ g/mol}$$

The atomic mass of Cl is 35.453, so the MW of RaCl_2 is $296.3 = \text{atomic mass of Ra} + 2(35.453)$

$$\text{Atomic mass of Ra} = \underline{\underline{225.5 \text{ g/mol}}}$$

7. The mercury in a 1.0451 g sample was precipitated with an excess of paraperiodic acid, H_5IO_6 :



The precipitate was filtered, washed free of precipitating agent, dried and weighed, and $Hg_5(IO_6)_2$ ($M_{Hg_5(IO_6)_2} = 1448.75$ g/mol) of 0.5718 g was recovered. Calculate the percentage of Hg_2Cl_2 ($M_{Hg_2Cl_2} = 472.18$ g/mol) in the sample. [10 %]

ANS:

$$\left(\frac{0.5718 \text{ g } Hg_5(IO_6)_2 \times \frac{1 \text{ mol } Hg_5(IO_6)_2}{1448.75 \text{ g } Hg_5(IO_6)_2} \times \frac{5 \text{ mol } Hg^{2+}}{1 \text{ mol } Hg_5(IO_6)_2} }{ \frac{1 \text{ mol } Hg_2Cl_2}{2 \text{ mol } Hg^{2+}} \times \frac{472.18 \text{ g } Hg_2Cl_2}{1 \text{ mol } Hg_2Cl_2} } \right) \times 100\% = 44.58\% \text{ } Hg_2Cl_2$$

8. Chromel is an alloy composed of nickel (Ni = 58.69 g/mol), iron (Fe = 55.847 g/mol) and chromium (Cr = 51.996 g/mol). A 0.6553 g sample was dissolved and diluted to 250.0 mL. When a 50.00 mL aliquot of 0.05173 M EDTA was mixed with an equal volume of the diluted sample, all three ions were chelated, and a 5.34 mL back-titration with 0.06139 M copper (II) was required. The chromium in a second 50.0 mL aliquot was masked through the addition of hexamethylenetetramine; titration of the Fe and Ni required 36.98 mL of 0.05173 M EDTA. Iron and chromium were masked with pyrophosphate in a third 50.0 mL aliquot, and the nickel was titrated with 24.53 mL of the EDTA solution. Calculate the percentages of nickel, chromium, and iron in the alloy. [15 %]

ANS:

$$\text{Amnt EDTA reacted in 50.00 mL} = \left(\frac{0.05173 \text{ mmol EDTA}}{\text{mL}} \times 50.00 \text{ mL EDTA} \right) - \left(\frac{0.06139 \text{ mmol Cu}^{2+}}{\text{mL}} \times 5.34 \text{ mL Cu}^{2+} \times \frac{1 \text{ mmol EDTA}}{\text{mmol Cu}^{2+}} \right) = 2.2587 \text{ mmol}$$

$$\text{Amnt EDTA reacted in 250.0 mL} = \text{Amnt (Ni + Fe + Cr)} = \frac{2.2587 \text{ mmol}}{\left(\frac{50.00 \text{ mL}}{250.0 \text{ mL}} \right)} = 11.2934 \text{ mmol}$$

$$\text{Amnt (Ni + Fe)} = \frac{\left(\frac{0.05173 \text{ mmol EDTA}}{\text{mL}} \times 36.98 \text{ mL EDTA} \right)}{\frac{50.00 \text{ mL}}{250.0 \text{ mL}}} = 9.5649 \text{ mmol}$$

$$\text{Amnt Cr} = 11.2934 \text{ mmol} - 9.5649 \text{ mmol} = 1.7285 \text{ mmol}$$

$$\text{Amnt Ni} = \frac{\left(\frac{0.05173 \text{ mmol EDTA}}{\text{mL}} \times 24.53 \text{ mL EDTA} \times \frac{1 \text{ mmol Ni}}{\text{mmol EDTA}} \right)}{\frac{50.00 \text{ mL}}{250.0 \text{ mL}}} = 6.3447 \text{ mmol}$$

$$\text{Amnt Fe} = 9.5649 \text{ mmol} - 6.3447 \text{ mmol} = 3.2202 \text{ mmol}$$

$$\% \text{Cr} = \frac{1.7285 \text{ mmol Cr} \times \frac{51.996 \text{ g Cr}}{1000 \text{ mmol}}}{0.6553 \text{ g}} \times 100\% = 13.72\%$$

$$\% \text{Ni} = \frac{6.3447 \text{ mmol Ni} \times \frac{58.69 \text{ g Ni}}{1000 \text{ mmol}}}{0.6553 \text{ g}} \times 100\% = 56.82\%$$

$$\% \text{Fe} = \frac{3.2202 \text{ mmol Fe} \times \frac{55.847 \text{ g Fe}}{1000 \text{ mmol}}}{0.6553 \text{ g}} \times 100\% = 27.44\%$$

9. The acid HA has $pK_a = 7.00$

- (i) Which is the principal species, HA or A^- , at pH 6.00? [1 %]
- (ii) Which is the principal species at pH 8.00? [1 %]
- (iii) What is the quotient $[A^-]/[HA]$ at pH 6.00? [3 %]

ANS:

- (i) HA
- (ii) A^-
- (iii) $6.00 = 7.00 + \log[A^-]/[HA]$
- $[A^-]/[HA] = \underline{\text{0.1}}$

- 10.** The acid HA has $pK_a = 4.00$. Find the fraction in the form HA (α_{HA}) and the fraction in the form A^- (α_{A^-}) at $pH = 5.00$. [5 %]

ANS:

$$\text{Fraction in form HA} = \alpha_{HA} = \frac{[H^+]}{[H^+] + K_a} = \frac{10^{-5}}{10^{-5} + 10^{-4}} = \underline{\underline{0.091}}$$

$$\text{Fraction in from } A^- = \alpha_{A^-} = \frac{K_a}{[H^+] + K_a} = \frac{10^{-4}}{10^{-5} + 10^{-4}} = \underline{\underline{0.909}}$$

~ End of Paper ~

TABLE 10-2

Activity Coefficients for Ions at 25°C

| Ion | α_x, nm | Activity Coefficient at Indicated Ionic Strength | | | | |
|--|----------------|--|-------|-------|-------|-------|
| | | 0.001 | 0.005 | 0.01 | 0.05 | 0.1 |
| H_3O^+ | 0.9 | 0.967 | 0.934 | 0.913 | 0.85 | 0.83 |
| $Li^+, C_6H_5COO^-$ | 0.6 | 0.966 | 0.930 | 0.907 | 0.83 | 0.80 |
| $Na^+, IO_3^-, HSO_3^-, HCO_3^-, H_2PO_4^-, H_2AsO_4^-, OAc^-$ | 0.4–0.45 | 0.965 | 0.927 | 0.902 | 0.82 | 0.77 |
| $OH^-, F^-, SCN^-, HS^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_3^-, MnO_4^-$ | 0.35 | 0.965 | 0.926 | 0.900 | 0.81 | 0.76 |
| $K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-, HCOO^-$ | 0.3 | 0.965 | 0.925 | 0.899 | 0.81 | 0.75 |
| $Rb^+, Cs^+, Ti^+, Ag^+, NH_4^+$ | 0.25 | 0.965 | 0.925 | 0.897 | 0.80 | 0.75 |
| Mg^{2+}, Be^{2+} | 0.8 | 0.872 | 0.756 | 0.690 | 0.52 | 0.44 |
| $Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Phthalate^{2-}$ | 0.6 | 0.870 | 0.748 | 0.676 | 0.48 | 0.40 |
| $Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}$ | 0.5 | 0.869 | 0.743 | 0.668 | 0.46 | 0.38 |
| $Pb^{2+}, CO_3^{2-}, SO_3^{2-}, C_2O_4^{2-}$ | 0.45 | 0.868 | 0.741 | 0.665 | 0.45 | 0.36 |
| $Hg_2^{2+}, SO_4^{2-}, S_2O_3^{2-}, Cr_4^{2-}, HPO_4^{2-}$ | 0.40 | 0.867 | 0.738 | 0.661 | 0.44 | 0.35 |
| $Al^{3+}, Fe^{3+}, Cr^{3+}, La^{3+}, Ce^{3+}$ | 0.9 | 0.737 | 0.540 | 0.443 | 0.24 | 0.18 |
| $PO_4^{3-}, Fe(CN)_6^{3-}$ | 0.4 | 0.726 | 0.505 | 0.394 | 0.16 | 0.095 |
| $Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}$ | 1.1 | 0.587 | 0.348 | 0.252 | 0.10 | 0.063 |
| $Fe(CN)_6^{4-}$ | 0.5 | 0.569 | 0.305 | 0.200 | 0.047 | 0.020 |

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