

11310CHEM311000-Analytical Chemistry (I) 分析化學一

Second Midterm Examination

Date: 19-11-2024, 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. Calculate the pH of water at (a) 25°C and (b) 50°C. The values for pK_w at these temperatures are 13.99 and 13.26, respectively. [10%]

Solution:

At 25°C, $pK_w = 13.99$, $K_w = 1.023 \times 10^{-14}$.

At 50°C, $pK_w = 13.26$, $K_w = 5.495 \times 10^{-14}$.

$[H_3O^+] = [OH^-]$ in pure water. Thus $[H_3O^+] = \sqrt{K_w}$.

At 25°C, $[H_3O^+] = \sqrt{1.023 \times 10^{-14}} = 1.011 \times 10^{-7} M$,

$$pH = -\log[H_3O^+] = 6.99_5 \approx 7.00.$$

At 50°C, $[H_3O^+] = \sqrt{5.495 \times 10^{-14}} = 2.3442 \times 10^{-7} M$,

$$pH = 6.63.$$

2. What the mass of sodium glycolic must be added to 400.0 mL of 1.00 M glycolic acid to produce a buffer solution that has a pH of 4.25? pKa of glycolic acid is 3.83. Molecular weight of glycolic acid is 76.05 g/mol. [10%]

Solution:

Let HGI = glycolic acid

$$\text{pH} = 4.25 = \text{pK}_a + \log \frac{[\text{GI}^-]}{[\text{HGI}]} = 3.83 + \log \frac{[\text{GI}^-]}{[\text{HGI}]}$$

$$\log \frac{[\text{GI}^-]}{[\text{HGI}]} = 4.25 - 3.83 = 0.42$$

$$\frac{[\text{GI}^-]}{[\text{HGI}]} = 2.63$$

$$\text{amount of HGI} = 400.0 \text{ mL} \times 1.00 \text{ M} = 400 \text{ mmol or } 0.400 \text{ mol}$$

$$\text{Need } 0.400 \times 2.63 = 1.052 \text{ mol NaGI}$$

$$\text{Mass of NaGI needed is } 1.052 \text{ mol} \times 98.01 \text{ g/mol} = 103.1 \text{ g}$$

3. Calculate the ionic strength of a solution that is:

- (a) 0.25 M in FeCl_3 and 0.15 M in 0.15 M in FeCl_2 . [5%]
(b) 0.025 M in $\text{La}(\text{NO}_3)_3$ and 0.050 M in $\text{Fe}(\text{NO}_3)_2$. [5%]

Solution:

- (a) 0.25 M in FeCl_3 and 0.15 M in 0.15 M in FeCl_2 .

$$\mu = \frac{1}{2}(0.25 \times 3^2 + 0.75 \times 1^2 + 0.15 \times 2^2 + 0.30 \times 1^2) = 1.95$$

- (b) 0.025 M in $\text{La}(\text{NO}_3)_3$ and 0.050 M in $\text{Fe}(\text{NO}_3)_2$.

$$\mu = \frac{1}{2}(0.025 \times 3^2 + 0.075 \times 1^2 + 0.050 \times 2^2 + 0.100 \times 1^2) = 0.30$$

4. Can Fe^{3+} and Mg^{2+} be separated quantitatively as hydroxides from a solution that is 0.10 M in each cation? If the separation is possible, what range of OH^- concentrations is permissible? $K_{\text{sp}}(\text{Fe}(\text{OH})_3) = 2 \times 10^{-39}$; $K_{\text{sp}}(\text{Mg}(\text{OH})_2) = 7.1 \times 10^{-12}$. (Assume that a precipitation is quantitative when $[\text{M}^+] < 1 \times 10^{-4}$ and activity effects can be neglected.)

[10%]

Solution:

Solubility-product constants for the two precipitates are

$$K_{\text{sp}} = [\text{Fe}^{3+}][\text{OH}^-]^3 = 2 \times 10^{-39}$$

$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 7.1 \times 10^{-12}$$

Because the K_{sp} for $\text{Fe}(\text{OH})_3$ is so much smaller than that for $\text{Mg}(\text{OH})_2$ that it appears likely that $\text{Fe}(\text{OH})_3$ will precipitate at a lower OH^- concentration.

Calculate the OH^- concentration in equilibrium with 1×10^{-4} M Fe^{3+} by substituting directly into the solubility-product expression:

$$K_{\text{sp}} = (1.0 \times 10^{-4})[\text{OH}^-]^3 = 2 \times 10^{-39}$$

$$[\text{OH}^-] = [(2 \times 10^{-39}) / (1.0 \times 10^{-4})]^{1/3} = 3 \times 10^{-12} \text{ M}$$

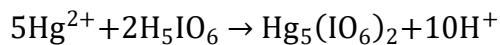
To determine what maximum concentration OH^- concentration can exist in the solution without causing formation of $\text{Mg}(\text{OH})_2$. Substitution of 0.1 (the molar Mg^{2+} concentration of the solution) into the solubility-product expression:

$$K_{\text{sp}} = 0.1[\text{OH}^-]^2 = 7.1 \times 10^{-12}$$

$$[\text{OH}^-] = 8.4 \times 10^{-6} \text{ M}$$

From these calculations, we conclude that **quantitative separation of $\text{Fe}(\text{OH})_3$ can be achieved if the OH^- concentration is greater than 3×10^{-12} M and that $\text{Mg}(\text{OH})_2$ will not precipitate until an OH^- concentration of 8.4×10^{-6} M is reached.** Therefore, it is possible to separate Fe^{3+} from Mg^{2+} by maintaining the OH^- concentration between these levels.

5. 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 0.5718 g was recovered. Calculate the percentage of Hg_2Cl_2 in the sample. Molecular weight of $\text{Hg}_5(\text{IO}_6)_2$ is 1448.75 g/mol, molecular weight of $\text{Hg}_2\text{Cl}_2 = 472.18$ g/mol.

[10%]

Solution:

$$n_{\text{Hg}_5(\text{IO}_6)_2} = \frac{0.5718 \text{ g}}{1448.75 \text{ g/mol}} = 3.95 \times 10^{-4} \text{ mol}$$

$$n_{\text{Hg}^{2+}} = 5 \times n_{\text{Hg}_5(\text{IO}_6)_2} = 5 \times 3.95 \times 10^{-4} \text{ mol} = 1.975 \times 10^{-3} \text{ mol}$$

$$n_{\text{Hg}_2\text{Cl}_2} = \frac{1}{2} \times n_{\text{Hg}^{2+}} = \frac{1}{2} \times 1.975 \times 10^{-3} \text{ mol} = 9.875 \times 10^{-4} \text{ mol}$$

$$W_{\text{Hg}_2\text{Cl}_2} = 9.875 \times 10^{-4} \text{ mol} \times 472.18 \text{ g/mol} = 0.466 \text{ g}$$

$$\% \text{Hg}_2\text{Cl}_2 = \frac{0.466 \text{ g}}{1.0451 \text{ g}} \times 100\% = 44.59\%$$

6. The aluminum in a 2.200 g sample of impure ammonium aluminum sulfate was precipitated with aqueous ammonia as the hydrous $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. The precipitate was filtered and ignited at 1000 °C to give anhydrous Al_2O_3 , which weighed 0.3006 g. Express the result of this analysis in terms of (a) % $\text{NH}_4\text{Al}(\text{SO}_4)_2$, (b) % Al_2O_3 , (c) %Al. molecular weight: $\text{NH}_4\text{Al}(\text{SO}_4)_2 = 237.14$ g/mol; $\text{Al}_2\text{O}_3 = 101.96$ g/mol; Al = 26.98 g/mol.

[10%]

Solution:

$$(a) n_{\text{Al}_2\text{O}_3} = \frac{0.3006 \text{ g}}{101.96 \text{ g/mol}} = 2.95 \times 10^{-3} \text{ mol}$$

$$n_{\text{NH}_4\text{Al}(\text{SO}_4)_2} = 2 \times n_{\text{Al}_2\text{O}_3} = 2 \times 2.95 \times 10^{-3} \text{ mol} = 5.90 \times 10^{-3} \text{ mol}$$

$$W_{\text{NH}_4\text{Al}(\text{SO}_4)_2} = 5.90 \times 10^{-3} \text{ mol} \times 237.14 \text{ g/mol} = 1.40 \text{ g}$$

$$\% \text{NH}_4\text{Al}(\text{SO}_4)_2 = \frac{1.40 \text{ g}}{2.200 \text{ g}} \times 100\% = 63.64\%$$

$$(b) \% \text{Al}_2\text{O}_3 = \frac{0.3006 \text{ g}}{2.200 \text{ g}} \times 100\% = 13.7\%$$

$$(c) n_{\text{Al}} = n_{\text{NH}_4\text{Al}(\text{SO}_4)_2} = 5.90 \times 10^{-3} \text{ mol}$$

$$W_{\text{Al}} = 5.90 \times 10^{-3} \text{ mol} \times 26.982 \text{ g/mol} = 0.159 \text{ g}$$

$$\% \text{Al} = \frac{0.159 \text{ g}}{2.200 \text{ g}} \times 100\% = 7.23\%$$

7. Calculate the concentration of Ni^{2+} in a solution that was prepared by mixing 50.0 mL of 0.0300 M Ni^{2+} with 50.00 mL of 0.0500 M EDTA. The mixture was buffered to a pH of 3.0. [10%]

| Calculation of α_4 for EDTA | | | | |
|------------------------------------|----------|------|----------|------------|
| | K values | pH | D values | α_4 |
| K₁ | 1.02E-02 | 1.0 | 1.10E-04 | 7.52E-18 |
| K₂ | 2.14E-03 | 2.0 | 2.24E-08 | 3.71E-14 |
| K₃ | 6.92E-07 | 3.0 | 3.30E-11 | 2.51E-11 |
| K₄ | 5.50E-11 | 4.0 | 2.30E-13 | 3.61E-09 |
| | | 5.0 | 2.34E-15 | 3.54E-07 |
| | | 6.0 | 3.69E-17 | 2.25E-05 |
| | | 7.0 | 1.73E-18 | 4.80E-04 |
| | | 8.0 | 1.54E-19 | 5.39E-03 |
| | | 9.0 | 1.60E-20 | 5.21E-02 |
| | | 10.0 | 2.34E-21 | 0.35 |
| | | 11.0 | 9.82E-22 | 0.85 |
| | | 12.0 | 8.46E-22 | 0.98 |
| | | 13.0 | 8.32E-22 | 1.00 |
| | | 14.0 | 8.31E-22 | 1.00 |

Solution:

Y = EDTA

$$c_{\text{NiY}^{2-}} = 50.00 \text{ mL} \times \frac{0.0300 \text{ M}}{100 \text{ mL}} = 0.0150 \text{ M}$$

$$c_{\text{EDTA}} = \frac{50.00 \text{ mL} \times 0.0500 \text{ M} - 50.0 \text{ mL} \times 0.0300 \text{ M}}{100 \text{ mL}} = 0.0100 \text{ M}$$

Assume that $[\text{Ni}^{2+}] \ll [\text{NiY}^{2-}]$ so that

$$[\text{NiY}^{2-}] = 0.0150 - [\text{Ni}^{2+}] \approx 0.0150 \text{ M}$$

At this point, the total concentration of uncomplexed EDTA is given by its concentration, c_{EDTA} :

$$c_T = c_{\text{EDTA}} = 0.0100 \text{ M}$$

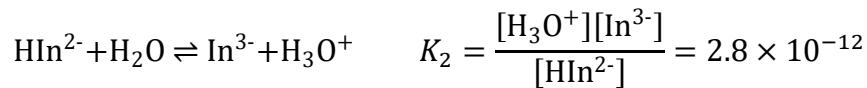
$$K'_{\text{NiY}} = \frac{0.0150}{[\text{Ni}^{2+}] \times 0.0100} = \alpha_4 K_{\text{NiY}}$$

Using the value of α_4 at pH 3.0 from the table, obtain

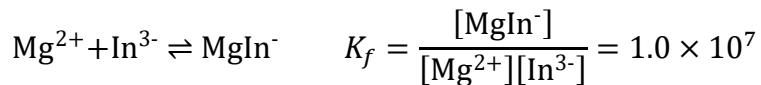
$$[\text{Ni}^{2+}] = \frac{0.0150}{0.0100 \times 2.51 \times 10^{-11} \times 4.2 \times 10^{18}} = 1.4 \times 10^{-8} \text{ M}$$

Note that the assumption that $[\text{Ni}^{2+}] \ll [\text{NiY}^{2-}]$ is valid.

8. Determine the transition ranges for Eriochrome Black T in titration of (a) Mg^{2+} and (b) Ca^{2+} at pH 10.0, given that the second acid dissociation constant for the indicator is



and that the formation constant for $MgIn^-$ is



and the analogous formation constant for Ca^{2+} is 2.5×10^5 .

(Assume that a detectable color change requires a ten-fold excess of one or the other color species.) [10%]

Solution:

(a) A detectable color change is observed when $0.10 < \frac{[MgIn^-]}{[HIn^{2-}]} < 10$. The product of K_2 for the indicator and K_f for $MgIn^-$ contains this ratio:

$$\frac{[MgIn^-][H_3O^+]}{[HIn^-][Mg^{2+}]} = 2.8 \times 10^{-12} \times 1.0 \times 10^7 = 2.8 \times 10^{-5}$$

Substituting 1.0×10^{-10} for $[H_3O^+]$ and 10 and 0.10 for the ratio yields, the range of $[Mg^{2+}]$ over which the color change occurs is

$$[Mg^{2+}] = 3.6 \times 10^{-5} \text{ to } 3.6 \times 10^{-7} \text{ M}$$

$$pMg = 5.4 \pm 1.0$$

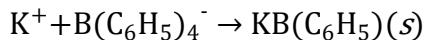
(b) Proceeding in the same way:

$$\frac{[CaIn^-][H_3O^+]}{[HIn^-][Ca^{2+}]} = 2.8 \times 10^{-12} \times 2.5 \times 10^5 = 7 \times 10^{-7}$$

$$[Ca^{2+}] = 1.4 \times 10^{-3} \text{ to } 1.4 \times 10^{-5} \text{ M}$$

$$pCa = 3.8 \pm 1.0$$

9. The potassium ion in a 250.0-mL sample of mineral water was precipitated with sodium tetraphenylborate:



The precipitate was filtered, washed, and redissolved in an organic solvent. An excess of the mercury(II)/EDTA chelate was added:



The liberated EDTA was titrated with 34.374 mL of 0.04813 M Mg^+ . Calculate the potassium ion concentration in parts per million. Atomic mass of potassium is 39.09 g/mol.

[10%]

Solution:

$$n_{EDTA} = 34.374 \text{ mL} \times 0.04813 \text{ M} = 1.654 \text{ mmol}$$

$$n_{EDTA} = \frac{1}{4} n_{B(C_6H_5)_4^-} = \frac{1}{4} n_{K^+}$$

$$n_{K^+} = \frac{1}{4} \times 1.654 \text{ mmol} = 0.4135 \text{ mmol}$$

$$c_{K^+} = \frac{0.4135 \text{ mmol} \times 39.098 \text{ mg/mmol}}{250 \text{ mL} \times \frac{1}{1000 \text{ mL}}} = 64.67 \text{ ppm}$$

10. A 0.3304-g sample of brass (containing lead, zinc, copper, and tin) was dissolved in nitric acid. The sparingly soluble $\text{SnO}_2 \cdot 4\text{H}_2\text{O}$ was removed by filtration, and the combined filtrate and washings were then diluted to 500.0 mL. A 10.00-mL aliquot was suitably buffered; titration of the lead, zinc, and copper in this aliquot required 34.78 mL of 0.002700 M EDTA. The copper in a 25.00-mL aliquot was masked with thiosulfate; the lead and zinc were then titrated with 25.62 mL of the EDTA solution. Cyanide ion was used to mask the copper and zinc in a 100-mL aliquot; 10.00 mL of the EDTA solution was needed to titrate the lead ion. Determine the composition of the brass sample; evaluate the percentage of tin by difference.

[10%]

Solution:

$$n_{\text{EDTA}} = n_{(\text{Pb}+\text{Zn}+\text{Cu})}$$

$$n_{(\text{Pb}+\text{Zn}+\text{Cu})} = \frac{0.002700 \text{ M} \times 34.78 \text{ mL}}{\frac{10.00 \text{ mL}}{500.0 \text{ mL}}} = 4.6953 \text{ mmol}$$

$$n_{(\text{Pb}+\text{Zn})} = \frac{0.002700 \text{ M} \times 25.62 \text{ mL}}{\frac{25.00 \text{ mL}}{500.0 \text{ mL}}} = 1.3835 \text{ mmol}$$

$$n_{\text{Cu}} = 4.6953 \text{ mmol} - 1.3835 \text{ mmol} = 3.3118 \text{ mmol}$$

$$n_{\text{Pb}} = \frac{0.002700 \text{ M} \times 10.00 \text{ mL}}{\frac{100 \text{ mL}}{500.0 \text{ mL}}} = 0.1350 \text{ mmol}$$

$$n_{\text{Zn}} = 1.3835 \text{ mmol} - 0.1350 \text{ mmol} = 1.2485 \text{ mmol}$$

$$\% \text{Cu} = \frac{3.3118 \text{ mmol} \times \frac{63.55 \text{ g}}{1000 \text{ mmol}}}{0.3304 \text{ g}} \times 100\% = 63.70\%$$

$$\% \text{Pb} = \frac{0.1350 \text{ mmol} \times \frac{207.2 \text{ g}}{1000 \text{ mmol}}}{0.3304 \text{ g}} \times 100\% = 8.47\%$$

$$\%Zn = \frac{1.2485 \text{ mmol} \times \frac{65.39 \text{ g}}{1000 \text{ mmol}}}{0.3304 \text{ g}} \times 100\% = 24.71\%$$

$$\%Sn = 100\% - 63.70\% - 8.47\% - 24.71\% = 3.12\%$$

~ End of Paper ~