10910CHEM311000-Analytical Chemistry (I) 分析化學一

Second Midterm Examination

Date: 15-12-2020, 10:10 am to 12:30 pm

Answer **all 12 questions** (total 110%). You have 2 hours and 20 minutes to finish this paper

1. The solubility products for a series of iodides are shown below:

CuI K_{sp} = 1 X 10^{-12}; AgI K_{sp} = 8.3 X10^{-17}; PbI$_2$ K_{sp} = 7.1 X 10^{-9}; BiI$_3$ K_{sp} = 8.1 X 10^{-19}

List these four compounds in the order of decreasing molar solubility in
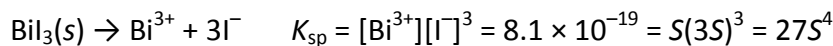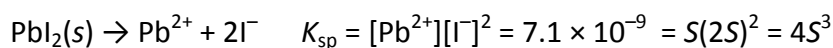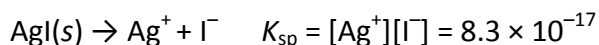
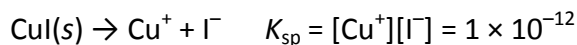(i) water   **[10 %]**

(ii) 0.20 M NaI   **[5 %]**

ANS:

$$CuI(s) \rightarrow Cu^+ + I^- \qquad K_{sp} = [Cu^+][I^-] = 1 \times 10^{-12}$$

$$AgI(s) \rightarrow Ag^+ + I^- \qquad K_{sp} = [Ag^+][I^-] = 8.3 \times 10^{-17}$$

$$PbI_2(s) \rightarrow Pb^{2+} + 2I^- \qquad K_{sp} = [Pb^{2+}][I^-]^2 = 7.1 \times 10^{-9} = S(2S)^2 = 4S^3$$

$$BiI_3(s) \rightarrow Bi^{3+} + 3I^- \qquad K_{sp} = [Bi^{3+}][I^-]^3 = 8.1 \times 10^{-19} = S(3S)^3 = 27S^4$$

(i)

For CuI, $S = [Cu^+] = [I^-] = \sqrt{1 \times 10^{-12}} = 1 \times 10^{-6}$ M

For AgI, $S = [Ag^+] = [I^-] = \sqrt{8.3 \times 10^{-17}} = 9.1 \times 10^{-9}$ M

For PbI$_2$, $S = \sqrt[3]{\dfrac{7.1 \times 10^{-9}}{4}} = 1.2 \times 10^{-3}$ M

For BiI$_3$ $S = \sqrt[4]{\dfrac{8.1 \times 10^{-19}}{27}} = 1.3 \times 10^{-5}$ M

So, solubilities are in the order PbI$_2$ > BiI$_3$ > CuI > AgI

(ii)

For CuI, $S = 1 \times 10^{-12}/0.20 = 5 \times 10^{-12}$ M

For AgI, $S = 8.3 \times 10^{-17}/0.20 = 4.2 \times 10^{-16}$ M

For PbI$_2$, $S = 7.1 \times 10^{-9}/(0.20)^2 = 1.8 \times 10^{-7}$ M

For BiI_3, $S = 8.1 \times 10^{-19}/(0.20)^3 = 1.0 \times 10^{-16}$ M

So, solubilities are in the order PbI_2 > CuI > AgI > BiI_3

2. 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 X 10^{-4}) to produce a buffer solution that has a pH of 3.50? **[10 %]**

ANS:

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

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

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

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 × 67.99 g/mol = **<u>19.54 g</u>**

3. 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 $AgI = 8.3 \times 10^{-17}$; $AgSCN = 1.1 \times 10^{-12}$

(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) $[Ag^+] = K_{sp}/[I^-] = 8.3 \times 10^{-17}/(1.0 \times 10^{-6}) = \underline{\mathbf{8.3 \times 10^{-11}\ M}}$

(ii) $[Ag^+] = K_{sp}/[SCN^-] = 1.1 \times 10^{-12}/(0.080) = 1.375 \times 10^{-11}\ M \approx \underline{\mathbf{1.4 \times 10^{-11}\ M}}$

(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

$[SCN^-]/[I^-] = 0.080/(6.0 \times 10^{-6}) = \underline{\mathbf{1.3 \times 10^4}}$

(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

$[SCN^-]/[I^-] = 1.1 \times 10^{-9}/(8.3 \times 10^{-14}) = \underline{\mathbf{1.3 \times 10^4}}$

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

4. In contrast to many salts, calcium sulfate is only partially dissociated in aqueous solution:

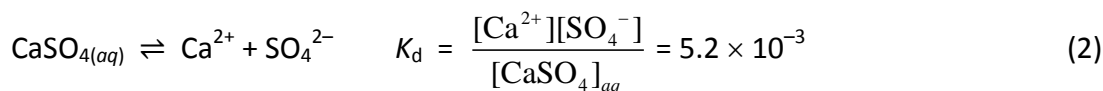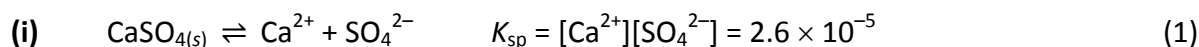$$CaSO_4(aq) \rightleftharpoons Ca^{2+} + SO_4^{2-} \qquad K_d = 5.2 \times 10^{-3}$$

The solubility product constant for $CaSO_{4(s)}$ is 2.6×10^{-5}. Calculate the percent solubility of $CaSO_{4(aq)}$ in

(i) Water   **[10 %]**

(ii) 0.0100 M Na_2SO_4 **[5 %]**

ANS:

(i) $CaSO_{4(s)} \rightleftharpoons Ca^{2+} + SO_4^{2-} \qquad K_{sp} = [Ca^{2+}][SO_4^{2-}] = 2.6 \times 10^{-5}$ (1)

$CaSO_{4(aq)} \rightleftharpoons Ca^{2+} + SO_4^{2-} \qquad K_d = \dfrac{[Ca^{2+}][SO_4^-]}{[CaSO_4]_{aq}} = 5.2 \times 10^{-3}$ (2)

$CaSO_{4(s)} \rightleftharpoons CaSO_{4(aq)}$ (3)

The mass balance gives

$[Ca^{2+}] = [SO_4^{2-}]$ (4)

We have 3 equations and 3 unknowns ($[Ca^{2+}]$, $[SO_4^{2-}]$, and $[CaSO_4]_{aq}$

To solve we divide (1) by (2) to give

$[CaSO_4]_{aq} = K_{sp}/K_d = (2.6 \times 10^{-5})/(5.2 \times 10^{-3}) = 5.0 \times 10^{-3}$

Note that this is the equilibrium constant expression for (3) and indicates that the

concentration of un-ionized $CaSO_4$ is always the same in a saturated solution of $CaSO_4$.

Substituting (4) into (1) gives

$[Ca^{2+}] = (2.6 \times 10^{-5})^{1/2} = 5.1 \times 10^{-3}$ M

and since $S = [CaSO_4]_{aq} + [Ca^{2+}]$, we obtain

$S = 5.0 \times 10^{-3} + 5.1 \times 10^{-3} = 1.01 \times 10^{-2}$ M

$\%CaSO_{4(aq)} = (5.0 \times 10^{-3}/1.01 \times 10^{-2}) \times 100\% = \underline{\textbf{49\%}}$

(ii)   Here $[CaSO_4]_{aq}$ is again equal to 5.0×10^{-3} and the mass balance gives

$[SO_4^{2-}] = 0.0100 + [Ca^{2+}]$ (5)

Substituting (1) into (5) and rearranging gives

$0 = [SO_4^{2-}]^2 - 0.0100[SO_4^{2-}] - K_{sp}$

which may be solved using the quadratic equation to give

$[SO_4^{2-}] = 0.0121$ and $[Ca^{2+}] = 2.14 \times 10^{-3}$

$S = 5.0 \times 10^{-3} + 2.14 \times 10^{-3} = 7.14 \times 10^{-3}$ M

%CaSO$_{4(aq)}$ = $(5.0 \times 10^{-3}/7.14 \times 10^{-3}) \times 100\%$ = **70%**

5. Treatment of a 0.2500 g sample of impure potassium chloride (KCl, MW = 74.55 g/mol) with an excess of $AgNO_3$ (MW = 169.87 g/mol) resulted in the formation of 0.2912 g of AgCl (MW = 143.32 g/mol). Calculate the percentage of KCl in the sample. **[5 %]**

ANS:

$\mathcal{M}_{AgCl} = 143.32$ g/mol $\qquad \mathcal{M}_{KCl} = 74.55$ g/mol

$$\frac{0.2912 \text{ g AgCl} \times \left(\dfrac{1 \text{ mol AgCl}}{143.32 \text{ g}}\right) \times \left(\dfrac{1 \text{ mol KCl}}{1 \text{ mol AgCl}}\right) \times \left(\dfrac{74.55 \text{ g KCl}}{\text{mol}}\right)}{0.2500 \text{ g impure sample}} \times 100\% = 60.59\%$$

6. What mass of $Cu(IO_3)_2$ can be formed from 0.650 g of $CuSO_4 \cdot 5H_2O$? **[5 %]**

$M_{CuSO4.5H2O}$ = 249.67 g/mol; $M_{Cu(IO3)2}$ = 413.35 g/mol.

ANS:

$$0.650 \text{ g CuSO}_4\bullet5\text{H}_2\text{O} \times \frac{1 \text{ mol CuSO}_4\bullet5\text{H}_2\text{O}}{249.67 \text{ g CuSO}_4\bullet5\text{H}_2\text{O}} \times \frac{1 \text{ mol Cu(IO}_3)_2}{1 \text{ mol CuSO}_4\bullet5\text{H}_2\text{O}}$$

$$\times \frac{413.35 \text{ g Cu(IO}_3)_2}{1 \text{ mol Cu(IO}_3)_2} = 1.076 \text{ g Cu(IO}_3)_2$$

7. The mercury in a 1.0451 g sample was precipitated with an excess of paraperiodic acid, H_5IO_6:
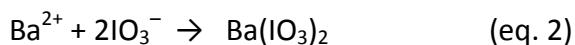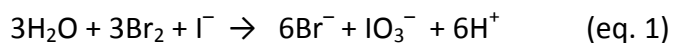
$$5Hg^{2+} + 2H_5IO_6 \rightarrow Hg_5(IO_6)_2 + 10H^+$$
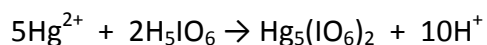
The precipitate was filtered, washed free of precipitating agent, dried and weighed, and $Hg_5(IO_6)_2$ ($M_{Hg5(IO6)2}$ = 1448.75 g/mol) of 0.5718 g was recovered. Calculate the percentage of Hg_2Cl_2 (M_{Hg2Cl2} = 472.18 g/mol) in the sample. **[10 %]**

ANS:

$$\frac{\left(\begin{array}{c} 0.5718 \text{ g Hg}_5(\text{IO}_6)_2 \times \dfrac{1 \text{ mol Hg}_5(\text{IO}_6)_2}{1448.75 \text{ g Hg}_5(\text{IO}_6)_2} \times \dfrac{5 \text{ mol Hg}^{2+}}{1 \text{ mol Hg}_5(\text{IO}_6)_2} \\ \times \dfrac{1 \text{ mol Hg}_2\text{Cl}_2}{2 \text{ mol Hg}^{2+}} \times \dfrac{472.18 \text{ g Hg}_2\text{Cl}_2}{1 \text{ mol Hg}_2\text{Cl}_2} \end{array} \right)}{1.0451 \text{ g sample}} \times 100\% = 44.58\% \text{ Hg}_2\text{Cl}_2$$

8. The iodide in a sample was converted to iodate by treatment with an excess of bromine (eq. 1). The unused bromine was removed by boiling, an excess of barium ion was then added to precipitate the iodate (eq. 2). In the analysis of a 1.59 g sample (KI, M_{KI} = 166.00g/mol), 0.0538 g of barium iodate ($Ba(IO_3)_2$, $M_{Ba(IO3)2}$ = 487.13 g/mol) was recovered. Express the results of this analysis as percent potassium iodide. **[5 %]**

$$3H_2O + 3Br_2 + I^- \rightarrow 6Br^- + IO_3^- + 6H^+ \qquad \text{(eq. 1)}$$

$$Ba^{2+} + 2IO_3^- \rightarrow Ba(IO_3)_2 \qquad \text{(eq. 2)}$$

ANS:

$$\mathcal{M}_{Ba(IO3)2\_} = 487.13 \text{ g/mol} \quad \mathcal{M}_{KI} = 166.00 \text{g/mol}$$

$$\frac{0.0538 \text{ g Ba(IO}_3)_2 \times \left(\dfrac{1 \text{ mol Ba(IO}_3)_2}{487.13 \text{ g}} \right) \times \left(\dfrac{2 \text{ mol KI}}{1 \text{ mol Ba(IO}_3)_2} \right) \times \left(\dfrac{166.00 \text{ g KI}}{\text{mol}} \right)}{1.59 \text{ g impure sample}} \times 100\% = 2.31\% \text{ KI}$$

9. 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:

$$\text{Amnt EDTA reacted in 50.00 mL} = \left(\frac{0.05173 \text{ mmol EDTA}}{\text{mL}} \times 50.00 \text{ mL EDTA} \right) -$$

$$\left(\frac{0.06139 \text{ mmol Cu}^{2+}}{\text{mL}} \times 5.34 \text{ mL Cu}^{2+} \times \frac{1 \text{ mmol EDTA}}{\text{mmol Cu}^{2+}} \right) = 2.2587 \text{ mmol}$$

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

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

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

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

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

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

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

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

10. **(i)** Write the charge and mass balances for a solution made by dissolving $MgBr_2$ to give Mg^{2+}, Br^-, $MgBr^+$, and $MgOH^+$.   **[5 %]**

(ii) Modify the mass balance if he solution was made by dissolving 0.2 mol $MgBr_2$ in 1 L. **[5 %]**

ANS:

(i)

Charge balance: $2[Mg^{2+}] + [H^+] + [MgBr^+] + [MgOH^+] = [Br^-] + [OH^-]$

Mass balance: total Br = 2 (total Mg)

$[MgBr^+] + [Br^-] = 2\{[Mg^{2+}] + [MgBr^+] + [MgOH^+]\}$

(ii) $[MgBr^+] + [Br^-] = 0.4\ M$

$[Mg^{2+}] + [MgBr^+] + [MgOH^+] = 0.2\ M$

11. The acid HA has pKa =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) $6.00 = 7.00 + \log[A^-]/[HA]$

$[A^-]/[HA] =$ **<u>0.1</u>**

12. The acid HA has pKa = 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:

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

Fraction in from A⁻ = $\alpha_{A^-} = \dfrac{K_a}{[H^+]+K_a} = \dfrac{10^{-4}}{10^{-5}+10^{-4}} =$ **0.909**

~ End of Paper ~