

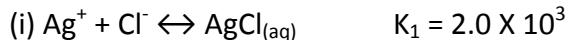
10810CHEM311000-Analytical Chemistry (I) 分析化學 (一)

Second Midterm Examination

Date: 10-12-2019, 10:10 am to 12:10 pm

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

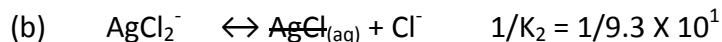
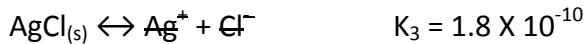
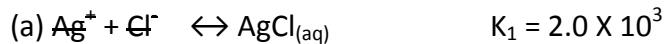
1. Consider the following equilibria in aqueous solution:



(a) Calculate the value of the equilibrium constant for the reaction $\text{AgCl}_{(\text{s})} \leftrightarrow \text{AgCl}_{(\text{aq})}$. [5%]

(b) Find the value of K for the reaction $\text{AgCl}_2^- \leftrightarrow \text{AgCl}_{(\text{s})} + \text{Cl}^-$. [5%]

Answer:



2. 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 × 10⁻⁸, Ce₂(C₂O₄)₃ K_{sp} = 5.9 × 10⁻³⁰. [10%]

Answer:

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 × 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 × 10⁻⁸), Ca²⁺ will not precipitate.

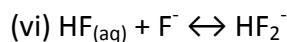
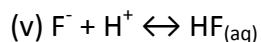
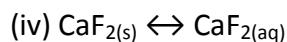
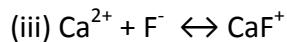
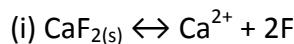
3. Assuming complete dissociation of the salts, calculate the ionic strength of

- (a) 0.2 mM KNO₃ [5%]
- (b) 0.2 mM Cs₂CrO₄ [5%]
- (c) 0.2 mM MgCl₂ and 0.3 mM AlCl₃ [5%]

Answer:

- (a) $\mu = 1/2 ([K^+] \times 1^2 + [NO_3^-] \times (-1)^2) = \underline{0.2 \text{ mM}}$
- (b) $\mu = 1/2 ([Cs^+] \times 1^2 + [CrO_4^{2-}] \times (-2)^2) = \underline{0.6 \text{ mM}}$
- (c) $\mu = 1/2 ([Mg^{2+}] \times 2^2 + [Cl^-] \times (-1)^2 + [Al^{3+}] \times (3)^2) = \underline{2.4 \text{ mM}}$

4. Write the (a) charge and (b) mass balances for dissolving CaF_2 in water. [5% each, no partial scores are given]



Answer:

(a) Charge balance:

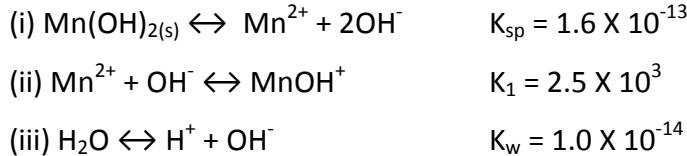
$$[\text{F}^-] + [\text{HF}_2^-] + [\text{OH}^-] = 2[\text{Ca}^{2+}] + [\text{CaOH}^+] + [\text{CaF}^+] + [\text{H}^+]$$

(b) Mass balance: CaF_2 gives 2 mol F for each mol Ca

$$[\text{F}^-] + [\text{CaF}^+] + 2[\text{CaF}_{2(\text{aq})}] + [\text{HF}_{(\text{aq})}] + 2[\text{HF}_2^-] = 2\{[\text{Ca}^{2+}] + [\text{CaOH}^+] + [\text{CaF}^+] + [\text{CaF}_{2(\text{aq})}]\}$$

$\underbrace{\hspace{10em}}_{\text{Species containing F}^-} \quad \underbrace{\hspace{10em}}_{\text{Species containing Ca}^{2+}}$

5. 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: [10%]



Answer:

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

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



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

(Mass balance gives the same result as charge balance)

Equilibrium constant expression in terms of activity

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

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

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

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

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} :

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

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

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

6. Using activities, (a) calculate the pH of a solution containing 0.010 M NaOH and 0.040 M LiNO₃. [5%]

(b) What would be the pH if you neglected activities? [5%]

Answer:

(a)

Ionic strength $\mu = 0.010 \text{ M from NaOH} + 0.040 \text{ M from LiNO}_3 = 0.05 \text{ M}$

Therefore, $\gamma_{\text{OH}^-} = 0.81$

$$[\text{H}^+] \gamma_{\text{H}^+} = \frac{K_w}{[\text{OH}^-] \gamma_{\text{OH}^-}} = 1.0 \times 10^{-14} / (0.010)(0.81) = 1.23 \times 10^{-12}$$

$$\text{pH} = -\log(1.23 \times 10^{-12}) = 11.90$$

(b) If we have neglected activities $\text{pH} = -\log[\text{H}^+] = -\log K_w/[\text{OH}^-] = 12.00$

7. 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%]

Answer:

(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 .

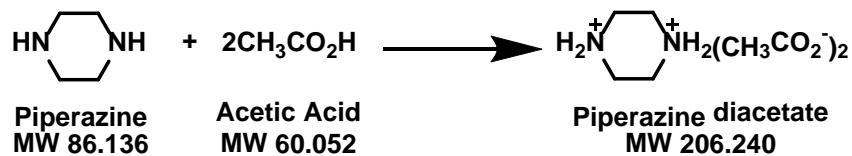
(b) For 2 mol of Cl^- , there must be 1 mol of Ra, so $\text{mol Ra} = 6.202 \times 10^{-4}/2 = 3.101 \times 10^{-4}$ mol. Let the MW of RaCl_2 be x. We found that 0.09192 g RaCl_2 contains 3.101×10^{-4} mol RaCl_2 . Therefore, $3.101 \times 10^{-4} = 0.09192/x$

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

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

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

8. The piperazine content of an impure commercial material can be determined by precipitating and weighing the diacetate:



In one experiment, 0.3126 g of sample was dissolved in 25 mL of acetone, and 1 mL of acetic acid was added. After 5 minutes, the precipitate was filtered, washed with acetone, dried at 110 °C, and found to weigh 0.7121 g. Find the weight % of piperazine in the sample. [10%]

Answer:

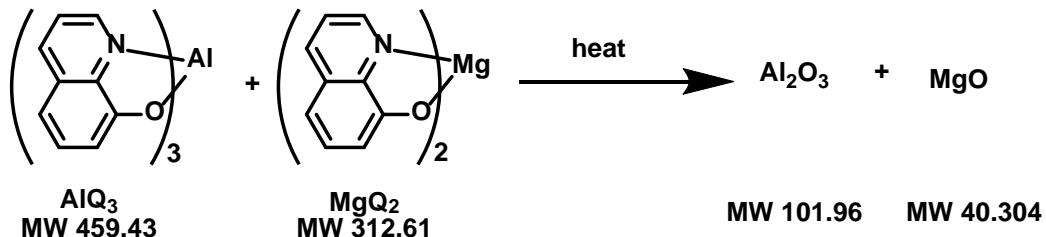
For each mole of piperazine in the impure material, 1 mol of product is formed.

$$\text{Moles of product} = 0.7121/206.240 = 3.453 \times 10^{-3} \text{ mol.}$$

$$\text{This value corresponds to grams of piperazine } (3.453 \times 10^{-3} \text{ mol})(86.136 \text{ g/mol}) = 0.2974 \text{ g.}$$

$$\text{This gives percentage of piperazine in analyte} = 0.2974/0.3126 = \underline{\underline{95.14\%}}$$

9. A mixture of the 8-hydroxyquinoline (Q) complexes of Al and Mg weighed 1.0843 g. When ignited in a furnace open to the air, the mixture decomposed, leaving a residue of Al_2O_3 and MgO weighing 0.1344 g. Find the weight percent of AlQ_3 in the original mixture. [10%]



Answer:

8-hydroxyquinoline was abbreviated as Q. Letting the mass of AlQ_3 be x and the mass of MgQ_2 be y , we can write $x + y = 1.0843$ g.

The moles of AlQ_3 are $x/459.43$, and the moles of MgQ_2 are $y/312.61$. The moles of Al_2O_3 are one-half of the total moles of AlQ_3 , because it takes 2 mol of AlQ_3 to make 1 mol of Al_2O_3 .

$$\text{Moles of } \text{Al}_2\text{O}_3 = (\frac{1}{2})(x/459.43)$$

The moles of MgO will equal the moles of $\text{MgQ}_2 = y/312.61$. Now we can write

$$(\frac{1}{2})(x/459.43)(101.96) + (y/312.61)(40.304) = 0.1344 \text{ g.}$$

Substituting $y = 1.0843 - x$ into the preceding equation gives

$$(\frac{1}{2})(x/459.43)(101.96) + (1.0843-x/312.61)(40.304) = 0.1344 \text{ g.}$$

For which we find $x = 0.3003$ g, which is 27.70% of the original mixture.

10. Please answer the following two questions:

- (a) Propose a complexometric method using EDTA for the determination of the individual components in a solution containing Th^{4+} , Zn^{2+} , and Mg^{2+} . Formation constants for EDTA complex $\text{Mg}^{2+} = 4.9 \times 10^8$, $\text{Zn}^{2+} = 3.2 \times 10^{16}$, and $\text{Th}^{4+} = 1.6 \times 10^{23}$. [5%]
- (b) Why is a small amount of MgY^{2-} often added to a water specimen that is to be titrated for hardness using Eriochrome Black T indicator? [5%]

Answer:

- (a) Titrate the three ions in an aliquot of the sample that has been buffered to a pH of about 10. Buffer a second aliquot to a pH of about 4 and titrate the zinc and thalium ions. Finally, titrate an aliquot that has been brought to a pH of about 2. Only the thalium is complexed under these conditions.
- (b) 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.

~ 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
$\text{Li}^+, \text{C}_6\text{H}_5\text{COO}^-$	0.6	0.966	0.930	0.907	0.83	0.80
$\text{Na}^+, \text{IO}_3^-, \text{HSO}_3^-, \text{HCO}_3^-, \text{H}_2\text{PO}_4^-, \text{H}_2\text{AsO}_4^-, \text{OAc}^-$	0.4–0.45	0.965	0.927	0.902	0.82	0.77
$\text{OH}^-, \text{F}^-, \text{SCN}^-, \text{HS}^-, \text{ClO}_3^-, \text{ClO}_4^-, \text{BrO}_3^-, \text{IO}_3^-, \text{MnO}_4^-$	0.35	0.965	0.926	0.900	0.81	0.76
$\text{K}^+, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{CN}^-, \text{NO}_2^-, \text{NO}_3^-, \text{HCOO}^-$	0.3	0.965	0.925	0.899	0.81	0.75
$\text{Rb}^+, \text{Cs}^+, \text{Ti}^+, \text{Ag}^+, \text{NH}_4^+$	0.25	0.965	0.925	0.897	0.80	0.75
$\text{Mg}^{2+}, \text{Be}^{2+}$	0.8	0.872	0.756	0.690	0.52	0.44
$\text{Ca}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Sn}^{2+}, \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}, \text{Phthalate}^{2-}$	0.6	0.870	0.748	0.676	0.48	0.40
$\text{Sr}^{2+}, \text{Ba}^{2+}, \text{Cd}^{2+}, \text{Hg}^{2+}, \text{S}^{2-}$	0.5	0.869	0.743	0.668	0.46	0.38
$\text{Pb}^{2+}, \text{CO}_3^{2-}, \text{SO}_3^{2-}, \text{C}_2\text{O}_4^{2-}$	0.45	0.868	0.741	0.665	0.45	0.36
$\text{Hg}_2^{2+}, \text{SO}_4^{2-}, \text{S}_2\text{O}_3^{2-}, \text{Cr}_4^{2-}, \text{HPO}_4^{2-}$	0.40	0.867	0.738	0.661	0.44	0.35
$\text{Al}^{3+}, \text{Fe}^{3+}, \text{Cr}^{3+}, \text{La}^{3+}, \text{Ce}^{3+}$	0.9	0.737	0.540	0.443	0.24	0.18
$\text{PO}_4^{3-}, \text{Fe}(\text{CN})_6^{3-}$	0.4	0.726	0.505	0.394	0.16	0.095
$\text{Th}^{4+}, \text{Zr}^{4+}, \text{Ce}^{4+}, \text{Sn}^{4+}$	1.1	0.587	0.348	0.252	0.10	0.063
$\text{Fe}(\text{CN})_6^{4-}$	0.5	0.569	0.305	0.200	0.047	0.020

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