

10710CHEM311000-Analytical Chemistry (I) 分析化學一

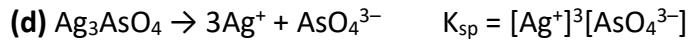
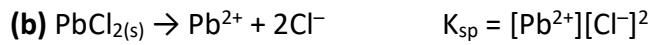
Second Midterm Examination

Date: 11-12-2018, 10:10 am to 12:10 pm

Answer all 10 questions (total 110%). You have 2 hours to finish this paper.

1. Generate the solubility-product equation and expression for (a) CuBr_(s), (b) PbCl_{2(s)}, (c) La(IO₃)_{3(s)}, and (d) Ag₃AsO_{4(s)}. [2.5% each]

Solution

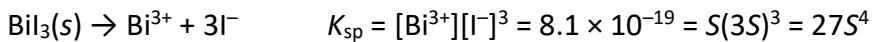
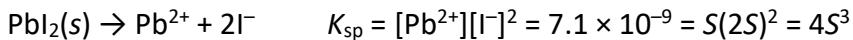


2. The solubility products for a series of metal iodides are shown below:

CuI	$K_{sp} = 1.0 \times 10^{-12}$
AgI	$K_{sp} = 8.3 \times 10^{-17}$
PbI ₂	$K_{sp} = 7.1 \times 10^{-9}$
BiI ₃	$K_{sp} = 8.1 \times 10^{-19}$

List these four compounds in the order of decreasing molar solubility in (a) water, and
 (b) 0.20 M NaI. [5% each]

Solution



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

$$\text{For AgI, } S = [\text{Ag}^+] = [\text{I}^-] = \sqrt[1]{8.3 \times 10^{-17}} = 9.1 \times 10^{-9} \text{ M}$$

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

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

So, the solubilities are in the order of PbI₂ > BiI₃ > CuI > AgI

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

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

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

$$\text{For BiI}_3, S = 8.1 \times 10^{-19}/(0.20)^3 = 1.0 \times 10^{-16} \text{ M}$$

So, the solubilities are in the order of PbI₂ > CuI > AgI > BiI₃

3. Calculate the ionic strength of a solution that is

(a) 0.030 M in FeSO_4 . [5%]

(b) 0.30 M in $(\text{NH}_4)_2\text{CrO}_4$. [5%]

Solution

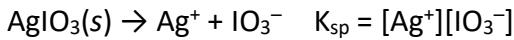
(a) $\mu = \frac{1}{2}[0.030 \times 2^2 + 0.030 \times 2^2] = 0.12$

(b) $\mu = \frac{1}{2}[0.60 \times 1^2 + 0.30 \times 2^2] = 0.90$

4. Calculate the solubility of AgIO_3 in a 0.0167 M solution of $\text{Ba}(\text{NO}_3)_2$ using

(1) activities and (2) molar concentrations. $K_{\text{sp}}(\text{AgIO}_3) = 3.1 \times 10^{-8}$. [5% each]

Solution



$\mu = \frac{1}{2}[0.0167 \times 2^2 + 2 \times 0.0167 \times 1^2] = 0.050$. You can use the data in Table 10-2.

$$(1) \quad \gamma_{\text{Ag}^+} = 0.80 \quad \gamma_{\text{IO}_3^-} = 0.82$$

$$[\text{Ag}^+][\text{IO}_3^-] = \frac{3.1 \times 10^{-8}}{\gamma_{\text{Ag}^+}\gamma_{\text{IO}_3^-}} = \frac{3.1 \times 10^{-8}}{(0.80)(0.82)} = 4.7 \times 10^{-8}$$

$$\text{Solubility} = S = [\text{Ag}^+] = [\text{IO}_3^-]$$

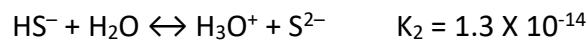
$$S^2 = 4.7 \times 10^{-8}$$

$$S = \sqrt{4.7 \times 10^{-8}} = 2.2 \times 10^{-4} \text{ M}$$

$$(2) \quad S = \sqrt{3.1 \times 10^{-8}} = 1.8 \times 10^{-4} \text{ M}$$

5. Cadmium sulfide (CdS) is less soluble than thallium(I) sulfide (Tl_2S). Find the $[\text{H}^+]$ concentrations under which Cd^{2+} and Tl^+ can, in theory, be separated quantitatively (99.9 %) with H_2S from a solution that is 0.1 M in each cation. Use the following constants to perform the calculation. [15%]

$$K_{sp}(\text{CdS}) = 1 \times 10^{-27}, K_{sp}(\text{Tl}_2\text{S}) = 6 \times 10^{-22}$$



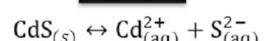
Solution

Example 11-11

Cadmium sulfide (CdS) is less soluble than thallium(I) Sulfide (Tl_2S). Find the conditions (pH) under which Cd^{2+} and Tl^+ can, in theory, be separated quantitatively with H_2S from a solution that is 0.1 M in each cation.

99.9% of CdS is removed

Equilibria



Equilibrium constant

$$K_{sp} = [\text{Cd}^{2+}][\text{S}^{2-}] = 1 \times 10^{-27}$$

$$K_{sp} = [\text{Tl}^+]^2[\text{S}^{2-}] = 6 \times 10^{-22}$$

the minimum $[\text{S}^{2-}]$ to precipitate 99.9% CdS :

$$[\text{S}^{2-}] = \frac{K_{sp}}{[\text{Cd}^{2+}]} = \frac{1 \times 10^{-27}}{0.1 \times (1 - 99.9\%)} = 1 \times 10^{-23} \text{ M}$$

99.9% of CdS is removed

the maximum $[\text{S}^{2-}]$ before Tl_2S precipitates:

$$[\text{S}^{2-}] = \frac{K_{sp}}{[\text{Tl}^+]^2} = \frac{6 \times 10^{-22}}{0.1^2} = 6 \times 10^{-20} \text{ M}$$

Tl₂S precipitation starts

99.9% CdS precipitation forms

$$[\text{S}^{2-}] = 1 \times 10^{-23} \text{ M}$$

$$[\text{S}^{2-}] = 6 \times 10^{-20} \text{ M}$$

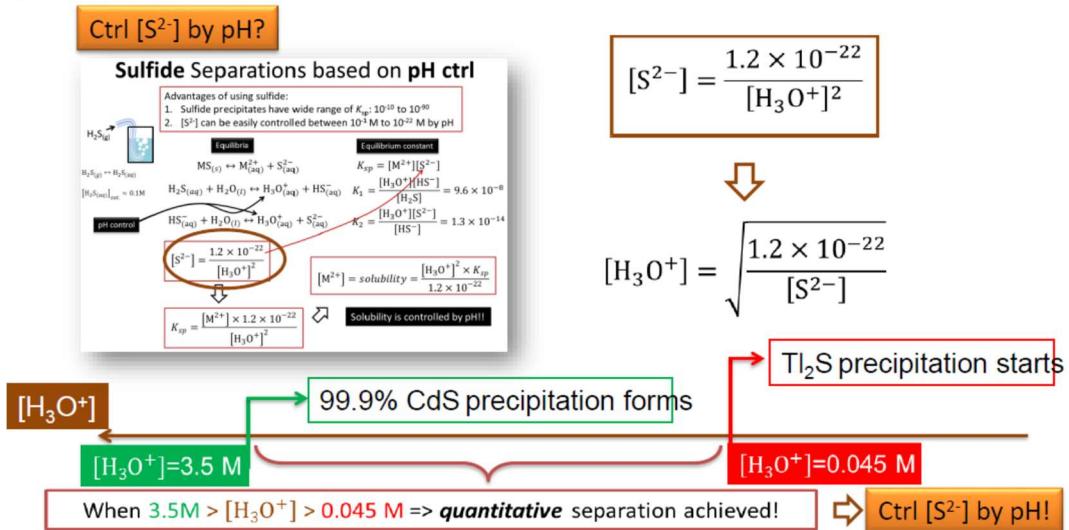
When $1 \times 10^{-23} \text{ M} < [\text{S}^{2-}] < 6 \times 10^{-20} \text{ M} \Rightarrow$ quantitative separation achieved!

Ctrl $[\text{S}^{2-}]$ by pH?

Example 11-11

Cadmium sulfide (CdS) is less soluble than thallium(I) Sulfide (Tl_2S). Find the conditions (pH) under which Cd^{2+} and Tl^+ can, in theory, be **separated quantitatively** with H_2S from a solution that is 0.1 M in each cation.

↑ 99.9% of CdS is removed



6.

- (a) In the presence of excess KIO_3 , what mass of $Cu(IO_3)_2$ can be formed from 0.650 g of $CuSO_4 \cdot 5H_2O$? (Molecular weight for $CuSO_4 \cdot 5H_2O$ = 249.67 g/mol, $Cu(IO_3)_2$ = 413.35 g/mol, and KIO_3 = 214.00 g/mol). [5%]
- (b) What mass of KIO_3 is needed to convert the copper in 0.2750 g of $CuSO_4 \cdot 5H_2O$ to $Cu(IO_3)_2$? [5%]

Solution

(a)

$$0.650 \text{ g } CuSO_4 \cdot 5H_2O \times \frac{1 \text{ mol } CuSO_4 \cdot 5H_2O}{249.67 \text{ g } CuSO_4 \cdot 5H_2O} \times \frac{1 \text{ mol } Cu(IO_3)_2}{1 \text{ mol } CuSO_4 \cdot 5H_2O}$$
$$\times \frac{413.35 \text{ g } Cu(IO_3)_2}{1 \text{ mol } Cu(IO_3)_2} = 1.076 \text{ g } Cu(IO_3)_2$$

(b)

$$0.2750 \text{ g } CuSO_4 \cdot 5H_2O \times \frac{1 \text{ mol } CuSO_4 \cdot 5H_2O}{249.67 \text{ g } CuSO_4 \cdot 5H_2O} \times \frac{1 \text{ mol } Cu(IO_3)_2}{1 \text{ mol } CuSO_4 \cdot 5H_2O}$$
$$\times \frac{2 \text{ mol } KIO_3}{1 \text{ mol } Cu(IO_3)_2} \times \frac{214 \text{ g } KIO_3}{1 \text{ mol } KIO_3} = 1.076 \text{ g } Cu(IO_3)_2$$

7. Calculate the concentration of free Ca^{2+} in a solution of 0.10 M CaY^{2-} ($\text{Y} = \text{EDTA}$) at pH 10.00 and pH 6.00. The formation constant (K_f) for CaY^{2-} is 5.0×10^{10} . At pH 10.00, $\alpha\text{Y}^{4-} = 0.30$. At pH 6.00, $\alpha\text{Y}^{4-} = 1.8 \times 10^{-5}$. [10%]

Solution:

The complex formation reaction is $\text{Ca}^{2+} + \text{EDTA} \leftrightarrow \text{CaY}^{2-}$ $K_f' = \alpha\text{Y}^{4-}K_f$

At pH 10.00: $K_f' = (0.3)(5.0 \times 10^{10}) = 1.34 \times 10^{10}$.

At pH 6.00: $K_f' = (1.8 \times 10^{-5})(5.0 \times 10^{10}) = 8.0 \times 10^5$.

Dissociation of CaY^{2-} must produce equal quantities of Ca^{2+} and EDTA, so we can write

Ca^{2+}	+	EDTA	\leftrightarrow	CaY^{2-}
Initial concentration	0	0		0.10
Final concentration	x	x		$0.10-x$

$$\frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}][\text{EDTA}]} = \frac{0.1 - x}{x^2} = 1.34 \times 10^{10} \text{ at pH } 10.00$$

$$= 8.0 \times 10^5 \text{ at pH } 6.00$$

If we assume that $\text{Ca}^{2+} \ll 0.1 \text{ M}$, an assumption that is almost certainly valid in light of the large formation constant of the complex, this equation simplifies to $\text{CaY}^{2-} = 0.1 \text{ M}$.

Solving for x , we find $[\text{Ca}^{2+}] = 2.7 \times 10^{-6} \text{ M}$ at pH 10.00 and $3.5 \times 10^{-4} \text{ M}$ at pH 6.00.

8.

(a) Write the charge balance for a solution containing H_2O , H^+ , OH^- , ClO_4^- , $\text{Fe}(\text{CN})_6^{3-}$,

CN^- , Fe^{3+} , Mg^{2+} , CH_3OH , HCN , NH_3 , and NH_4^+ . [5%]

(b) What would be the charge balance if you add MgCl_2 to the solution and it

dissociate into $\text{Mg}^{2+} + 2\text{Cl}^-$? [5%]

Solution

(a) Neutral species (H_2O , CH_3OH , HCN , and NH_3) contribute no charge, so the charge balance is

$$[\text{H}^+] + 3[\text{Fe}^{3+}] + 2[\text{Mg}^{2+}] + [\text{NH}_4^+] = [\text{OH}^-] + [\text{ClO}_4^-] + 3[\text{Fe}(\text{CN})_6^{3-}] + [\text{CN}^-]$$

(b) $[\text{H}^+] + 3[\text{Fe}^{3+}] + 2[\text{Mg}^{2+}] + [\text{NH}_4^+] = [\text{OH}^-] + [\text{ClO}_4^-] + 3[\text{Fe}(\text{CN})_6^{3-}] + [\text{CN}^-] + [\text{Cl}^-]$

9. Calculate the pH of water containing 0.10 M KCl at 25°C. $K_w = 1.0 \times 10^{-14}$. [10%]

Solution

$$[H^+] = [OH^-]$$

However, the ionic strength of 0.10 M KCl is 0.10 M. The activity coefficients of H^+ and OH^- in Table 10-2 are 0.83 and 0.76, respectively, when $\mu = 0.10$ M.

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

$$1.0 \times 10^{-14} = (\chi)(0.83)(\chi)(0.76)$$

$$\chi = 1.26 \times 10^{-7} M$$

The concentration of H^+ and OH^- are equal and are both greater than 1.0×10^{-7} M. The activity of H^+ and OH^- are not equal in this solution:

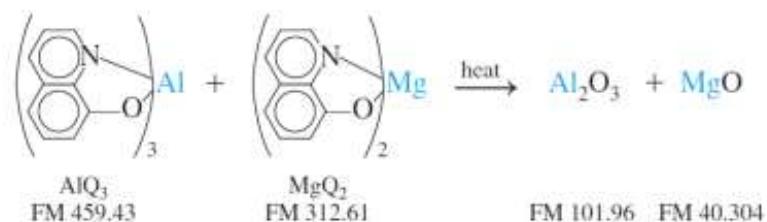
$$\mathcal{A}_{H^+} = [H^+] \gamma_{H^+} = (1.26 \times 10^{-7})(0.83) = 1.05 \times 10^{-7}$$

$$\mathcal{A}_{OH^-} = [OH^-] \gamma_{OH^-} = (1.26 \times 10^{-7})(0.76) = 0.96 \times 10^{-7}$$

Finally, we calculate $pH = -\log \mathcal{A}_{H^+} = -\log(1.05 \times 10^{-7}) = 6.98$

10. A mixture of 8-hydroxyquinoline complex 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.

[15%]



Solution

We will abbreviate the 8-hydroxyquinoline anion as Q. Letting the mass of AlQ_3 be x and the mass of MgQ_2 be y , we can write

$$x + y = 1.0843 \text{ g}$$

The mole 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 Al, because it takes 2 mol of Al to make 1 mol of Al_2O_3 .

$$\text{The moles of } \text{Al}_2\text{O}_3 = \left(\frac{1}{2}\right) \frac{x}{459.43}$$

$$\text{The moles of } \text{MgO} = \frac{y}{312.61}.$$

Now we can write

$$\frac{\left(\frac{1}{2}\right) \frac{x}{459.43} (101.96) + \frac{y}{312.61} (40.304)}{\text{Mass of } \text{Al}_2\text{O}_3 \quad \text{Mass of } \text{MgO}} = 0.1344 \text{ g}$$

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

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

from which we can find $x = 0.3003 \text{ g}$, which is 27.70 % of the original mixture.

Table of Activity Coefficients for Ions at 25°C

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
$\text{Rb}^+, \text{Cs}^+, \text{Tl}^+, \text{Ag}^+, \text{NH}_4^+$	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
$\text{Hg}_2^{2+}, \text{SO}_4^{2-}, \text{S}_2\text{O}_3^{2-}, \text{Cr}_2^{2+}, \text{HPO}_4^{2-}$	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

Source: Reprinted with permission from J. Kielland, *J. Am. Chem. Soc.*, 1937, 59, 1675. Copyright 1937 American Chemical Society.

© 2004 Thomson - Brooks/Cole