

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

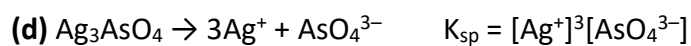
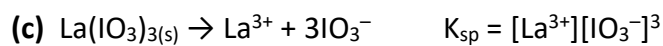
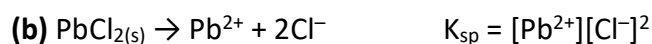
Second Midterm Examination

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) $\text{CuBr}_{(s)}$, (b) $\text{PbCl}_{2(s)}$, (c) $\text{La}(\text{IO}_3)_{3(s)}$, and (d) $\text{Ag}_3\text{AsO}_{4(s)}$. [2.5% each]

Solution

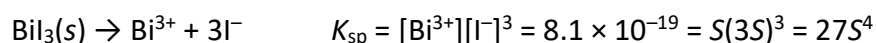
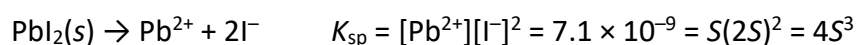


2. The solubility products for a series of metal iodides are shown below:

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

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

For PbI₂, $S = \sqrt[3]{\frac{7.1 \times 10^{-9}}{4}} = 1.2 \times 10^{-3} \text{ M}$

For BiI₃, $S = \sqrt[4]{\frac{8.1 \times 10^{-19}}{27}} = 1.3 \times 10^{-5} \text{ M}$

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

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

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

For PbI₂, $S = 7.1 \times 10^{-9}/(0.20)^2 = 1.8 \times 10^{-7} \text{ M}$

For BiI₃, $S = 8.1 \times 10^{-19}/(0.20)^3 = 1.0 \times 10^{-16} \text{ M}$

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%]

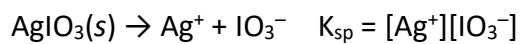
Solution

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

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

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

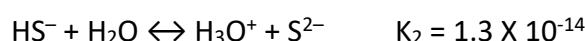
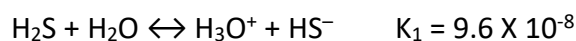
$$S^2 = 4.7 \times 10^{-8}$$

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

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

5. Cadmium sulfide (CdS) is less soluble than thallium(I) sulfide (Tl₂S). Find the [H⁺] concentrations under which Cd²⁺ and Tl⁺ can, in theory, be separated quantitatively (99.9 %) with H₂S from a solution that is 0.1 M in each cation. Use the following constants to perform the calculation. [15%]

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

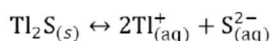
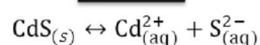


Solution

Example 11-11

Cadmium sulfide (CdS) is less soluble than thallium(I) Sulfide (Tl₂S). Find the conditions (pH) under which Cd²⁺ and Tl⁺ can, in theory, be separated quantitatively with H₂S from a solution that is 0.1 M in each cation.
↖ 99.9% of CdS is removed

Equilibria



Equilibrium constant

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

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

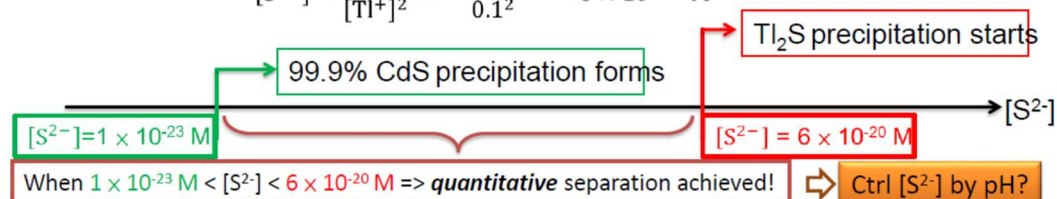
the minimum [S²⁻] to precipitate 99.9% CdS:

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

the maximum [S²⁻] before Tl₂S precipitates:

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

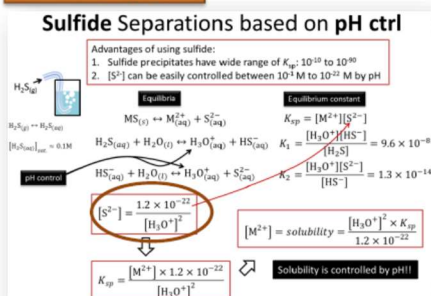
↖ 99.9% of CdS is removed



Example 11-11

Cadmium sulfide (CdS) is less soluble than thallium(I) Sulfide (Tl₂S). Find the conditions (pH) under which Cd²⁺ and Tl⁺ can, in theory, be **separated quantitatively** with H₂S from a solution that is 0.1 M in each cation. 99.9% of CdS is removed

Ctrl [S²⁻] by pH?



$$[S^{2-}] = \frac{1.2 \times 10^{-22}}{[H_3O^+]^2}$$

$$[H_3O^+] = \sqrt{\frac{1.2 \times 10^{-22}}{[S^{2-}]}}$$

Tl₂S precipitation starts

[H₃O⁺]

99.9% CdS precipitation forms

[H₃O⁺]=3.5 M

[H₃O⁺]=0.045 M

When $3.5M > [H_3O^+] > 0.045M \Rightarrow$ **quantitative** separation achieved!

Ctrl [S²⁻] by pH!

6.

- (a) In the presence of excess KIO_3 , what mass of $\text{Cu}(\text{IO}_3)_2$ can be formed from 0.650 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$? (Molecular weight for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ = 249.67 g/mol, $\text{Cu}(\text{IO}_3)_2$ = 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 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ to $\text{Cu}(\text{IO}_3)_2$? [5%]

Solution

(a)

$$0.650 \text{ g CuSO}_4 \cdot 5\text{H}_2\text{O} \times \frac{1 \text{ mol CuSO}_4 \cdot 5\text{H}_2\text{O}}{249.67 \text{ g CuSO}_4 \cdot 5\text{H}_2\text{O}} \times \frac{1 \text{ mol Cu}(\text{IO}_3)_2}{1 \text{ mol CuSO}_4 \cdot 5\text{H}_2\text{O}} \\ \times \frac{413.35 \text{ g Cu}(\text{IO}_3)_2}{1 \text{ mol Cu}(\text{IO}_3)_2} = 1.076 \text{ g Cu}(\text{IO}_3)_2$$

(b)

$$0.2750 \text{ g CuSO}_4 \cdot 5\text{H}_2\text{O} \times \frac{1 \text{ mol CuSO}_4 \cdot 5\text{H}_2\text{O}}{249.67 \text{ g CuSO}_4 \cdot 5\text{H}_2\text{O}} \times \frac{1 \text{ mol Cu}(\text{IO}_3)_2}{1 \text{ mol CuSO}_4 \cdot 5\text{H}_2\text{O}} \\ \times \frac{2 \text{ mol KIO}_3}{1 \text{ mol Cu}(\text{IO}_3)_2} \times \frac{214 \text{ g KIO}_3}{1 \text{ mol KIO}_3} = 1.076 \text{ g Cu}(\text{IO}_3)_2$$

7. Calculate the concentration of free Ca^{2+} in a solution of 0.10 M CaY^{2-} (Y = 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, $\alpha_{Y^{4-}} = 0.30$. At pH 6.00, $\alpha_{Y^{4-}} = 1.8 \times 10^{-5}$. [10%]

Solution:

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

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.

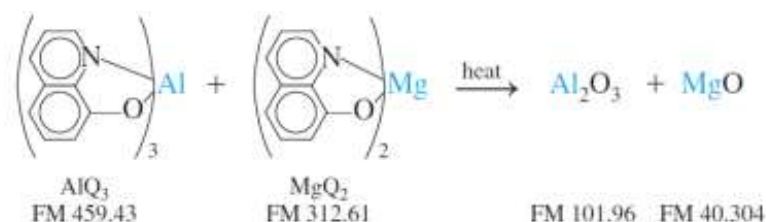
$$\begin{aligned}K_w &= [H^+]\gamma_{H^+}[OH^-]\gamma_{OH^-} \\1.0 \times 10^{-14} &= (\chi)(0.83)(\chi)(0.76) \\ \chi &= 1.26 \times 10^{-7} \text{ M}\end{aligned}$$

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:

$$\begin{aligned}\mathcal{A}_{H^+} &= [H^+]\gamma_{H^+} = (1.26 \times 10^{-7})(0.83) = 1.05 \times 10^{-7} \\ \mathcal{A}_{OH^-} &= [OH^-]\gamma_{OH^-} = (1.26 \times 10^{-7})(0.76) = 0.96 \times 10^{-7}\end{aligned}$$

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

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 .

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

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

Now we can write

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

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	Activity Coefficient at Indicated Ionic Strength					
	α_X , nm	0.001	0.005	0.01	0.05	0.1
H ₃ O ⁺	0.9	0.967	0.934	0.913	0.85	0.83
Li ⁺ , C ₆ H ₅ COO ⁻	0.6	0.966	0.930	0.907	0.83	0.80
Na ⁺ , IO ₃ ⁻ , HSO ₃ ⁻ , HCO ₃ ⁻ , H ₂ PO ₄ ⁻ , H ₂ AsO 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 ⁺ , Tl ⁺ , 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 ₂ O ₄ ²⁻	0.45	0.868	0.741	0.665	0.45	0.36
Hg ₂ ²⁺ , SO ₄ ²⁻ , S ₂ O 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 ⁴⁻	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 ³⁻	0.5	0.569	0.305	0.200	0.047	0.020

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