

1. Solve the following problem related to the solubility equilibria of some metal hydroxides in aqueous solution.  
- 1998

- a) The solubility of  $\text{Cu}(\text{OH})_2$  is  $1.72 \times 10^{-6}$  gram per 100. milliliters of solution at  $25^\circ\text{C}$ .  
 (i) Write the balanced chemical equation for the dissociation of  $\text{Cu}(\text{OH})_2(\text{s})$  in aqueous solution.  
 (ii) Calculate the solubility (in moles per liter) of  $\text{Cu}(\text{OH})_2$  at  $25^\circ\text{C}$ .  
 (iii) Calculate the value of the solubility-product constant,  $K_{\text{sp}}$ , for  $\text{Cu}(\text{OH})_2$  at  $25^\circ\text{C}$ .  
 b) The value of the solubility-product constant,  $K_{\text{sp}}$ , for  $\text{Zn}(\text{OH})_2$  is  $7.7 \times 10^{-17}$  at  $25^\circ\text{C}$ .  
 (i) Calculate the solubility (in moles per liter) of  $\text{Zn}(\text{OH})_2$  at  $25^\circ\text{C}$  in a solution with a pH of 9.35.  
 (ii) At  $25^\circ\text{C}$ , 50.0 milliliters of 0.100-molar  $\text{Zn}(\text{NO}_3)_2$  is mixed with 50.0 milliliters of 0.300-molar  $\text{NaOH}$ . Calculate the molar concentration of  $\text{Zn}^{2+}(\text{aq})$  in the resulting solution once equilibrium has been established. Assume that volumes are additive.

ANSWER:

- (a) (i)  $\text{Cu}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2 \text{OH}^{-}(\text{aq})$  (one point)  
 Correct stoichiometry and charges (but not phases) necessary  
 No credit earned if water as a reactant or product  
 (ii)  $1.72 \times 10^{-6} \text{ g} / 97.57 \text{ g/mol} = 1.763 \times 10^{-8} \text{ mol Cu}(\text{OH})_2$  (one point)  
 $1.763 \times 10^{-8} \text{ mol Cu}(\text{OH})_2 / 0.100 \text{ L} = 1.76 \times 10^{-7} \text{ moles per liter}$  (one point)  
 One point earned for conversion of mass to moles (need not to be computed explicitly)  
 One point earned for calculation of moles per liter  
 (iii)  $[\text{Cu}^{2+}] = 1.76 \times 10^{-7} \text{ M}$   
 $[\text{OH}^{-}] = 2 \times (1.76 \times 10^{-7} \text{ M}) = 3.52 \times 10^{-7}$  (one point)  
 $K_{\text{sp}} = [\text{Cu}^{2+}][\text{OH}^{-}]^2 = (1.76 \times 10^{-7})(3.52 \times 10^{-7})^2 = 2.18 \times 10^{-20}$  (one point)  
 One point earned for correct  $[\text{Cu}^{2+}]$  and  $[\text{OH}^{-}]$   
 One point for correct substitution into  $K_{\text{sp}}$  expression and answer  
 Response need not include explicit statement of  $[\text{OH}^{-}]$  if  $K_{\text{sp}}$  expression is written with correct values of  $[\text{Cu}^{2+}]$  and  $[\text{OH}^{-}]$   
 (b) (i)  $\text{pH} = 9.35 \rightarrow \text{pOH} = 4.65 \rightarrow [\text{OH}^{-}] = 2.24 \times 10^{-5} \text{ M}$  (one point)  
 $[\text{Zn}^{2+}] = K_{\text{sp}} / [\text{OH}^{-}]^2 = 7.7 \times 10^{-17} / (2.24 \times 10^{-5})^2 = 1.5 \times 10^{-7} \text{ M}$  (one point)  
 One point earned for correct determination of  $[\text{OH}^{-}]$   
 One point for correct answer (assume  $[\text{Zn}^{2+}]$  equals solubility in moles per liter)  
 No points earned if  $[\text{OH}^{-}]$  is assumed equal to twice  $[\text{Zn}^{2+}]$   
 (b) (ii)
- |                  |   |                   |               |                          |            |
|------------------|---|-------------------|---------------|--------------------------|------------|
| $\text{Zn}^{2+}$ | + | $2 \text{OH}^{-}$ | $\rightarrow$ | $\text{Zn}(\text{OH})_2$ |            |
| initial amount   |   | 0.0050 mol        |               | 0.0150 mol               | 0 mol      |
| final amount     |   | 0 mol             |               | 0.0050 mol               | 0.0050 mol |
- OR
- $[\text{OH}^{-}] = 0.0050 \text{ mol} / 0.100 \text{ L} = 0.0050 \text{ M}$  (one point)  
 One point earned if precipitation reaction is clearly indicated and moles or concentration of  $\text{OH}^{-}$  is calculated correctly
- |                                    |               |                  |   |                 |
|------------------------------------|---------------|------------------|---|-----------------|
| $\text{Zn}(\text{OH})_2(\text{s})$ | $\rightarrow$ | $\text{Zn}^{2+}$ | + | $\text{OH}^{-}$ |
| x                                  |               | (0.050 + 2x)     |   | (0.050 + 2x)    |
- $K_{\text{sp}} = 7.7 \times 10^{-17} = [\text{Zn}^{2+}][\text{OH}^{-}]^2 = (x)(0.050 + 2x)^2 = (x)(0.050)^2 \rightarrow [\text{Zn}^{2+}] = 3.1 \times 10^{-14} \text{ M}$  (one point)
- OR
- |                                    |               |                  |   |                   |
|------------------------------------|---------------|------------------|---|-------------------|
| $\text{Zn}(\text{OH})_2(\text{s})$ | $\rightarrow$ | $\text{Zn}^{2+}$ | + | $2 \text{OH}^{-}$ |
| (0.050-x)                          |               | (0.150-2x)       |   | (0.150-2x)        |
- $K_{\text{sp}} = 7.7 \times 10^{-17} = [\text{Zn}^{2+}][\text{OH}^{-}]^2 = (0.050 - x)(0.150 - 2x)^2$  (one point)  
 Solve for x, then subtract x from 0.050 M to obtain  $[\text{Zn}^{2+}]$  (one point)

2.  $\text{MgF}_2(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2 \text{F}^{-}(\text{aq})$  - 1994

In a saturated solution of  $\text{MgF}_2$  at  $18^\circ\text{C}$ , the concentration of  $\text{Mg}^{2+}$  is  $1.21 \times 10^{-3}$  molar. The equilibrium is represented by the equation above.

- (a) Write the expression for the solubility-product constant,  $K_{\text{sp}}$ , and calculate its value at  $18^\circ\text{C}$ .  
 (b) Calculate the equilibrium concentration of  $\text{Mg}^{2+}$  in 1.000 liter of saturated  $\text{MgF}_2$  solution at  $18^\circ\text{C}$  to which 0.100 mole of solid  $\text{KF}$  has been added. The  $\text{KF}$  dissolves completely. Assume the volume change is negligible.

**(c) Predict whether a precipitate of MgF<sub>2</sub> will form when 100.0 milliliters of a 3.00 x 10<sup>-3</sup> molar Mg(NO<sub>3</sub>)<sub>2</sub> solution is mixed with 200.0 milliliters of a 2.00 x 10<sup>-3</sup> molar NaF solution at 18°C. Calculations to support your prediction must be shown.**

**(d) At 27°C the concentration of Mg<sup>2+</sup> in a saturated solution of MgF<sub>2</sub> is 1.17 x 10<sup>-3</sup> molar. Is the dissolving of MgF<sub>2</sub> in water an endothermic or an exothermic process? Give an explanation to support your conclusion.**

ANSWER:

a) two points

$$\begin{aligned}K_{sp} &= [\text{Mg}^{2+}][\text{F}^{-}]^2 \\&= (1.21 \times 10^{-3})(2 \times 1.21 \times 10^{-3})^2 \\&= 7.09 \times 10^{-9}\end{aligned}$$

b) two points

$$\begin{aligned}K_{sp} &= [\text{Mg}^{2+}](2x + 0.100)^2 \\&\text{since } 2x \text{ is much less than } 0.100 \\&= 7.09 \times 10^{-9} = [\text{Mg}^{2+}](0.100)^2 \\[\text{Mg}^{2+}] &= (7.09 \times 10^{-9}) / (10^{-2}) \\&= 7.09 \times 10^{-7} \text{ M}\end{aligned}$$

Note: OK if 0.102 is used for [F<sup>-</sup>], then K<sub>sp</sub> = 6.76 x 10<sup>-7</sup>

c) three points (first point earned if both concentrations are correct; correct substitution and calculation of the wrong concentration values earns the second point [calc. of Q], but not the first

$$\begin{aligned}[\text{Mg}^{2+}]: \\100.0 \times 3.00 \times 10^{-3} &= 300.0 \times [\text{Mg}^{2+}]\end{aligned}$$

$$[\text{Mg}^{2+}] = 1.00 \times 10^{-3} \text{ M}$$

$$\begin{aligned}[\text{F}^{-}]: \\200.0 \times 2.00 \times 10^{-3} &= 300.0 \times [\text{F}^{-}]\end{aligned}$$

$$[\text{F}^{-}] = 1.33 \times 10^{-3} \text{ M}$$

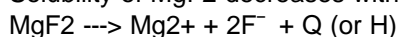
$$\begin{aligned}Q = \text{Ion Product} &= [\text{Mg}^{2+}][\text{F}^{-}]^2 \\&= (1.00 \times 10^{-3})(1.33 \times 10^{-3})^2 \\&= 1.77 \times 10^{-9}\end{aligned}$$

Since Q < K<sub>sp</sub>, no precipitate will form.

Note: conclusion must be consistent with Q value.

d) two points

Solubility of MgF<sub>2</sub> decreases with the increasing temperature, thus dissolution process is exothermic.



Reason:

i) Increased temperature puts a stress on the system (LeChâtelier). The system will reduce the stress by shifting the equilibrium in the endothermic (left) direction.

OR

ii) A data supported argument such as comparing ion concentrations, calculating second K<sub>sp</sub> and giving proper interpretations.

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**3. At 25 °C the solubility product constant, K<sub>sp</sub>, for strontium sulfate, SrSO<sub>4</sub>, is 7.6 x 10<sup>-7</sup>. The solubility product constant for strontium fluoride, SrF<sub>2</sub>, is 7.9 x 10<sup>-10</sup> - 1987**

**(a) What is the molar solubility of SrSO<sub>4</sub> in pure water at 25 °C?**

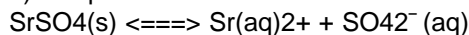
**(b) what is the molar solubility of SrF<sub>2</sub> in pure water at 25 °C?**

**(c) An aqueous solution of Sr(NO<sub>3</sub>)<sub>2</sub> is added slowly to 1.0 liter of a well-stirred solution containing 0.020 mole F<sup>-</sup> and 0.10 mole SO<sub>4</sub><sup>2-</sup> at 25 °C. (You may assume that the added Sr(NO<sub>3</sub>)<sub>2</sub> solution does not materially affect the total volume of the system.) Which salt precipitates first? What is the concentration of strontium ion, Sr<sup>2+</sup>, in the solution when the first precipitate begins to form?**

**(d) As more Sr(NO<sub>3</sub>)<sub>2</sub> is added to the mixture in (c) a second precipitate begins to form. At that stage, what percent of the anion of the first precipitate remains in solution?**

ANSWER:

a) two points

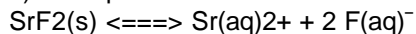


at equilibrium:  $[\text{SO}_4^{2-}] = x = [\text{Sr}^{2+}]$

$$(x)(x) = K_{\text{sp}} = 7.6 \times 10^{-7}$$

$$(x) = 8.7 \times 10^{-4} \text{ mol / liter} = \text{solubility of SrSO}_4$$

b) three points



at equilibrium:  $[\text{Sr}^{2+}] = x$ ,  $[\text{F}^{-}] = 2x$

$$K_{\text{sp}} = [\text{Sr}^{2+}][\text{F}^{-}]^2 = (x)(2x)^2 = 7.9 \times 10^{-10}$$

$$x = 5.8 \times 10^{-4} \text{ mol / liter} = \text{solubility of SrF}_2$$

c) two points

Solve for  $[\text{Sr}^{2+}]$  required for precipitation of each salt.

$$K_{\text{sp}} = [\text{Sr}^{2+}][\text{F}^{-}]^2 = 7.9 \times 10^{-10}$$

$$= (x)(0.020 \text{ mole} / 1.0 \text{ L})^2 = 7.9 \times 10^{-10}$$

$$x = 2.0 \times 10^{-6} \text{ M}$$

$$K_{\text{sp}} = [\text{Sr}^{2+}][\text{SO}_4^{2-}] = 7.6 \times 10^{-7}$$

$$= (y)(0.10 \text{ mole} / 1.0 \text{ liter}) = 7.6 \times 10^{-7}$$

$$y = 7.6 \times 10^{-6} \text{ M}$$

Since  $2.0 \times 10^{-6} \text{ M} < 7.6 \times 10^{-6} \text{ M}$ ,  $\text{SrF}_2$  must precipitate first.

When  $\text{SrF}_2$  precipitates,  $[\text{Sr}^{2+}] = 2.0 \times 10^{-6} \text{ M}$

d) two points

The second precipitate to form is  $\text{SrSO}_4$ , which appears when  $[\text{Sr}^{2+}] = 7.6 \times 10^{-6} \text{ M}$  (Based on calculation in Part c.)

When  $[\text{Sr}^{2+}] = 7.6 \times 10^{-6} \text{ M}$ ,  $[\text{F}^{-}]$  is determined as follows:

$$K_{\text{sp}} = [\text{Sr}^{2+}][\text{F}^{-}]^2 = 7.9 \times 10^{-10}$$

$$= (7.6 \times 10^{-6})(z)^2 = 7.9 \times 10^{-10}$$

$$z = 1.0 \times 10^{-2} \text{ M}$$

$$\% \text{F}^{-} \text{ still in solution} = 1.0 \times 10^{-2} / 2.0 \times 10^{-2} \times 100 = 50.0\%$$

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4. 1) A saturated solution of lead iodate in pure water has a lead ion concentration of  $4.0 \times 10^{-5}$  mole per liter at  $25^\circ\text{C}$  - 1979

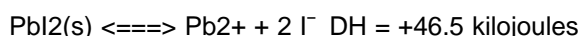
(a) Calculate the value for the solubility-product constant of  $\text{Pb}(\text{IO}_3)_2$  at  $25^\circ\text{C}$

(b) Calculate the molar solubility of  $\text{Pb}(\text{IO}_3)_2$  in a 0.10-molar  $\text{Pb}(\text{NO}_3)_2$  solution at  $25^\circ\text{C}$

(c) To 333 milliliters of a 0.120-molar  $\text{Pb}(\text{NO}_3)_2$  solution, 667 milliliters of 0.435-molar  $\text{KIO}_3$  is added. Calculate the concentration of  $\text{Pb}^{2+}$  and  $\text{IO}_3^{-}$  in the solution at equilibrium at  $25^\circ\text{C}$

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5. Lead iodide is a dense, golden yellow, slightly soluble solid. At  $25^\circ\text{C}$ , lead iodide dissolves in water forming a system represented by the following equation.



The solubility-product constant,  $K_{\text{sp}}$ , for  $\text{PbI}_2$  is  $7.1 \times 10^{-9}$  at  $25^\circ\text{C}$ .

(a) How does the entropy of the system  $\text{PbI}_2(\text{s}) + \text{H}_2\text{O}(\text{l})$  change as  $\text{PbI}_2(\text{s})$  dissolves in water at  $25^\circ\text{C}$ ? Explain.

(b) If the temperature of the system were lowered from  $25^\circ\text{C}$  to  $15^\circ\text{C}$ , what would be the effect on the value of  $K_{\text{sp}}$ ? Explain.

(c) If additional solid  $\text{PbI}_2$  were added to the system at equilibrium, what would be the effect on the concentration of  $\text{I}^{-}$  in the solution? Explain.

(d) At equilibrium,  $\text{DG} = 0$ . What is the initial effect on the value of  $\text{DG}$  of adding a small amount of  $\text{Pb}(\text{NO}_3)_2$  to the system at equilibrium? Explain.

ANSWER:

a) two points

$[\Delta]S$  increases

Dissolving converts highly organized solid to less organized hydrated ions

OR

dissociates, break down, etc.

OR

less particles => more particles

OR

$[\Delta]G$  negative,  $[\Delta]H$  positive =>  $-T[\Delta]S$  negative =>  $[\Delta]S$  positive

b) two points

$K_{sp}$  decreases

lowering  $T$  decreases the solubility since the reaction is endothermic

OR

if  $T$  decreases,  $-T[\Delta]S$  becomes less negative or  $[\Delta]G$  becomes more positive, i.e., less soluble;  $K_{sp}$  decreases

c) two points

There is no effect on  $[I^-]$

$PbI_2$  is a solid; its concentration does NOT change on addition of more  $PbI_2$

OR

$PbI_2(s)$  is NOT included in the expression for  $K_{sp}$  or  $Q$

OR

the solution is saturated => no more solid will dissolve

d) two points

$[\Delta]G$  becomes more positive (increases, gets larger, etc.)

Due to the common ion effect; the increase in  $[Pb^{2+}]$  shifts the equilibrium to the left.

OR

the reverse reaction becomes more spontaneous as  $[Pb^{2+}]$  increases due to the common ion effect

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6.  $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$  - 1987

Ammonia is a weak base that dissociates in water as shown above. At 25 °C, the base dissociation constant,  $K_b$ , for  $NH_3$  is  $1.8 \times 10^{-5}$ .

(a) Determine the hydroxide ion concentration and the percentage dissociation of a 0.150-molar solution of ammonia at 25 °C.

(b) Determine the pH of a solution prepared by adding 0.0500 mole of solid ammonium chloride to 100. milliliters of a 0.150-molar solution of ammonia.

(c) If 0.0800 mole of solid magnesium chloride,  $MgCl_2$ , is dissolved in the solution prepared in part (b) and the resulting solution is well-stirred, will a precipitate of  $Mg(OH)_2$  form? Show calculation to support your answer. (Assume the volume of the solution is unchanged. The solubility product constant for  $Mg(OH)_2$  is  $1.5 \times 10^{-11}$ ).

ANSWER

a) three points

$$[NH_4^+] = [OH^-] = x$$

$$[NH_3] = 0.150 \text{ mol/L} - x$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$1.8 \times 10^{-5} = \frac{(x)(x)}{(0.150 - x)}$$

approximately equals  $x^2 \div 0.150$

$$x = [OH^-] = 1.6 \times 10^{-3} \text{ mol/L}$$

$$\% \text{ diss} = \frac{(1.6 \times 10^{-3})}{(0.150)} \times 100\% = 1.1\%$$

b) three points

$$[NH_4^+] = 0.0500 \text{ mol} / 0.100 \text{ L} = 0.500 \text{ mol/L } NH_4^+$$

$$[NH_3] = 0.150 \text{ mol/L}$$

OR

$$\text{mol } NH_4^+ = 0.0500 \text{ mol } NH_4^+$$

$$\text{mol } NH_3 = 0.150 \text{ mol/L} \times 0.100 \text{ L} = 0.0150 \text{ mol}$$

THEN

$$1.8 \times 10^{-5} = [(0.500)(x)] \div (0.150)$$

OR

$$\text{pOH} = 4.74 + \log(0.500 / 0.150)$$

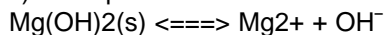
THEN

$$x = [\text{OH}^-] = 5.4 \times 10^{-6} \text{ mol/L}$$

$$\text{pOH} = 5.27$$

$$\text{pH} = 14.00 - 5.27 = 8.73$$

c) three points



$$[\text{Mg}^{2+}] = 0.0800 \text{ mol} / 0.100 \text{ L} = 0.800 \text{ mol/L} \quad (0.800 \pm x = \text{no credit})$$

$$([\text{OH}^-] = 5.4 \times 10^{-6} \text{ mol/L from b.})$$

$$Q = [\text{Mg}^{2+}][\text{OH}^-]^2 = (0.800)(5.4 \times 10^{-6})^2$$

$$Q = 2.3 \times 10^{-11}$$

$$K_{\text{sp}} = 1.5 \times 10^{-11}$$

since  $Q > K_{\text{sp}}$ ,  $\text{Mg(OH)}_2$  precipitates

(Q must be defined in the same way as  $K_{\text{sp}}$ )

OR

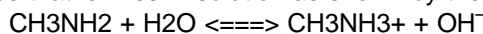
$$K_{\text{sp}} = 1.5 \times 10^{-11} = (0.800)[\text{OH}^-]^2$$

$$[\text{OH}^-] = 4.3 \times 10^{-6} \text{ mol/L}$$

since  $5.4 \times 10^{-6} > 4.3 \times 10^{-6} \text{ mol/L}$ , then  $\text{Mg(OH)}_2$  precipitates

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7. Methylamine,  $\text{CH}_3\text{NH}_2$ , is a weak base that ionizes in solution as shown by the following equation.



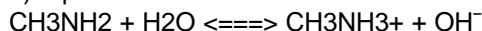
(a) At 25 °C, the percentage ionization in a 0.160-molar solution of  $\text{CH}_3\text{NH}_2$  is 4.7%. Calculate  $[\text{OH}^-]$ ,  $[\text{CH}_3\text{NH}_3^+]$ ,  $[\text{CH}_3\text{NH}_2]$ ,  $[\text{H}_3\text{O}^+]$ , and the pH of a 0.160-molar solution of  $\text{CH}_3\text{NH}_2$  at 25 °C.

(b) Calculate the value for  $K_{\text{b}}$ , the ionization constant for  $\text{CH}_3\text{NH}_2$ , at 25 °C.

(c) If 0.050 mole of crystalline lanthanum nitrate is added to 1.00 liter of a solution containing 0.20 mole of  $\text{CH}_3\text{NH}_2$  and 0.20 mole of its salt  $\text{CH}_3\text{NH}_3\text{Cl}$  at 25 °C, and the solution is stirred until equilibrium is attained, will any  $\text{La(OH)}_3$  precipitate? Show the calculations that prove your answer. (The solubility product constant for  $\text{La(OH)}_3$ ,  $K_{\text{sp}}$ , is  $1 \times 10^{-19}$  at 25 °C.)

ANSWER:

a) 7 points



$$(0.160)(0.047) = \text{moles} / \text{CH}_3\text{NH}_2 \text{ ionizing} = 7.5 \times 10^{-3} \text{ M}$$

$$(0.160 - 7.5 \times 10^{-3}) = 0.152 \text{ M} = [\text{CH}_3\text{NH}_2] \text{ at equilibrium}$$

$$[\text{CH}_3\text{NH}_3^+] = [\text{OH}^-] = 7.5 \times 10^{-3} \text{ M}$$

$$[\text{H}_3\text{O}^+] = (1.0 \times 10^{-14} / 7.5 \times 10^{-3}) = 1.3 \times 10^{-12} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 11.89$$

b) 3 points

$$K_{\text{b}} = ([\text{CH}_3\text{NH}_3^+][\text{OH}^-]) / [\text{CH}_3\text{NH}_2]$$

$$= (7.5 \times 10^{-3})^2 / 0.152 = 3.7 \times 10^{-4}$$

c) 5 points

$$K_{\text{b}} = 3.7 \times 10^{-4} = [(0.20 + x)(x)] / (0.20 - x) = x = [\text{OH}^-]$$

$$Q = [\text{La}^{3+}][\text{OH}^-]^3 = (0.050)(3.7 \times 10^{-4})^3 = 2.5 \times 10^{-12}$$

$Q > K_{\text{sp}}$ , therefore  $\text{La(OH)}_3$  precipitation occurs.