

# Chem 108

## (Acid-base titration, Solubility products & Spontaneity)

Problem set # 3

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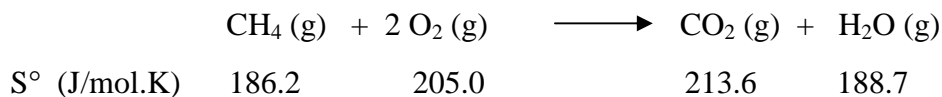
**Part I: Multiple Choices.** Please circle the **ONE** best answer:

- Which of the following sulfides has the greater molar solubility? CdS ( $K_{sp} = 8 \times 10^{-28}$ ), CoS ( $K_{sp} = 8 \times 10^{-22}$ ), CuS ( $K_{sp} = 6 \times 10^{-37}$ ) and ZnS ( $K_{sp} = 2 \times 10^{-25}$ ):  
a) CuS                      b) ZnS                      c) CoS                      d) CdS
- Zn(OH)<sub>2</sub> is a relatively insoluble base. A saturated solution has a pH of 8.65. Calculate the  $K_{sp}$  for Zn(OH)<sub>2</sub>.  
a)  $9.1 \times 10^{-17}$               b)  $1.1 \times 10^{-17}$               c)  $4.5 \times 10^{-17}$               d) None of the above
- In the titration of 20.0 mL of 0.200 M HOBr with 0.100 M NaOH, what is the pH at the equivalence point? ( $K_a$  HOBr =  $2.5 \times 10^{-9}$ )  
a) 7.00                      b) 3.29                      c) 10.86                      d) 10.71
- Calculate the pH of a solution formed by adding 50.0 mL of 6.0 M NH<sub>3</sub> to 75.0 mL of 1.0 M HCl.  
a) 9.26                      b) 9.73                      c) 8.79                      d) 5.22
- In a saturated solution of Pb(OH)<sub>2</sub>, the concentration of lead ions is  $4.2 \times 10^{-6}$  M and the concentration of hydroxide ions is  $8.3 \times 10^{-6}$  M. What is the predicted value of  $K_{sp}$  for Pb(OH)<sub>2</sub>?  
a)  $2.9 \times 10^{-16}$               b)  $5.8 \times 10^{-16}$               c)  $1.5 \times 10^{-16}$               d)  $3.5 \times 10^{-13}$
- Calculate the pH of a solution that is formed by mixing 20.0 mL of 0.15 M HCl with 30.0 mL of 0.12 M NaOH?  
a) 1.62                      b) 7.00                      c) 0.82                      d) 12.08
- Which of the following statements is CORRECT?  
a) Ag<sub>2</sub>CO<sub>3</sub> ( $K_{sp} = 8.1 \times 10^{-12}$ ) is considered soluble in water.  
b) Ag<sub>2</sub>CO<sub>3</sub> is more soluble in Na<sub>2</sub>CO<sub>3</sub> solution than in water.  
c) Ag<sub>2</sub>CO<sub>3</sub> is less in aqueous HCl than in water.  
d) None of these.
- Calculate the pH of a solution formed by mixing 20.0 mL of 0.25 M formic acid, HCOOH, and 8.0 mL of 0.400 M NaOH.  $K_a$  HCOOH =  $1.8 \times 10^{-4}$   
a) 3.99                      b) 3.74                      c) 2.17                      d) 2.47

9. Which of the following processes would lead to a decrease in entropy?

- a)  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \longrightarrow 2 \text{NH}_3(\text{g})$
- b)  $\text{N}_2\text{O}_4(\text{g}) \longrightarrow 2 \text{NO}_2(\text{g})$
- c)  $\text{I}_2(\text{s}) \longrightarrow \text{I}_2(\text{aq})$
- d)  $\text{NH}_4\text{NO}_3(\text{s}) \longrightarrow \text{N}_2\text{O}(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$

10. Given the following standard molar entropies, calculate  $\Delta S^\circ$  for the reaction:



- a) 5.2
- b) 11.1
- c) -11.1
- d) -193.3

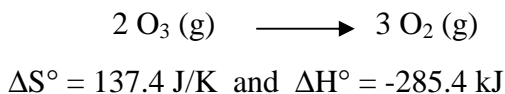
11. The following reaction is endothermic:  $3 \text{O}_2(\text{g}) \longrightarrow 2 \text{O}_3(\text{g})$ . The reaction is:

- a) spontaneous at high temperatures
- b) non-spontaneous at all temperatures
- c) spontaneous at all temperatures
- d) spontaneous at high temperature

12. Consider the reaction:  $\text{PCl}_5(\text{g}) \longrightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ ,  $\Delta H = +87.9 \text{ kJ/mol.K}$  and  $\Delta S = +170.2 \text{ J/mol.K}$ . At what temperature in C, does the reaction become spontaneous?

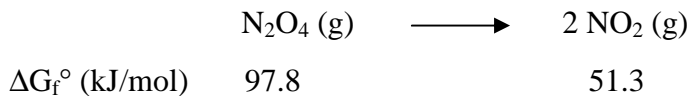
- a) 25
- b) 343
- c) 616
- d) 243

13. Consider following data and calculate  $\Delta G^\circ$ , in kJ at  $55^\circ \text{C}$  for the reaction:



- a)  $-4.51 \times 10^5$
- b) -292.9
- c)  $-7.59 \times 10^4$
- d) -330.5

14. Determine the value of  $K_{\text{eq}}$  at  $25^\circ \text{C}$  for the following reaction:



- a) 1.0
- b)  $1.4 \times 10^8$
- c)  $6.2 \times 10^{-8}$
- d) 0.14

**Part II Show all work for full credit. Please express all answers with proper units and correct number of significant figures.**

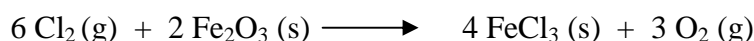
1. In the titration of 25.0 mL of 0.120 M formic acid,  $\text{HCO}_2\text{H}$  ( $K_a = 1.8 \times 10^{-4}$ ) with 0.105 M NaOH solution:

- a) What is the pH of  $\text{HCO}_2\text{H}$  solution before the titration begins?
- a) What is the pH at the mid point of the titration?
- c) What is the pH at the equivalence point?
- d) What indicator would be best to detect the equivalence point?

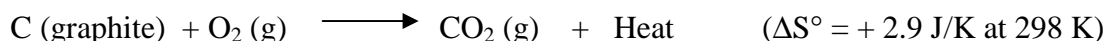
2. In the titration of 25.0 mL of 0.250 M propanoic acid,  $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$  ( $\text{pK}_a = 4.89$ ) with 0.330 M NaOH solution:
- What is the pH of  $\text{HCO}_2\text{H}$  solution before the addition of any NaOH?
  - What is the pH at the mid point of the titration?
  - What is the pH at the equivalence point?
3. Will a precipitate form when 100. mL of  $8.0 \times 10^{-3}$  M  $\text{Pb}(\text{NO}_3)_2$  is added to 400. mL of  $5.0 \times 10^{-3}$  M  $\text{Na}_2\text{SO}_4$ ? ( $K_{\text{sp}}$  for  $\text{PbSO}_4 = 6.3 \times 10^{-7}$ )
4. The value for  $K_{\text{sp}}$  for manganese(II) hydroxide,  $\text{Mn}(\text{OH})_2$  is  $1.6 \times 10^{-13}$ . Calculate the molar solubility of  $\text{Mn}(\text{OH})_2$ :
- in pure water
  - in a solution that contains 0.020 M NaOH
5. Should  $\text{Mg}(\text{OH})_2$  (s) ( $K_{\text{sp}} = 1.8 \times 10^{-11}$ ) precipitate from a solution of that is 0.010 M  $\text{MgCl}_2$  and also 0.10 M  $\text{NH}_3$  ( $K_b = 1.8 \times 10^{-5}$ )?
6. Calculate the solubility of copper(II) hydroxide,  $\text{Cu}(\text{OH})_2$  in g/L ( $K_{\text{sp}} = 2.2 \times 10^{-20}$  & molar mass of  $\text{Cu}(\text{OH})_2$  is 97.57g/mol). What could be the pH of the saturated solution of  $\text{Cu}(\text{OH})_2$ ?

7. Answer the following questions:

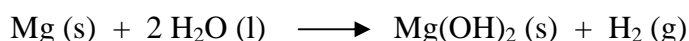
a) Predict whether the entropy change is positive (+) or negative (-) for the following reaction:



b) Predict whether the following reaction is *product-favored* or *reactant-favored*:



8. Calculate  $\Delta H^\circ$  and  $\Delta S^\circ$  values at 25° C for the following reaction:



|                             | Mg (s) | H <sub>2</sub> O (l) | Mg(OH) <sub>2</sub> (s) | H <sub>2</sub> (g) |
|-----------------------------|--------|----------------------|-------------------------|--------------------|
| $\Delta H_f^\circ$ (kJ/mol) | 0      | -285.8               | -924.5                  | 0                  |
| $S^\circ$ (J/K.mol)         | 32.68  | 69.91                | 63.18                   | 130.7              |

Is the calculated entropy change consistent with what you expected? Why?

9. Calculate the standard free energy change,  $\Delta G_f^\circ$  for the reaction:




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|                              |         |        |        |
|------------------------------|---------|--------|--------|
| $\Delta H_f^\circ$ (kJ/mol): | -1095.8 | -601.7 | -393.5 |
| $S_f^\circ$ (J/K.mol):       | 65.7    | 26.9   | 213.7  |

- Is the reaction product-favored at room temperature?
- Is the reaction enthalpy or entropy driven?
- What is the value of  $K_p$  at 25°C?
- At what temperature does  $K_p = 1$ ?
- Does high temperature make the reaction more or less product-favored?

## Answers:

**Part I. MC:** 1) c, 2) c, 3) d, 4) b, 5) a, 6) d, 7) d, 8) a, 9) a, 10) d, 11) d, 12) d, 13) d, 14) d

**Part II:** 1) a, pH = 2.3; b, pH = 3.7; c, pH = 8.24; d, phenolphthalein

2) a, pH = 2.74; b, pH = 4.89; c, pH = 9.02

3) Yes,  $P (6.4 \times 10^{-6}) > K_{sp}$

4) a,  $3.4 \times 10^{-5} \text{ M}$ ; b,  $4.0 \times 10^{-10} \text{ M}$

5)

6)  $1.72 \times 10^{-5} \text{ g/L}$ ; pH = 7.55

7) a, negative because less molecules in the product are in the gas phase

b, product-favored; negative enthalpy & positive entropy (spontaneous process)

8)  $\Delta H^\circ_{rxn} = -352.9 \text{ kJ/mol}$ ,  $\Delta S^\circ_{rxn} = +21.4 \text{ J/mol.K}$  & entropy change is expected to be positive as calculated because one mole of  $\text{H}_2$  gas is formed in product as well as the solid  $\text{Mg(OH)}_2$  has more atoms than any compound in the reactant side.

## Answer of problem # 9:

1. We need to calculate  $\Delta G^\circ_f$  and its sign:

$$\begin{aligned}\Delta H^\circ_{rxn} &= \{\Delta H^\circ_f [\text{MgO (s)}] + \Delta H^\circ_f [\text{CO}_2 \text{ (g)}]\} - \Delta H^\circ_f [\text{MgCO}_3 \text{ (s)}] \\ &= \{(1 \text{ mol}) (-601.7 \text{ kJ/mol}) + (1 \text{ mol}) (-393.5 \text{ kJ/mol})\} - (1 \text{ mol}) (1095.8 \text{ kJ/mol}) \\ &= +100.6 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ_{rxn} &= \{S^\circ_f [\text{MgO (s)}] + S^\circ_f [\text{CO}_2 \text{ (g)}]\} - S^\circ_f [\text{MgCO}_3 \text{ (s)}] \\ &= \{(1 \text{ mol}) (26.9 \text{ J/K.mol}) + (1 \text{ mol}) (213.7 \text{ J/K.mol})\} - (1 \text{ mol}) (65.7 \text{ J/K.mol}) \\ &= +174.9 \text{ J/K}\end{aligned}$$

$$\begin{aligned}\Delta G^\circ_{rxn} &= \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn} \\ &= (100.6 \text{ kJ}) - (298 \text{ K})(174.9 \text{ J/K})(1000\text{J/kJ}) \\ &= +48.5 \text{ kJ}\end{aligned}$$

The + sign of  $\Delta G^\circ_{rxn}$  indicates that decomposition of  $\text{MgCO}_3$  at R.T. is *Reactant-Favored*.

2. Since  $\Delta S^\circ_{rxn}$  is +; reaction is *Entropy-Driven*.

3. To calculate  $K_p$ :  $\Delta G^\circ_{rxn} = -RT \ln K_p$

$$\begin{aligned}\ln K_p &= -\Delta G^\circ_{rxn} / RT \\ &= -(48.5 \text{ kJ})(1000 \text{ J/kJ}) / (8.315 \text{ J/K.mol})(298 \text{ K}) = -19.6\end{aligned}$$

$$K_p = e^{-19.6} = 3.0 \times 10^{-9} \text{ (} K_p \ll 1; \text{ product-favored)}$$

4.  $K_p = 1$  when  $\Delta G^\circ_{rxn} = 0$

$$\Delta G^\circ_{rxn} = 0 = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$$

$$T = \Delta H^\circ_{rxn} / \Delta S^\circ_{rxn} \text{ (The minimum temperature at which } K_p = 1)$$

$$= (100 \text{ kJ}) / (0.1749 \text{ kJ/K}) = 575.2 \text{ K}$$

$$= 575.2 - 273 = 302 \text{ }^\circ\text{C}$$

5. Higher temperatures make the reaction to be more product-favored; at  $T \geq 302 \text{ }^\circ\text{C}$ . Under this conditions  $-T\Delta S^\circ_{rxn}$  (*the entropy term*)  $> \Delta H^\circ_{rxn}$  (*enthalpy term*) and  $\Delta G^\circ_{rxn}$  has a negative sign; reaction is becoming spontaneous.