Chem 108

(Acid-base titration, Solubility products & Spontaneity)

Problem set # 3 **Salah S. Massoud**

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

1. Which of the following sulfides has the greater molar solubility? CdS (K_{sp} = 8 x 10^{-28}), CoS (K_{sp} = 8 x 10^{-22}), CuS (K_{sp} = 6 x 10^{-37}) and ZnS (K_{sp} = 2 x 10^{-25}):

   a) CuS b) ZnS c) CoS d) CdS

2. $Zn(OH)_2$ is a relatively insoluble base. A saturated solution has a pH of 8.65. Calculate the Ksp for $Zn(OH)_2$.

   a) 9.1 x 10^{-17} b) 1.1 x 10^{-17} c) 4.5 x 10^{-17} d) None of the above

3. 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? (Ka HOBr = 2.5 x 10^{-9})

   a) 7.00 b) 3.29 c) 10.86 d) 10.71

4. Calculate the pH of a solution formed by adding 50.0 mL of 6.0 M NH_3 to 75.0 mL of 1.0 M HCl.

   a) 9.26 b) 9.73 c) 8.79 d) 5.22

5. In a saturated solution of $Pb(OH)_2$, the concentration of lead ions is 4.2 x 10^{-6} M and the concentration of hydroxide ions is 8.3 x 10^{-6} M. What is the predicted value of K_{sp} for $Pb(OH)_2$?

   a) 2.9 x 10^{-16} b) 5.8 x 10^{-16} c) 1.5 x 10^{-16} d) 3.5 x 10^{-13}

6. 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

7. Which of the following statements is CORRECT?

   a) Ag_2CO_3 (K_{sp} = 8.1 x 10^{-12}) is considered soluble in water.
   b) Ag_2CO_3 is more soluble in Na_2CO_3 solution than in water.
   c) Ag_2CO_3 is less in aqueous HCl than in water.
   d) None of these.

8. 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. Ka HCOOH = 1.8 x 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) $N_2 (g) + 3 H_2 (g) \longrightarrow 2 NH_3 (g)$

b) $N_2O_4 (g) \longrightarrow 2 NO_2 (g)$

c) $I_2 (s) \longrightarrow I_2 (aq)$

d) $NH_4NO_3 (s) \longrightarrow N_2O (g) + 2 H_2O (g)$

10. Given the following standard molar entropies, calculate ΔS° for the reaction:

	$CH_4 (g)$	$+ 2 O_2 (g)$	$\longrightarrow$	$CO_2 (g)$	$+ H_2O (g)$
S° (J/mol.K)	186.2	205.0		213.6	188.7

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

11. The following reaction is endothermic: $3 O_2 (g) \longrightarrow 2 O_3 (g)$. 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: $PCl_5 (g) \longrightarrow PCl_3 (g) + Cl_2 (g)$, ΔH = +87.9 kJ/mol.K and ΔS = +170.2 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 ΔG°, in kJ at 55° C for the reaction:

$$2 O_3 (g) \longrightarrow 3 O_2 (g)$$

ΔS° = 137.4 J/K and ΔH° = -285.4 kJ

a) -4.51×10^5 b) -292.9 c) -7.59×10^4 d) -330.5

14. Determine the value of K_{eq} at 25° C for the following reaction:

	$N_2O_4 (g)$	$\longrightarrow$	$2 NO_2 (g)$
$\Delta G_f°$ (kJ/mol)	97.8		51.3

a) 1.0 b) 1.4×10^8 c) 6.2×10^{-8} d) 0.14

<u>Part II</u> <u>Show all work for full credit</u>. 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, HCO_2H (Ka = 1.8×10^{-4}) with 0.105 M NaOH solution:

a) What is the pH of HCO_2H 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, $CH_3CH_2CO_2H$ (pK_a = 4.89) with 0.330 M NaOH solution:

   a) What is the pH of HCO_2H solution before the addition of any NaOH?
   b) What is the pH at the mid point of the titration?
   c) What is the pH at the equivalence point?

3. Will a precipitate form when 100. mL of 8.0×10^{-3} M $Pb(NO_3)_2$ is added to 400. mL of 5.0×10^{-3} M Na_2SO_4? (K_{sp} for $PbSO_4 = 6.3 \times 10^{-7}$)

4. The value for Ksp for manganese(II) hydroxide, $Mn(OH)_2$ is 1.6×10^{-13}. Calculate the molar solubility of $Mn(OH)_2$:
   b) in pure water
   b) in a solution that contains 0.020 M NaOH

5. Should $Mg(OH)_2$ (s) ($K_{sp} = 1.8 \times 10^{-11}$) precipitate from a solution of that is 0.010 M $MgCl_2$ and also 0.10 M NH_3 ($K_b = 1.8 \times 10^{-5}$)?

6. Calculate the solubility of copper(II) hydroxide, $Cu(OH)_2$ in g/L ($K_{sp} = 2.2 \times 10^{-20}$ & molar mass of $Cu(OH)_2$ is 97.57g/mol). What could be the pH of the saturated solution of $Cu(OH)_2$?

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

   $$6\,Cl_2\,(g) + 2\,Fe_2O_3\,(s) \longrightarrow 4\,FeCl_3\,(s) + 3\,O_2\,(g)$$

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

   $$C\,(\text{graphite}) + O_2\,(g) \longrightarrow CO_2\,(g) + \text{Heat} \qquad (\Delta S° = +\,2.9\text{ J/K at 298 K})$$

8. Calculate ΔH° and ΔS° values at 25° C for the following reaction:

   $$Mg\,(s) + 2\,H_2O\,(l) \longrightarrow Mg(OH)_2\,(s) + H_2\,(g)$$

	Mg (s)	H_2O (l)	$Mg(OH)_2$ (s)	H_2 (g)
$\Delta H_f°$ (kJ/mol)	0	-285.8	-924.5	0
S° (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, $\Delta G°_f$ for the reaction:

   $$MgCO_3\,(s) \longrightarrow MgO\,(s) + CO_2\,(g)$$

	$MgCO_3$ (s)	MgO (s)	CO_2 (g)
$\Delta H°_f$ (kJ/mol):	-1095.8	-601.7	-393.5
$S°_f$ (J/K.mol):	65.7	26.9	213.7

1. Is the reaction product-favored at room temperature?
2. Is the reaction enthalpy or entropy driven?
3. What is the value of Kp at 25ºC?
4. At what temperature does Kp = 1?
5. Does high temperature make the reaction more or less product-favored?

<u>Answers:</u>

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 (6.4×10^{-6}) > K_{sp}
4) a, 3.4×10^{-5} M; b, 4.0×10^{-10} M
5)
6) 1.72 x 10-5 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) ΔH^o_{rxn} = -352.9 KJ/mol, ΔS^o_{rxn} = + 21.4 J/mol.K & entropy change is expected to be positive as calculated because one mole oh H_2 gas is formed in product as well as the solid $Mg(OH)_2$ has more atoms than any compound in the reactant side.

<u>Answer of problem # 9</u>:

1. We need to calculate ΔG^o_f and its sign:

$$\Delta H^o_{rxn} = \{\Delta H^o_f\ [MgO\ (s)] + \Delta H^o_f\ [CO_2\ (g)]\} - \Delta H^o_f\ [MgCO_3\ (s)]$$
$$= \{(1\ mol)\ (-601.7\ kJ/mol) + (1\ mol)\ (-393.5\ kJ/mol)\} – (1\ mol)\ (1095.8\ kJ/mol)$$
$$= +\ 100.6\ kJ$$

$$\Delta S^o_{rxn} = \{S^o_f\ [MgO\ (s)] + S^o_f\ [CO_2\ (g)]\} - S^o_f\ [MgCO_3\ (s)]$$
$$= \{(1\ mol)\ (26.9\ J/K.mol) + (1\ mol)\ (213.7\ J/K.mol)\} – (1\ mol)\ (65.7\ J/K.mol)$$
$$= +\ 174.9\ J/K$$

$$\Delta G^o_{rxn} = \Delta H^o_{rxn} - T\Delta S^o_{rxn}$$
$$= (100.6\ kJ) - (298\ K)(174.9\ J/K)(1000J/kJ)$$
$$= +\ 48.5\ kJ$$

The + sign of ΔG^o_{rxn} indicates that decomposition of $MgCO_3$ at R.T. is *Reactant-Favored*.

2. Since ΔS^o_{rxn} is +; reaction is *Entropy-Driven*.

3. To calculate K_p: $\Delta G^o_{rxn} = -RT \ln K_p$
$\ln K_p = -\Delta G^o_{rxn} / RT$
$= -(48.5\ kJ)(1000\ J/kJ) / (8.315\ J/K.mol)(298\ K) = -19.6$

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

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

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

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

$= (100\ kJ)/(0.1749\ kJ/K) = 575.2\ K$

$= 575.2 – 273 = 302\ ^oC$

5. Higher temperatures make the reaction to be more product-favored; at T ≥ 302 ºC. Under this conditions $-T\Delta S^o_{rxn}$ *(the entropy term)* > ΔH^o_{rxn} (enthalpy term) and ΔG^o_{rxn} has a negative sign; reaction is becoming spontaneous.