

Chem 108

(Acid-base titration, Solubility products & Spontaneity)

Problem set # 3

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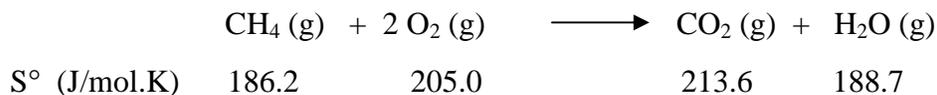
Part I: Multiple Choices. Please circle the **ONE** best answer:

- 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)₂ is a relatively insoluble base. A saturated solution has a pH of 8.65. Calculate the K_{sp} for Zn(OH)₂.
a) 9.1×10^{-17} b) 1.1×10^{-17} c) 4.5×10^{-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? ($K_a \text{ HOBr} = 2.5 \times 10^{-9}$)
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 NH₃ 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)₂, the concentration of lead ions is 4.2×10^{-6} M and the concentration of hydroxide ions is 8.3×10^{-6} M. What is the predicted value of K_{sp} for Pb(OH)₂?
a) 2.9×10^{-16} b) 5.8×10^{-16} c) 1.5×10^{-16} d) 3.5×10^{-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) Ag₂CO₃ ($K_{sp} = 8.1 \times 10^{-12}$) is considered soluble in water.
b) Ag₂CO₃ is more soluble in Na₂CO₃ solution than in water.
c) Ag₂CO₃ 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. $K_a \text{ HCOOH} = 1.8 \times 10^{-4}$
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 ΔS° for the reaction:



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

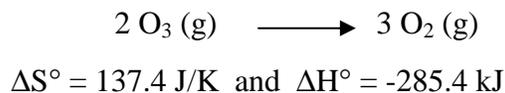
11. The following reaction is endothermic: $3 \text{O}_2(\text{g}) \longrightarrow 2 \text{O}_3(\text{g})$. The reaction is:

- 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?

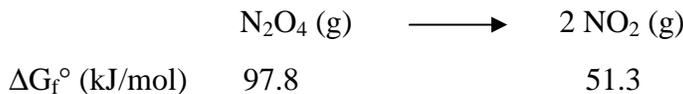
- a) 25
- b) 343
- c) 616
- d) 243

13. Consider following data and calculate ΔG° , in kJ at 55°C for the reaction:



- 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:



- a) 1.0
- b) 1.4×10^8
- c) 6.2×10^{-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, HCO_2H ($K_a = 1.8 \times 10^{-4}$) 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?

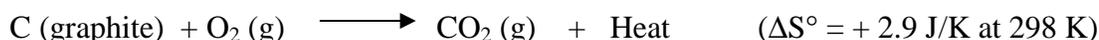
- In the titration of 25.0 mL of 0.250 M propanoic acid, $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ ($\text{pK}_a = 4.89$) with 0.330 M NaOH solution:
 - What is the pH of HCO_2H solution before the addition of any NaOH?
 - What is the pH at the mid point of the titration?
 - What is the pH at the equivalence point?
- Will a precipitate form when 100. mL of 8.0×10^{-3} M $\text{Pb}(\text{NO}_3)_2$ is added to 400. mL of 5.0×10^{-3} M Na_2SO_4 ? (K_{sp} for $\text{PbSO}_4 = 6.3 \times 10^{-7}$)
- The value for K_{sp} for manganese(II) hydroxide, $\text{Mn}(\text{OH})_2$ is 1.6×10^{-13} . Calculate the molar solubility of $\text{Mn}(\text{OH})_2$:
 - in pure water
 - in a solution that contains 0.020 M NaOH
- 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 MgCl_2 and also 0.10 M NH_3 ($K_b = 1.8 \times 10^{-5}$)?
- 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 ΔH° and ΔS° values at 25° C for the following reaction:



	Mg (s)	H ₂ O (l)	Mg(OH) ₂ (s)	H ₂ (g)
ΔH_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, ΔG_f° for the reaction:



ΔH_f° (kJ/mol):	-1095.8	-601.7	-393.5
S_f° (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 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.

Answer of problem # 9:

1. We need to calculate ΔG°_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 ΔG°_{rxn} indicates that decomposition of MgCO_3 at R.T. is *Reactant-Favored*.

2. Since ΔS°_{rxn} is +; reaction is *Entropy-Driven*.

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

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

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

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

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

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

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

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

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*) $>$ ΔH°_{rxn} (*enthalpy term*) and ΔG°_{rxn} has a negative sign; reaction is becoming spontaneous.