DAWSON COLLEGE
DEPARTMENT OF CHEMISTRY & CHEMICAL TECHNOLOGY

FINAL EXAMINATION CHEMISTRY 202-NYB-05
May 21, 2010
9:30 – 12:30

Print your Name: __________________________________________
Student Number: ____________________________

INSTRUCTORS: Please circle the name of your instructor:

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INSTRUCTIONS:
This exam set consists of 16 questions. Please ensure that your copy of this examination is complete.

Answer all questions in the space provided.

1. Calculators may not be shared. Programmable calculators are not permitted.
2. No books or extra paper are permitted.
3. In order to obtain full credit, you must show the method used to solve all problems involving calculations and express your answers to the correct number of significant figures.
4. Your attention is drawn to the College policy on cheating.
5. A Periodic Table is provided. (last page).
6. If a mathematical equation is used to solve a problem, the equation should be clearly written.
7. Write your answer in the appropriate space when required.

USEFUL DATA:

Avogadro’s Number \( N_A = 6.022 \times 10^{23} \text{ mol}^{-1} \)
Gas Constant \( R \approx 0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \)
\( R \approx 8.314 \text{ L} \cdot \text{kPa} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \)
\( R \approx 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \)

1 atm = 101.3 kPa = 760 mmHg = 760 torr
1 J = 1 kg⋅m²⋅s⁻²
101.3 J = 1 L⋅atm
Question 1

Ethanol is the common alcohol with molecular formula \( \text{C}_2\text{H}_5\text{OH} \). An alcohol-water solution is prepared by dissolving 10.00 cm\(^3\) of ethanol, with density \( d_{\text{ethanol}} = 0.789 \text{ g/cm}^3 \), in a sufficient volume of water to produce 100.00 cm\(^3\) of solution. Density of solution is \( d_{\text{soln}} = 0.932 \text{ g/cm}^3 \).

For a given solution calculate the following for ethanol:

a. the mass percent

For 10.00 cm\(^3\) of solution: \( 10.00 \text{ cm}^3 \times 0.932 \frac{\text{g}}{\text{cm}^3} = 9.32 \text{ g solution} \)

In this solution 10.00 cm\(^3\) ethanol are present: \( 10.00 \text{ cm}^3 \times 0.789 \frac{\text{g}}{\text{cm}^3} = 7.89 \text{ g ethanol} \)

Mass percent = \( \frac{7.89 \text{ g}}{93.2 \text{ g}} \times 100\% = 8.46\% \text{ ethanol} \)

Ans. Mass%: _____________

b. the molarity

For 1.00 L of solution: \( 1.00 \text{ L} \times 0.932 \frac{\text{g}}{\text{mL}} \times 1000 \frac{\text{mL}}{\text{L}} = 932 \text{ g solution} \)

In this solution 8.46% is ethanol then: \( 932 \text{ g solution} \times \frac{7.80 \text{ g ethanol}}{100. \text{ g solution}} = 78.8 \text{ g ethanol} \)

Molarity = \( \frac{\text{mol solute}}{\text{L solution}} = \frac{78.8 \text{ g} \times \frac{1 \text{ mol ethanol}}{46.07 \text{ g ethanol}}}{1.00 \text{ L}} = 1.71 \text{ M ethanol} \)

Ans. molarity: _____________

c. the molality

Mole of ethanol for 1.00L solution = \( 78.8 \text{ g} \times \frac{1 \text{ mol}}{46.07 \text{ g}} = 1.71 \text{ mol} \)

Number of kilogram of solvent in one liter of solution: 932 g solution - 78.8 g ethanol = 853 g solvent

Molality = \( \frac{\text{mol solute}}{\text{kg solvent}} = \frac{1.71 \text{ mol}}{853 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} \text{ solvent}} = 2.00 \text{ molal ethanol} \)

Ans. Molality: _____________

d. the mole fraction

Mole of ethanol for 1.00 L solution = \( 78.8 \text{ g} \times \frac{1 \text{ mol}}{46.07 \text{ g}} = 1.71 \text{ mol} \)

Mole of solvent for 1.00 L solution = \( 853 \text{ g solvent} \times \frac{1 \text{ mol}}{18.015 \text{ g}} = 47.3 \text{ mol} \)

Mole fraction = \( \frac{\text{mol solute}}{\text{total mol solution}} = \frac{1.71 \text{ mol}}{1.71 \text{ mol} + 47.3 \text{ mol}} = 3.49 \times 10^{-2} \text{ ethanol} \)

Ans. Mole fraction: _____________
Question 2
Toluene, C₇H₈, is a component of gasoline (octane, C₈H₁₈). It is present in gasoline as an octane booster at concentrations between 3 to 5% by mass (25% in racing cars gasoline).
Consider a solution of octane with 20% by mass of toluene at 20°C

a. Calculate the total vapor pressure of this solution

Data:  
\( P_{\text{octane}}^o = 10.5 \text{ mm Hg at } 20°C, \ T_b = 126°C \)  
\( P_{\text{toluene}}^o = 22 \text{ mm Hg at } 20°C, \ T_b = 111°C \)

For 100 g of solution you have: (keep one extra sig.fig. for calculations)

\[ n_{\text{toluene}} = 20 \text{ g} \times \frac{1 \text{ mol toluene}}{92.14 \text{ g}} = 0.217 \text{ mol} \]
\[ n_{\text{octane}} = 80 \text{ g} \times \frac{1 \text{ mol octane}}{114.23 \text{ g}} = 0.700 \text{ mol} \]

\[ \chi_{\text{toluene}} = \frac{0.217 \text{ mol}}{0.217 \text{ mol} + 0.700 \text{ mol}} = 0.237 \]

\[ \chi_{\text{octane}} = 1 - 0.237 = 0.763 \text{ (only 2 components)} \]

Total vapor pressure:

\[ P_{\text{total}} = P_{\text{toluene}}^o \times \chi_{\text{toluene}} + P_{\text{octane}}^o \times \chi_{\text{octane}} \]

\[ = (22 \text{ mm Hg} \times 0.237) + (10.5 \text{ mm Hg} \times 0.763) = 13 \text{ mm Hg} \]

**ans. total vapor pressure:**_____________  (1 mark)

b. Calculate the mole ratio of toluene to octane in the vapor phase above the solution

\[ \text{Molar ratio} = \frac{n_{\text{toluene Vap.}}}{n_{\text{octane Vap.}}} \]

Since \( PV = nRT \) then \( P \propto n \) therefore:

\[ \frac{n_{\text{toluene Vap.}}}{n_{\text{octane Vap.}}} \times \frac{P_{\text{toluene}}}{P_{\text{octane}}} = \frac{22 \text{ mm Hg} \times 0.237}{10.5 \text{ mm Hg} \times 0.763} = 0.65 \]

**ans. mole ratio: toluene/octane:**_____________

c. If the actual vapor pressure measured is 15.2 mm Hg, will the boiling point of this solution be higher or lower than the one expected from Raoult's law? Explain.

The actual vapor pressure is higher than the ideal one (calculated) therefore, the boiling point will be lower than the one expected. The intermolecular forces between toluene - octane are weaker than the one of the pure compounds.
Question 3
A 0.461 g sample of cumene, a non-volatile non-ionic compound, is dissolved in 10.0 g cyclohexane (C₆H₁₂), producing a solution that freezes at -1.25°C. Cyclohexane has a normal freezing point of 6.50°C and a freezing point depression constant of 20.2°C/m. What is the molar mass of cumene? (3 marks)

Colligative properties involving the freezing point depression of a non ionic solute:

\[ \Delta T_f = K_f \times m \]

where \( \Delta T_f = 6.50°C - (-1.25°C) = 7.25°C \)

The concentration of cumene can be found:

\[ \frac{\Delta T_f}{K_f} = m = \frac{7.75°C}{20.2°C.m^{-1}} = 0.384 \text{ m} \]

The number of mole of cumene is:

\[
\text{molality} = \frac{\text{mole solute}}{\text{kg solvent}} \\
Mole \text{ solute} = \text{molality} \times \text{kg solvent} = 0.384 \text{ m} \times 10.0 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 3.84 \times 10^{-3} \text{ mol} \\
\]

Finally, the molar mass of cumene:

\[ \text{mole cumene} = \frac{\text{mass cumene}}{\text{mole cumene}} = \frac{0.461 \text{ g}}{0.00384 \text{ mol}} = 120 \text{ g/mol} \] (or \( 1.20 \times 10^2 \text{ g/mol} \))

Ans. Mol. mass cumene: _______________
Question 4

Hydrofluoric acid, (HF) is a weak acid that can be used in the fluoridation of water. An aqueous solution of 0.100 M HF has an osmotic pressure of 2.64 atm at 25°C.

a. Calculate the van't Hoff factor for HF at this concentration

\[ \text{Colligative properties involving the osmotic pressure of an ionic compound in solution: } \Pi = i \cdot M \cdot R \cdot T \]

\[ i = \frac{\Pi}{M \cdot R \cdot T} = \frac{2.64 \text{ atm}}{(0.100 \text{ mol/L})(0.0821 \text{ L.atm/mol.K})(25 + 273)K} = 1.08 \]

Ans. van't Hoff factor: _____________

b. Does it differ from the maximum van't Hoff factor expected for a monoprotic acid? If so, explain why.

Yes it differs from the expected van't Hoff factor of 2 for a monoprotic acid.

Therefore, HF is a weak acid since its dissociation is partial because of **ion pairing** at this concentration corresponding to an incomplete dissociation of the acid (weak acid).

(2 marks)

(c. What is the percent ionization of HF at this concentration?

\[ \text{HF} \rightarrow \text{H}^+ + \text{F}^- \]

\[ i = \frac{\text{mole of particle in solution}}{\text{mole solute added}} = \frac{2x + (c - x)}{x + c} = \frac{x + c}{c} \]

Since \( i = 1.08 \) and \( c = 0.100 \text{ M} \) \( \rightarrow 1.08 = \frac{x + 0.100}{0.100} \) then \( x = 0.008 \)

\[ \% \text{ ionization} = \frac{x}{c} \times 100\% = \frac{0.008 \text{ M}}{0.100 \text{ M}} \times 100\% = 8\% \]

Ans. % ionization: _____________
**Question 5**

Iodide ion is oxidized in acidic solution to triiodide ion $I_3^-$ by hydrogen peroxide.

\[ H_2O_2(aq) + 3 I^-(aq) + 2 H^+(aq) \rightarrow I_3^-(aq) + 2H_2O(l) \]

A series of four experiments was run at different concentrations, and the initial rates of $I_3^-$ formation were determined (see table).

<table>
<thead>
<tr>
<th>Initial concentration (mol·L$^{-1}$)</th>
<th>Initial concentration (mol·L$^{-1}$)</th>
<th>Initial concentration (mol·L$^{-1}$)</th>
<th>Initial rate (mol·L$^{-1}$·s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O_2$</td>
<td>$I^-$</td>
<td>$H^+$</td>
<td></td>
</tr>
<tr>
<td>Exp 1 0.010</td>
<td>0.010</td>
<td>0.00050</td>
<td>1.15x10$^{-6}$</td>
</tr>
<tr>
<td>Exp 2 0.020</td>
<td>0.010</td>
<td>0.00050</td>
<td>2.30x10$^{-6}$</td>
</tr>
<tr>
<td>Exp 3 0.010</td>
<td>0.020</td>
<td>0.00050</td>
<td>2.30x10$^{-6}$</td>
</tr>
<tr>
<td>Exp 4 0.010</td>
<td>0.010</td>
<td>0.00100</td>
<td>1.15x10$^{-6}$</td>
</tr>
</tbody>
</table>

a. From the table above, obtain the reaction orders with respect to each of the following species: $H_2O_2$, $I^-$, $H^+$.

Ans. Reaction order: $H_2O_2$: ___1___ $I^-$: ___1___ $H^+$: ___0___

b. Find the rate constant with its units.

The reaction rate is given by: rate = $k [H_2O_2]^\alpha [I^-]^\beta [H^+]^\gamma$

For $\alpha$:
\[ \frac{\text{Exp.2}}{\text{Exp.1}} = \frac{2.30 \times 10^{-6}}{1.15 \times 10^{-6}} = \frac{k(0.020)^\alpha(0.010)^\beta(0.00050)^\gamma}{k(0.010)^\alpha(0.010)^\beta(0.00050)^\gamma} \rightarrow 2 = 2^\alpha \text{ then } \alpha = 1 \]

For $\beta$:
\[ \frac{\text{Exp.3}}{\text{Exp.1}} = \frac{2.30 \times 10^{-6}}{1.15 \times 10^{-6}} = \frac{k(0.010)^\alpha(0.020)^\beta(0.00050)^\gamma}{k(0.010)^\alpha(0.010)^\beta(0.00050)^\gamma} \rightarrow 2 = 2^\beta \text{ then } \beta = 1 \]

For $\gamma$:
\[ \frac{\text{Exp.4}}{\text{Exp.1}} = \frac{1.15 \times 10^{-6}}{1.15 \times 10^{-6}} = \frac{k(0.010)^\alpha(0.010)^\beta(0.00100)^\gamma}{k(0.010)^\alpha(0.010)^\beta(0.00050)^\gamma} \rightarrow 1 = 2^\gamma \text{ then } \gamma = 0 \]

The reaction orders are: $H_2O_2$: ___1___ $I^-$: ___1___ $H^+$: ___0___

Ans. Reaction order: $H_2O_2$: ____ $I^-$: ____ $H^+$: ____

(3 marks)

(2 marks)

Using Exp.4:
\[ 1.16 \times 10^{-6} \text{ M·s}^{-1} = k (0.010 \text{ M}) (0.010 \text{ M}) \]

\[ k = \frac{1.16 \times 10^{-6} \text{ M·s}^{-1}}{(1.0 \times 10^{-2} \text{ M})^2} = 1.2 \times 10^{-2} \text{ M}^{-1} \text{s}^{-1} \]

Ans. rate constant: _______________
Question 6

The reaction below was monitored as a function of time at a temperature of 400 K:

\[ 2\text{NOC} \rightleftharpoons 2\text{NO} + \text{Cl}_2 \]

A plot of \(1/[\text{NOC}]\) against time yielded a straight line with slope of \(6.7 \times 10^{-4} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}\).

a. Write the rate law for the reaction.  

\[
\text{rate} = 6.7 \times 10^{-4} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \ [\text{NOC}]^2 \quad \text{(second order)}
\]

(2 marks)

b. What is the half-life for the reaction if the initial concentration of NOC is 0.20 M?  

\[
t_{\frac{1}{2}} = \frac{1}{k[A]^0} = \frac{1}{6.7 \times 10^{-4} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \ [0.20 \text{ mol} \cdot \text{L}^{-1}]} = 7.5 \times 10^3 \text{ s}.
\]

Ans. half-life: ________________

(2 marks)

c. If the initial concentration of NOC is 0.35 M, what is the concentration of NOC after 5.0 min?  

\[
\frac{1}{[\text{NOC}]} = k t + \frac{1}{[\text{NOC}]_o}
\]

\[
\frac{1}{[\text{NOC}]} = \left(6.7 \times 10^{-4} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}\right) \times 5.0 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} + \frac{1}{0.35 \text{ M}} = 3.06 \text{ M}^{-1} \text{ or } [\text{NOC}] = 0.33 \text{ M}
\]

Ans. [NOC] after 5.0 min: ________________

(2 marks)

d. If the initial concentration of NOC is 0.35 M, How long will it take for the concentration to drop to 20% of its original value?  

\[
t = \frac{1}{k} \times \left(\frac{1}{[\text{NOC}]} - \frac{1}{[\text{NOC}]_o}\right) = \frac{1}{6.7 \times 10^{-4} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}} \times \left(\frac{1}{0.35 \text{ M} \times 20/100} - \frac{1}{0.35 \text{ M}}\right) = 1.7 \times 10^4 \text{ s}.
\]

Ans. time after 20% drop: ________________

(2 marks)
Question 7

a. Consider the potential energy profiles for three different chemical reactions. (2 marks)

![Potential Energy Profiles]

Indicate which reaction is the slowest one. Explain your choice.

Reaction 1 is the slowest one since its activation energy is the highest.

b. Consider the potential energy profiles for a chemical reaction. (2 marks)

![Mechanism Diagrams]

Circle the proposed mechanism that is consistent with the reaction profile shown and explain your choice.

The curve is consistent with mechanism 2 since the slow step is the first one (highest \( E_a \)).

The rate law will be \( \text{rate} = k [A]^2 \).

c. Beside concentration and pressure, give two parameters you can change that could affect the reaction rate of a chemical reaction. (2 marks)

Temperature  
Catalyst or enzyme
At elevated temperature (997°C) limestone dissociates according to the equation

\[
\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g}) \quad \Delta H = +42.5 \text{ kJ}
\]

a. If 50.0 g \( \text{CaCO}_3 \) (100.1 g/mol) is placed in an evacuated 4.00 L container and heated up to 997°C, how many grams of \( \text{CaCO}_3 \) will decompose if the pressure at equilibrium is 392 kPa? (2 marks)

Mole of \( \text{CO}_2 \) produced = \( PV = nRT \)

\[
n = \frac{PV}{RT} = \frac{392 \text{ kPa} \times 4.00 \text{ L}}{8.31 \text{ L}\cdot\text{kPa} / \text{K}\cdot\text{mol} \times (977 + 273)\text{K}} = 0.149 \text{ mole}
\]

Since it is a 1:1 ratio between \( \text{CO}_2 \) and \( \text{CaCO}_3 \) then:

Mass of \( \text{CaCO}_3 \) consumed = 0.149 mol \( \text{CO}_2 \) \( \times \frac{1 \text{CaCO}_3}{1 \text{CO}_2} \times 100.1 \text{ g/mol} = 14.9 \text{ g} \)

b. If the volume of the container is expanded to 10.0 L at 997°C, what will be the \( \text{CO}_2 \) pressure at equilibrium? (1 mark)

\[ K = [\text{CO}_2] \]

The concentration of \( \text{CO}_2 \) remains the same whatever the volume

For a gas, concentration = pressure.

Therefore, pressure does not change = 392 kPa or 3.87 atm.

K = \( [\text{CO}_2] \) since the other reactants are all solids.

In part A, the number of mole of \( \text{CO}_2 \) for a container of 4.00 L was 0.149 mole.

\[
K = \frac{0.149 \text{ mol}}{4.00 \text{ L}} = 0.0373 \quad \text{also } K = \frac{K_p}{RT} = \frac{P}{RT} = \text{ where } P \text{ is also obtained from } PV = nRT
\]

(2 marks)

d. Predict the effect of each of the following changes will have on the equilibrium position.

<table>
<thead>
<tr>
<th>Change</th>
<th>Equilibrium Position Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2) is added</td>
<td>![ ]</td>
</tr>
<tr>
<td>CaCO(_3) is added</td>
<td>![ ]</td>
</tr>
<tr>
<td>Pressure is increased (adding N(_2) gas, volume unchanged)</td>
<td>![ ]</td>
</tr>
<tr>
<td>The temperature is increased</td>
<td>![ ]</td>
</tr>
</tbody>
</table>
Question 9

Consider the following set of data:

<table>
<thead>
<tr>
<th>Formula</th>
<th>$K_a$ (at 25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Al(H}_2\text{O)}_6]^{3+}$</td>
<td>$1.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>HNO$_2$</td>
<td>$4.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>HF</td>
<td>$7.2 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

a. What is the strongest acid in the table? _______HF___________  (1 mark)

b. With the help of the table, arrange the following in order of most basic to least basic:  (2 marks)

$$ \text{H}_2\text{O}, \ \text{NO}_2^- , \ [\text{Al(H}_2\text{O)}_5\text{OH}]^{2+} $$

Most basic $[\text{Al(H}_2\text{O)}_5\text{OH}]^{2+}$ > $\text{NO}_2^-$ > $\text{H}_2\text{O}$  Least basic

---

c. What is the value of $K_b$ for $\text{F}^-$ at 25°C ?  (2 marks)

$$ K_b = \frac{10^{-14}}{7.2 \times 10^{-4}} = 1.4 \times 10^{-11} $$

**Ans.** $K_b = 1.4 \times 10^{-11}$

d. Write the chemical reaction represented by the $K_b$ for $\text{F}^-$ in water and place the species involved in the appropriate place  (2 marks)

$$ \text{H}_2\text{O} + \text{F}^- \rightleftharpoons \text{HF} + \text{OH}^- $$

Acid  Base  Conjugate acid  Conjugate base

e. At 40°C, $K_w = 2.9 \times 10^{-14}$. What is the neutral $pH$ of water at this temperature?  (2 marks)

$$ \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}^+ \text{ then } K_w = [\text{H}^+][\text{OH}^-] $$

at neutral $pH$: $[\text{H}^+] = [\text{OH}^-]$ then $\sqrt{K_w} = [\text{H}^+] = \sqrt{2.9 \times 10^{-14}} = 1.7 \times 10^{-7}$

$$ \text{pH} = -\log(1.7 \times 10^{-7}) = 6.77 $$
Question 10

a. A solution of the basic oxide CaO is prepared by adding water to 0.28 g CaO to make 0.50 L of solution.
   
i. Write the equations for the reactions that occur when CaO is dissolved in water
   
   \[
   \begin{align*}
   1) & \quad \text{CaO(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Ca(OH)}_2(\text{aq}) \\
   2) & \quad \text{Ca(OH)}_2(\text{aq}) \rightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{OH}^- (\text{aq})
   \end{align*}
   \]
   
or
   \[
   \begin{align*}
   1) & \quad \text{CaO(s)} \rightarrow \text{Ca}^{2+}(\text{aq}) + \text{O}^2^- (\text{aq}) \\
   2) & \quad \text{O}^2^- (\text{aq}) + \text{H}_2\text{O(l)} \rightarrow 2\text{OH}^- (\text{aq})
   \end{align*}
   \]
   
   (2 marks)
   
   ii. Assuming that ion-pairing is non-existent, what is the expected pH of this solution?
   
   
   \[
   \begin{align*}
   \text{Mole of OH}^- \text{ in solution: } & \quad 0.28 \text{ g CaO} \times \frac{1 \text{ mol}}{56.08 \text{ g}} \times \frac{\text{Ca(OH)}_2}{\text{CaO}} \times \frac{2 \text{ OH}^-}{\text{Ca(OH)}_2} = 0.010 \text{ mol OH}^- \\
   \text{Concentration of OH}^- \text{ in solution: } & \quad \frac{0.010 \text{ mol OH}^-}{0.50 \text{ L}} = 0.020 \text{ M} \\
   \text{Finally, the pH will be: } & \quad \text{pOH} = -\log(0.020 \text{ M}) = 1.70 \\
   & \quad \text{pH} = 14 - \text{pOH} = 12.30
   \end{align*}
   \]
   
   ans. pH:__________
   
   (2 marks)

b. For which of the following salts will the solubility depend on pH?

<table>
<thead>
<tr>
<th></th>
<th>pH sensitive</th>
<th>pH independent</th>
</tr>
</thead>
<tbody>
<tr>
<td>i.</td>
<td>KClO₄</td>
<td></td>
</tr>
<tr>
<td>ii.</td>
<td>Pb(OH)₂</td>
<td></td>
</tr>
<tr>
<td>iii.</td>
<td>AgF</td>
<td></td>
</tr>
<tr>
<td>iv.</td>
<td>Ba(NO₃)₂</td>
<td></td>
</tr>
</tbody>
</table>

   (2 marks)

c. For each of the following salts dissolved in water, predict whether the aqueous solution will be acidic, neutral or basic.

<table>
<thead>
<tr>
<th></th>
<th>acid</th>
<th>neutral</th>
<th>basic</th>
</tr>
</thead>
<tbody>
<tr>
<td>i.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ii.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>iii.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>iv.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

   (2 marks)
Question 11

a. Consider 0.500 L of a buffer that consists of 1.50 M KClO (K_a HC\ell\ell\ell\ell O = 3.5x10^{-8}) and 0.50 M HClO. What will be the pH of this buffer after the addition of 250 mL of 1.0 M HNO_3?

The system is the following: HClO(aq) \rightleftharpoons H^+(aq) + ClO^-(aq) \quad \text{(note H}^+ = H_3O^+\text{)}

\text{Mol of HClO = 0.500 L} \times 0.50 \text{ mol L}^{-1} = 0.25 \text{ mol}

\text{Mol of ClO}^- = 0.500 L \times 1.50 \text{ mol L}^{-1} = 0.750 \text{ mol}

\text{Mol of H}^+ \text{ added} = 0.250 L \times 1.0 \text{ mol L}^{-1} = 0.25 \text{ mol}

First we have a reaction between a strong acid and a weak base:

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<th>Initial</th>
<th>Reaction</th>
<th>After reaction</th>
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<tbody>
<tr>
<td>H^+</td>
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<td>+0.25</td>
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After, the system reach equilibrium:

\begin{align*}
\text{I} & \quad \text{0.50} & \quad 0 & \quad 0.50 \\
\text{C} & \quad -x & \quad +x & \quad +x \\
\text{E} & \quad 0.50-x & \quad +x & \quad 0.50+x \\
\end{align*}

Since we have a buffer, \( x \ll 0.50 \) AND the number of mole for the acid and the conjugated base are the same, then \( \text{pH} = \text{pKa} \quad \text{pH} = -\log(3.5x10^{-8}) = 7.46 \)

\text{ans. pH: ____________}

b. Which of the following mixtures would result in a buffer solution when 100 mL of each of the two solutions are mixed together? (2 marks)

<table>
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<th>not a buffer</th>
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<tbody>
<tr>
<td>i.</td>
<td>0.1 M KOH and 0.2 M NH_3</td>
<td>[ ]</td>
</tr>
<tr>
<td>ii.</td>
<td>0.2 M HC\ell\ell\ell\ell and 0.2 M NH_3</td>
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</tr>
<tr>
<td>iii.</td>
<td>0.2 M HNO_3 and 0.4 M NaNO_3</td>
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</tr>
<tr>
<td>iv.</td>
<td>0.1 M HNO_3 and 0.2 M NaF</td>
<td>[ ]</td>
</tr>
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</table>
Consider the following titration curve of trimethylamine (C₃H₉N) a weak base with 0.100 M HCl at 23°C.

Initial solution:
50.0 mL of C₃H₉N, 4.00x10⁻² M

a. Draw on the graph the shape of the titration curve if this base had a smaller $K_b$ value.

b. Which letter (A to F) on the graph corresponds to each of the following?

<table>
<thead>
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<th>letter</th>
<th>The equivalence point</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>The point of half-neutralization</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>The point corresponding to the $pK_a$ of C₃H₉NH⁺</td>
<td>B</td>
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</table>

c. When 15.0 mL of 0.100 M HCl is added, the pH of the solution is 9.255. Calculate $K_b$ of trimethylamine.

Let's call trimethylamine TMA an its conjugated acid TMAH⁺

\[
\begin{align*}
\text{Mole of TMA} & = 4.00\times10^{-2} \text{ M} \times 0.0500 \text{ L} = 2.00\times10^{-3} \text{ mol} \\
\text{Mole of acid added} & = 1.00\times10^{-1} \text{ M} \times 0.0150 \text{ L} = 1.50\times10^{-3} \text{ mol}
\end{align*}
\]

The HCl reacts to completion (strong acid) with TMA according to:

\[
\begin{align*}
\text{TMA} & + \text{H}^+ \rightleftharpoons \text{TMAH}^+ \\
\text{Initial} & = 2.00\times10^{-3} \quad 1.50\times10^{-3} \quad 0 \\
\text{Reaction} & = -1.50\times10^{-3} \quad -1.50\times10^{-3} \quad +1.50\times10^{-3} \\
\text{After reaction} & = 0.50\times10^{-3} \quad 0 \quad 1.50\times10^{-3}
\end{align*}
\]

Then, the system will reach equilibrium from those initial conditions:

\[
\begin{align*}
\text{TMA} & + \text{H}_2\text{O} \rightleftharpoons \text{TMAH}^+ + \text{OH}^- \\
0.50\times10^{-3} \text{-} x \text{ mole} & \quad 1.50\times10^{-3} + x \text{ mole} \quad x \text{ mole}
\end{align*}
\]

In a buffer regime, $x$ is small compared to [base] or [conjugated acid] and can be neglected. In this case ONLY the ratio of mole of TMAH⁺ / TMA is the same as the one of concentrations. Therefore:

\[
K_b = \frac{[\text{TMAH}^+][\text{OH}^-]}{[\text{TMA}]} = \frac{(1.50\times10^{-3})(10^{-14-9.255})}{0.50\times10^{-3}} = 5.4\times10^{-5}
\]
(1 mark)

(3 marks)

(3 marks)
Question 13

a. A saturated aqueous solution of Mg(OH)$_2$ has a pH of 10.08, what is the $K_{sp}$ of Mg(OH)$_2$? 

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2 OH^-(aq) \quad K_{sp} = [Mg^{2+}][OH^-]^2$$

I
Solid
0
0

C
-x
+x
+2x

E
solid
x
+2x
$K_{sp} = (x)(2x)^2 = 4x^3$

We can use the pH to know $[OH^-]$ that is equal to 2x.

$pOH = 14 - 10.08 = 3.92, \quad [OH^-] = 10^{-3.92} = 1.2 \times 10^{-4} \text{ M}.$

since $2x = 1.2 \times 10^{-4} \text{ M}.$ then $x = 6.0 \times 10^{-5}.$

finally: $K_{sp} = 4 (6.0 \times 10^{-5})^3$

$K_{sp} = 8.6 \times 10^{-13}$

---

b. The $K_{sp}$ of cobalt(III) hydroxide is $2.5 \times 10^{-43}.$ Calculate the solubility of Co(OH)$_3$ in water in mol/L

According to the $K_{sp}$ value, the concentration of OH⁻ generated by the salt will be small compared to the one of natural ionization of water $[OH^-] = 10^{-7} \text{ M}$ therefore, common ion effect.

$$Co(OH)_3(s) \rightleftharpoons Co^{3+}(aq) + 3OH^-(aq) \quad K_{sp} = [Co^{3+}][OH^-]^3$$

I
Solid
0
10$^{-7}$

C
-x
+x
+3x

E
solid
x
3x$\times 10^{-7}$

if $x \ll 10^{-7}$ then $K_{sp} = (x)(10^{-7})^3$

And the solubility (or x) is $x = \frac{K_{sp}}{10^{-21}} = \frac{2.5 \times 10^{-43}}{10^{-21}} = 2.5 \times 10^{-22} \text{ M} \quad \text{ (check: } x = 2.5 \times 10^{-22} \ll 10^{-7} \text{ )}$

---

c. Does a precipitate form when 25 mL of 0.10 M lithium nitrate LiNO$_3$, is mixed with 35 mL of 0.75 M sodium carbonate Na$_2$CO$_3$? ($K_{sp}$ Li$_2$CO$_3 = 8.15 \times 10^{-4}$) Show your work.

A precipitation will occur if $Q > K_{sp}$

$$Li_2CO_3(s) \rightleftharpoons 2Li^+(aq) + CO_3^{2-}(aq) \quad K_{sp} = [Li^+]^2[CO_3^{2-}]$$

Li$^+$ concentration $= \frac{0.025 \text{ L} \times 0.10 \text{ M}}{0.025 + 0.035\text{L}} = 0.042 \text{ M}$

$CO_3^{2-}$ concentration $= \frac{0.035 \text{ L} \times 0.75 \text{ M}}{0.025 + 0.035\text{L}} = 0.44 \text{ M}$

$$Q = [Li^+]^2[CO_3^{2-}] = (0.042)^2(0.44) = 7.8 \times 10^{-4}. \quad \text{Since } Q < K_{sp} \text{ then: No precipitation.}$$
Question 14

a. A system is made of a cylinder of gas with a piston. When 4.0 kJ of heat is transferred from the surroundings to the system, the gas in the piston expands from 12 L to 27 L and performs work on the surroundings. If the system gains 201 J of internal energy from this process, against what constant external pressure, in atmospheres, is the piston working?

\[ \Delta H = \Delta E + P\Delta V \] (first law: conservation of the energy)

\[ \Delta H - \Delta E = P\Delta V \]

\[ \Delta H = [+4000 \text{ J} - (+201 \text{ J})] \times \frac{1 \text{ L.atm}}{101.3 \text{ J}} = 37.50 \text{ L.atm} \]

37.5 L.atm = P\Delta V and \( \Delta V = V_{\text{final}} - V_{\text{initial}} \)

\[ P = \frac{37.5 \text{ L.atm}}{27L - 12L} = 2.5 \text{ atm} \]

Ans. pressure (atm): ____________

b. Bromine is a liquid at room temperature. Calculate the freezing point of bromine if its heat of fusion is +5.79 kJ mol\(^{-1}\) and its entropy of fusion is 21.8 J K\(^{-1}\) mol\(^{-1}\).

\[ \Delta G = \Delta H - T\Delta S \] (second law: spontaneity of a system)

The freezing point occurs when all the heat added to a system is converted to entropy. At this point, the system is highly reversible (equilibrium condition, therefore \( \Delta G = 0 \))

The equation becomes: \( 0 = \Delta H - T\Delta S \) and \( \frac{\Delta H}{\Delta S} = T \)

\[ T = \frac{\Delta H}{\Delta S} = \frac{5.79 \times 10^3 \text{ J.mol}^{-1}}{21.8 \text{ J.K}^{-1}. \text{ mol}^{-1}} = 266 \text{ K} \text{ or } -7^\circ \text{C} \]

Ans. \( T_f \) bromine: ____________
Question 15

a. Circle the substance in each of the following pairs that would have the greater entropy. (2 marks)

i. H₂O (l, 1 mol, 75°C, 1 atm) or H₂O (g, 1 mol, 75°C, 1 atm)

ii. Fe (s, 50.0 g, 5°C, 1 atm) or Fe (s, 0.80 mol, 5°C, 1 atm)

iii. Br₂ (l, 1 mol, 8°C, 1 atm) or Br₂ (s, 1 mol, -8°C, 1 atm)

iv. SO₂ (g, 0.312 mol, 32.5°C, 0.110 atm) or SO₂ (g, 0.284 mol, 22.3°C, 15 atm)

b. Methyl isothiocyanate, CH₃—N=C=S, is a highly irritating pesticide. It can be prepared by reacting carbon disulfide with methylvamine. Given the thermodynamic data at 25°C below, calculate the standard molar entropy of methyl isothiocyanate. (4 marks)

\[
\begin{array}{cccc}
\text{CS₂} (g) + \text{CH₃NH₂} (g) & \rightarrow & \text{CH₃—N=C=S} (g) + \text{H₂S} (g) \\
\Delta G^\circ (kJ \cdot mol^{-1}) & & 67.15 & 32.09 & 144.35 & -33.56 \\
\Delta H^\circ (kJ \cdot mol^{-1}) & & 117.36 & -22.98 & 130.96 & -20.63 \\
S^\circ (J \cdot mol^{-1} \cdot K^{-1}) & & 237.73 & 243.30 & ? & 205.69 \\
\end{array}
\]

\[
\Delta G^\circ = (-33.56) + (144.35) - [(67.15) + (32.09)] = 11.55 \text{ kJ}
\]

\[
\Delta H^\circ = (-20.63) + (130.96) - [(117.36) + (-22.98)] = 15.95 \text{ kJ}
\]

\[
\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{(15950 - 11550)J}{(25 + 273)K} = 14.8 \text{ J/K}
\]

finally:

\[
\Delta S = \sum S_{\text{product}} - \sum S_{\text{reactant}}
\]

\[
14.8 \text{ J/K} = (205.69 + x) \text{ J/K} - (237.73 + 243.30) \text{ J/K}
\]

\[
x = S^\circ \text{CH₃—NCS} = 290.1 \text{ J/K} =
\]

Ans: ________________
Question 16

In the laboratory experiment 4, you want to determine the activation energy of the following reaction: (5 marks)

\[ 2\bar{I}(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2S_2O_4^{2-} \]

Where the reaction rate is: \( \text{Rate} = -\frac{[\Delta \bar{I}]}{2\Delta t} \) and the rate law for this reaction is: \( \text{Rate} = k[I][S_2O_8^{2-}] \)

By recording the reaction rate of several experiments at different temperatures, the following graph based on the linear form of the Arrhenius equation is obtained.

**Arrhenius plot for the determination of the activation energy for the reaction of iodide with peroxydisulfate**

From this graph, calculate the activation energy (with units) for this reaction.

We will be using the linear form of the Arrhenius equation: \( \ln k = -\frac{E_a}{R} \frac{1}{T} + \text{constant} \)

The graph of \( \ln k \) vs. \( \frac{1}{T} \) gives a slope = \( -\frac{E_a}{R} \)

\[ \text{Slope} = \frac{Y_2 - Y_1}{X_2 - X_1} = \frac{(-4.80) - (-5.60)}{(3.2 \times 10^{-3}) - (3.35 \times 10^{-3}) \text{K}^{-1}} = \frac{0.80}{-1.5 \times 10^{-4} \text{K}^{-1}} = \frac{-5.3 \times 10^3 \text{K}}{} \]

Since: slope = \( -\frac{E_a}{R} \) then \( E_a = \frac{-8.31 J}{K\text{.mol}} \times -5.3 \times 10^3 \text{K} = 44 \times 10^3 \frac{J}{\text{mol}} \) or \( 44 \frac{kJ}{\text{mol}} \).
### Periodic Table of the Elements

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<th>Pu</th>
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<th>Bk</th>
<th>Cf</th>
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</table>

= metalloid

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* = Lanthanides

* = Actinides