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:

J. Ali  I. Dionne  M. Haniff
D. Baril  M. Di Stefano  S. Holden
O. Behar  N. Duxin / Y-S. Uh  S. Mutic

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  \( R = 0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \)
\( R = 8.314 \text{ L} \cdot \text{kPa} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \)
\( R = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \)

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

MARK DISTRIBUTION

<table>
<thead>
<tr>
<th>Question</th>
<th>Mark</th>
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<tbody>
<tr>
<td>1.</td>
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<td>2.</td>
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<td>10.</td>
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<td>/ 7</td>
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<td>13.</td>
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<td>14.</td>
<td>/ 6</td>
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<td>15.</td>
<td>/ 6</td>
</tr>
<tr>
<td>16.</td>
<td>/ 5</td>
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<tr>
<td>TOTAL</td>
<td>/100</td>
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</table>
Question 1
Ethanol is the common alcohol with molecular formula $C_2H_5OH$. 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

(2 marks)

Ans. Mass%: 

b. the molarity

(2 marks)

Ans. Molarity: 

c. the molality

(2 marks)

Ans. Molality: 

d. the mole fraction.

(2 marks)

Ans. Mole fraction:
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:  
\( P^\circ_{\text{octane}} = 10.5 \text{ mm Hg at 20} ^\circ \text{C, } T_b = 126 \text{ } ^\circ \text{C} \)  
\( P^\circ_{\text{toluene}} = 22 \text{ mm Hg at 20} ^\circ \text{C, } T_b = 111 \text{ } ^\circ \text{C} \)

\[ \text{ans. total vapor pressure: } \]

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

\[ \text{ans. mole ratio: toluene/octane: } \]

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.
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)

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 \text{ M} HF has an osmotic pressure of 2.64 \text{ atm} at 25^\circ\text{C}.

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

\text{Ans. van’t Hoff factor: } \underline{\text{ }} \text{ } \underline{\text{ }}

(2 \text{ marks})

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

\text{Ans. } \underline{\text{ }} \underline{\text{ }} \underline{\text{ }} \underline{\text{ }} \underline{\text{ }} \underline{\text{ }} \underline{\text{ }} \underline{\text{ }} \underline{\text{ }}

(2 \text{ mark})

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

\text{Ans. } \underline{\text{ }} \underline{\text{ }} \underline{\text{ }}

(2 \text{ marks})
**Question 5**

Iodide ion is oxidized in acidic solution to triiodide ion $\text{I}_3^-$ by hydrogen peroxide.

$$
\text{H}_2\text{O}_2(\text{aq}) + 3 \text{I} (\text{aq}) + 2 \text{H}^+ (\text{aq}) \rightarrow \text{I}_3 (\text{aq}) + 2\text{H}_2\text{O}(l)
$$

$$\text{Rate} = \frac{\Delta [\text{I}_3^-]}{\Delta t}$$

A series of four experiments was run at different concentrations, and the initial rates of $\text{I}_3^-$ formation were determined (see table).

<table>
<thead>
<tr>
<th>Initial concentration ($\text{mol} \cdot \text{L}^{-1}$)</th>
<th>Initial concentration ($\text{mol} \cdot \text{L}^{-1}$)</th>
<th>Initial concentration ($\text{mol} \cdot \text{L}^{-1}$)</th>
<th>Initial rate ($\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}_2$</td>
<td>$\text{I}$</td>
<td>$\text{H}^+$</td>
<td>1.15x10^{-6}</td>
</tr>
<tr>
<td>Exp 1 0.010</td>
<td>0.010</td>
<td>0.00050</td>
<td></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:

$$
\text{H}_2\text{O}_2, \quad \text{I}, \quad \text{H}^+.
$$

(3 marks)

Ans. Reaction order: $\text{H}_2\text{O}_2$: _____  $\text{I}$: _____  $\text{H}^+$: _____

b. Find the rate constant with its units.

(2 marks)

Ans. rate constant: ____________________
Question 6

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

\[ \text{2NOC} \ell (g) \rightarrow \text{2NO(g) + C} \ell _2(g) \]

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

a. Write the rate law for the reaction. \((2 \text{ marks})\)

b. What is the half-life for the reaction if the initial concentration of NOCl is 0.20 M? \((2 \text{ marks})\)

\[ \text{Ans. half-life: } \]  

(c). If the initial concentration of NOCl is 0.35 M, what is the concentration of NOCl after 5.0 min? \((2 \text{ marks})\)

\[ \text{Ans. } [\text{NOCl}] \text{ after 5.0 min: } \]  

d. If the initial concentration of NOCl is 0.35 M, How long will it take for the concentration to drop to 20% of its original value? \((2 \text{ marks})\)

\[ \text{Ans. time after 20% drop: } \]
Question 7

a. Consider the potential energy profiles for three different chemical reactions.

![Potential Energy Profiles](image)

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

b. Consider the potential energy profiles for a chemical reaction.

![Mechanisms](image)

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

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

i. ____________________________  ii. ____________________________
Question 8

At elevated temperature (997°C) limestone dissociates according to the equation

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

a. If 50.0 g 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 CaCO\(_3\) will decompose if the pressure at equilibrium is 392 kPa? (2 marks)

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

c. Calculate \(K_c\) for this reaction at 997°C (1 mark)

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

<table>
<thead>
<tr>
<th>change</th>
<th>CO(_2) is added</th>
<th>CaCO(_3) is added</th>
<th>Pressure is increased (adding N(_2) gas, volume unchanged)</th>
<th>The temperature is increased</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>to the left</td>
<td>no change</td>
<td>to the right</td>
<td>to the left</td>
</tr>
<tr>
<td>i.</td>
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<td></td>
</tr>
<tr>
<td>ii.</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>iii.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>iv.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Consider the following set of data:

<table>
<thead>
<tr>
<th>Formula</th>
<th>$K_a$ (at 25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Al(H$_2$O)$_6$]$^{3+}$</td>
<td>1.4x10$^{-5}$</td>
</tr>
<tr>
<td>HNO$_2$</td>
<td>4.0x10$^{-4}$</td>
</tr>
<tr>
<td>HF</td>
<td>7.2x10$^{-4}$</td>
</tr>
</tbody>
</table>

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

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

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

Most basic _________ > _________ > _________ Least basic

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

Ans. $K_b$: ___________

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

$$\text{_____} + \text{_____} \leftrightarrow \text{_____} + \text{_____}$$

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)

Ans. __________
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
      \( \text{(1 mark)} \)

   ii. Assuming that ion-pairing is non-existent, what is the expected pH of this solution?
      \( \text{(2 marks)} \)

ans. pH:___________

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>
\( \text{(2 marks)} \)

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>RbOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ii.</td>
<td>NaIO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>iii.</td>
<td>NH₄OH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>iv.</td>
<td>LiClO₃</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
\( \text{(2 marks)} \)
Question 11

a. Consider 0.500 L of a buffer that consists of 1.50 M \( KC\ell O \) \( (K_a \ HC\ell O = 3.5 \times 10^{-8}) \) and 0.50 M \( HC\ell O \). What will be the \( pH \) of this buffer after the addition of 250 mL of 1.0 M \( HNO_3 \)?

\[ \text{ans. } pH: \_\_\_\_\_\_\_\_ \]

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

<table>
<thead>
<tr>
<th></th>
<th>buffer</th>
<th>not a buffer</th>
</tr>
</thead>
<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 ( HCl ) and 0.2 M ( NH_3 )</td>
<td></td>
</tr>
<tr>
<td>iii.</td>
<td>0.2 M ( HNO_3 ) and 0.4 M ( NaNO_3 )</td>
<td></td>
</tr>
<tr>
<td>iv.</td>
<td>0.1 M ( HNO_3 ) and 0.2 M ( NaF )</td>
<td></td>
</tr>
</tbody>
</table>
Question 12

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>
<tr>
<th>letter</th>
<th>The equivalence point</th>
<th>The point of half-neutralization</th>
<th>The point corresponding to the $pK_a$ of C₃H₉NH⁺</th>
</tr>
</thead>
<tbody>
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<td></td>
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</tbody>
</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.
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)$_2$?  

ans. $K_{sp}$: ____________  

(2 marks)

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  

ans. solubility (mol/L): ____________  

(2 marks)

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.  

ans: yes  no  

(3 marks)
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? (3 marks)

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\(^{-1}\). (3 marks)

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. $\text{H}_2\text{O} (\ell, 1 \text{ mol}, 75^\circ \text{C}, 1 \text{ atm})$ or $\text{H}_2\text{O} (\text{g}, 1 \text{ mol}, 75^\circ \text{C}, 1 \text{ atm})$

ii. $\text{Fe} (\text{s}, 50.0 \text{ g}, 5^\circ \text{C}, 1 \text{ atm})$ or $\text{Fe} (\text{s}, 0.80 \text{ mol}, 5^\circ \text{C}, 1 \text{ atm})$

iii. $\text{Br}_2 (\ell, 1 \text{ mol}, 8^\circ \text{C}, 1 \text{ atm})$ or $\text{Br}_2 (\text{s}, 1 \text{ mol}, -8^\circ \text{C}, 1 \text{ atm})$

iv. $\text{SO}_2 (\text{g}, 0.312 \text{ mol}, 32.5^\circ \text{C}, 0.110 \text{ atm})$ or $\text{SO}_2 (\text{g}, 0.284 \text{ mol}, 22.3^\circ \text{C}, 15 \text{ atm})$

b. Methyl isothiocyanate, $\text{CH}_3\text{—N═C═S}$, is a highly irritating pesticide. It can be prepared by reacting carbon disulfide with methylamine. Given the thermodynamic data at 25$^\circ$C below, calculate the standard molar entropy of methyl isothiocyanate. (4 marks)

\[
\begin{array}{cccc}
\text{CS}_2 (\text{g}) & + & \text{CH}_3\text{NH}_2 (\text{g}) & \rightarrow & \text{CH}_3\text{—N═C═S} (\text{g}) & + & \text{H}_2\text{S} (\text{g}) \\
\Delta G^\circ (\text{kJ} \cdot \text{mol}^{-1}) & 67.15 & 32.09 & 144.35 & -33.56 \\
\Delta H^\circ (\text{kJ} \cdot \text{mol}^{-1}) & 117.36 & -22.98 & 130.96 & -20.63 \\
S^\circ (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) & 237.73 & 243.30 & ? & 205.69 \\
\end{array}
\]

Ans: __________________
Question 16

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

\[ 2\text{I}^- (aq) + \text{S}_2\text{O}_8^{2-} (aq) \rightleftharpoons \text{I}_2 (aq) + 2\text{S}_2\text{O}_4^{2-} \]

Where the reaction rate is: Rate = \( -\frac{\Delta \text{I}^-}{2\Delta t} \) and the rate law for this reaction is: Rate = \( k [\text{I}^-][\text{S}_2\text{O}_8^{2-}] \)

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.

Ans. \( E_a \): _________________
### Periodic Table of the Elements

<table>
<thead>
<tr>
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<th>1</th>
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<th>1.008</th>
<th>2A</th>
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<td>3</td>
<td>4</td>
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</tr>
<tr>
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<th>C</th>
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<th>O</th>
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- **= metalloid**

#### *Lanthanides*

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#### *Actinides*

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