Print your Name: SOLUTIONS

Student Number: ____________________________

INSTRUCTORS: Please circle the name of your instructor:

J. Ali   D. Baril   Y. Brouillette
I. Dionne  M. Di Stefano  N. Duxin
M. Haniff   S. Holden

INSTRUCTIONS:
This exam set consists of 17 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.
6. If a mathematical equation is used to solve a problem, the equation should be clearly written.
7. Write your answer in the appropriate box when required

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

1 \( \text{atm} = 101.3 \text{ kPa} = 760 \text{ mmHg} = 760 \text{ torr} \)
1 \( \text{J} = 1 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} = 1 \text{ kPa} \cdot \text{L} \)
101.3 \( \text{J} = 1 \text{ L} \cdot \text{atm} \)
**Question 1**  
(8 marks)

To make an antifreeze solution, 40.0 mL of ethylene glycol (C₉H₈O₂, density: 1.08 g·mL⁻¹) is added to 60.0 mL water (density: 1.00 g·mL⁻¹). Assume ideal behavior for this solution (volumes are additive). Calculate:

a. the mass percent of ethylene glycol

\[
\text{Mass of water in 1 L of solution (60% v/v): } 600. \text{ mL} \times 1.00 \text{ g mL}^{-1} = 600. \text{ g} \\
\text{Mass of ethylene glycol in 1 L (40%): } 400 \text{ mL} \times 1.08 \text{ g mL}^{-1} = 432 \text{ g} \\
\text{Mass% ethylene glycol: } \frac{432 \text{ g}}{432 \text{ g} + 600 \text{ g}} \times 100\% = 41.9\% 
\]

b. mole fraction

\[
\text{Mole of water in 1 L: } 600. \text{ g} \times \frac{1 \text{ mol}}{18.015 \text{ g}} = 33.3 \text{ mol} \\
\text{Mole of ethylene glycol in 1 L: } \frac{432 \text{ g}}{62.068 \text{ g L}^{-1}} \times 1 \text{ mol L}^{-1} = 6.96 \text{ mol L}^{-1} \\
\text{Molar fraction ethylene glycol: } \frac{6.96 \text{ mol}}{6.96 \text{ mol} + 33.3 \text{ mol}} = 0.173 
\]

c. molality

\[
\text{Molality (mol solute/kg solvent): } \frac{6.96 \text{ mol}}{0.600 \text{ kg}} = 11.6 \text{ mol kg}^{-1} 
\]

d. molarity

\[
\text{Molarity (mol solute/L solution): } \frac{6.96 \text{ mol}}{1.00 \text{ L}} = 6.96 \text{ mol L}^{-1} 
\]

| ans. a: 41.9% | ans. b: 0.173 | ans. c: 11.6 mol/kg | ans. d: 6.96 mol/L |
Question 2

At 25°C Henry’s Law constant for oxygen in water is $1.3 \times 10^{-3}$ mol·L$^{-1}$·atm$^{-1}$.

a. If the partial pressure of oxygen in the atmosphere at sea level is 159 mmHg calculate the molar solubility (concentration) of oxygen in water at 25°C.

\[
\text{Solubility} = (1.3 \times 10^{-3} \text{ mol \cdot L}^{-1} \cdot \text{atm}^{-1}) \times 159 \text{ mmHg} \times \frac{1.00 \text{ atm}}{760 \text{ mmHg}} = 2.7 \times 10^{-4} \text{ mol/L}
\]

Ans. a: $2.7 \times 10^{-4}$ mol/L

b. When water is cooled the solubility of oxygen in water increases. Is the enthalpy of hydration of oxygen positive or negative? Explain your answer.

\[
\text{The more heat you add, the less soluble it becomes: } \quad \text{O}_2(g) \rightarrow \text{O}_2(aq) + \text{heat}
\]

Therefore, heat as a product = $\Delta H < 0$ (exothermic)

---

c. The vapor pressure of pure liquid benzene (C$_6$H$_6$, 78.11 g/mol) at 75°C is 640.0 torr. A solution made of 20.21 g anthracene in 117.2 g benzene has a vapor pressure of 595.0 torr at 75°C. (anthracene is a non ionic and non volatile solid). Calculate the molar mass of anthracene.

\[
\frac{P_{\text{TOT}}}{P_{\text{sol}}} = \frac{P_{\text{sol}} \chi_{\text{sol}}}{595.0 \text{ torr}} = \frac{(640.0 \text{ torr})(\chi_{\text{sol}})}{595.0 \text{ torr}} = 0.9297
\]

\[
\chi_{\text{solvent}} = \frac{595.0 \text{ torr}}{640.0 \text{ torr}} = 0.9297
\]

\[
n_{\text{solute}} = \frac{n_{\text{solvent}}}{\chi_{\text{solvent}}} = \frac{1.500 \text{ mol}}{0.9297} = 1.620 \text{ mol}
\]

\[
n_{\text{solute}} - n_{\text{solvent}} = \frac{1.500 \text{ mol}}{0.9297} - 1.500 \text{ mol} = 0.1134 \text{ mol solute}
\]

The molar mass of anthracene is:

\[
\frac{20.21 \text{ g}}{0.1134 \text{ mol}} = 178 \text{ g/mol}
\]

Ans. c: 178 g/mol
Question 3

a. What mass of ethylene glycol (non electrolyte) must be added to 1525 g of water at 1.000 atm to raise the boiling point to 103.9°C? The molal boiling point elevation constant of water is 0.52°C/m and the molar mass of ethylene glycol (C\(_2\)H\(_6\)O\(_2\)) is 62.07 g/mol. (2 marks)

\[\Delta T_b = k_b \cdot m \]
\[m = \frac{T_b}{k_b} = \frac{(103.9 - 100.0) \, ^\circ C}{0.52 \, ^\circ C/m} = 7.5 \, m\]

\[m = \text{mol} / \text{kg solvent} \quad \text{mol ethylene glycol} = (m) \times (\text{kg solvent}) = 7.5 \frac{\text{mol}}{\text{kg}} \times 1.525 \, g = 11.43 \, \text{mol}\]

\[\text{mass of ethylene glycol} = 11.43 \, \text{mol} \times \frac{62.07 \, g}{\text{mol}} = 709.9 \, g = 710 \, g \quad \text{(or} \quad 7.1 \times 10^2 \, g)\]

**Ans. a:** 710 g

b. Arrange the following aqueous solutions in order of increasing boiling point: (2 marks)

i. 0.10 m Na\(_3\)PO\(_4\)

ii. 0.20 m MgCl\(_2\)

iii. 0.15 m C\(_6\)H\(_{12}\)O\(_6\) (sugar)

iv. 0.15 m HNO\(_2\) (weak acid)

<table>
<thead>
<tr>
<th>iii</th>
<th>iv</th>
<th>i</th>
<th>ii</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>lowest boiling point</strong></td>
<td><strong>highest boiling point</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

c. How will the following compounds change the percent dissociation of nitrous acid (HNO\(_2\)) when added to an aqueous solution of HNO\(_2\) at equilibrium? (2 marks)

<table>
<thead>
<tr>
<th>compounds</th>
<th>decrease in % dissociation</th>
<th>no change</th>
<th>increase in % dissociation</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Ca(NO(_2))(_2)</td>
<td>□</td>
<td>□</td>
<td>□</td>
</tr>
<tr>
<td>ii. HNO(_3)</td>
<td>□</td>
<td>□</td>
<td>□</td>
</tr>
<tr>
<td>iii. NaNO(_3)</td>
<td>□</td>
<td>□</td>
<td>□</td>
</tr>
<tr>
<td>iv. H(_2)O</td>
<td>□</td>
<td>□</td>
<td>□</td>
</tr>
</tbody>
</table>
Question 4

3.70 g of calcium bromide (CaBr$_2$ mol. mass: 199.9 g·mol$^{-1}$) is added to water to make a total of 100.0 mL CaBr$_2$ aqueous solution. The osmotic pressure of this solution is determined to be 10.3 atm at 25.0°C.

a. Calculate the actual van't Hoff factor $i$ for this aqueous calcium bromide solution. (3 marks)

\[
\Pi = i \frac{MRT}{\Pi} = \frac{i}{MRT} = \frac{10.3 \text{ atm}}{\frac{3.70 \text{ g}}{0.1000 \text{ L}} \cdot \frac{1 \text{ mol}}{199.9 \text{ g}} \cdot \frac{0.08206 \text{ L atm}}{\text{mol K}} \cdot \frac{273 + 25.0}{1000}} = 2.28
\]

Ans. a: 2.28

b. What is the theoretical value of $i$ for calcium bromide? (1 mark)

CaBr$_2$ → Ca$^{2+}$(aq) + 2Br$^-$ (aq) 3 particles/mole: $i = 3$

Ans. b: $i = 3$
Question 5

a. The balanced equation for the reaction of bromate ion with bromide ion in acidic solution is given by:

\[ \text{BrO}_3^- + 5 \text{Br}^- + 6 \text{H}^+ \rightarrow 3 \text{Br}_2 + 3 \text{H}_2\text{O} \]

At a particular instant in time, the value of \(- \frac{\Delta [\text{Br}^-]}{\Delta t}\) is \(2.9 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}\).

What is the value of \(\frac{\Delta [\text{Br}_2]}{\Delta t}\) in the same units?

\[
(3 \text{ Br}_2 / 5 \text{ Br}^-) \times (2.9 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}) = +1.7 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}
\]

b. The reaction between nitric oxide (NO) and hydrogen (H\(_2\)) was studied at a constant temperature,

\[ 2 \text{NO}(g) + \text{H}_2(g) \rightarrow \text{N}_2\text{O}(g) + \text{H}_2\text{O}(g) \]

and the following results were obtained:

<table>
<thead>
<tr>
<th>experiment</th>
<th>Initial [NO], M</th>
<th>Initial [H(_2)], M</th>
<th>Initial rate of NO consumption, mol\cdot\text{L}^{-1}\cdot\text{s}^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.4 x 10(^{-3})</td>
<td>2.2 x 10(^{-3})</td>
<td>3.0 x 10(^{-5})</td>
</tr>
<tr>
<td>2</td>
<td>12.8 x 10(^{-3})</td>
<td>2.2 x 10(^{-3})</td>
<td>1.2 x 10(^{-4})</td>
</tr>
<tr>
<td>3</td>
<td>6.4 x 10(^{-3})</td>
<td>4.5 x 10(^{-3})</td>
<td>6.1 x 10(^{-5})</td>
</tr>
<tr>
<td>4</td>
<td>12.8 x 10(^{-3})</td>
<td>4.5 x 10(^{-3})</td>
<td>?</td>
</tr>
</tbody>
</table>

What is the rate law for this reaction?

\[
\text{Exp} \quad k \times [\text{NO}]^a \times [\text{H}_2]^b = \text{rate}
\]

\[
\frac{\text{Exp} 2}{\text{Exp} 1} = \frac{k \left( \frac{12.8 \times 10^{-3}}{6.4 \times 10^{-3}} \right)^a \times \left( \frac{2.2 \times 10^{-3}}{2.2 \times 10^{-3}} \right)^b}{k \left( \frac{6.4 \times 10^{-3}}{6.4 \times 10^{-3}} \right)^a \times \left( \frac{2.2 \times 10^{-3}}{2.2 \times 10^{-3}} \right)^b} = \frac{1.2 \times 10^{-4}}{3.0 \times 10^{-5}} = \frac{2.0}{3.3} = 4 \quad \text{order for [NO] is 2}
\]

\[
\frac{\text{Exp} 3}{\text{Exp} 1} = \frac{k \left( \frac{6.4 \times 10^{-3}}{6.4 \times 10^{-3}} \right)^a \times \left( \frac{4.5 \times 10^{-3}}{2.2 \times 10^{-3}} \right)^b}{k \left( \frac{6.4 \times 10^{-3}}{6.4 \times 10^{-3}} \right)^a \times \left( \frac{2.2 \times 10^{-3}}{2.2 \times 10^{-3}} \right)^b} = \frac{6.1 \times 10^{-5}}{3.0 \times 10^{-5}} = \frac{2.0}{3.3} = 2 \quad \text{order for [H}_2\text{] is 1}
\]

Rate = \(k \times [\text{NO}]^2 \times [\text{H}_2]\)

c. Calculate the rate constant for this reaction, with the appropriate units.

\[
k = \frac{\text{Rate}}{[\text{NO}]^2[\text{H}_2]} = \frac{3.0 \times 10^{-5} \text{ M}\cdot\text{s}^{-1}}{(6.4 \times 10^{-3} \text{ M})^2(2.2 \times 10^{-3} \text{ M})} = 333 = 3.3 \times 10^2 \text{ M}^{-2}\cdot\text{s}^{-1}
\]

d. What will the initial rate (in mol\cdot\text{L}^{-1}\cdot\text{s}^{-1}) be in experiment 4?

\[
\text{Rate} = 3.3 \times 10^2 \text{ M}^{-1}\cdot\text{s}^{-1} \times [\text{NO}]^2 \times [\text{H}_2] = (3.3 \times 10^2 \text{ M}^{-2}\cdot\text{s}^{-1})(12.8 \times 10^{-3} \text{ M})^2(4.5 \times 10^{-3} \text{ M}) = 2.4 \times 10^{-4} \text{ M}\cdot\text{s}^{-1}
\]
**Question 6**

The decomposition of hydrogen iodide follows the equation,

\[ 2 \text{HI}(g) \rightarrow \text{H}_2(g) + \text{I}_2(g) \]

The reaction is **second order** and has a rate constant equal to \(1.60 \times 10^{-3} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}\) at 700°C.

a. If the initial concentration of HI in a container is \(3.40 \times 10^{-2} \text{ M}\), how many minutes will it take for the concentration to be reduced to 75.0 % of its initial value at 700°C? (2 marks)

\[
\text{second order:} \quad \frac{1}{[\text{HI}]} = \frac{1}{[\text{HI}]}_0 + kt
\]

To find \(t\):

\[
(\frac{1}{[\text{HI}]} - \frac{1}{[\text{HI}]}_0) \times \frac{1}{k} = t
\]

\[
t = \frac{1}{(75/100 \times 3.40 \times 10^{-2} \text{M}) - 3.40 \times 10^{-2} \text{M}} \times \frac{1}{1.60 \times 10^{-3} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}} = 6127 \text{ s}
\]

\[
t = 6127 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} = 102 \text{ min}
\]

b. What is the half–life, in minutes, for the reaction at 700°C? (2 marks)

\[
\frac{1}{k[\text{HI}]}_0 = \frac{1}{(1.60 \times 10^{-3} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1})(3.40 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1})} \times \frac{1 \text{ min}}{60 \text{ s}} = 306 \text{ min}
\]

\text{ans. a: 102 min} \quad \text{ans. b: 306 min}
A two step mechanism has been suggested for the reaction of nitric oxide with bromine:

1. \[ \text{NO}(g) + \text{Br}_2(g) \rightarrow \text{NOBr}_2(g) \]
2. \[ \text{NOBr}_2(g) + \text{NO}(g) \rightarrow 2 \text{NOBr}(g) \]

a. Write the overall reaction

\[ 2 \text{NO}(g) + \text{Br}_2(g) \rightarrow 2 \text{NOBr}(g) \]

b. What is the role of NOBr$_2$ in this reaction?

Intermediate species

c. Based on the proposed mechanism and the energy profile of the reaction shown below, write the rate law for this reaction?

The slowest step is the first one. Therefore:

\[ \text{Rate} = k [\text{NO}] [\text{Br}_2] \]

d. Write on the energy profile of the reaction the position of the chemicals: Br$_2$, NOBr$_2$, NOBr.
2.0 mol of C(s) and 3.0 mol of CO\(_2\)(g) were initially placed in a 6.0 L container and heated to 100°C and allowed to reach equilibrium according to the following equation.

\[
\text{C(s) + CO}_2(g) \rightleftharpoons 2 \text{CO}(g)
\]

Analysis of the contents of the container at 100°C determined that 0.50 mol of C(s) remained.

a. Calculate the value of the equilibrium constant \(K\) (or \(K_c\)) for this reaction at 100°C. (2 marks)

\[
\begin{array}{c|ccc}
& \text{C(s)} & \text{CO}_2(g) & \text{2 CO}(g) \\
\hline
\text{initial} & 2.0 \text{ mol} & 3.0 \text{ mol} \\
\text{change} & -x & -x & + 2x \\
\text{final} & 0.50 & 1.5 & + 3.0 \\
\end{array}
\]

Since the final amount of C(s) is 0.50 mol and the initial number of mole was 2.0 mol, then

\[x = 2.0 - 0.5 = 1.5 \text{ mol}.
\]

The concentration of a solid is constant, therefore, it is not part of the equilibrium constant:

\[
\begin{align*}
\text{CO}_2(g) \text{ concentration} &= 1.5 \text{ mol} / 6.0 \text{ L} = 0.25 \text{ M} \\
\text{CO(g) concentration} &= 3.0 \text{ mol} / 6.0 \text{ L} = 0.50 \text{ M}
\end{align*}
\]

\[
K = \frac{[\text{CO}]^2}{[\text{CO}_2]} = \frac{[\text{CO}]^2}{[\text{CO}_2]} = \frac{(0.50)^2}{(0.25)} = 1.0
\]

ans. a: \(K = 1.0\)

b. If the initial amount of CO\(_2\)(g) added to the equilibrium above was doubled to 6.0 mol instead of 3.0 mol, how would the value of \(K\) change at 100°C? (circle one answer) (1 mark)

i. Increase ii. Decrease iii. Stay the same iv. Not enough information to say

Question 8, continue on the next page…
Question 8 (Cont.)

\[ C(s) + CO_2(g) \rightleftharpoons 2 CO(g) \]

c. If the value of \( K \) for the reaction is 0.050 at 25°C, what is the value of the equilibrium constant in terms of partial pressures, \( K_p \), at 25°C? (2 marks)

\[
K_p = K(RT)^{\Delta n} \\
K_p = (0.050) \times \left[ \frac{0.08206 \text{ L atm \cdot K}}{\text{mol \cdot K}} \right] \times (273+25)^2 \times (2-1) = 1.2
\]

ans. c: \( K_p = 1.2 \)

d. Find the value for the pressure equilibrium constant, \( K_p \), at 25°C for the equilibrium (2 marks)

\[ 2 \text{H}_2\text{O}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{H}_2\text{O}_2(g) \]

from the following information.

i. \( \text{H}_2(g) + \text{O}_2(g) \rightleftharpoons \text{H}_2\text{O}_2(g) \) \( K_{p,1} = 1.0 \times 10^6 \) at 25°C

ii. \( \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{H}_2\text{O}(g) \) \( K_{p,2} = 1.8 \times 10^{37} \) at 25°C

\[
\begin{align*}
\text{i.} & \quad 2\text{H}_2(g) + 2\text{O}_2(g) \rightleftharpoons 2\text{H}_2\text{O}_2(g) \\
& \quad (K_{p,1})^2 = (1.0 \times 10^6)^2 \\
\text{ii.} & \quad 2\text{H}_2\text{O}(g) \rightleftharpoons 2\text{H}_2(g) + \text{O}_2(g) \\
& \quad (1/ K_{p,2})^2 = (1.8 \times 10^{37})^{-2} \\
& \quad 2 \text{H}_2\text{O}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{H}_2\text{O}_2(g) \\
& \quad K_p = 3.1 \times 10^{-63}
\end{align*}
\]

ans. d: \( 3.1 \times 10^{-63} \)
Question 9
Select from the equilibria (i to v) at 25°C below the one that best fits the statements in a. to d. (2 marks)

i. \( \text{H}_2(g) + \text{O}_2(g) \rightleftharpoons \text{H}_2\text{O}_2(g) \quad K_{p,1} = 1.0 \times 10^6 \)
ii. \( \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{H}_2\text{O}(g) \quad K_{p,2} = 1.8 \times 10^{37} \)
iii. \( \text{Cl}_2(g) + \text{H}_2(g) \rightleftharpoons 2 \text{HCl}(g) \quad K_{p,3} = 3.4 \times 10^2 \)
iv. \( 2 \text{NOCl}_2(g) \rightleftharpoons 2 \text{NO}(g) + \text{Cl}_2(g) \quad K_{p,4} = 4.0 \times 10^{-1} \)
v. \( \text{C}(s) + \text{CO}_2(g) \rightleftharpoons 2 \text{CO}(g) \quad K_{p,5} = 9.9 \times 10^{-10} \)

a. The equilibrium that would be considered “going to completion”. Answer: _____ii_____

b. The equilibrium that lies furtherest “to the left”. Answer: _____v_____

c. The equilibrium whose \( K_c \) equals its \( K_p \). Answer: _____iii_____ 

d. The heterogeneous equilibrium. Answer: _____v_____ 

Consider the following chemical equation:

\[ \text{CO}(g) + \text{Fe}_3\text{O}_4(s) \rightleftharpoons \text{CO}_2(g) + 3 \text{FeO}(s) \quad \Delta H^o = +18 \text{ kJ} \]

How does the equilibrium position shift as a result of each of the following disturbance? (3 marks)

<table>
<thead>
<tr>
<th>shift of the equilibrium</th>
<th>to the left</th>
<th>no change</th>
<th>to the right</th>
</tr>
</thead>
<tbody>
<tr>
<td>e. CO(g) is added.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>f. CO(_2)(g) is removed by adding solid NaOH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>g. Additional Fe(_3)O(_4)(s) is added to the system</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>h. Increasing the volume of the container</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>i. Add a catalyst</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>j. Increase temperature (while keeping pressure constant)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Question 10

What is the pH of the following aqueous solutions at 25°C (Show calculation and circle your choice)?

a. 0.012 M HBr
   i. 0.012
   ii. 1.92
   iii. 7.00
   iv. 12.08
   v. None of the above

\[ \text{pH} = - \log (0.012) = 1.92 \]

b. 0.030 M HOBr. \( K_a \) for HOBr is \( 2.0 \times 10^{-9} \)
   i. 1.52
   ii. 4.35
   iii. 9.22
   iv. 9.39
   v. None of the above

\[
\begin{array}{c|ccc}
\text{HOBr} & H^+ & \text{OBr}^- \\
\hline
i & 0.030 & 0 & 0 \\
\text{c} & -x & +x & +x \\
\text{e} & 0.030 - x & x & x \\
\end{array}
\]

\[ K_a = \frac{[H^+][\text{OBr}^-]}{[\text{HOBr}]} = \frac{(x)^2}{(0.030 - x)} \]

If \( x << 0.030 \) then \( \sqrt{K_a(0.030)} = x \)

\[ x = 7.7 \times 10^{-6} \text{ M} \]

(note \( 7.7 \times 10^{-6} / 0.03 << 5\% \), check!)

\[ \text{pH} = - \log(7.7 \times 10^{-6}) = 5.11 \]

c. 0.021 M NaOBr \( K_a \) for HOBr is \( 2.0 \times 10^{-9} \)
   i. 3.49
   ii. 5.19
   iii. 7.00
   iv. 8.81
   v. 10.51

\[
\begin{array}{c|ccc}
\text{OBr}^- & \text{H}^+ & \text{H}_2\text{O} & \text{OH}^- & \text{HOBr} \\
\hline
\text{i} & 0.021 & - & 0 & 0 \\
\text{c} & -x & -x & +x & +x \\
\text{e} & 0.021 - x & - & x & x \\
\end{array}
\]

\[ K_b = \frac{[\text{OH}^-][\text{HOBr}]}{[\text{OBr}^-]} = \frac{(x)^2}{(0.021 - x)} \]

If \( x << 0.021 \) then \( \sqrt{K_b(0.021)} = x \)

\[ x = 3.2 \times 10^{-4} \text{ M} = [\text{OH}^-] \]

(note \( \frac{3.2 \times 10^{-4}}{0.021} \times 100\% = 1.5\% \), check!)

\[ \text{pOH} = - \log(3.2 \times 10^{-4}) = 3.49, \quad \text{pH} = 14 - 3.49 = 10.51 \]
Question 11

a. Are the aqueous solutions of the following salts acidic, basic or neutral? (3 marks)

<table>
<thead>
<tr>
<th></th>
<th>basic</th>
<th>neutral</th>
<th>acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>i.</td>
<td>CsNO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ii.</td>
<td>NaF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>iii.</td>
<td>KOI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>iv.</td>
<td>NH₄Br</td>
<td></td>
<td></td>
</tr>
<tr>
<td>v.</td>
<td>CsCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>vi.</td>
<td>Li₂SO₄</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

b. At 25°C, a 250.0 mL KCN solution has a pH of 11.00. Calculate the initial molarity of KCN in this solution. ($K_a$ HCN = 4.9x10⁻¹⁰ at 25°C, mol. mass KCN = 65.12 g.mol⁻¹) (3 marks)

\[
K_b = \frac{[OH^-][HCN]}{[CN^-]} = \frac{(x)^2}{(M-x)}
\]

Since x = [OH⁻] this value can be obtained from the pH

\[
pOH = 14 - pH = 3.00 \quad \text{therefore, } [OH^-] = 10^{-3.00}
\]

\[
M = \frac{(x)^2}{K_b} + x = \frac{(1.0\times10^{-3})^2}{10^{-14}/4.9\times10^{-10}} + 1.0\times10^{-3} = 5.0\times10^{-2} \text{ M}
\]

Ans. b: $5.0\times10^{-2}$ M
Question 12

a. Which of the following combinations can be used to prepare a buffer? (2 marks)

<table>
<thead>
<tr>
<th></th>
<th>buffer</th>
<th>not buffer</th>
</tr>
</thead>
<tbody>
<tr>
<td>i.</td>
<td>HCl / Cl(^{-})</td>
<td>☐</td>
</tr>
<tr>
<td>ii.</td>
<td>NH(_4)(^{+}) / H(^{+})</td>
<td>☐</td>
</tr>
<tr>
<td>iii.</td>
<td>HNO(_2) / NO(_2)(^{-})</td>
<td>☐</td>
</tr>
<tr>
<td>iv.</td>
<td>HNO(_3) / NO(_3)(^{-})</td>
<td>☐</td>
</tr>
</tbody>
</table>

b. Consider 1.0 L of a solution that is 0.85 M formic acid (HCOOH, \(K_a = 1.7 \times 10^{-4}\)) and 1.4 M sodium formate (HCOO\(_{\text{Na}}\)). What is the pH of this solution? (2 marks)

\[
\begin{align*}
\text{HCOOH} & \rightleftharpoons H^+ + \text{HCOO}^- \\
i & 0.85 \text{ M} & - & 1.4 \text{ M} \\
c & -x & +x & +x \\
e & 0.85 - x & +x & 1.4 + x
\end{align*}
\]

\[
K_a = \frac{[H^+][\text{HCOO}^-]}{[\text{HCOOH}]} \quad \text{since \([\text{HCOOH}] \text{ and } [\text{HCOO}^-] \gg [H^+]\), then you have a buffer}
\]

\[
[H^+] = \frac{K_a [\text{HCOOH}]}{[\text{HCOO}^-]} = \frac{(1.7 \times 10^{-4})(0.85)}{(1.4)} = 1.03 \times 10^{-4} \text{ M.}
\]

\[
pH = -\log(1.03 \times 10^{-4}) = 3.99
\]

c. Calculate the pH of the solution in 12b above after the addition of 0.15 mol HCl. Assume the addition causes no volume change. (2 marks)

\[
\begin{align*}
\text{HCOOH} & \rightleftharpoons H^+ + \text{HCOO}^- \\
l & 0.85 \text{ M} & 0.15 & 1.4 \text{ M} \\
r & +0.15 & -0.15 & -0.15 \\
f & 1.00 & - & 1.25
\end{align*}
\]

The problem is solved the same way as part 12b

\[
[H^+] = \frac{K_a [\text{HCOOH}]}{[\text{HCOO}^-]} = \frac{(1.7 \times 10^{-4})(1.00)}{(1.25)} = 1.36 \times 10^{-4} \text{ M.}
\]

\[
pH = -\log(1.36 \times 10^{-4}) = 3.87
\]

ans. b: 3.99

ans. c: 3.87
Question 13
A 30.0 mL sample of 0.150 mol/L HOCl solution was titrated with 0.300 mol/L KOH solution at 25°C. (\(K_a\) for HOCl is 3.5x10^{-8}).

a. What volume of KOH is needed to reach the equivalence point? (1 mark)

\[
\text{mole of acid} = 30.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times 0.150 \frac{\text{mol}}{\text{L}} = 4.50 \times 10^{-3} \text{ mole}
\]

\[
\text{volume of KOH needed} = 4.50 \times 10^{-3} \text{ mole acid} \times \frac{1 \text{ base}}{1 \text{ acid}} \times \frac{1 \text{ L}}{0.300 \text{ mol}} = 1.50 \times 10^{-2} \text{ L} \text{ (or 15.0 mL)}
\]

b. Calculate the pH of the solution in the flask at the equivalence point. (3 marks)

At the equivalence point, the 4.50x10^{-3} mol of acid is neutralised. Therefore, we have 4.50x10^{-3} mol conjugated base in the solution.

\[
[\text{OCl}^-] = \frac{\text{mol}}{\text{L}} = \frac{4.50 \times 10^{-3} \text{ mol}}{(0.030 + 0.015) \text{ L}} = 0.10 \text{ M}
\]

\[
\begin{align*}
\text{ OCl}^- & + \quad \text{H}_2\text{O} & \quad \rightleftharpoons & \quad \text{HOCl} & + & \quad \text{OH}^- \\
\text{i} & 0.10 & - & - & - \\
\text{c} & -x & -x & +x & +x \\
\text{e} & 0.10 - x & - & +x & +x
\end{align*}
\]

\[
K_b = \frac{1.0 \times 10^{-14}}{3.5 \times 10^{-8}} = 2.9 \times 10^{-7}
\]

\[
K_b = \frac{[\text{OH}^-][\text{HOCl}]}{[\text{OCl}^-]} = \frac{(x)^2}{0.10 - x}
\]

assume \(x \ll 0.1 \text{ M}\) then \(x = [\text{OH}^-] = \sqrt{K_b(0.10)} = 1.7 \times 10^{-4}\)

finally, \(\text{pH} = 14 - \text{pOH}\) \(\text{pH} = 14 - (-\log 1.7 \times 10^{-4}) = 10.23\)

c. Calculate the pH in the flask upon the addition of 45.0 ml of KOH solution. (3 marks)

Since 15 mL were used to neutralize the acid, the remaining KOH is in excess:

\[
[\text{OH}^-] \text{ in solution} = \frac{\text{mole of OH}^- \text{ in excess}}{\text{total volume of the solution}} = \frac{(45.0 \text{ mL} - 15.0 \text{ mL})(0.300 \text{ M})}{(30.0 \text{ mL} + 45.0 \text{ mL})} = 0.120 \text{ M}
\]

\[
\text{pH} = 14 - (-\log 0.120) = 13.08
\]

ans. a: 15.0 mL  
ans. b: pH = 10.23  
ans. c: pH = 13.08
Question 14

Sodium chloride is added slowly to a solution that is 0.010 M in Cu\(^{+}\), Ag\(^{+}\), and Au\(^{+}\). (1 mark)

a. Which compound will precipitate first? (circle one answer)

\(K_{sp}\) CuCl: 1.9x10\(^{-7}\), AgCl: 1.6x10\(^{-10}\), AuCl: 2.0x10\(^{-13}\)

i. CuCl

ii. AgCl

iii. AuCl

iv. All will precipitate at the same time.

v. Cannot be determined.

A solution is prepared by mixing 100.0 mL of 0.0400 M ZnCl\(_2\) and 300.0 mL of 0.020 M NaOH. (2 marks)

b. Does precipitation occur? Show your calculations. (\(K_{sp}\) of Zn(OH)\(_2\) = 4.5x10\(^{-17}\)).

\[K_{sp} = [Zn^{2+}][OH^-]^2\]
\[Q = [Zn^{2+}][OH^-]^2\]

\[Q = \left(\frac{100.0 \text{ mL}}{400.0 \text{ mL}}\right)(0.0400 \text{ M Zn}^{2+}) \left(\frac{300.0 \text{ mL}}{400.0 \text{ mL}}\right)(0.0200 \text{ M OH}^-)^2 = 2.25 \times 10^{-6}\]

Q > K. Yes, you will have a precipitation.

c. Calculate the concentration of Zn\(^{2+}\) at equilibrium with solid Zn(OH)\(_2\). (3 marks)

First assume complete precipitation reaction (OH\(^-\) is the limiting reactant):

\[
\begin{align*}
\text{Zn}^{2+}(aq) + 2 \text{OH}^-(aq) &\rightarrow \text{Zn(OH)}_2(s) \\
\text{I} &\quad 0.0100 \quad 0.015 \quad - \\
\text{R} &\quad -0.0075 \quad -0.015 \quad + 0.0075(s) \\
\text{F} &\quad 0.0025 \quad 0 \quad 0.0075
\end{align*}
\]

Then let the system coming back to equilibrium:

\[
\begin{align*}
\text{Zn(OH)}_2(s) &\rightarrow 2 \text{OH}^-(aq) + \text{Zn}^{2+}(aq) \\
\text{I} &\quad 0.0075 \quad 0 \quad 0.0025 \\
\text{C} &\quad -x \quad +2x \quad +x \\
\text{E} &\quad \text{solid} \quad 2x \quad x + 0.0025
\end{align*}
\]

\[K_{sp} = [\text{Zn}^{2+}][\text{OH}^-]^2 = [x + 0.0025][2x]^2\]

If x << 0.0025, then

\[\sqrt{\frac{K_{sp}}{0.0025(4)}} = x = 6.71 \times 10^{-8}\]

Finally, the Zn\(^{2+}\) at equilibrium in solution is: (6.71x10\(^{-8}\) + 0.0025) M = 2.5x10\(^{-3}\) M

d. How does the concentration of Zn\(^{2+}\) vary if the pH is increased (more basic conditions)? (1 mark)

- increases
- decreases
- does not change
- can not tell
Question 15

A balloon is filled with 8.00 g helium early in the morning at 15.0°C and 1.00 atm. It is then transported down south where the temperature increased to 30.0°C at 1.00 atm.

a. Assuming He behaves like an ideal gas, calculate the initial and final volumes. (2 marks)

\[ V = \frac{nRT}{P} = \frac{(8.00 \text{ g})(1 \text{ mol/4.003 g})(0.08205 \text{ atm.L/K.mol})(273 + 15)K}{1.00 \text{ atm}} = 47.2 \text{ L (initial volume)} \]

\[ \frac{V_1}{T_1} = \frac{V_2}{T_2} \]

\[ V_2 = \frac{V_1 T_2}{T_1} = \frac{(47.2 \text{ L})(30. + 273)K}{(15 + 273)K} = 49.7 \text{ L (final volume)} \]

b. Calculate the work \( (w) \) done by the balloon (in J). (1 mark)

\[ w = -P \Delta V = -(1.00 \text{ atm}) \left( \frac{101.3 \text{ kPa}}{1 \text{ atm}} \right)(49.7 \text{ L} - 47.2 \text{ L}) = -253 \text{ kPa.L or J} \text{ (work done)} \]

c. Calculate the heat \( (q) \) transferred (in J) assuming a specific heat capacity of 5.33 J·K⁻¹·g⁻¹ for He at \( P = 1.00 \text{ atm} \). (2 marks)

\[ q = m C_p \Delta T = (8.00 \text{ g})(5.33 \text{ J·K}^{-1} \cdot \text{g}^{-1})(30.0 - 15.0)\text{°C} = +640 \text{ J} \text{ (endothermic)} \]

(note \( \Delta T \) in °C or K = same)

d. Calculate the change in internal energy, \( \Delta E \) (in J). (1 mark)

\[ \Delta E = q + w = 640 \text{ J} + (-253 \text{ J}) = +387 \text{ J} \]
The fermentation of glucose (C₆H₁₂O₆) from corn yields ethanol (C₂H₅OH) which can then be used in automobile fuel.

\[
\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) \rightarrow 2 \text{C}_2\text{H}_5\text{OH}(\text{f}) + 2 \text{CO}_2(\text{g})
\]

a. Calculate \(\Delta H^\circ\), \(\Delta S^\circ\), and \(\Delta G^\circ\) for the reaction at 25°C using the data in the table below.

<table>
<thead>
<tr>
<th>Substance</th>
<th>(\Delta H^\circ) (kJ mol(^{-1}))</th>
<th>(S^\circ) (J K(^{-1}) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}<em>6\text{H}</em>{12}\text{O}_6(\text{s}))</td>
<td>-1275</td>
<td>212</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_5\text{OH}(\text{f}))</td>
<td>-278</td>
<td>161</td>
</tr>
<tr>
<td>(\text{CO}_2(\text{g}))</td>
<td>-393.5</td>
<td>214</td>
</tr>
</tbody>
</table>

\[
\Delta H^\circ = \Sigma \Delta H^\circ_{\text{products}} - \Sigma \Delta H^\circ_{\text{reactants}}
\]

\[
\Delta H^\circ = [2(-278) + 2(-393.5)] \text{kJ} - (-1275) \text{kJ} = -68 \text{kJ} \text{ or } -6.8 \times 10^4 \text{J}
\]

\[
\Delta S^\circ = \Sigma S^\circ_{\text{products}} - \Sigma S^\circ_{\text{reactants}}
\]

\[
\Delta S^\circ = [2(161) + 2(214)] \text{kJ} - (212) \text{kJ} = +538 \text{J/K}
\]

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (-68000 \text{J}) - (273 + 25) \text{K}(538 \text{J/K}) = -2.28 \times 10^5 \text{J}
\]

The reaction is spontaneous.

\[
\begin{array}{ccc}
\Delta H^\circ &=& -68 \text{kJ} \\
\Delta S^\circ &=& +540 \text{J/K} \\
\Delta G^\circ &=& -229 \text{kJ}
\end{array}
\]

b. Is the spontaneity of the reaction dependent on temperature? Explain.

Whatever the temperature, this system will always be spontaneous because the entropy is positive and the enthalpy is exothermic.

c. Consider the Haber-Bosch process for synthesizing ammonia:

\[
\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})
\]

Knowing that \(\Delta G^\circ\) of \(\text{NH}_3(\text{g})\) is \(-16.5 \text{kJ/mol}\), calculate its equilibrium constant at 25°C.

Since there is 2 moles of \(\text{NH}_3\) in this equation, \(\Delta G^\circ\) will be:
\[
\Delta G^\circ = 2 \text{mol} \times (-16.5 \text{kJ/mol}) = -33.0 \text{kJ}.
\]

\[
\Delta G^\circ = -RT \ln K \text{ then } K = e^{\frac{-\Delta G^\circ}{RT}} = e^{\left(\frac{-33.0 \times 10^3 \text{J}}{8.31 \text{ J/K mol} (273 + 25) \text{K}}\right)} = e^{13.3} = 6.1 \times 10^5.
\]
Having studied a similar reaction during the semester you are asked to determine the nature of the rate law for the main reaction below.

\[
\text{H}_2\text{O}_2(\text{aq}) + 2 \Gamma(\text{aq}) + 2 \text{H}^+(\text{aq}) \rightarrow I_2(\text{aq}) + 2 \text{H}_2\text{O}(\ell)
\]

To monitor the main reaction, very small quantities of thiosulphate (\(\text{S}_2\text{O}_3^{2-}\)) and starch were also included in the reaction flask. Thiosulphate and starch react at a much faster rate than the main reaction according to the following equations:

\[
2 \text{S}_2\text{O}_3^{2-}(\text{aq}) + I_2(\text{aq}) \rightarrow \text{S}_4\text{O}_6^{2-}(\text{aq}) + 2I^-(\text{aq})
\]

\[
\text{Starch} + I_2(\text{aq}) \rightarrow \text{Starch–I}_2(\text{a blue product})
\]

a. Complete the equations below to show how the rates of each reaction compare to each other during the reaction.

\[
\text{Rate} = -\frac{\Delta[H_2O_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[I^-]}{\Delta t} = -\frac{1}{2}\frac{\Delta[S_2O_3^{2-}]}{\Delta t}
\]

The following solutions were used to prepare 2 flasks.

<table>
<thead>
<tr>
<th>Flask 1</th>
<th>Flask 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 mL of 0.10 M KI and 10 mL of 0.00050 M (\text{Na}_2\text{S}_2\text{O}_3)</td>
<td>20 mL of 0.10 M (\text{H}_2\text{O}_2) and 10 mL of 0.30 M (\text{H}_2\text{SO}_4) and 3 drops of Starch Solution</td>
</tr>
</tbody>
</table>

When Flask 1 and Flask 2 were combined it was found that it took 21 s for the solution to turn a dark blue colour.

b. Calculate the rate of the reaction \(-\frac{\Delta[H_2O_2]}{\Delta t}\) for the example shown.

*Hint: thiosulphate is used to monitor the main reaction rate*

\[
-\frac{1}{2}\frac{\Delta[S_2O_3^{2-}]}{\Delta t} = -\frac{[0 \ M \ (5.0 \times 10^{-4} \ M \times 10 \ mL / 60 \ mL)]}{2 \times 21 \ s} = 2.0 \times 10^{-6} \ M/\text{s}
\]
**Question 17 (Cont.)**

The results of a series of reactions are shown below. For each graph the reactant in the title had its initial concentration changed and the others kept constant.

c. Write the differential rate law (or rate law) for the reaction.

\[
\text{Rate} = -\frac{\Delta [\text{H}_2\text{O}_2]}{\Delta t} = k [\text{H}_2\text{O}_2]^2 [\text{I}^-] \quad \text{(answer)}
\]

([H^+] not written since its order = zero)

Dependence of the reaction rate on [H_2O_2]_0 concentration

![Graph showing the dependence of the reaction rate on [H_2O_2]_0 concentration.]

Dependence of the reaction rate on [I^-]_0 concentration

![Graph showing the dependence of the reaction rate on [I^-]_0 concentration.]

Dependence of the reaction rate on [H^+]_0 concentration

![Graph showing the dependence of the reaction rate on [H^+]_0 concentration.]

d. Determine the value of the rate constant.

\[
[\text{H}_2\text{O}_2]_0 = \frac{20 \text{ mL} \times 0.10 \text{ M}}{60 \text{ mL}} = 0.033 \text{ M}
\]

\[
[\text{I}^-]_0 = \frac{20 \text{ mL} \times 0.10 \text{ M}}{60 \text{ mL}} = 0.033 \text{ M}
\]

\[
k = \frac{\text{rate}}{[\text{H}_2\text{O}_2]^2 [\text{I}^-]} = \frac{2.0 \times 10^{-6} \text{ M.s}^{-1}}{[0.033 \text{ M}]^2 [0.033 \text{ M}]}
\]

\[
k = 0.056 \text{ M}^2\text{s}^{-1}
\]