Memorial University of Newfoundland

Chemistry 1051

Final Examination **Winter 2014** **Time: 3 hours**

NAME: ____________________________ MUN STUDENT #: ______________________

PROFESSOR: (circle the appropriate name) **C. Flinn** **P. Warburton**

READ THE FOLLOWING CAREFULLY

1. This examination paper has 17 numbered pages. Ensure that this examination is complete.

2. Failure to submit this paper in its entirety at the end of the examination may result in disqualification.

3. A Periodic Table and physical constants are provided, as are a sheet of useful equations. These are on the last two pages of the examination and may be detached for use during the examination.

4. Answer each question in the space provided. Should you require more space, use the back of the page and indicate clearly when this has been done.

5. When answering questions, **show all relevant calculations and justify simplifying assumptions.**

6. Numerical answers should include units where appropriate and be reported to the correct number of significant digits.

7. Do not write in the enclosed area below.

QUESTION	**TOPIC**	**VALUE**	**MARK**
1, 2, 3	Kinetics	16	
4, 5, 6	Equilibrium	13	
7, 8, 9	Acid-Base Equilibrium	20	
10, 11, 12	Solubility Equilibrium	14	
13, 14	Thermodynamics	12	
15, 16, 17	Electrochemistry	13	
18, 19, 20	Short Answer	12	
TOTAL		100	

[MARKS]

1. Consider the reaction between nitric oxide and hydrogen at 904 ˚C:

$$2\ NO\ (g) + 2\ H_2\ (g) \rightarrow N_2\ (g) + 2\ H_2O\ (g)$$

The data obtained are listed in the table:

Exp.	[NO], M	$[H_2]$, M	Rate of Formation of N_2 , M s^{-1}
1	0.420	0.122	0.136
2	0.210	0.122	0.0339
3	0.210	0.244	0.0678
4	0.105	0.488	0.0339

[4] (a) Determine the rate law for the reaction.

[2] (b) Calculate the rate constant at 904 ˚C.

[4] 2. When heated to high temperature cyclobutane, C_4H_8, decomposes to ethylene:

$$C_4H_8\ (g) \rightarrow 2\ C_2H_4\ (g)$$

The activation energy, E_a, for the reaction is 260 kJ mol^{-1}. At 527 °C the rate constant k = 0.0315 s^{-1}. Calculate the rate constant at 800 °C.

[6] 3. A mechanism is proposed for the reaction

$$2\ NO\ (g) + O_2\ (g) \rightarrow 2\ NO_2\ (g)$$

Mechanism:

$$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} N_2O_2$$

$$O_2 + N_2O_2 \xrightarrow{k_2} NO_2 + NO_2$$

(a) Define the rate law of the reaction in terms of the rate of disappearance of O_2. Apply the steady state approximation to the concentration of any intermediates and determine the rate law for the reaction.

(b) Determine the **simplified rate law** for the reaction under the following conditions:

(i) very high $[O_2]$

(ii) very low $[O_2]$

[5] 4. 2.00 mol of CO_2 (g) and an excess of solid carbon is placed in a 2.00 L flask. When the reaction is conducted at 700 °C and equilibrium is established, 19.3% of the CO_2 has reacted according to the following equation.

$$CO_2\ (g) + C\ (s) \rightleftharpoons 2\ CO\ (g)$$

Calculate both K_c and K_p for this reaction at 700 °C.

[2] 5. We know the equilibrium constants for the following two reactions at a given temperature:

$$NOBr\ (g) \rightarrow NO\ (g) + \tfrac{1}{2}\ Br_2\ (g) \qquad K_1 = 0.12$$
$$2\ BrCl\ (g) \rightarrow Br_2\ (g) + Cl_2\ (g) \qquad K_2 = 0.14$$

What is the equilibrium constant for the following reaction at the same temperature?

$$2\ NOBr\ (g) + Cl_2\ (g) \rightarrow 2\ NO\ (g) + 2\ BrCl\ (g)$$

[6] 6. An **equilibrium** mixture at a particular temperature contains 0.310 M CO (g), 0.140 M Cl_2 (g) and 0.780 M $COCl_2$ (g) in a 2.00 L container. Calculate the number of moles of Cl_2 (g) which must be **added** to the equilibrium mixture in the 2.00 L flask to reduce the concentration of CO (g) to 0.250 M when **equilibrium is re-established** at the same temperature for the chemical system shown below:

$$Cl_2\ (g) + CO\ (g) \rightleftharpoons COCl_2\ (g)$$

[6] 7. Calculate the pH, $[HSeO_3^-]$ and $[SeO_3^{2-}]$ in 0.0250 M selenous acid (H_2SeO_3) at 25°C.

For selenous acid $K_{a1} = 2.3 \times 10^{-3}$ and $K_{a2} = 5.4 \times 10^{-9}$ at 25°C.

[4] 8. Ephedrine ($C_{10}H_{15}ON$) is a weak organic base. A 0.035 M solution of ephedrine at 25 °C has a pH = 11.33. Calculate K_b for ephedrine at 25 °C.

[5] 9 (a) 25.00 mL of a 0.700 M solution of the weak acid $HC_3H_5O_3$ (aq) is titrated with 1.05 M NaOH (aq). Calculate the pH after 12.50 mL of titrant solution has been added to the solution of $HC_3H_5O_3$.

$$K_a\ HC_3H_5O_3 = 1.4 \times 10^{-4}$$

[5] (b) The titration started in part a) is continued to the equivalence point. What volume of strong base has been added, and what is the final pH?

[4] 10. The molar solubility of PbF_2 (s) in 0.0084 M KF (aq) is 3.91×10^{-4} M at 25 ºC. Calculate the K_{sp} of PbF_2 at 25 ºC.

[5] 11. Determine whether or not $Cd(OH)_2$ (s) will precipitate when 250.0 mL of an aqueous solution of 8.0×10^{-9} M $Cd(NO_3)_2$ (aq) is mixed with 250.0 mL of aqueous 0.160 M NH_3 at 25 ºC.

K_{sp} $Cd(OH)_2 = 7.2 \times 10^{-15}$, K_b $NH_3 = 1.8 \times 10^{-5}$ at 25 ºC.

[5] 12. Consider an aqueous solution that is 2.00×10^{-9} M in Al^{3+} and 5.00×10^{-9} M in Cu^{2+}. A solution of Na_3PO_4 is used to selectively precipitate one of the cations from solution, leaving the other unprecipitated.

$$K_{sp} \text{ for } AlPO_4 = 9.84 \times 10^{-21} \text{ and } K_{sp} \text{ for } Cu_3(PO_4)_2 = 1.40 \times 10^{-37}$$

(a) Determine the $[PO_4^{3-}]$ required to precipitate each ion

(b) What is the concentration of the cation which precipitates first that remains in solution when the second cation just begins to precipitate?

(c) What % of the first ion to precipitate remains in solution when the second cation just begins to precipitate?

[4] 13. The reaction for the formation of nitrogen dioxide is:

$$N_2\,(g) + 2\,O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

Using the following data, at what temperature does this reaction have an thermodynamic equilibrium constant value of 2.00 x 10^{-10}?

$$\Delta H_f^\circ\,(N_2) = 0\text{ kJ mol}^{-1} \quad \Delta H_f^\circ\,(O_2) = 0\text{ kJ mol}^{-1} \quad \Delta H_f^\circ\,(NO_2) = 33.2\text{ kJ mol}^{-1}$$

$$S^\circ\,(N_2) = 191.6\ \text{J K}^{-1}\text{ mol}^{-1} \quad S^\circ\,(O_2) = 205.2\ \text{J K}^{-1}\text{ mol}^{-1} \quad S^\circ\,(NO_2) = 240.1\ \text{J K}^{-1}\text{ mol}^{-1}$$

14. The steam-methane reforming reaction is

$$CH_4\,(g) + H_2O\,(g) \rightleftharpoons CO\,(g) + 3\,H_2\,(g)$$

$$\Delta_rH° = +205.9 \text{ kJ mol}^{-1},\ \Delta_rG° = +141.9 \text{ kJ mol}^{-1} \text{ at } 298.15 \text{ K}$$

[2] (a) Calculate $\Delta_rS°$ for the reaction at 298.15 K. Is the sign of $\Delta_rS°$ reasonable? Briefly explain.

[3] (b) Calculate the value of the equilibrium constant K at 350 ºC.

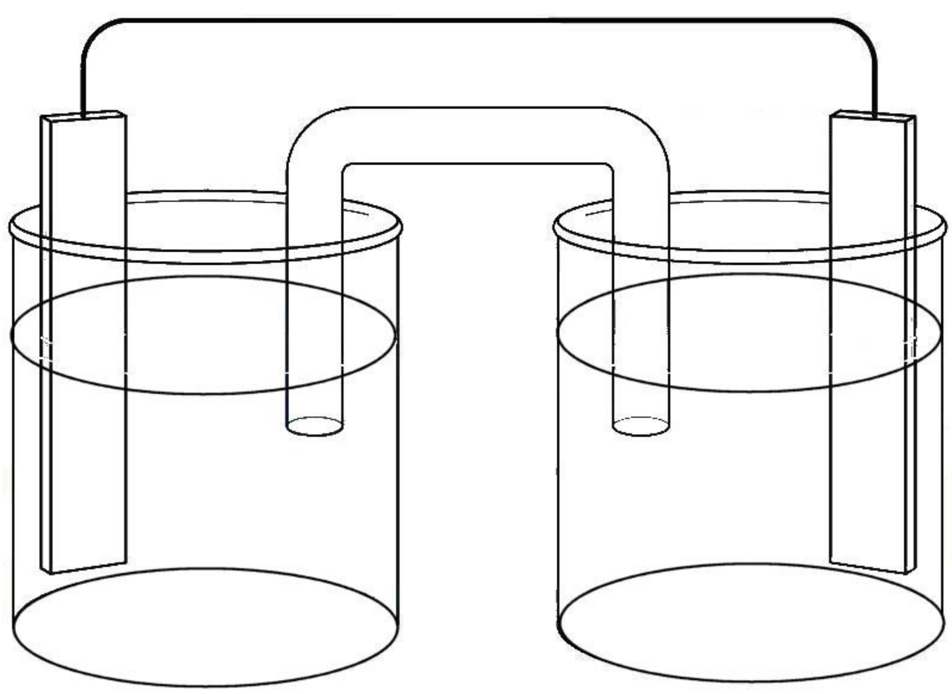
[3] (c) Calculate Δ_rG for the reaction at 298.15 K when

$$CH_4\,(g) = H_2O\,(g) = 20.0 \text{ bar and } CO(g) = H_2\,(g) = 0.0250 \text{ bar}$$

[5] 15. Calculate the concentration of Au^{3+} (aq) remaining in 155 mL of a solution that was originally 0.141 M $Au(NO_3)_3$ (aq) after a current of 2.68 A has passed through the cell for 4 minutes and 42 seconds and gold is deposited at the cathode.

[3] 16. A voltaic cell is created where one half-cell contains a bar of chromium immersed in a $Cr(NO_3)_3$ solution, while the other half-cell has a silver bar in a $AgNO_3$ solution. The two half-cells are joined by a salt bridge containing KNO_3, and a wire connects the two metal bars. Measurements indicate the Cr bar loses mass as the reaction proceeds.

i) Label each electrode by metal type, indicate whether it is the anode or cathode, and show the sign of each electrode.
ii) Below each half-cell write the correct balanced half-reaction.
iii) Indicate the direction of electron flow through the wire.
iv) Label the ions of the salt bridge and indicate their direction of movement.



reduction half-reaction	E°, V
$IO_3^-(aq) + 6\ H^+(aq) + 5\ e^- \rightarrow \frac{1}{2}\ I_2\ (aq) + 3\ H_2O\ (l)$	+1.20
$PtCl_4^{2-}\ (aq) + 2\ e^- \rightarrow Pt\ (s) + 4\ Cl^-\ (aq)$	+0.76

17. Consider the **galvanic** cell based on the following reaction:

$$2\ IO_3^-\ (aq) + 12\ H^+\ (aq) + 20\ Cl^-\ (aq) + 5\ Pt\ (s) \rightarrow I_2\ (aq) + 6\ H_2O\ (l) + 5\ PtCl_4^{2-}\ (aq)$$

[2 ½] (a) Write the anode and cathode half–reactions based on the reaction above and calculate $E°_{cell}$. Is the reaction spontaneous at standard conditions?

[2] (b) Calculate E_{cell} at 25 °C when the concentrations within the cell are

$$[Cl^-] = [PtCl_4^{2-}] = 0.00800\ M \text{ and } [H^+] = [IO_3^-] = [I_2] = 0.100\ M.$$

[½] (c) Is the reaction spontaneous at the non-standard conditions of part (b)?

[4] 18. Balance the following unbalanced oxidation-reduction reaction in **basic** solution.

$$MnO_4^- (aq) + CN^- (aq) \rightarrow CNO^- (aq) + MnO_2 (s)$$

[6] 19. Give a brief explanation or a definition for six of the following.
If more than six are answered, only the first six will be marked.

a) Termolecular elementary reactions are very rare.

b) The levelling effect for acids in aqueous solution.

c) The reaction between NH_3 (aq) and Cu^{2+} (aq) to form $[Cu(NH_3)_4]^{2+}$ (aq) is considered to be a Lewis acid/Lewis base reaction.

d) The third law of thermodynamics.

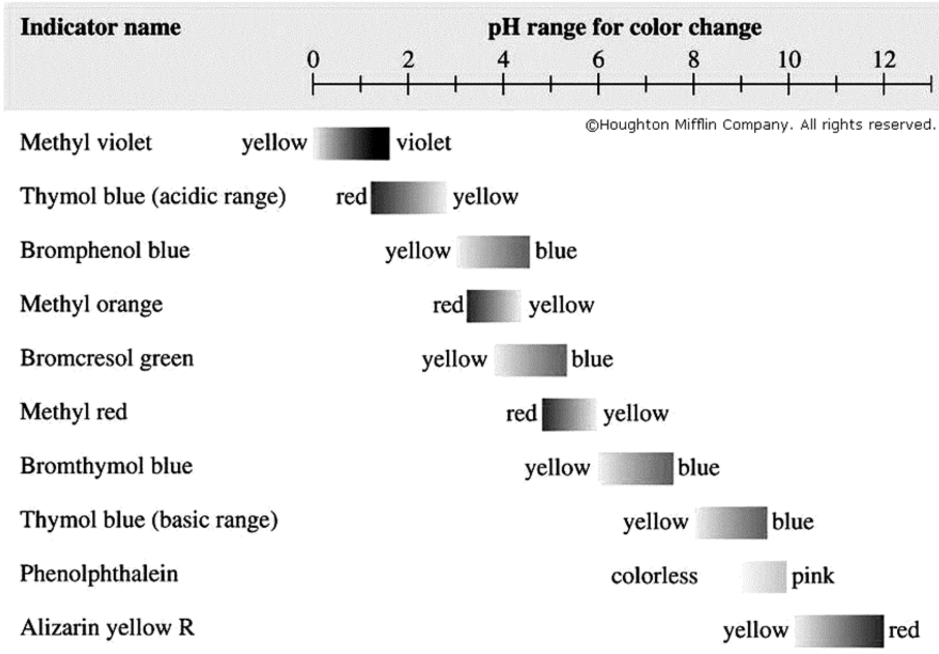
e) The reaction $2A + 2B \rightarrow$ products with the rate law, rate = $k[A]^2[B]$, can be made to behave as if it were a first order reaction.

f) Of the three bases, CH_3NH_2, NH_2OH and NH_3, CH_3NH_2 is the strongest and NH_2OH is the weakest.

g) Of the three acids, $HClO_2$, $HBrO_2$ and $HClO_3$, $HClO_3$ is the strongest and $HBrO_2$ is the weakest.

h) The entropy of a sample of molecules increases with temperature.

[2] 20. Use the diagram and the experiment described below to answer the questions found in ***bold italics***:



An aqueous solution of the anticoagulant drug dicoumarol is prepared. One sample of the solution has the indicator **methyl violet** added, and the result is **violet**. A second sample of the solution has the indicator **phenolphtalein** added, and the result is **colorless**. A third sample has the indicator **methyl red** added, and the result is **red**. A final sample has the indicator **bromphenol blue** added, and the result is **blue**.

① ***What information does each indicator tell us about the pH of the solution?***

② ***Based on this information estimate the range of pH values (<u>nearest integer only</u>) that the actual pH of the solution lies between.***

Chemistry 1051 Equations

$$k = A\,e^{-E_a/RT}$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln K = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}$$

$$\Delta G^\circ = -RT \ln K$$

$$\Delta G^\circ = -nFE^\circ$$

$$E^\circ = \frac{RT}{nF}\ln K$$

$$E^\circ = \frac{0.0257\ V}{n}\ln K \quad \text{at } 25\ ^\circ C$$

$$E = E^\circ - \frac{RT}{nF}\ln Q$$

$$E = E^\circ - \frac{0.0257\ V}{n}\ln Q \quad \text{at } 25\ ^\circ C$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$