Department of Chemistry
Memorial University
Chemistry 1051
Winter 2017 Final Examination
Time 3 hours

Read the Following Carefully

1. This exam has 15 pages. Question are on pages 2 through 13 and a periodic table and equation sheet is at the end of the exam. Ensure that all pages for the examination paper are present.

2. The sheets containing the periodic table, physical constants and equations which may be useful to you are provided. These **should be detached for easier use.**

3. **Read each question carefully** and answer each question in the space provided.

4. Show all relevant calculations.

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

Questions	Points	Grade
1 - 3	9	
4	8	
5	4	
6	9	
7 - 8	10	
9 - 12	11	
13	7	
14	7	
15 - 16	6	
17	10	
18	11	
19	3	
total	95	

1. Water has a boiling point of 100.00 ^{o}C at 1 atm. What mass of sodium chloride is required to increase the boiling point of 500.0 g of water to 101.50 ^{o}C? $K_b(H_2O)$ = 0.51 ^{o}C kg mol^{-1} and the molar mass of sodium chloride, NaCl, is 58.44 g mol^{-1}. **(3 marks)**

2. Hemoglobin is a globular iron-containing protein responsible for the transport of oxygen in the body. In an experiment, 0.5515 g of hemoglobin was dissolved in 100.00 mL of solution at 25.0 ^{o}C. The osmotic pressure was measured to be 1.985x10^{-3} bar. Determine the molar mass of hemoglobin. **(3 marks)**

3. A solution is made by dissolving 17.1 g of sucrose (342.08 g mol^{-1}) in 90.0 g of water at 30.0 ^{o}C. What is the vapour pressure of water above the solution if the vapour pressure of pure water at 30.0 ^{o}C is 31.86 Torr. **(3 marks)**

4. Consider the reaction that occurs when a ClO_2 solution and a solution containing OH^- are mixed:

$$2\,ClO_2(aq) + 2\,OH^-(aq) \rightarrow ClO_3^-(aq) + ClO_2^-(aq) + H_2O(l)$$

The following three experiments were conducted in which the initial rates of reaction were measured at various concentrations of reactants:

$[ClO_2]$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	initial rate / mol L^{-1} s^{-1}
1.25×10^{-2}	1.30×10^{-3}	2.33×10^{-4}
2.50×10^{-2}	1.30×10^{-3}	9.34×10^{-4}
4.25×10^{-2}	2.50×10^{-3}	5.19×10^{-3}

a) Determine the order of the reaction for each reactant. **(4 marks)**

b) Determine the rate constant for this reaction. **(2 marks)**

c) What would you expect to happen to the rate constant (increase or decrease) if the temperature were increased? Briefly explain why the rate constant would change in value. **(2 mark)**

5. The reaction of gaseous NO with H_2 produces N_2O and H_2O:

$$2\,NO(g) \;+\; H_2(g) \longrightarrow N_2O(g) \;+\; H_2O(g)$$

The following mechanism has been proposed for the reaction:

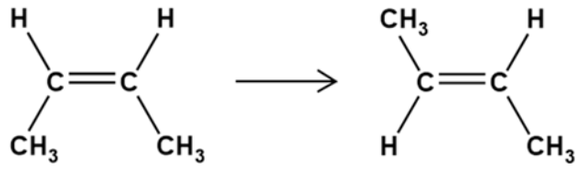
$$2\,NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$$

$$N_2O_2 \;+\; H_2 \xrightarrow{k_2} N_2O \;+\; H_2O$$

a) Determine the rate law for the reaction using the steady state approximation?

Use $r = \dfrac{d[N_2O]}{dt}$. **(4 marks)**

6. For the isomerization of cis-2-butene to trans-2-butene:



a) The rate constants at 480. °C and 550. °C are 3.75×10^{-5} s^{-1} and 1.28×10^{-3} s^{-1}, respectively. Determine the activation energy for the reaction? **(3 marks)**

b) The standard enthalpy change for the reaction is -3.1 kJ mol^{-1}. The thermodynamic equilibrium constant at 25 °C is 3.42. Using this information, determine the equilibrium constant at 480. °C **(4 marks)**

c) With your computed activation energy from a), and the enthalpy change for the reaction given in b), sketch the potential energy diagram for the reaction of cis-2-butene to trans-2-butene on the axis below indicating reactants, products, E_a, and $\Delta_r H^\circ$. **(2 marks)**

7. In an experiment, 9.50 bar of NO and 6.5 bar H_2 were placed into a flask at 1950 K. The reaction that occurs is as follows:

$$2\,NO(g) \;+\; H_2(g) \longrightarrow N_2O(g) \;+\; H_2O(g)$$

a) At equilibrium, the total pressure is 11.64 bar. Determine the partial pressures of each of the reactants and products and the equilibrium constant, *K*. **(4 marks)**

b) Once at equilibrium, the reaction chamber was compressed. What effect, if any, would this have on the partial pressures of the reactants and products once equilibrium was re-established? Explain your answer. **(1 mark)**

8. Lactic acid, $C_3H_5O_6$, is a weak monoprotic acid that occurs naturally in sour milk, apples, wine, and—very sadly—in beer. The K_a of lactic acid is 1.38×10^{-4}. Determine the pH and the % ionization of lactic acid in a 0.0150 mol L^{-1} lactic acid solution. **(5 marks)**

9. Would you expect PH_3 to be an acid or base? Explain your answer. A Lewis structure and a reaction might help your answer. **(2 marks)**

10. Explain why CH_3NH_2 is a stronger base than NH_3. **(2 marks)**

11. What initial concentration of $HClO_2$, $K_a = 1.1 \times 10^{-2}$ is required to produce a solution of pH = 1.38? **(4 marks)**

12. Consider the following equilibrium

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad \Delta_r H^o = -31.6 \text{ kJ mol}^{-1}$$

a) Write the expression for the thermodynamic equilibrium constant, *K.* **(1 mark)**

b) What would happen to the concentration of NH_4^+ if the temperature were increased? Briefly explain your answer. **(1 mark)**

c) What would happen to the pressure of NH_3 above the solution if a small amount of acid such as HCl were added to the solution? Briefly Explain your answer. **(1 mark)**

13. a) Determine the pH of a buffer solution (100.0 mL) containing 0.150 mol L^{-1} ammonia and 0.120 mol L^{-1} ammonium chloride. $K_b(NH_3) = 1.76 \times 10^{-5}$. **(3 marks)**

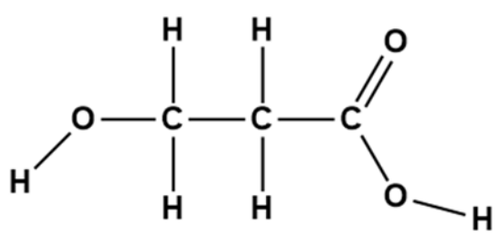
b) Determine the pH of the same buffer solution in a), but after the addition of 15.0 mL of 0.0500 mol L^{-1} HCl solution. **(4 marks)**

14. 3-Hydroxypropanoic acid ($C_3H_5O_3H$) is an organic acid used in polymer plastics. It is a weak acid with a $K_a = 1.3x10^{-5}$. In an experiment, a 25.00 mL aliquot of 0.2750 mol L^{-1} 3-hydroxypropanoic acid is titrated with 0.1500 mol L^{-1} NaOH.

a) What volume of NaOH solution is required to reach the equivalence point of the titration? **(1 mark)**

b) What is the pH at the equivalence point of the titration? **(4 marks)**

c) The structure of 3-hydroxypropanoic acid is show to the left. Circle the acidic hydrogen and briefly explain why you chose it. **(2 marks)**



15. The K_{sp} of aluminum hydroxide is 1.3×10^{-33}. What is the concentration in mol L^{-1} of Al^{3+} in a saturated aqueous solution when the pH is buffered at 9.50? **(3 marks)**

16. The K_{sp} of $PbCl_2$ is 1.2×10^{-5}. If a 500.0 mL solution is 1.0×10^{-4} mol L^{-1} in NaCl, how many mg of $Pb(NO_3)_2$ can be added before a precipitate occurs? **(3 marks)**

17. Given the thermochemical information in the table to the right.

	$\Delta_f H^\circ$ / kJ mol^{-1}	S° / J K^{-1} mol^{-1}
$Al(OH)_3(s)$	-1284	85.4
$Al^{3+}(aq)$	-538.4	-325
$OH^-(aq)$	-230.02	-10.90

a) Compute the standard enthalpy change, $\Delta_r H^\circ$, the standard entropy change, $\Delta_r S^\circ$, and the 298 K Gibbs energy change, $\Delta_r G^\circ$, for the following dissolution of aluminum hydroxide. **(3 marks)**

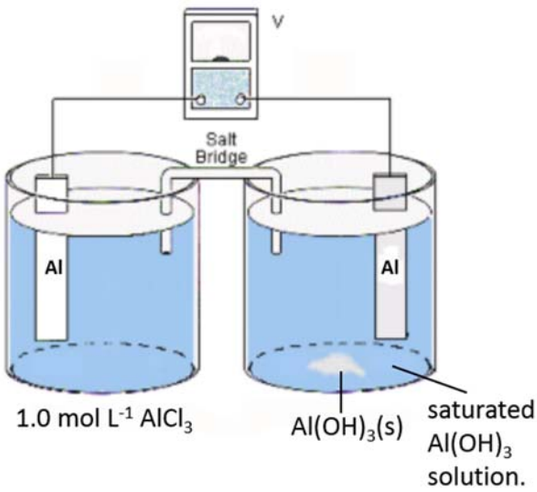
$$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3\ OH^-(aq)$$

b) Determine the equilibrium constant, K_{sp}, for the dissolution of $Al(OH)_3$ at 298 K. **(3 marks)**

c) Determine $\Delta_r G$ when the pH of the solution is 9.50 and the concentration of Al^{3+} is 1.0×10^{-5}. **(3 marks)**

d) What does the sign of $\Delta_r G$ determined in d) tell us about the direction of the reaction? **(1 mark)**

18. To the right is a concentration cell. The half-cell on the right-hand side is composed of a saturated $Al(OH)_3$ solution, a salt which is not very soluble and an aluminum electrode. The left half-cell also has an aluminum electrode in a 1.0 mol L^{-1} Al^{3+} solution.



a) Indicate in the diagram in which direction the electrons spontaneously flow in this cell. Explain your answer. Note that the concentration of Al^{3+} in the right half-cell is far less than 1.0 mol L^{-1}. **(2 marks)**

b) Based on your answer in a) which half-cell is the anode and which is the cathode? Label them on the figure. **(1 mark)**

c) The cell potential for the Al concentration cell was measured to be 0.17 V. Determine the concentration of Al^{3+}, $[Al^{3+}]$ in the saturated $Al(OH)_3$ solution in the half-cell. **(3 marks)**

d) Based on the $[Al^{3+}]$ determined in c), which is the solubility of $Al(OH)_3$, determine the K_{sp} of $Al(OH)_3$. **(2 marks)**

e) Determine $\Delta_r G$ and $\Delta_r G^\circ$ for the electrochemical cell. **(3 marks)**

19. The industrial production of aluminium occurs by electrolysis of molten Al_2O_3 dissolved in Na_3AlF_6.

The simplified reaction is:

$$Al^{3+}(l) + 3e \rightarrow Al(s)$$

What mass of aluminum can be produced if 20.0 A of electricity is passed for 1.0 h? (By the way, this is about 25 cents worth of electricity in NL.) **(3 marks)**

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

$$\ln [\mathrm{A}]_\mathrm{t} = -kt + \ln [\mathrm{A}]_\mathrm{o}$$

$$\frac{1}{[\mathrm{A}]_\mathrm{t}} = kt + \frac{1}{[\mathrm{A}]_\mathrm{o}}$$

$$[\mathrm{A}]_\mathrm{t} = -kt + [\mathrm{A}]_\mathrm{o}$$

$$S_{\text{gas}} = k_H P_{\text{gas}}$$

$$\Delta \mathrm{T_b} = \mathrm{K_b} \times i\mathrm{m}$$

$$\Delta \mathrm{T_f} = \mathrm{K_f} \times i\mathrm{m}$$

$$\Pi = i(\mathrm{MRT})$$

$$\mathrm{P_{solvent}} = \frac{n_{\text{solvent}}}{in_{\text{solute}} + n_{\text{solvent}}} \times \mathrm{P^o_{solvent}}$$

$$\mathrm{P_{solvent}} = \mathrm{X_{solvent}} \times \mathrm{P^o_{solvent}}$$

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

$$\ln \frac{\mathrm{K_2}}{\mathrm{K_1}} = \frac{-\Delta_\mathrm{r}H^o}{\mathrm{R}}\left(\frac{1}{\mathrm{T_2}} - \frac{1}{\mathrm{T_1}}\right) = \frac{\Delta_\mathrm{r}H^o}{\mathrm{R}}\left(\frac{1}{\mathrm{T_1}} - \frac{1}{\mathrm{T_2}}\right)$$

$$\ln K = \frac{-\Delta_\mathrm{r}H^o}{\mathrm{RT}} + \frac{\Delta_\mathrm{r}S^o}{\mathrm{R}}$$

$$K_\mathrm{P} = K_\mathrm{C}(RT)^{\Delta n_{\text{gases}}}$$

$$\Delta_\mathrm{r}G^\mathrm{o} = -\mathrm{RT}\ \ln K$$

$$\Delta_\mathrm{r}G^\mathrm{o} = -\mathrm{nF}E^\mathrm{o}_{\text{cell}}$$

$$E^\mathrm{o}_{\text{cell}} = \frac{\mathrm{RT}}{\mathrm{nF}} \ln K$$

$$E^\mathrm{o}_{\text{cell}} = \frac{0.0257\ \mathrm{V}}{\mathrm{n}} \ln K \quad \text{at } 25\ ^\mathrm{o}\mathrm{C}$$

$$E_{\text{cell}} = E^\mathrm{o}_{\text{cell}} - \frac{\mathrm{RT}}{\mathrm{nF}} \ln Q$$

$$E_{\text{cell}} = E^\mathrm{o}_{\text{cell}} - \frac{0.0257\ \mathrm{V}}{\mathrm{n}} \ln Q \quad \text{at } 25\ ^\mathrm{o}\mathrm{C}$$

$$\Delta_\mathrm{r}G^\mathrm{o} = \Delta_\mathrm{r}H^\mathrm{o} - \mathrm{T}\,\Delta_\mathrm{r}S^\mathrm{o}$$

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

$$\Delta_\mathrm{r}G = \Delta_\mathrm{r}G^\mathrm{o} + \mathrm{RT}\ \ln Q$$

$$\mathrm{R} = 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$$
$$= 0.08314\ \mathrm{bar\ L\ K^{-1}\ mol^{-1}}$$

$$\mathrm{F} = 96\,485\ \mathrm{C\ mol^{-1}}$$

$$\mathrm{J} = \mathrm{kg\ m^2\ s^{-1}}$$

Chemistry 1051

PERIODIC TABLE OF THE ELEMENTS

atomic mass — 6 C 12.0107 — atomic number

KEY

1																	18
1 H 1.0079	2											13	14	15	16	17	2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.0107	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.1797
11 Na 22.9898	12 Mg 24.3050	3	4	5	6	7	8	9	10	11	12	13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.065	17 Cl 35.453	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9380	26 Fe 55.8475	27 Co 58.9332	28 Ni 58.6934	29 Cu 63.546	30 Zn 65.409	31 Ga 69.723	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.798
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.9055	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.75	52 Te 127.60	53 I 126.9045	54 Xe 131.29
55 Cs 132.9054	56 Ba 137.327	57 La 139.9055	72 Hf 178.49	73 Ta 180.9479	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.9665	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.9804	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (269)	109 Mt (268)									

d-block

Lanthanides	58 Ce 140.116	59 Pr 140.9077	60 Nd 144.24	61 Pm (147)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.9303	68 Er 167.259	69 Tm 168.9342	70 Yb 173.04	71 Lu 174.967
Actinides	90 Th 232.0381	91 Pa 231.0359	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Parenthesis Indicates the most stable isotope

SOME USEFUL CONSTANTS

Quantity and Symbol	Value	Quantity and Symbol	Value
ΔH_{fusion}, $H_2O(s)$ at 273 K	6.01 kJ mol^{-1}	Rydberg constant, R_H	1.0973 x 10^{7} m^{-1}
$\Delta H_{vaporization}$, $H_2O(\ell)$ at 373 K	40.7 kJ mol^{-1}	Velocity of light in a vacuum, c	2.998 x 10^{8} m s^{-1}
Specific Heat Capacity of $H_2O(\ell)$	4.184 J g^{-1} K^{-1}	Planck's Constant, h	6.626 x 10^{-34} J s
Specific Heat Capacity of $H_2O(s)$ at 0°C	1.960 J g^{-1} K^{-1}	Density of $H_2O(\ell)$ (near 0°C)	1.000 g mL^{-1}

Faraday Constant, F 9.6485 x 10^4 C mol^{-1} Avogadro Constant, N 6.022 x 10^{23} particles·mol^{-1}

Ideal Gas Constant, R 8.314 L kPa mol^{-1} K^{-1} = 8.314 J mol^{-1} K^{-1} = 8.206 x 10^{-2} L atm mol^{-1} K^{-1} = 0.08314 L bar mol^{-1} K^{-1}

CONVERSION FACTORS

1 bar = 10^5 Pa = 100 kPa = 750.1 mmHg = 750.1 torr = 0.9869 atm

1 L = 1 dm^3 (exactly)

1 L bar = 100 J

1 cal = 4.184 J (exactly)

K_w = 1.008 x 10^{-14} at 25ºC

Do not turn the paper over until you are told that you may do so.

You may not leave the examination room during the first half hour or during the last half hour of the examination.

At the end of the examination:
When you are told to stop writing you must do so.

ACADEMIC OFFENCES

Academic offences shall be deemed to include, but shall not be limited to, the following:

1. **Cheating on examinations, theses, assignments, work term reports, projects, internship reports, or any other tests.**
   Cheating includes copying from another student's work or allowing another student to copy from one's own work, consulting with any unauthorized person during an examination or test, or using unauthorized aids; or knowingly recording or reporting false empirical or statistical data. The work referred to includes examinations, theses, assignments, work term reports, projects, internship reports, or any other tests which are to be used in judging the student's performance in a course or programme of study, or on any special tests which the University may offer.
2. **Impersonating another student or allowing oneself to be impersonated**.
   By impersonation is meant the imitation of a student or entrance into an arrangement with another person to be impersonated for purposes of taking examinations or tests or carrying out laboratory or other assignments.
3. **Plagiarism.**
   Plagiarism is the act of presenting the ideas or works of another as one's own. This applies to all material such as essays, laboratory reports, work term reports, design projects, seminar presentations, statistical data, computer programmes and research results. The properly acknowledged use of sources is an accepted and important part of scholarship. Use of such material without acknowledgement, however, is contrary to accepted norms of academic behaviour.
4. **Theft of examination papers or other material.**
   By theft is meant obtaining by any improper means examination papers, tests, or any other such material.
5. **Use and/or distribution of stolen material.**
   The use of material which the student knows to have been improperly obtained and/or the distribution of such material is considered to be an academic offence.
6. **Submitting false information**.
   This offence includes falsifying academic forms or records, submitting false credentials, medical or other certificates, or making a false, misleading or incomplete declaration to the University.
7. **Submitting work for one course which has been or is being submitted for another course without express permission to do so.**
   This includes the presentation of an essay, report or assignment to satisfy some or all of the requirements of a course when that essay, report, or assignment has been previously submitted or is concurrently being submitted for another course without the express permission of the professor(s) involved.

NOTE: Procedures to be followed and penalties to be assessed in cases of academic dishonesty are outlined in the University Calendar.