

Memorial University of Newfoundland

Chemistry 1051

Final Examination

Winter 2015

TIME: 3 hours

NAME: _____ MUN STUDENT #: _____

READ THE FOLLOWING CAREFULLY

1. This examination paper has 13 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. These are on the last page 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 previous page and indicate clearly where 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.

QUESTIONS	VALUE	MARK
Part A		
A1–A10	17	
Part B		
B1–B2	10	
B3	6	
B4–B5	11	
B6	7	
B7–B8	12	
B9–B11	12	
B12	10	
B13	4	
B14	11	
TOTAL	100	

Part A Short Answer Questions

Value = 17 points

[2] A1. State two reasons why collisions do not always result in product formation.

[1] A2. Briefly explain the difference between the equivalence point and the endpoint of a titration.

[2] A3. Define
Lewis base

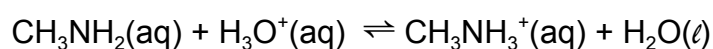
Brönsted acid

[1] A4. Explain the purpose of a salt bridge in a voltaic cell.

[1] A5. State the second law of thermodynamics.

[2] A6. What are ion pairs? How do they affect the solubility of a slightly soluble compound e.g. Ca(OH)_2 ?

- [2] A7. Given $K_b \text{CH}_3\text{NH}_2 = 4.3 \times 10^{-4}$ at 25°C , determine the value of the equilibrium constant K for the following reaction:



- [1] A8. Explain what is meant by the steady state approximation.

- [2] A9. Estimate the boiling point of benzene (liquid and vapor are in equilibrium) from the following data:

$$\Delta_{\text{vap}}H^\circ = 33.90 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{vap}}S^\circ = 96.51 \text{ J K}^{-1} \text{ mol}^{-1}$$

- [3] A10. A plot of $\left(\frac{1}{[A]}\right)$ versus time in seconds for the reaction

$A \rightarrow \text{products}$ gave a straight line with a slope equal to $1.49 \text{ L mol}^{-1} \text{ s}^{-1}$ and an intercept equal to 100.2 L mol^{-1} .

What is the order of the reaction with respect to $[A]$? _____

Determine the rate constant: _____

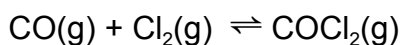
How long is the **second** half-life period? _____

Part B Longer Answer Questions

Value 83 points

[Marks]

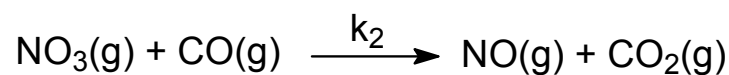
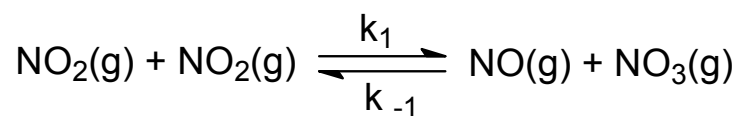
- B1. The following experimental data were obtained for the formation of phosgene COCl_2 at a particular temperature:



[CO] (mol L ⁻¹)	[Cl ₂] (mol L ⁻¹)	Initial rate of reaction (mol L ⁻¹ s ⁻¹)
0.0500	0.250	3.64×10^{-5}
0.100	1.00	1.46×10^{-4}
0.150	0.250	1.09×10^{-4}

- [4] (a) Determine the order of the reaction for each reactant.
- [1] (b) Determine the **overall order** of the reaction. Answer: _____
- [2] (c) Calculate the rate constant at this temperature.
- [3] B2. The activation energy for the decomposition of iodoethane was determined by measuring the rate constants at two different temperatures. At 600 K the rate constant was found to be $1.6 \times 10^{-5} \text{ s}^{-1}$ and at 700 K it was $6.36 \times 10^{-3} \text{ s}^{-1}$. What was the activation energy?

- [6] B3. The reaction between NO_2 and CO is proposed to occur by the following mechanism.



- (a) Define the rate of reaction in terms of the rate of formation of $\text{CO}_2(\text{g})$. 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**

(i) at the beginning of the reaction when there is mostly reactants

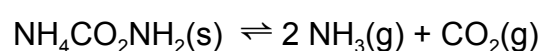
(ii) near the end of the reaction when there is mostly products.

[5] B4. Ammonia, $\text{NH}_3(\text{g})$, at a pressure of 1.35 bar is placed in a container at a certain temperature. When equilibrium is established at that temperature, the pressure of $\text{H}_2(\text{g})$ is 0.630 bar.

(a) Determine the value of K_p for the decomposition of NH_3 at that temperature
 $2 \text{NH}_3(\text{g}) \rightleftharpoons 3 \text{H}_2(\text{g}) + \text{N}_2(\text{g})$.

(b) Determine the mole fraction of NH_3 in the gas mixture at equilibrium.

[6] B5. When heated, solid ammonium carbonate decomposes as follows:



$K = 4.95 \times 10^{-3}$ at 90°C .

(a) Calculate the total pressure in a flask at 90°C when equilibrium has been established.

(b) Calculate **the minimum mass** of $\text{NH}_4\text{CO}_2\text{NH}_2$ (molar mass = 78.07 g mol^{-1}) needed to reach equilibrium in a 10.0 L container at 90°C .

- [7] B6. Calculate $[\text{H}_2\text{SO}_4]$, $[\text{HSO}_4^-]$, $[\text{SO}_4^{2-}]$ and the pH of 0.020 M $\text{H}_2\text{SO}_4(\text{aq})$ at 25 °C. K_{a_1} H_2SO_4 is very large and K_{a_2} $\text{H}_2\text{SO}_4 = 1.0 \times 10^{-2}$ at 25 °C.

[6] B7. A 32.00 mL volume of 0.1800 mol L⁻¹ HOCN(aq), a weak acid, is titrated with 0.2400 mol L⁻¹ NaOH(aq). K_a HOCN = 3.3×10^{-4} at 25 °C.

(a) Calculate the equivalence volume for the titration.

(b) Calculate the pH at the equivalence point.

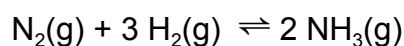
[6] B8. Calculate the number of moles of NaOH which must be added to 2.000 L of a 0.2500 mol L⁻¹ aqueous solution of HCHO₂(HCOOH) to give a buffer of pH = 4.00. Assume no change in solution volume.
 K_a HCHO₂(HCOOH) = 1.8×10^{-4}

- [3] B9. Determine the molar solubility of $\text{Mg}(\text{OH})_2$. $K_{\text{sp}} \text{Mg}(\text{OH})_2 = 1.8 \times 10^{-11}$ at 25°C .
- [4] B10. Determine whether or not a precipitate of PbBr_2 will form when 200.0 mL of $0.0200 \text{ mol L}^{-1} \text{Pb}(\text{NO}_3)_2(\text{aq})$ is mixed with 300.0 mL of $0.0400 \text{ mol L}^{-1} \text{KBr}(\text{aq})$. $K_{\text{sp}} \text{PbBr}_2 = 4.67 \times 10^{-6}$ at 25°C .
- [5] B11. What initial concentration of the weak base hydroxylamine, HONH_2 ($K_{\text{b}} = 9.1 \times 10^{-9}$ at 25°C), is required to just precipitate the $\text{Mg}(\text{OH})_2$ from a solution that is $0.0050 \text{ mol L}^{-1}$ in $\text{Mg}(\text{NO}_3)_2$? $K_{\text{sp}} \text{Mg}(\text{OH})_2 = 1.8 \times 10^{-11}$ at 25°C .

Use the following table to help answer question B12.

Data is for P = 1 bar and 25°C		
	$\Delta_f H^\circ$ (kJ mol ⁻¹)	S° (J K ⁻¹ mol ⁻¹)
N ₂ (g)	0	191.5
H ₂ (g)	0	130.6
NH ₃ (g)	-46.1	192.3

[3] B12. (a) Calculate $\Delta_r G^\circ$ for the following reaction at 25°C.



[1] (b) Account for the sign of $\Delta_r S^\circ$. Give your reasoning.

[3] (c) Calculate the value of K_p for the reaction at 300.0°C. State any assumptions required.

[2] (d) Calculate $\Delta_r G$ at 300.0°C when $P(\text{N}_2) = 3.00$ bar $P(\text{H}_2) = 12.00$ bar and $P(\text{NH}_3) = 0.0010$ bar.

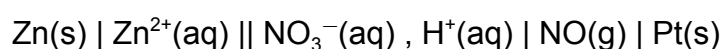
[1] (e) Is the reaction to form NH₃ spontaneous under these conditions? Explain briefly.

- [4] B13. A current of 2.68 A is passed through 455 mL of 0.366 mol L⁻¹ CuSO₄(aq) for 282 seconds depositing copper metal at the cathode. Determine the mass of copper deposited.

Data from the following table is applicable to question B14.

	<i>E</i> ^o volts at 25°C
$\text{Cl}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{Cl}^-(\text{aq})$	1.358
$\text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow 2 \text{H}_2\text{O}(\ell)$	1.229
$\text{NO}_3^-(\text{aq}) + 4 \text{H}^+(\text{aq}) + 3 \text{e}^- \rightarrow \text{NO}(\text{g}) + 2 \text{H}_2\text{O}(\ell)$	0.956
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	0.800
$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g})$	0.00
$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.760

- B14. Consider a voltaic cell at standard conditions at 25°C represented by the following.



- [1] (a) Fill in the blanks below with appropriate answers.

$$[\text{Zn}^{2+}] = \underline{\hspace{2cm}} \quad P_{\text{NO}} = \underline{\hspace{2cm}}$$

- [1] (b) Indicate the direction of electron movement in the cell.

- [1] (c) The half-cells are connected by a salt bridge containing KNO₃. Towards which electrodes do the K⁺ and NO₃⁻ ions move?

- [1] (d) Determine the **cell potential** at standard conditions.
- [2] (e) **Write** the balanced equation for the cell reaction at standard conditions.
- [1] (f) Determine $\Delta_r G^\circ$ for the cell reaction.
- [2] (g) Determine the cell potential for the following conditions:
 $P_{\text{NO}} = 0.200 \text{ bar}$, $[\text{Zn}^{2+}] = 0.10 \text{ M}$, $[\text{NO}_3^-] = 0.50 \text{ M}$, $\text{pH} = 4.00$.
- [2] (h) When a Zn^{2+}/Zn half cell is combined with a Ti^{2+}/Ti half cell at standard conditions, $E^\circ = +0.867 \text{ V}$. Determine the standard reduction potential E° for $\text{Ti}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Ti}(\text{s})$ if the titanium (Ti) electrode is the anode.

Chemistry 1051 Equations

$$[A]_t = -kt + [A]_o$$

$$\ln[A]_t = -kt + \ln [A]_o \text{ or } \ln \left(\frac{[A]_t}{[A]_o} \right) = -kt$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$$

$$\ln \left(\frac{k_2}{k_1} \right) = \frac{-E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad k = Ae^{-E_a/RT}$$

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

$$K_p = K_c (RT)^{\Delta n}$$

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

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

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

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

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

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

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

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

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

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 0.08314 \text{ bar L K}^{-1} \text{ mol}^{-1}$$

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

Chemistry 1051

PERIODIC TABLE OF THE ELEMENTS

6 C 12.0107	atomic number
atomic mass	

KEY

1 H 1.0079																	18 He 4.0026
3 Li 6.941	4 Be 9.0122	← d-block →										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											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)									

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
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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)
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Parenthesis Indicates the most stable isotope

SOME USEFUL CONSTANTS

Quantity and Symbol	Value	Quantity and Symbol	Value
ΔH_{fusion} , $\text{H}_2\text{O}(\text{s})$ at 273 K	6.01 kJ mol ⁻¹	Rydberg constant, R_H	1.0973 x 10 ⁷ m ⁻¹
$\Delta H_{\text{vaporization}}$, $\text{H}_2\text{O}(\ell)$ 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 $\text{H}_2\text{O}(\ell)$	4.184 J g ⁻¹ K ⁻¹	Planck's Constant, h	6.626 x 10 ⁻³⁴ J s
Specific Heat Capacity of $\text{H}_2\text{O}(\text{s})$ at 0°C	1.960 J g ⁻¹ K ⁻¹	Density of $\text{H}_2\text{O}(\ell)$ (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 = 10⁵ Pa = 100 kPa = 750.1 mmHg = 750.1 torr = 0.9869 atm
 1 L = 1 dm³ (exactly)
 1 cal = 4.184 J (exactly)
 1 L bar = 100 J

SOME USEFUL FORMULAS

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

$$K_p = K_c (RT)^{\Delta n}$$

$$k = Ae^{\frac{-E_a}{RT}} \quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

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.