

Memorial University of Newfoundland

Chemistry 1051

Final Examination

Winter 2016

TIME: 3 hours

NAME: _____ MUN STUDENT #: _____

READ THE FOLLOWING CAREFULLY

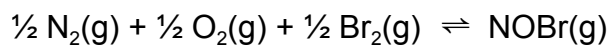
1. This examination paper has 13 numbered pages. Ensure that this examination is complete.
2. Failure to submit this paper in its entirety at the end of the examination may result in disqualification.
3. A Periodic Table and physical constants are provided. These are on the last page of the examination 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–B10	8	
B11	10	
B12–B13	8	
B14	11	
TOTAL	100	

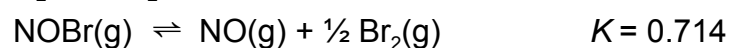
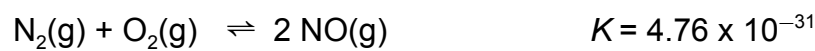
Part A Short Answer Questions**Value = 17 points**

- [1] A1. Give an example of a diprotic acid.
- [1] A2. Briefly describe the leveling effect.
- [1] A3. The solubility, of CO_2 in water at 25°C is $8.5 \times 10^{-3} \text{ mol L}^{-1}$ when the pressure of CO_2 above the solution is 0.250 bar. Calculate the Henry's law constant k_{H} for CO_2 in water at 25°C .
- [2] A4. Give two reasons why a collision between reactants does not result in product formation.
- [2] A5. Consider the following reaction: $\text{CO}_2(\text{g}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{HCO}_3^-(\text{aq})$. Draw Lewis structures for the reactants and show how this reaction takes place according to Lewis acid/Lewis base theory. Explain briefly.
- [1] A6. Explain why a 0.10 m ($m = \text{mol kg}^{-1}$) CaCl_2 solution has a higher boiling point than a 0.10 m solution of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$).

- [3] A7. Determine K for the reaction at 298 K



from the following data at 298 K:



- [1] A8. **Given:** $2 \text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3 \text{H}_2(\text{g})$. What is the rate of disappearance of NH_3 when the rate of formation of H_2 is $3.00 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$?

- [3] A9. Briefly explain how a catalyst acts to increase the rate of a chemical reaction.

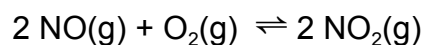
- [2] A10. A buffer contains lactic acid $\text{HC}_3\text{H}_5\text{O}_3(\text{aq})$ and sodium lactate $\text{NaC}_3\text{H}_5\text{O}_3(\text{aq})$. What ratio of $[\text{NaC}_3\text{H}_5\text{O}_3]$ to $[\text{HC}_3\text{H}_5\text{O}_3]$ is required to give a $\text{pH} = 3.50$? $K_a \text{HC}_3\text{H}_5\text{O}_3 = 1.4 \times 10^{-4}$ at 25°C .

Part B Longer Answer Questions

Value 83 points

[Marks]

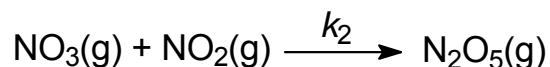
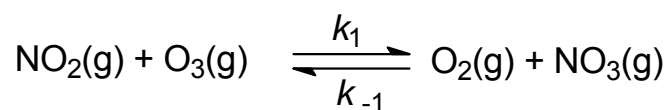
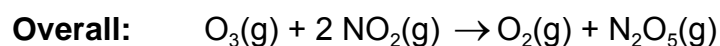
- B1. The following experimental data were obtained for the following reaction at 1000 K:



[NO] (mol L ⁻¹)	[O ₂] (mol L ⁻¹)	Initial rate of reaction (mol L ⁻¹ s ⁻¹)
0.0100	0.0200	3.02 x 10 ⁻⁵
0.0200	0.0500	3.02 x 10 ⁻⁴
0.0300	0.0200	2.72 x 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 conversion of C₅H₁₁Br to C₅H₁₀ and HBr follows first order kinetics with a half-life of 9.35 x 10³ seconds. How long will it take for 85.0% of a sample of C₅H₁₁Br to decompose to products?

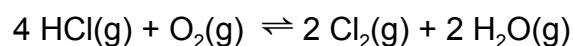
- [6] B3. The reaction between O_3 and NO_2 is proposed to occur by the following mechanism.



- (a) Define the rate of reaction in terms of the rate of formation of $N_2O_5(g)$. Apply the steady-state approximation to the concentration of any intermediates and determine the rate law for the reaction.
- (b) Under what set of conditions is the reaction second order in NO_2 ? Backup your answer by showing how the rate law from part(a) is affected by your chosen set of conditions.

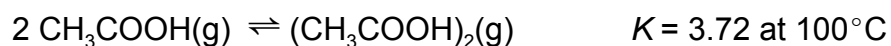
[6] B4. HCl at a pressure of 2.300 bar and O₂ at a pressure of 1.00 bar are placed in a container and allowed to come to equilibrium at 750 K. When equilibrium is established, the total pressure of the gases present is 2.835 bar.

(a) Determine the value of K at 750 K for the reaction:



(b) If a catalyst were present in the container, would the total pressure at equilibrium be increased, decreased or remain the same? Explain your answer briefly.

[5] B5. Acetic acid forms hydrogen bonded dimers in the gas phase.



A sample of pure acetic acid is placed in a container and allowed to come to equilibrium at 100°C. The pressure of the dimer in the equilibrium mixture was 0.576 bar. Determine the initial pressure of acetic acid.

- [7] B6. Calculate $[\text{H}_2\text{C}_2\text{O}_4]$, $[\text{HC}_2\text{O}_4^-]$, $[\text{C}_2\text{O}_4^{2-}]$ and the pH of 0.020 M $\text{H}_2\text{C}_2\text{O}_4(\text{aq})$ at 25°C. For $\text{H}_2\text{C}_2\text{O}_4$, $K_{a_1} = 6.0 \times 10^{-2}$ and $K_{a_2} = 6.1 \times 10^{-5}$ at 25°C.

[6] B7. A 32.00 mL volume of 0.1800 mol L⁻¹ CH₃NH₂(aq), a weak base, is titrated with 0.2400 mol L⁻¹ HCl(aq). K_b CH₃NH₂ = 4.4 × 10⁻⁴ at 25 °C.

(a) Calculate the equivalence volume for the titration.

(b) Calculate the pH at the equivalence point.

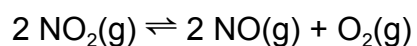
- [6] B8. Calculate the number of moles of HCl which must be dissolved in 500.0 mL of a 0.600 mol L^{-1} aqueous solution of NaF to give a buffer of $\text{pH} = 3.00$. Assume no change in solution volume. $K_a \text{ HF} = 3.5 \times 10^{-4}$ at 25°C .

- [3] B9. Determine the molar solubility of $\text{Ni}(\text{OH})_2$ in a solution buffered at $\text{pH} = 7.00$. $K_{\text{sp}} \text{Ni}(\text{OH})_2 = 5.48 \times 10^{-16}$ at 25°C .
- [5] B10. Determine the **maximum mass** of NaOH that can be added to 200.0 mL of $0.0200 \text{ mol L}^{-1} \text{CaCl}_2(\text{aq})$ before precipitation of $\text{Ca}(\text{OH})_2$ occurs. $K_{\text{sp}} \text{Ca}(\text{OH})_2 = 4.68 \times 10^{-6}$ at 25°C .

Use the following table to help answer question B11.

Data is for P = 1 bar and 25°C		
	$\Delta_f H^\circ$ (kJ mol ⁻¹)	S° (J K ⁻¹ mol ⁻¹)
NO ₂	33.2	240.1
NO	91.3	210.8
O ₂	0	205.2

[3] B11. (a) Calculate $\Delta_r G^\circ$ for the following reaction at 25°C.



[1] (b) Does the sign of the entropy change for the reaction make sense? Briefly explain your answer.

[3] (c) Determine the temperature at which the reaction becomes spontaneous at standard conditions. State any assumptions required.

[3] (d) Determine the value of K_p at 1000 K.

- [4] B12. A current of 3.000 amperes is passed through 0.500 mol L⁻¹ MCl₃(aq) for 29.07 minutes depositing 3.561 grams of metal M at the cathode. Identify metal M.

Data from the following table is applicable to questions B13 and B14.

	<i>E</i> [°] / V at 25°C
Cl ₂ (g) + 2 e ⁻ → 2 Cl ⁻ (aq)	1.36
Br ₂ (ℓ) + 2 e ⁻ → 2 Br ⁻ (aq)	1.09
NO ₃ ⁻ (aq) + 4 H ⁺ (aq) + 3 e ⁻ → NO(g) + 2 H ₂ O(ℓ)	0.96
Ag ⁺ (aq) + e ⁻ → Ag(s)	0.80
Cu ²⁺ (aq) + 2 e ⁻ → Cu(s)	0.34
Zn ²⁺ (aq) + 2 e ⁻ → Zn(s)	-0.76

- [2] B13. (a) Will Br₂(ℓ) oxidize Cl⁻(aq) to form Cl₂ at standard conditions? Explain your answer briefly.
- [2] (b) Which metal, Ag, Cu or Zn would be easiest to oxidize as the anode of an electrolytic cell? Explain briefly.

- [3] B14. A Cu^{2+}/Cu half cell and an Ag^+/Ag half cell are connected using a salt bridge to make a Galvanic cell at 25°C .
- (a) What is the cell potential and cell reaction at standard conditions?
- [2] (b) Identify the anode, the cathode and the direction of electron movement.
- [1] (c) The half-cells are connected by a salt bridge containing KNO_3 . Towards which electrodes do the K^+ and NO_3^- ions move?
- [2] (d) Find $\Delta_r G^\circ$ and K for the cell reaction at 25°C .
- [2] (e) If the cell potential is 0.36 volts and the concentration of Cu^{2+} is 0.100 mol L^{-1} , what is the concentration of Ag^+ in the cell?
- [1] (f) Find $\Delta_r G$ for the cell in part (e).

$$k = Ae^{-E_a/RT}$$

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

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

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

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

$$\Delta T_b = K_b \times im$$

$$\Delta T_f = K_f \times im$$

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

$$P_{\text{solvent}} = \frac{n_{\text{solvent}}}{in_{\text{solute}} + n_{\text{solvent}}} \times P_{\text{solvent}}^o$$

$$P_{\text{solvent}} = X_{\text{solvent}} \times P_{\text{solvent}}^o$$

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

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

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

$$K_p = K_c (RT)^{\Delta n_{\text{gases}}}$$

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

$$\Delta_r G^o = -nFE_{\text{cell}}^o$$

$$E_{\text{cell}}^o = \frac{RT}{nF} \ln K$$

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

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

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

$$\Delta_r G^o = \Delta_r H^o - T \Delta_r S^o$$

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

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

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

$$F = 96485 \text{ C mol}^{-1}$$

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

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)									

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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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 L bar = 100 J
 1 cal = 4.184 J (exactly)
 $K_w = 1.008 \times 10^{-14}$ at 25°C

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.