

Memorial University of Newfoundland

Chemistry 1051

Final Examination

Winter 2018

TIME: 3 hours

NAME: _____

MUN STUDENT #:

READ THE FOLLOWING CAREFULLY

1. This examination paper has 12 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–A8	18	
Part B		
B1–B2	12	
B3–B4	10	
B5–B6	10	
B7–B9	9	
B10	10	
B11–B12	11	
B13	7	
B14–B15	9	
TOTAL	96	

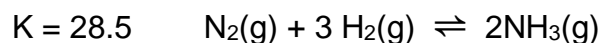
Part A Short Answer Questions

Value 18 points

- [2] A1. Define
Lewis acid

Bronsted base
- [2] A2. Buffer A, 0.50 M $\text{NH}_3(\text{aq})/0.50 \text{ M NH}_4\text{Cl}(\text{aq})$ and Buffer B, 0.20 M $\text{NH}_3(\text{aq})/0.20 \text{ M NH}_4\text{Cl}(\text{aq})$ have the same pH. Consider equal volumes of both buffers. Which buffer is more effective at resisting pH change? Briefly explain your choice.
- [1] A3. A salt bridge in a voltaic cell contains saturated KNO_3 . Toward which electrode do the K^+ ions move when the cell is operating?
- [3] A4. A biochemical engineer isolates a gene fragment and dissolves a 10.0 mg sample in enough water to make 30.0 mL of solution. The osmotic pressure of the solution is 4.53×10^{-5} bar at 25.0°C . Determine the molar mass of the gene fragment.
- [3] A5. Determine the $[\text{Ag}^+]$ in a saturated solution of Ag_2CrO_4 at 25°C .
 $K_{\text{sp}} \text{Ag}_2\text{CrO}_4 = 2.6 \times 10^{-12}$ at 25°C .

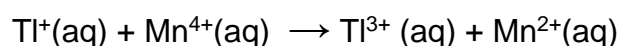
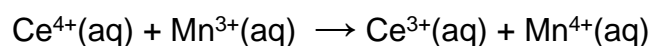
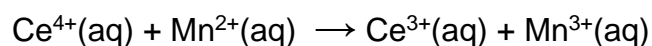
[2] A6. At a particular temperature the following reaction has



Determine K at the same temperature for $\text{NH}_3(\text{g}) \rightleftharpoons \frac{1}{2} \text{N}_2(\text{g}) + \frac{3}{2} \text{H}_2(\text{g})$

[2] A7. The Henry's law constant for CO_2 in water at 25°C is $3.4 \times 10^{-2} \text{ mol L}^{-1} \text{ bar}^{-1}$. Determine the concentration of CO_2 in mol L^{-1} in water exposed to air at a pressure of 1.02 bar containing CO_2 at a mole fraction of 0.0350.

[3] A8. The oxidation of Tl^+ by Ce^{4+} is thought to occur by the following mechanism:



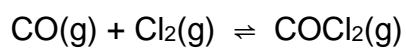
(a) Determine the balanced overall reaction.

(b) Identify any intermediates in the mechanism.

(c) What is the role of Mn^{2+} ?

Part B Longer Answer Questions**Value 82 points****[Marks]**

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

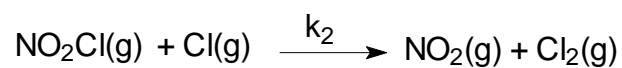
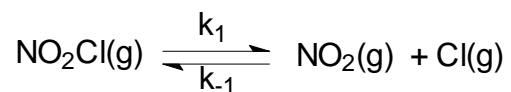
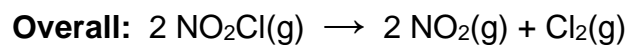


	[CO] (mol L ⁻¹)	[Cl ₂](mol L ⁻¹)	Initial rate of reaction (mol L ⁻¹ s ⁻¹)
1	0.0500	0.225	3.60×10^{-5}
2	0.100	0.900	1.44×10^{-4}
3	0.150	0.225	1.08×10^{-4}

- [4] (a) Determine the order of the reaction for each reactant.

- [2] (b) Calculate the rate constant at this temperature. Include units.

B2. A possible mechanism for the decomposition of NO_2Cl is as follows.



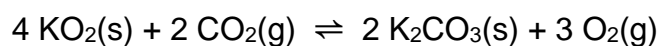
- [5] (a) Define the rate of reaction in terms of the rate of formation of $\text{Cl}_2(\text{g})$. Apply the steady state approximation to the concentration of any intermediates and determine the rate law for the reaction.

- [1] (b) Determine the **simplified rate law** if the concentration of the reactant, NO_2Cl , is very high compared to the concentration of products.

- B3. For the **first order** decomposition of an antibiotic in a person with a normal temperature of 310.15 K, $k = 3.1 \times 10^{-5} \text{ s}^{-1}$. For a person with a fever of 311.95 K, $k = 3.9 \times 10^{-5} \text{ s}^{-1}$.
- [4] (a) Calculate the activation energy E_a for the decomposition of the antibiotic.
- [2] (b) If the person with the fever of 311.95 K must take another pill when $\frac{3}{4}$ of the first pill has decomposed, how many hours should he/she wait to take the second pill?
- [4] B4. Determine the mass of KCl which must be dissolved in 500.0 g of water to lower the freezing point by 2.00°C. $K_f \text{ H}_2\text{O} = 1.86^\circ\text{C kg mol}^{-1}$.

- [5] B5. Determine whether or not $\text{Mg}(\text{OH})_2(\text{s})$ will precipitate in a solution containing $8.0 \times 10^{-4} \text{ mol L}^{-1} \text{Mg}(\text{NO}_3)_2(\text{aq})$ and $0.100 \text{ mol L}^{-1} \text{C}_6\text{H}_5\text{NH}_2(\text{aq})$ at 25°C . $K_b = 7.5 \times 10^{-10}$ at 25°C . $K_{\text{sp}} \text{Mg}(\text{OH})_2 = 2.06 \times 10^{-13}$.

- B6. Consider the following reaction.



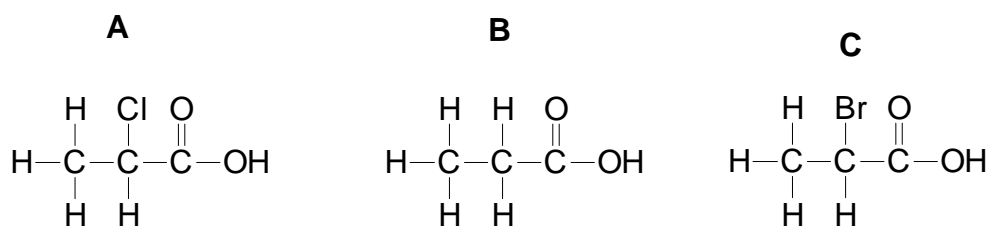
A large excess of $\text{KO}_2(\text{s})$ and $\text{CO}_2(\text{g})$ at a pressure of 2.500 bar are placed in a 10.0 L container and allowed to come to equilibrium at 25°C . At that time, the total pressure of gas was 3.362 bar.

- [5] Calculate K_p for the reaction at 25°C .

[4] B7. Calculate the pH of 0.100 mol L⁻¹ HClO₂(aq) at 25°C. Given K_a for HClO₂ at 25°C is 1.1 x 10⁻².

[3] B8. Determine the pH of a solution formed by mixing 2.00 L of 0.0800 mol L⁻¹ HCl(aq) with 3.00 L of 0.0300 mol L⁻¹ Ba(OH)₂(aq).

[2] B9. Arrange the following acids in order of increasing acid strength. Briefly explain your choice in terms of electron donation/withdrawal.



weakest acid _____ < _____ < _____ strongest acid

B10. 20.00 mL of a $0.1800 \text{ mol L}^{-1}$ solution of the weak acid HOCN(aq) is titrated with $0.2400 \text{ mol L}^{-1}$ NaOH(aq) . $K_a \text{ HOCN} = 3.3 \times 10^{-4}$ at 25°C .

[5] (a) Calculate the pH after 9.00 mL of titrant have been added to the solution of HOCN.

[5] (b) Calculate the pH at the equivalence point of the titration.

B11. Consider the reaction $\text{C}_6\text{H}_6(\text{g}) \rightleftharpoons 3 \text{C}_2\text{H}_2(\text{g})$. Use data in the table below to answer each part of this question.

	S°	$\Delta_f H^\circ \text{ kJ mol}^{-1}$
$\text{C}_2\text{H}_2(\text{g})$	200.96	226.73
$\text{C}_6\text{H}_6(\text{g})$	269.31	82.93

[3] (a) Calculate ΔG° at 298.15 K.

[2] (b) Calculate the temperature for which the reaction is at equilibrium at standard conditions.

[3] (c) Calculate K_p at 1750 K.

[3] B12. Determine whether the synthesis of ammonia is spontaneous at 700 K, when $P_{\text{NH}_3} = 50.0 \text{ bar}$, $P_{\text{H}_2} = 200 \text{ bar}$, $P_{\text{N}_2} = 10.0 \text{ bar}$.



Reduction half-reaction	E° , V
$\text{Cl}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{Cl}^-(\text{aq})$	1.358
$\text{Cr}^{3+}(\text{g}) + \text{e}^- \rightarrow \text{Cr}^{2+}(\text{aq})$	-0.740

B13. Consider a voltaic cell at standard conditions based on half cells constructed from the half-reactions in the table above.

- [2] (a) Write the half-reactions occurring at the anode and the cathode and the overall cell reaction.

anode:

cathode:

cell:

- [1] (b) Calculate E°_{cell} .

- [1] (c) Calculate ΔG° for the cell reaction at 25°C.

- [3] (d) Under a particular set of non-standard conditions, the cell potential $E_{\text{cell}} = 1.958 \text{ V}$ at 25°C, $[\text{Cl}^-] = 0.200 \text{ M}$, $[\text{Cr}^{2+}] = 3.00 \times 10^{-3} \text{ M}$ and $[\text{Cr}^{3+}] = 0.500 \text{ M}$. Calculate the pressure of Cl_2 in bar.

Use the data from the table below to answer question B14.

Reductions half-reaction	E° , V
$\text{Cl}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{Cl}^-(\text{aq})$	+1.358
$\text{Br}_2(\ell) + 2 \text{e}^- \rightarrow 2 \text{Br}^-(\text{aq})$	+1.065
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.771
$\text{I}_2(\text{s}) + 2 \text{e}^- \rightarrow 2 \text{I}^-(\text{aq})$	+0.535
$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.340
$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.760
$\text{Mn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Mn}(\text{s})$	-1.182

- [2] B14. (a) Consider the halogens Cl_2 , Br_2 and I_2 . Which halogen(s) will oxidize $\text{Fe}^{2+}(\text{aq})$ to $\text{Fe}^{3+}(\text{aq})$? Briefly explain your choice.
- [2] (b) An alloy of copper and zinc is made the anode in an electrolytic cell. The voltage is controlled so that only one metal is oxidized. Which one is it? Explain your choice.
- [1] (c) What is the best reducing agent in the table above? Briefly explain your choice.
- [4] B15. Determine the time in hours needed to deposit 10.0 g of chromium on a car bumper as a cathode immersed in a solution of $\text{CrCl}_3(\text{aq})$ using a current of 25.0 amperes.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\Delta P_{\text{solvent}} = X_{\text{solute}} \times P_{\text{solvent}}^\circ$$

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

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

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

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

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

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

$$Q = It \quad Q = n_e F$$

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

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} , H ₂ O(s) at 273 K	6.01 kJ mol ⁻¹	Rydberg constant, R _H	1.0973 x 10 ⁷ m ⁻¹
$\Delta H_{\text{vaporization}}$, H ₂ O(l) 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 ₂ O(l)	4.184 J g ⁻¹ K ⁻¹	Planck's Constant, h	6.626 x 10 ⁻³⁴ J s
Specific Heat Capacity of H ₂ O(s) at 0°C	1.960 J g ⁻¹ K ⁻¹	Density of H ₂ O(l) (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 x 10⁻¹⁴ at 25°C
 0 °C = 273.15 K