NAME:	Section: Student Number:
Spring 2020	Chemistry 2000 Midterm #2A/ 65 marks
INSTRUCTIONS:	<ol> <li>Please read over the test carefully before beginning. You should have 8 pages of questions, a blank "overflow" page and two pages of data sheets with periodic table.</li> <li>If your work is not legible, it will be given a mark of zero.</li> <li>Marks will be deducted for incorrect information added to an otherwise correct answer.</li> <li>Marks will be deducted for improper use of significant figures and for missing or incorrect units.</li> <li>Show your work for all calculations. Numerical answers without supporting calculations will not be given full credit.</li> <li>You may use a calculator but only for the purposes of calculation. No text-capable calculators are allowed.</li> <li>You have 90 minutes to complete this test.</li> </ol>

### **Confidentiality Agreement:**

I agree not to discuss (or in any other way divulge) the contents of this exam until after 8:30 pm Mountain Time on Tuesday, March 17<sup>th</sup>, 2020. I understand that breaking this agreement would constitute academic misconduct, a serious offense with serious consequences. The minimum punishment would be a mark of 0/65 on this exam and removal of the "overwrite midterm mark with final exam mark" option for my grade in this course; the maximum punishment would include expulsion from this university.

Date:

Signature: \_\_\_\_\_ Course: CHEM 2000 (General Chemistry II) Semester: Spring 2020 The University of Lethbridge

 Question Breakdown

 Q1
 / 7

 Q2
 / 6

 Q3
 / 13

 Q4
 / 10

 Q5
 / 3

 Q6
 / 8

 Q7
 / 18

**Total** / 65

1.

[4 marks]

- (a) Complete each statement with one of the following symbols: >, < or =For an allowed process at constant temperature and pressure,
  - i.  $\Delta S_{universe} > 0$ ii.  $\Delta G < 0$ E > 0iii. K > 0iv.
- One of the statements in part (a) is true under any conditions (not just at constant temperature and (b) pressure). Which one? [1 mark]

 $\Delta S_{universe} > 0$ 

(c) In statement (a) i., why do we have to write  $\Delta S_{universe}$ ? Why can't we just write  $\Delta S$ ? [1 mark]

 $\Delta S$  refers to the entropy change for the system only.  $\Delta S_{universe}$  also includes the entropy change for the surroundings, and the second law of thermodynamics states that the entropy of the universe must increase in any thermodynamically allowed process.

(d) In statement ii. in part (a), can  $\Delta G$  be replaced by  $\Delta G^{\circ}$ ? Why or why not? [1 mark] No.

 $\Delta G^{\circ}$  refers specifically to the free energy change of a reaction under standard conditions.  $\Delta G$ refers to the free energy change of a reaction under whatever conditions it is actually being run.

- Consider the following reaction that takes place in aqueous acid. 2. [6 marks]  $Cr_2 O_{7(aa)}^{2-} + Zn_{(s)} \rightarrow Zn_{(aa)}^{2+} + Cr_{(aa)}^{3+}$ Balance this equation under acidic conditions. [3 marks] (a) For full marks, your answer must include balanced half reactions.  $(Zn_{(s)} \rightarrow Zn_{(aa)}^{2+} + 2e^{-}) \times 3$  $Cr_2 O_{7(aq)}^{2-} + 14 H_{(aq)}^+ + 6 e^- \rightarrow 2 Cr_{(aq)}^{3+} + 7 H_2 O_{(l)}$  $Cr_2 O_{7(aq)}^{2-} + 3 Zn_{(s)} + 14 H_{(aq)}^+ \rightarrow 2 Cr_{(aq)}^{3+} + 3 Zn_{(aq)}^{2+} + 7 H_2 O_{(l)}$ (b) Identify the oxidizing agent. [1 mark]  $Cr_2 O_7^{2-}$
- Identify the reducing agent. (c) [1 mark] Zn
- What is  $v_e$  for this reaction? [1 mark] (d)
  - 6

Section: \_\_\_\_ Student Number:\_\_

[1 mark]

3. Ethene, essential in making plastics, can be produced electrolytically from carbon dioxide and water using surplus electricity. The two half-reactions involved are shown below. [13 marks] *Water is written in the gas phase for consistency with later parts of the question which will deal with this process at high temperature.* 

cathode 
$$2 CO_{2(g)} + 8 H_2O_{(g)} + 12 e^- \rightarrow C_2H_{4(g)} + 12 OH_{(aq)}^-$$
  
anode  $4 OH_{(aq)}^- \rightarrow O_{2(g)} + 2 H_2O_{(g)} + 4 e^-$ 

- (a) Clearly label which half-reaction occurs at the anode and which occurs at the cathode. [1 mark] see above
- (b) Write the overall balanced reaction for this process. [1 mark]  $2 CO_{2(g)} + 2 H_2O_{(g)} \rightarrow C_2H_{4(g)} + 3 O_{2(g)}$
- (c) What is  $v_e$  for this process? 12
- (d) Calculate the standard Gibbs free energy change for this process. [2 marks] For consistency with later parts of the question, please use data for water in the gas phase.  $\Delta_r G^\circ = \Delta_f G^\circ (C_2 H_{4(g)}) + 3 \Delta_f G^\circ (O_{2(g)}) - [2 \Delta_f G^\circ (CO_{2(g)}) + 2 \Delta_f G^\circ (H_2 O_{(g)})]$   $\Delta_r G^\circ = (68.36 \frac{kJ}{mol}) + 3 (0 \frac{kJ}{mol}) - [2 (-394.37 \frac{kJ}{mol}) + 2 (-228.6 \frac{kJ}{mol})]$   $\Delta_r G^\circ = 1314.3 \frac{kJ}{mol}$
- (e) Calculate the standard cell potential (or standard emf) for this process. [2 marks]

$$\Delta_{r}G^{\circ} = -\nu_{e}FE^{\circ}$$

$$E^{\circ} = -\frac{\Delta_{r}G^{\circ}}{\nu_{e}F}$$

$$E^{\circ} = -\frac{\left(\frac{1314.3 \frac{kJ}{mol}\right)\left(\frac{1000 J}{1 kJ}\right)}{(12)\left(96485 \frac{C}{mol}\right)}$$

$$E^{\circ} = -1.1352 \frac{J}{c} = -1.1352 V$$

#### 3. ...continued

Calculate Q for this process when it is performed at 800 °C and the partial pressures of carbon (f) dioxide and water vapour are both 1.00 kbar while the partial pressures of ethene and oxygen are both 1.00 *mbar*. [3 marks]

$$a_{CO_2} = \frac{1.00 \ kbar}{1 \ bar} \times \frac{1000 \ bar}{1 \ kbar} = 1.00 \times 10^3$$
$$a_{H_2O} = \frac{1.00 \ kbar}{1 \ bar} \times \frac{1000 \ bar}{1 \ kbar} = 1.00 \times 10^3$$

$$a_{C_2H_4} = \frac{1.00 \ mbar}{1 \ bar} \times \frac{1 \ bar}{1000 \ mbar} = 1.00 \times 10^{-3}$$
$$a_{O_2} = \frac{1.00 \ mbar}{1 \ bar} \times \frac{1 \ bar}{1000 \ mbar} = 1.00 \times 10^{-3}$$

$$Q = \frac{(a_{C_2H_4})(a_{O_2})^3}{(a_{CO_2})^2(a_{H_2O})^2}$$
$$Q = \frac{(1.00 \times 10^{-3})(1.00 \times 10^{-3})^3}{(1.00 \times 10^3)^2(1.00 \times 10^{-3})^2}$$
$$Q = 1.00 \times 10^{-24}$$

Calculate the cell potential (or emf) for this process under the conditions described in part (f). The (g) standard cell potential for this process <u>at 800 °C</u> is -1.120 V. [3 marks]

$$E = E^{\circ} - \frac{RT}{v_e F} lnQ$$

$$E = (-1.120 V) - \frac{\left(\frac{8.314462 \frac{J}{mol \cdot K}}{(12)\left(96485 \frac{C}{mol}\right)}\right)(1073.15 K)}{(12)\left(96485 \frac{C}{mol}\right)} ln(1.00 \times 10^{-24}) \left(\frac{1 V}{1 \frac{J}{c}}\right)$$

$$E = (-1.120 V) - (-0.42587 V)$$

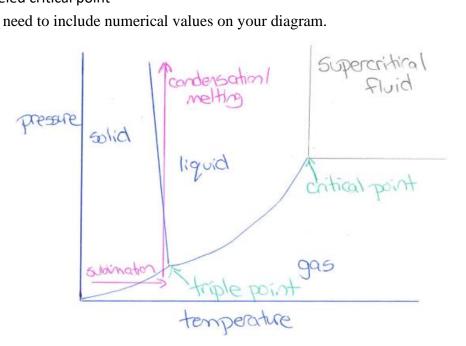
$$E = -0.694 V$$

Student Number:

4.

- (a) Draw a phase diagram for water. Your diagram must include:
  - Labeled axes •
  - Labeled phases •
  - Labeled triple point
  - Labeled critical point •

You do not need to include numerical values on your diagram.



- (b) On your phase diagram, draw a line of constant pressure where only sublimation occurs. Label your line "sublimation". [1 mark]
- On your phase diagram, draw a line of constant temp. where condensation is followed by melting. (c) Label your line "condensation/melting". [1 mark]
- The dissociation of water into  $H^+_{(aq)}$  and  $OH^-_{(aq)}$  is an endothermic process. Would you expect 5. the pH of water to increase or decrease as the temperature of water increases at constant pressure? [3 marks] Justify your answer.

*Hint: remember that*  $pH = -log\left(a_{H_{(ag)}^{+}}\right)$ 

 $H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$ 

This process is endothermic, so heating the system will push the equilibrium more toward the products side (Le Châtelier's principle). Therefore, as temperature increases, concentration of  $H^+$ increases and the pH decreases.

[10 marks]

[8 marks]

NAME:

6. In CHEM 1000, you would have learned that the following reaction does NOT occur (unlike the analogous reaction of water with any of the other Group 2 metals): [8 marks]

$$Be_{(s)} + 2H_2O_{(l)} \rightarrow Be(OH)_{2(s)} + H_{2(g)}$$

(a) Is this reaction thermodynamically allowed at 25 °C if the pressure of  $H_{2(a)}$  is 0.05 bar?

[6 marks]

$$\begin{split} \Delta_r G^\circ &= \left[ \Delta_f G^\circ \left( Be(OH)_{2(s)} \right) + \Delta_f G^\circ \left( H_{2(g)} \right) \right] - \left[ \Delta_f G^\circ \left( Be_{(s)} \right) + 2\Delta_f G^\circ \left( H_2 O_{(l)} \right) \right] \\ \Delta_r G^\circ &= \left[ \left( -818 \frac{kJ}{mol} \right) + \left( 0 \frac{kJ}{mol} \right) \right] - \left[ \left( 0 \frac{kJ}{mol} \right) + 2 \left( -237.140 \frac{kJ}{mol} \right) \right] \\ \Delta_r G^\circ &= -344 \frac{kJ}{mol} \end{split}$$

$$Q = \frac{(a_{Be(OH)_2})(a_{H_2})}{(a_{Be})(a_{H_2O})^2}$$
$$Q = \frac{(1)(0.05)}{(1)(1)^2}$$

- Q = 0.05
- T = 298.15 K

$$\Delta_r G = \Delta_r G^\circ + RT lnQ$$
  

$$\Delta_r G = \left(-344 \frac{kJ}{mol}\right) + \left(8.314462 \frac{J}{mol \cdot K}\right) (298.15 K) ln(0.05)$$
  

$$\Delta_r G = -351 \frac{kJ}{mol}$$

 $\Delta_r G$  is negative, so the reaction is <u>thermodynamically allowed</u>.

(b) Discuss briefly the agreement or disagreement between the result of your calculation and the observation that beryllium does not react with water. [2 marks]

The fact that the reaction is thermodynamically allowed means that it \*may\* happen not that it must happen. In order for a reaction to occur, it must be both thermodynamically and kinetically favourable, so it's possible that the activation energy for this reaction may be too high. It's also possible that a passivation layer of *BeO* means that the beryllium wouldn't actually be in contact with water if a sample of beryllium were placed in water.

NAME:\_\_\_\_\_ Section:\_\_\_\_ Student Number:\_\_\_\_\_

[18 marks]

[1 mark]

$$2 CO_{(g)} \rightleftharpoons CO_{2(g)} + C_{(s)}$$

This reaction is a serious nuisance in industrial processes involving carbon monoxide since it results in the deposition of graphite, which leads to fouling of the lines transporting this gas.

Is this a redox reaction? Justify your answer. (a)

> Yes. The oxidation state of carbon is different in the products than in the reactant. In CO, it is +2. In  $CO_2$ , it is +4. In C, it is 0.

Calculate the equilibrium constant for this reaction at 25 °C. Is the reaction reactant-favoured or (b) product-favoured under standard conditions? [5 marks]

$$\Delta_r G^\circ = \left[\Delta_f G^\circ (CO_{2(g)}) + \Delta_f G^\circ (C_{(s)})\right] - 2\Delta_f G^\circ (CO_{(g)})$$
  
$$\Delta_r G^\circ = \left[\left(-394.37 \frac{kJ}{mol}\right) + \left(0 \frac{kJ}{mol}\right)\right] - 2\left(-137.17 \frac{kJ}{mol}\right)$$
  
$$\Delta_r G^\circ = -120.03 \frac{kJ}{mol}$$
  
$$\Delta_r G^\circ = -1.2003 \times 10^5 \frac{J}{mol}$$

T = 298.15 K

$$\Delta_r G^{\circ} = -RT lnK$$

$$K = e^{\frac{-\Delta_r G^{\circ}}{RT}}$$

$$K = e^{\frac{-(-1.2003 \times 10^5 \frac{J}{mol})}{(8.314462 \frac{J}{mol \cdot K})(298.15 K)}}$$

$$K = e^{48.420}$$

$$K = 1.07 \times 10^{21}$$

K is very large, so this is a strongly product-favoured reaction under standard conditions.

7. ...continued

Estimate the equilibrium constant for this reaction at 250 °C. (c)

[6 marks]

$$T_1 = 25 \text{ °C} = 298.15 \text{ K}$$
  
 $K_1 = 1.07 \times 10^{21}$ 
 $T_2 = 250 \text{ °C} = 523.15 \text{ K}$   
 $K_2 = ???$ 

$$\Delta_r H^\circ = \left[\Delta_f H^\circ(CO_{2(g)}) + \Delta_f H^\circ(C_{(s)})\right] - 2\Delta_f H^\circ(CO_{(g)})$$
  
$$\Delta_r H^\circ = \left[\left(-393.51 \frac{kJ}{mol}\right) + \left(0 \frac{kJ}{mol}\right)\right] - 2\left(-110.53 \frac{kJ}{mol}\right)$$
  
$$\Delta_r H^\circ = -172.45 \frac{kJ}{mol}$$
  
$$\Delta_r H^\circ = -1.7245 \times 10^5 \frac{J}{mol}$$

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

$$ln\left(\frac{K_2}{1.07 \times 10^{21}}\right) = \left(\frac{-1.7245 \times 10^5 \frac{J}{mol}}{8.314 \, 462 \frac{J}{mol \cdot K}}\right) \left(\frac{1}{298.15 \, K} - \frac{1}{523.15 \, K}\right)$$

$$ln\left(\frac{K_2}{1.07 \times 10^{21}}\right) = -29.919$$

$$\frac{K_2}{1.07 \times 10^{21}} = e^{-29.919}$$

$$\frac{K_2}{1.07 \times 10^{21}} = 1.01 \times 10^{-13}$$

$$K_2 = (1.07 \times 10^{21})(1.01 \times 10^{-13})$$

$$K_2 = 1.08 \times 10^8$$

#### 7. ...continued

At 975 K, the equilibrium constant for the Boudouard reaction is 1. Suppose that a container holds (d) 58 bar of CO at 975 K. What will the partial pressures of CO and  $CO_2$  be when the system reaches equilibrium in this container? [6 marks]

	2 <i>CO</i> <sub>(g)</sub>	$\rightleftharpoons$	$CO_{2(g)}$	+	$C_{(s)}$
I bar)	58		0		0
C (bar)	-2x		+x		+ <i>x</i>
E (bar)	58 - 2x		x		x

$$K = \frac{(a_{CO_{2}(g)})(a_{C_{(s)}})}{(a_{CO_{(g)}})^{2}}$$

$$a_{CO(g)} = \frac{(58-2x)\,bar}{1\,bar} = 58 - 2x \qquad a_C$$

$$a_{CO_{2(g)}} = \frac{x \, bar}{1 \, bar} = x$$
$$a_{C_{(s)}} = 1$$

$$K = \frac{(x)(1)}{(58-2x)^2}$$
  

$$1 = \frac{x}{(58-2x)^2}$$
  

$$(58-2x)^2 = x$$
  

$$3364 - 232x + 4x^2 = x$$
  

$$4x^2 - 233x + 3364 = 0$$

$$x = \frac{-(-233)\pm\sqrt{(-233)^2 - 4(4)(3364)}}{2(4)}$$
$$x = \frac{233\pm\sqrt{465}}{8}$$
$$x = 31.8 \text{ or } 26.4$$

But x cannot be 31.8 because that would give a negative value for the pressure of CO. Therefore, x = 26.4.

$$p_{CO_{2(g)}} = (x)(1 \text{ bar}) = (26.4)(1 \text{ bar}) = 26.4 \text{ bar}$$
$$p_{CO_{(g)}} = (58 - 2x)(1 \text{ bar}) = (58 - 2(26.4))(1 \text{ bar}) = (58 - 52.8) \text{ bar} = 5 \text{ bar}$$

## Some Useful Constants and Formulae Fundamental Constants and Conversion Factors

Atomic mass unit (u)	$1.660~539 \times 10^{-27} \text{ kg}$	Kelvin temperature scale	0 K = -273.15 °C
Avogadro's number (NA)	$6.022 \ 141 \times 10^{23} \ \text{mol}^{-1}$	K <sub>w</sub> (at 25 °C)	10 <sup>-14</sup>
Boltzmann constant (k <sub>B</sub> )	$1.380~649 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$	Planck's constant (h)	$6.626\ 070 \times 10^{-34}\ J \cdot Hz^{-1}$
Charge of electron	$-1.602\ 176 \times 10^{-19}\ C$	Speed of light in vacuum (c)	2.997 925 x 10 <sup>8</sup> m·s <sup>-1</sup>
Faraday's constant (F)	96 485 C·mol⁻¹	Volume conversion	$1000 L = 1 m^3$
Ideal gas constant (R)	8.314 462 J·mol <sup>-1</sup> ·K <sup>-1</sup>	Pressure conversions	1  bar = 100  kPa
	8.314 462 $m^3 \cdot Pa \cdot mol^{-1} \cdot K^{-1}$		1  atm = 1.01325  bar

# <u>Formulae</u>

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

$$S = k_B \ln \Omega$$
  $\Delta S = \frac{q_{rev}}{T}$   $\Delta_r G = \Delta_r H - T \Delta_r S$ 

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q \qquad \Delta_r G^\circ = -RT \ln K \qquad \ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$P_{A} = X_{A}P_{A}^{\bullet} \qquad [A] = k_{H}P_{A} \qquad X = \frac{n}{\sum n} \qquad \Delta_{r}G = -\upsilon_{e}FE \qquad E = E^{\circ} - \frac{RT}{\upsilon_{e}F}\ln Q$$

 $pH = -\log a_{H^+}$   $pK_a = -\log K_a$   $pK_b = -\log K_b$   $K_w = K_a \cdot K_b$   $pH = pK_a + \log \left(\frac{a_{A^-}}{a_{HA}}\right)$ 

$$\Delta H_{rxn}^{0} = \sum (\Delta H_{f}^{0}(products) - \sum (\Delta H_{f}^{0}(reactants))$$

$$\Delta S_{rxn}^{0} = \sum (S^{0}(products) - \sum (S^{0}(reactants)))$$

$$\Delta G_{rxn}^{0} = \sum (\Delta G_{f}^{0}(products) - \sum (\Delta G_{f}^{0}(reactants)))$$

### **Activities**

Solid	<i>a</i> = 1
Pure liquid	a = 1
Ideal Solvent	a = X
Ideal Solute	$a = \frac{c}{c^{\circ}}$
Ideal Gas	$a = \frac{P}{P^{\circ}}$

1	_		CH	EM 2(	)00 Sta	ndard	l Perio	odic Ta	able								18
1.0079																	4.0026
$\mathbf{H}_{1}$	2											13	14	15	16	17	<b>He</b> 2
6.941	9.0122											10.811	12.011	14.0067	15.9994	18.9984	20.179
Li	Be											В	С	Ν	0	F	Ne
3	4											5	6	7	8	9	10
22.9898	24.3050											26.9815	28.0855	30.9738	32.066	35.4527	39.948
Na	Mg	-		_		_	•	0	4.0			Al	Si	Р	S	Cl	Ar
11	12	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
39.0983	40.078	44.9559	47.88	50.9415	51.9961	54.9380	55.847	58.9332	58.693	63.546	65.39	69.723	72.61	74.9216	78.96	79.904	83.80
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
85.4678	87.62	88.9059	91.224	92.9064	95.94	(98)	101.07	102.906	106.42	107.868	112.411	114.82	118.710	121.757	127.60	126.905	131.29
Rb	Sr	Y	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	Ι	Xe
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
132.905	137.327		178.49	180.948	183.85	186.207	190.2	192.22	195.08	196.967	200.59	204.383	207.19	208.980	(210)	(210)	(222)
Cs	Ba	La-Lu	Hf	Та	W	Re	Os	Ir	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn
55	56		72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
(223)	226.025		(265)	(268)	(271)	(270)	(277)	(276)	(281)	(280)	(285)	(284)	(289)	(288)	(293)	(294)	(294)
Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
87	88		104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
		138.906	140.115	140.908	144.24	(145)	150.36	151.965	157.25	158.925	162.50	164.930	167.26	168.934	173.04	174.967	1
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dv	Но	Er	Tm	Yb	Lu	
		57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	
		227.028	232.038	231.036	238.029	237.048	(240)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(262)	1
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	
		20	00	01	02	- · F	0.4	05	06	07	00	~~~	100	101	102	102	1

Substance	$\Delta_f H^{\circ}\left(\frac{kJ}{mol}\right)$	$\Delta_f G^{o}\!\!\left(rac{kJ}{mol} ight)$
$Be(OH)_{2(s)}$	-904	-818
$C_2H_{4(g)}$	52.47	68.36
$CO_{(g)}$	-110.53	-137.17
$CO_{2(g)}$	-393.51	-394.37
$H_2O_{(g)}$	-241.8	-228.6
$H_2O_{(l)}$	-285.830	-237.140

# Some Useful Thermodynamic Properties