NAME:	Section:	Student Number:	
Spring 2017	Chemistry 2000 Midt	erm #2A	/ 50 marks
INSTRUCTIONS: 1)	Please read over the test carefully of questions, a blank "overflow" periodic table.	0 0	1 0
2)	If your work is not legible, it will	be given a mark of zero.	
	Marks will be deducted for incorreanswer.	•	n otherwise correct
4)	Marks will be deducted for improor incorrect units.	per use of significant figur	es and for missing
5)	Show your work for all calculations will not be given full		without supporting
6)	You may use a calculator but on capable calculators are allowed.		lculation. No text-
7)	You have 90 minutes to complete	this test.	
Time on <u>Thursday</u> , Maracademic misconduct, a sa a mark of 0/50 on this ex	ent: in any other way divulge) the content of 23 rd , 2017. I understand that serious offense with serious consequam and removal of the "overwrite se; the maximum punishment would	t breaking this agreement uences. The minimum pur midterm mark with final of	t would constitute nishment would be exam mark" option
Signature:Course: CHEM 2000 (Ge Semester: Spring 2017 The University of Lethbr	eneral Chemistry II)		

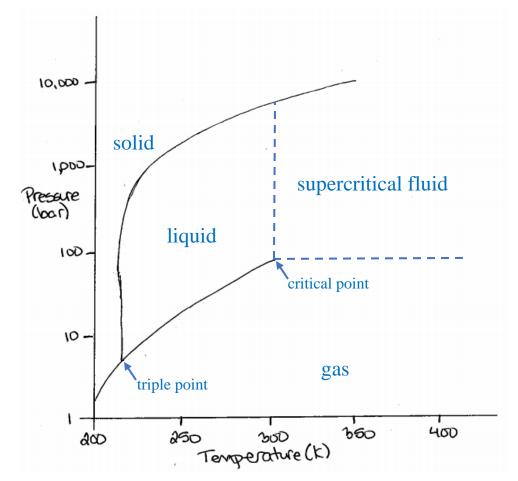
Question Breakdown

Q1	/ 5
Q2	/ 11
Q3	/ 9
Q4	/ 5
Q5	/ 8
Q6	/ 12

Total	/ 50

1. Consider the unlabeled phase diagram below.

[5 marks]



(a) On the diagram, label:

[3 marks]

- the critical point
- the triple point
- regions corresponding to the <u>four</u> states of matter discussed in class
- (b) A sample of this substance is initially at 200 K and 10 bar. The temperature is raised to 300 K while the pressure is maintained at 10 bar. What phase change(s) will occur? [1 mark]

solid \rightarrow liquid \rightarrow gas

(solid melts to give liquid; liquid vaporizes to give gas)

(c) A sample of this substance is initially at 200 K and 1 bar. The pressure is raised to 10 bar. What phase change(s) will occur? [1 mark]

gas \rightarrow solid

("deposition" or "desublimation")

NAME	E: Section: Student Number:
2.	Two chlorine atoms react to form a chlorine molecule under standard conditions: [11 marks] $2 Cl_{(g)} \rightarrow Cl_{2(g)}$
(a)	What information does the phrase "standard conditions" give you about the conditions under which this reaction is being studied? [2 marks] temperature is 25 °C (298.15 K) partial pressures of all gases are 1 bar
(b)	Is $\Delta_r G^\circ$ positive, negative or zero for this reaction? Briefly, justify your answer. [2 marks] $\Delta_r G^\circ$ must be negative
	For a reaction to proceed in the forward direction, $\Delta_r G$ must be negative for those conditions. Since this reaction proceeds in the forward direction under standard conditions, $\Delta_r G^{\circ}$ must be negative.
(c)	Is $\Delta_r S^\circ$ positive, negative or zero for this reaction? Briefly, justify your answer. [2 marks] $\Delta_r S^\circ$ should be negative Gases have larger entropy values than other states of matter. Since this reaction consumes two moles of gas but only generates one mole of gas, the entropy of the system is expected to decrease.
(d)	Is $\Delta_r H^\circ$ positive, negative or zero for this reaction? Briefly, justify your answer. [2 marks] $\Delta_r H^\circ$ should be negative
either:	In this reaction, no bonds are broken while one bond is formed. Heat is released when bonds are formed. Therefore, this reaction is exothermic (negative $\Delta_r H$).
or:	In order for a reaction to proceed, it must be favoured by enthalpy and/or entropy. This reaction proceeds but is not favoured by entropy. Therefore, it must be favoured by enthalpy (exothermic therefore negative $\Delta_r H$).
(e)	Will there be any temperature at which this reaction is not favoured in the forward direction? If 'yes', will it be high or low temperatures (and why)? If 'no', why not? [3 marks]
	This reaction will not be favoured at sufficiently high temperatures.
	$\Delta_r G = \Delta_r H - T \Delta_r S$
	$\Delta_r H$ and $T\Delta_r S$ are both negative.
	At high temperatures, the $T\Delta_rS$ term will dominate: a larger negative number will be subtracted from a smaller negative number. This will give a positive number for Δ_rG , and reactions with positive Δ_rG are not favoured in the forward direction.

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- 3. Fill in each blank with the word or short phrase that best completes the sentence. [9 marks]
- (a) The term for "heat at constant pressure" is _enthalpy_.
- (b) The only time that Q = K is when _the system is at equilibrium_.
- (c) If Q > K, we can expect that the reaction will proceed in the <u>reverse</u> direction.
- (d) The entropy of _the universe_ increases in every thermodynamically allowed process.
- (e) The <u>_reduction_</u> half reaction occurs at the cathode of an electrochemical cell.
- (f) The activity of a pure solid is $_1$.
- (g) The activity of $Cl_{(aq)}^-$ in an ideal 0.1 M solution of $MgCl_{2(aq)}$ is $\frac{0.2\frac{mol}{L}}{1\frac{mol}{l}} = 0.2$.
- (h) Henry's law states that the concentration of dissolved gas in a solution is directly proportional to_partial pressure of the gas above the solution_.
- (i) The third law of thermodynamics states that _entropy of a perfect crystal at 0 K is 0_.
- 4. In the qualitative analysis lab, you used aqua regia, a mixture of concentrated $HNO_{3(aq)}$ and $HCl_{(aq)}$ to isolate for certain Group II/III cations. The use of aqua regia was originally developed by alchemists to "dissolve" gold but, in reality, this is just a redox reaction under acidic conditions.

The incomplete and unbalanced equation is shown below:

[5 marks]

$$Au_{(s)} + NO_{3(aq)}^{-} + Cl_{(aq)}^{-} \rightarrow AuCl_{4(aq)}^{-} + NO_{2(g)}$$

(a) Balance the equation using either the half reaction method or the oxidation method. [3 marks] Show your work.

Oxidation Half-Reaction:

$$Au_{(s)} + 4Cl_{(aq)}^{-} \rightarrow AuCl_{4(aq)}^{-} + 3e^{-}$$

Reduction Half-Reaction:

$$(NO_{3(aq)}^{-} + 2H_{(aq)}^{+} + 1e^{-} \rightarrow NO_{2(q)} + H_{2}O_{(l)}) \times 3$$

Overall Balanced Equation:

$$Au_{(s)} + 6H_{(aa)}^{+} + 3NO_{3(aa)}^{-} + 4Cl_{(aa)}^{-} \rightarrow AuCl_{4(aa)}^{-} + 3NO_{2(a)} + 3H_{2}O_{(l)}$$

(b) Identify the oxidizing agent.

[1 mark]

 $NO_{3(aq)}^{-}$ is the oxidizing agent. It is reduced from +5 to +4.

(c) Identify the reducing agent.

[1 mark]

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5. Consider the following electrochemical cell, run at 25.00°C: [8 marks]

$$Cu_{(s)} \mid Cu_{(aq)}^{2+}(0.0100 M) \parallel Ag_{(aq)}^{+}(0.500 M) \mid Ag_{(s)}$$

Write a balanced chemical equation for the reaction that proceeds in this electrochemical cell. (a) [1 mark]

Oxidation Half-Reaction:

$$Cu_{(s)} \rightarrow Cu_{(aq)}^{2+} + 2e^-$$

 $E^{\circ} = -0.34 V$ (E° for reverse reaction is +0.34 V)

Reduction Half-Reaction:

$$(Ag_{(aq)}^+ + 1e^- \rightarrow Ag_{(s)}) \times 2$$
 $E^\circ = +0.80 \ V \text{ (std. reduction potential for } Ag_{(aq)}^+)$

Overall Balanced Equation:

$$Cu_{(s)} + 2Ag_{(aq)}^{+} \rightarrow Cu_{(aq)}^{2+} + 2Ag_{(s)}$$
 $v_e = 2$

(b) Calculate the cell potential for this electrochemical cell. [7 marks]

Step 1: Calculate cell potential under standard conditions.

$$E^{\circ} = (+0.80 \text{ V}) + (-0.34 \text{ V}) = +0.46 \text{ V}$$

Step 2: Convert temperature into Kelvin.

$$T = 25.00 + 273.15 = 298.15 K$$

Step 3: Find ν_e .

2 electrons were cancelled when the half-reactions were added, so $v_e = 2$.

Step 4:Find activities and calculate the reaction quotient (Q).

Activities of both solids are 1. Activities of both cations are $\frac{concentration}{1 \text{ M}}$.

$$Q = \frac{\left(a_{Cu_{(aq)}^{2+}}\right)\left(a_{Ag_{(s)}}\right)^{2}}{\left(a_{Cu_{(s)}}\right)\left(a_{Ag_{(aq)}^{+}}\right)^{2}} = \frac{\left(\frac{0.0100 \text{ M}}{1 \text{ M}}\right)(1)^{2}}{\left(1\right)\left(\frac{0.500 \text{ M}}{1 \text{ M}}\right)^{2}} = \frac{(0.0100)(1)^{2}}{(1)(0.500)^{2}} = 0.0400$$
3 sig. fig.

Step 5:Use Nernst equation to calculate cell potential under actual conditions.

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

$$E = (+0.46 V) - \left[\frac{\left(8.314462 \frac{J}{mol \cdot K}\right) (298.15 K)}{(2) \left(96485 \frac{C}{mol}\right)} ln(0.0400) \right] \times \frac{1 V}{1 \frac{J}{C}}$$

$$E = (+0.46 V) - (-0.04135 V)$$

$$E = +0.50 V$$
 2 decimal places therefore 2 sig. fig.

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6. The K_a value for $HF_{(aq)}$ at 25.00 °C is 6.8×10^{-4} .

[12 marks]

 $K_a = 6.8 \times 10^{-4}$

$$HF_{(aq)} \rightleftharpoons H_{(aq)}^+ + F_{(aq)}^-$$

1 1 1

(a) Calculate ΔG° for the reaction above.

[2 marks]

$$\Delta_r G^{\circ} = -RT lnK = -\left(8.314462 \frac{J}{mol \cdot K}\right) (298.15 K) ln(6.8 \times 10^{-4}) = +18080 \frac{J}{mol}$$
$$\Delta_r G^{\circ} = +18080 \frac{J}{mol} \times \frac{1 kJ}{1000 J} = +18.1 \frac{kJ}{mol}$$

 $ln(6.8 \times 10^{-4}) = -7.29$ therefore the answer has 3 sig. fig.

(2 sig. fig. in 6.8×10^4 therefore 2 decimal places in -7.29)

(b) Calculate $\Delta_f G^{\circ}$ for $HF_{(aq)}$.

[3 marks]

$$\Delta_r G^{\circ} = \sum \Delta_f G^{\circ}(products) - \sum \Delta_f G^{\circ}(reactants)$$

$$\Delta_r G^{\circ} = \Delta_f G^{\circ} (H_{(aq)}^+) + \Delta_f G^{\circ} (F_{(aq)}^-) - \Delta_f G^{\circ} (HF_{(aq)})$$

$$\Delta_f G^{\circ} \big(HF_{(aq)} \big) = \Delta_f G^{\circ} \big(H_{(aq)}^+ \big) + \Delta_f G^{\circ} \big(F_{(aq)}^- \big) - \Delta_r G^{\circ}$$

$$\Delta_f G^{\circ}(HF_{(aq)}) = \left(0 \frac{kJ}{mol}\right) + \left(-278.79 \frac{kJ}{mol}\right) - \left(+18.1 \frac{kJ}{mol}\right)$$

$$\Delta_f G^{\circ}(HF_{(aq)}) = -296.9 \frac{kJ}{mol}$$

1 decimal place therefore 4 sig. fig.

(c) Calculate the K_a value for $HF_{(aa)}$ at 50.00 °C.

[6 marks]

Step 1: Get organized

This question compares K values at different temperatures, so it must involve:

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

"integrated van't Hoff equation"

Assign one temperature to each number:

$$K_1 = 6.8 \times 10^{-4}$$
 and $T_1 = 298.15$ K.

$$K_2 = ???$$
 and $T_2 = 50.00 + 273.15 = 323.15 \text{ K}$

Then you just need $\Delta_r H^{\circ}$ and you can use the integrated van't Hoff equation to solve for K_2 .

Step 2: Solve for Standard Enthalpy Change for the Reaction

$$\Delta_r H^{\circ} = \sum \Delta_f H^{\circ}(products) - \sum \Delta_f H^{\circ}(reactants)$$

$$\Delta_r H^{\circ} = \Delta_f H^{\circ} (H_{(aq)}^+) + \Delta_f H^{\circ} (F_{(aq)}^-) - \Delta_f H^{\circ} (HF_{(aq)})$$

$$\Delta_r H^{\circ} = \left(0 \frac{kJ}{mol}\right) + \left(-332.63 \frac{kJ}{mol}\right) - \left(-320.08 \frac{kJ}{mol}\right) = -12.55 \frac{kJ}{mol} = -1.255 \times 10^4 \frac{J}{mol}$$

Step 3: Solve for K₂

$$ln\left(\frac{K_2}{K_1}\right) = \frac{\left(-1.255 \times 10^4 \frac{J}{mol}\right)}{\left(8.314462 \frac{J}{mol \cdot K}\right)} \left(\frac{1}{298.15 \, K} - \frac{1}{323.15 \, K}\right)$$

$$ln\left(\frac{K_2}{K_1}\right) = \frac{\left(-1.255 \times 10^4 \frac{J}{mol}\right)}{\left(8.314462 \frac{J}{mol}\right)} (2.5948 \times 10^{-4})$$

$$ln\left(\frac{K_2}{K_1}\right) = -0.3917$$

$$\frac{K_2}{K_1} = e^{-0.3917} = 0.6759$$

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$K_2 = 0.6759 \cdot K_1$		
$K_2 = (0.6759)(6.8 \times 10^{-4}) = 4.4$	6×10^{-4}	2 sig. fig. (because K_1 had 2 sig. fig.)

(d) Is $HF_{(aq)}$ a stronger acid at 50.00 °C or at 25.00 °C? How do you know? [1 mark] In other words, at which temperature is the reaction more product-favoured?

 $K_1 > K_2$ therefore the reaction is more product-favoured at 25.00 °C. Therefore, HF is a stronger acid at 25.00 °C.

Some Useful Constants and Formulae

Fundamental Constants and Conversion Factors

Kelvin temperature scale Atomic mass unit (u) $1.660\,539\times10^{-27}\,\mathrm{kg}$ $0 \text{ K} = -273.15 ^{\circ}\text{C}$ 10^{-14} $6.022\ 141 \times 10^{23}\ mol^{-1}$ Avogadro's number (N_A) K_w (at 25 °C) $1.380649 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$ $6.626\ 070 \times 10^{-34}\ J \cdot Hz^{-1}$ Planck's constant (h) Boltzmann constant (k_B) $2.997 925 \times 10^8 \text{ m} \cdot \text{s}^{-1}$ $-1.602\ 176 \times 10^{-19}\ C$ Speed of light in vacuum (c) Charge of electron 96 485 C·mol⁻¹ $1000 L = 1 m^3$ Volume conversion Faraday's constant (F) Ideal gas constant (R) 8.314 462 J·mol⁻¹·K⁻¹ Pressure conversions 1 bar = 100 kPa8.314 462 m³·Pa·mol⁻¹·K⁻¹ 1 atm = 1.01325 bar

Formulae

$$\overline{K} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}RT$$
 $v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3RT}{M}}$ $PV = nRT$

 $\Delta_r G = \Delta_r G^{\circ} + RT \ln Q$ $\Delta_r G^{\circ} = -RT \ln K$

$$S = k_B \ln \Omega \qquad \Delta S = \frac{q_{rev}}{T} \qquad \Delta_r G = \Delta_r H - T \Delta_r S \qquad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

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

$$P_A = X_A P_A^{\bullet}$$
 $[A] = k_H P_A$ $X = \frac{n}{\sum n}$ $\Delta_r G = -v_e FE$ $E = E^{\circ} - \frac{RT}{v_e F} \ln Q$

$$pH = -\log a_{H^{+}} \qquad pK_{a} = -\log K_{a} \qquad pK_{b} = -\log K_{b} \qquad K_{w} = K_{a} \cdot K_{b} \qquad pH = pK_{a} + \log \left(\frac{a_{A^{-}}}{a_{\mu A}}\right)$$

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

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

Activities

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

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu 60 58 70 61 227.028 (262) 232.038 231.036 238.029 237.048 (240) (243) (247) (251) (252) (257) (258)(247)(259)Th Pa \mathbf{U} Pu Cm Bk Es Fm MdAc Np Am Cf No Lr 92 99 90 94 96 97 100 101 91 93 95 103

Developed by Prof. R. T. Boeré (updated 2016)

Some Useful Thermodynamic Properties

Substance	$\Delta_f H^{\circ} \left(\frac{kJ}{mol} \right)$	$\Delta_f G^{\circ}\!\!\left(rac{kJ}{mol} ight)$	$S^{\circ}\left(\frac{J}{mol \cdot K}\right)$
$F_{(aq)}^{-}$	-332.63	-278.79	-13.8
$HF_{(aq)}$	-320.08	see question 6	88.7

Half Reaction	$E^{\circ}(V)$
$Ag_{(aq)}^+ + e^- \rightarrow Ag_{(s)}$	+0.80
$Cu_{(aq)}^{2+} + 2e^- \rightarrow Cu_{(s)}$	+0.34
$Cu_{(aq)}^{2+} + e^- \rightarrow Cu_{(aq)}^+$	+0.15
$2 H_{(aq)}^+ + 2 e^- \rightarrow H_{2(g)}$	0