Spring 2023 **Chemistry 2000 Midterm #2** ____/60 marks

Confidentiality Agreement:
I agree not to discuss (or in any other way divulge) the contents of this exam with (or in the presence of) any CHEM 2000 student who has yet to write it. I understand that breaking this agreement would constitute academic misconduct. The minimum penalty would be a mark of 0/60 on this exam.

Signature: _____ Date: _____

1) Please read the test carefully before starting. It has 8 pages of questions (four pages double-sided).
2) You have also been given a data sheet. It does not have a QR code, so nothing written on it will be graded.
3) **DO NOT WRITE ON ANY QR CODE!!!** Work on pages without a QR code will not be graded.
4) You may use a calculator but only for calculation. No other electronic devices are allowed. Any non-trivial use of a calculator must be described. For example, if you use a calculator to solve a nonlinear equation, you need to make it clear what equation was solved and provide any other inputs you used to the calculation.
5) If your work is not legible, it will be given a mark of zero.
6) Show your work. Answers without supporting reasoning or calculations will not get full credit
7) Marks will be deducted for incorrect information added to an otherwise correct answer.
8) You have 90 minutes to complete this test.

Question Breakdown

Q1	**Q2**	**Q3**	**Q4**	**Q5**									**Total**
/ 10	/ 16	/ 15	/ 15	/ 4									/ 60

1. The following data were obtained for mercury (Hg), the only metal which is liquid under standard conditions. **[10 marks]**

	$\Delta_f H° \left(\frac{kJ}{mol}\right)$	$S° \left(\frac{J}{mol \cdot K}\right)$
$Hg_{(l)}$		76.0
$Hg_{(g)}$	61.3	175.0

(a) Calculate the standard entropy change for the vaporization of mercury $(\Delta_{vap}S°)$. Comment on why the sign of your answer makes sense for the $Hg_{(l)} \rightarrow Hg_{(g)}$ reaction. *[4 marks]*

$\Delta_{vap}S° = S°(Hg_{(g)}) - S°(Hg_{(l)})$

$\Delta_{vap}S° = \left(175.0 \frac{J}{mol \cdot K}\right) - \left(76.0 \frac{J}{mol \cdot K}\right)$

$\Delta_{vap}S° = 99.0 \frac{J}{mol \cdot K}$

The fact that the sign of $\Delta_{vap}S°$ is positive means that entropy of the system increases.

This makes sense given there are more moles of gas in the products than the reactants.

(b) Calculate the standard free energy change for the vaporization of mercury $(\Delta_{vap}G°)$ at 25 °C. *[3 marks]*

$\Delta_{vap}H° = \Delta_f H°(Hg_{(g)}) - \Delta_f H°(Hg_{(l)})$

$\Delta_{vap}H° = \left(61.3 \frac{kJ}{mol}\right) - \left(0 \frac{kJ}{mol}\right)$

$\Delta_{vap}H° = 61.3 \frac{kJ}{mol}$

$\Delta_{vap}G° = \Delta_{vap}H° - T\Delta_{vap}S°$

$\Delta_{vap}G° = \left(61.3 \frac{kJ}{mol}\right) - (298.15\ K)\left(99.0 \frac{J}{mol \cdot K}\right)\left(\frac{1\ kJ}{1000\ J}\right)$

$\Delta_{vap}G° = 31.8 \frac{kJ}{mol}$

(c) Calculate the normal boiling point for mercury. *[3 marks]*

You may assume that $\Delta_{vap}H°$ and $\Delta_{vap}S°$ do not vary significantly within the relevant temperature range.

Recall that $\Delta G = 0$ at equilibrium…

$\Delta_{vap}G = \Delta_{vap}H - T\Delta_{vap}S$ therefore $T = \frac{\Delta_{vap}H - \Delta_{vap}G}{\Delta_{vap}S}$

$T = \frac{\left(61.3 \frac{kJ}{mol}\right) - \left(0 \frac{kJ}{mol}\right)}{\left(99.0 \frac{J}{mol \cdot K}\right)} \times \frac{1000\ J}{1\ kJ} = 619\ K$

2. The unbalanced chemical equation below shows the reactants and products for the partial combustion of ammonia (which is the first step in the industrial production of nitric acid). **[16 marks]**

$$_4_\, NH_{3(g)} + _5_\, O_{2(g)} \rightleftharpoons _4_\, NO_{(g)} + _6_\, H_2O_{(g)}$$

	$\Delta_f G° \left(\frac{kJ}{mol}\right)$
$NH_{3(g)}$	-16.4
$NO_{(g)}$	86.55
$H_2O_{(g)}$	-228.6

(a) Balance the reaction equation above and write the coefficients on the blanks provided. *[1 mark]*

see above

(b) Calculate the standard free energy change for the partial combustion of ammonia at 25 °C. *[3 marks]*

$$\Delta_r G° = \left[4\Delta_f G°\left(NO_{(g)}\right) + 6\Delta_f G°\left(H_2O_{(g)}\right)\right] - \left[4\Delta_f G°\left(NH_{3(g)}\right) + 5\Delta_f G°\left(O_{2(g)}\right)\right]$$

$$\Delta_r G° = \left[4\left(86.55\frac{kJ}{mol}\right) + 6\left(-228.6\frac{kJ}{mol}\right)\right] - \left[4\left(-16.4\frac{kJ}{mol}\right) + 5\left(0\frac{kJ}{mol}\right)\right]$$

$$\Delta_r G° = -959.8\frac{kJ}{mol}$$

(c) Calculate the equilibrium constant for the partial combustion of ammonia at 25 °C. *[3 marks]*

You may leave your answer in the format e^x; however, you must provide a numerical value for 'x'.

$\Delta_r G° = -RT\ln K$ therefore $K = e^{-\frac{\Delta_r G°}{RT}}$

$$K = e^{-\frac{\left(-959.8\frac{kJ}{mol}\right)\left(\frac{1000\ J}{1\ kJ}\right)}{\left(8.314462\frac{J}{mol\cdot K}\right)(298.15\ K)}} = e^{387}$$

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2. *…continued*

(d) Is the partial combustion of ammonia thermodynamically favoured ("spontaneous") at 25 °C for the following mixture of gases? For full marks, your logic must be clearly explained. *[4 marks]*

- $P(NH_3) = 0.001\ bar$
- $P(O_2) = 0.001\ bar$
- $P(NO) = 10{,}000\ bar$
- $P(H_2O) = 10{,}000\ bar$

$$Q = \frac{(a_{NO})^4(a_{H_2O})^6}{(a_{NH_3})^4(a_{O_2})^5}$$

$$Q = \frac{(10{,}000)^4(10{,}000)^6}{(0.001)^4(0.001)^5}$$

$$Q = 1 \times 10^{67}$$

$Q < K$ therefore the reaction is thermodynamically favoured

(e) The standard free energy change for the partial combustion of ammonia at 1000 °C is $-674.4\ \frac{kJ}{mol}$ (for the equation balanced using simplest whole numbers). Is the partial combustion of ammonia thermodynamically favoured ("spontaneous") at 1000 °C for the mixture of gases described in part (d)? For full marks, your logic must be clearly explained. *[5 marks]*

There are two reasonable approaches to this question. Either calculate a new equilibrium constant for the reaction at 1000 °C or calculate $\Delta_r G$ from the new $\Delta_r G°$ and $RTlnQ$.

Approach #1

$\Delta_r G° = -RTlnK$ therefore $K = e^{-\frac{\Delta_r G°}{RT}}$

$$K = e^{-\frac{\left(-674.4\frac{kJ}{mol}\right)\left(\frac{1000\ J}{1\ kJ}\right)}{\left(8.314462\frac{J}{mol \cdot K}\right)(1273.15\ K)}} = e^{63.7} = 5 \times 10^{27}$$

$Q > K$ therefore the reaction is **not** thermodynamically favoured

Approach #2

$$\Delta_r G = \Delta_r G° + RTlnQ$$

$$\Delta_r G = \left(-674.4\frac{kJ}{mol}\right) + \left(8.314462\frac{J}{mol \cdot K}\right)(1273.15\ K)\left(\frac{1\ kJ}{1000\ J}\right) ln(1 \times 10^{67})$$

$$\Delta_r G = \left(-674.4\frac{kJ}{mol}\right) + \left(1633\frac{kJ}{mol}\right)$$

$$\Delta_r G = +959\frac{kJ}{mol}$$

$\Delta_r G > 0$ therefore the reaction is **not** thermodynamically favoured

3. The unbalanced chemical equation below shows the reactants and products for the partial combustion of ammonia (which is the first step in the industrial production of nitric acid). **[15 marks]**

$$___\ NH_{3(g)} + ___\ O_{2(g)} \rightleftharpoons ___\ NO_{(g)} + ___\ H_2O_{(g)}$$

(a) Balance the oxidation half-reaction under acidic conditions. *[2 marks]*

$NH_3 + H_2O \rightleftharpoons NO + 5\,H^+ + 5\,e^-$

(b) Balance the reduction half-reaction under acidic conditions. *[2 marks]*

$O_2 + 4\,H^+ + 4\,e^- \rightleftharpoons 2\,H_2O$

(c) What is ν_e (the coefficient for the electrons cancelled when the two half-reactions are combined) for the partial combustion of ammonia under acidic conditions? *[1 mark]*

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(d) Copy your final answers to questions 2(a) and 2(b) onto this page. *[0 marks]*

$$_4_\ NH_{3(g)} + _5_\ O_{2(g)} \rightleftharpoons _4_\ NO_{(g)} + _6_\ H_2O_{(g)} \qquad \Delta_r G° = -959.8\frac{kJ}{mol}$$

This was simply requested for everyone's convenience. No marks were associated with doing it.

(e) Calculate the standard potential for the partial combustion of ammonia at 25 °C. *[3 marks]*

$\Delta_r G° = -\nu_e F E°$ therefore $E° = -\frac{\Delta_r G°}{\nu_e F}$

$$E° = -\frac{\left(-959.8\frac{kJ}{mol}\right)}{(20)\left(96485\frac{C}{mol}\right)} \times \frac{1000\ J}{1\ kJ} \times \frac{1\ V}{1\ \frac{J}{C}} = 0.4974\ V$$

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3. *…continued*

(f) If an electrochemical cell is built based on this reaction, calculate the value of Q that would be needed to give a cell potential of $+0.60\ V$ at 25 °C. *[3 marks]*

$E = E° - \frac{RT}{\nu_e F} lnQ$ therefore $\frac{RT}{\nu_e F} lnQ = E° - E$ therefore $lnQ = \frac{\nu_e F}{RT}(E° - E)$

$$lnQ = \frac{(20)\left(96485\frac{C}{mol}\right)}{\left(8.314462\frac{J}{mol \cdot K}\right)(298.15\ K)}(0.4974\ V - 0.60\ V) \times \frac{1\frac{J}{C}}{1\ V}$$

$$lnQ = -80$$

$$Q = e^{-80}$$

$$Q = 2 \times 10^{-35}$$

(g) What pressure of $NH_{3(g)}$ would be required for the electrochemical cell described in part (f) ($E = +0.60V$, 25 °C) if the pressure of $O_{2(g)}$ were 0.20 bar and the pressures of $NO_{(g)}$ and $H_2O_{(g)}$ were both 0.0010 bar? *[4 marks]*

$$Q = \frac{(a_{NO})^4 (a_{H_2O})^6}{(a_{NH_3})^4 (a_{O_2})^5}$$

$$(a_{NH_3})^4 = \frac{(a_{NO})^4 (a_{H_2O})^6}{(Q)(a_{O_2})^5}$$

$$a_{NH_3} = \sqrt[4]{\frac{(a_{NO})^4 (a_{H_2O})^6}{(Q)(a_{O_2})^5}}$$

$$a_{NH_3} = \sqrt[4]{\frac{(0.0010)^4 (0.0010)^6}{(2\times10^{-35})(0.20)^5}}$$

$$a_{NH_3} = \sqrt[4]{2 \times 10^8}$$

$$a_{NH_3} = 1 \times 10^2$$

The required pressure of $NH_{3(g)}$ would therefore be 111 bar (1×10^2 bar).

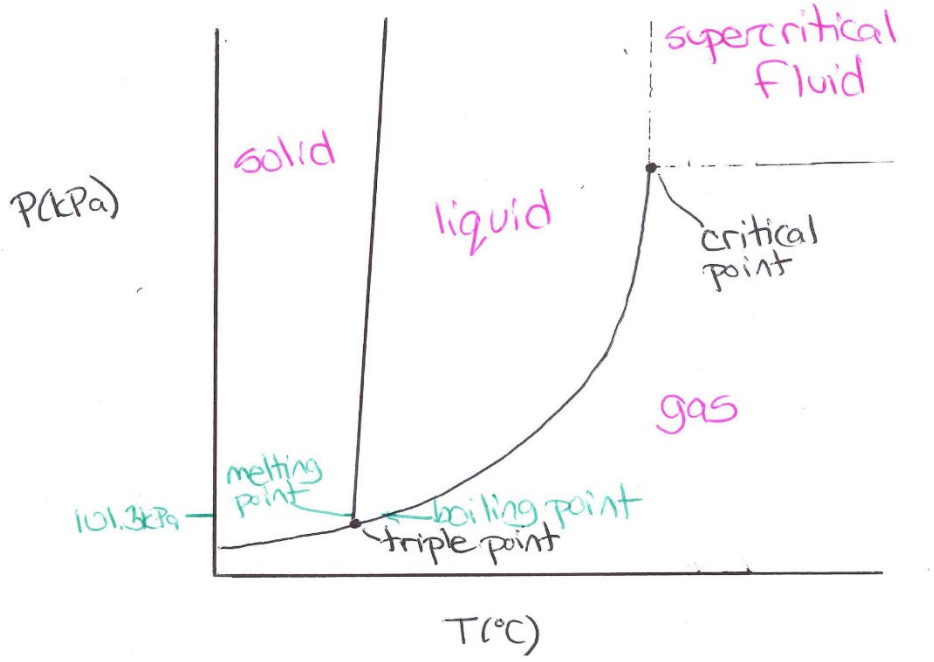
4. The following data were obtained for iodine (I_2). **[15 marks]**

	temperature (°C)	pressure (kPa)
triple point	113.5	12.1
critical point	546	11,700
normal melting point	113.7	101.3
normal boiling point	184.3	101.3

(a) Sketch a phase diagram for iodine. On your diagram, you must label: *[5 marks]*

- both axes
- the points listed in the table above
- regions corresponding to the <u>four</u> states of matter discussed in class

Your sketch does not need to be to-scale; however, it must be neat, and all points used to make it must be clearly labeled. Relative values must be preserved. In other words, it must be clear which pressures/temperatures are larger/smaller/approximately the same.



(b) If solid iodine is heated at a constant pressure of 50 kPa, will it sublime? Why or why not? *[2 marks]*

No, it will not sublime.

This pressure is above the triple point, so the solid will first melt (become liquid) then the liquid will evaporate.

(c) Describe the phase changes that will be experienced by a sample of iodine kept at a constant temperature of 120 °C as pressure is increased from 1 kPa to 100,000 kPa. *[2 marks]*

The iodine will start in gas phase, condense to liquid phase then freeze/solidify to solid phase.

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4. *…continued*

(d) Calculate the boiling point of iodine at 506.5 kPa (5.065 bar) given that $\Delta_{vap}H(I_2) = 20.752\frac{kJ}{mol}$. *[6 marks]*

Organize information:

Reaction Equation: $I_{2(l)} \rightarrow I_{2(g)}$ $\Delta_r H = 20.752\frac{kJ}{mol}$

$K = \frac{a_{I_{2(g)}}}{a_{I_{2(l)}}}$ By definition, $a_{I_{2(l)}} = 1$

Temperature 1 = "normal boiling point" therefore $T_1 = 184.3\ ℃ = 457.45\ K$

At the normal boiling point, $a_{I_{2(g)}} = \frac{101.3\ kPa}{1\ bar} \times \frac{1\ bar}{100\ kPa} = 1.013$

Therefore, $K_1 = \frac{a_{I_{2(g)}}}{a_{I_{2(l)}}} = \frac{1.013}{1} = 1.013$

Temperature 2 = "5 bar boiling point" therefore $T_2 = ???$

At the normal boiling point, $a_{I_{2(g)}} = \frac{5.065\ bar}{1\ bar} = 5.065$

Therefore, $K_2 = \frac{a_{I_{2(g)}}}{a_{I_{2(l)}}} = \frac{5.065}{1} = 5.065$

Crunch Numbers:

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

$$\frac{1}{T_2} = \frac{1}{457.45\ K} - \frac{\left(8.314462\frac{J}{mol \cdot K}\right)}{\left(20.752\frac{kJ}{mol}\right)\left(\frac{1000\ J}{1\ kJ}\right)} ln\left(\frac{5.065}{1.013}\right)$$

$$\frac{1}{T_2} = (0.002186\ K^{-1}) - (0.00040066\ K^{-1}) ln(5.000)$$

$$\frac{1}{T_2} = (0.002186\ K^{-1}) - (0.00040066\ K^{-1})(1.609)$$

$$\frac{1}{T_2} = (0.002186\ K^{-1}) - (0.0006448 K^{-1})$$

$$\frac{1}{T_2} = 0.001541\ K^{-1}$$

$$T_2 = \frac{1}{0.001541\ K^{-1}}$$

$$T_2 = 649\ K$$

$$T_2 = 376\ ℃$$

There was a copy error on the original test in which the terms "boiling point" and "melting point" had been swapped. If this calculation was performed using 113.7 ℃ *for the normal boiling point (as per the original table), the answers ought to be as shown below. Full credit was awarded to students who did the correct procedure using this value.*

Organize information:

Reaction Equation: $I_{2(l)} \rightarrow I_{2(g)}$ $\Delta_r H = 20.752 \frac{kJ}{mol}$

$K = \frac{a_{I_{2(g)}}}{a_{I_{2(l)}}}$ By definition, $a_{I_{2(l)}} = 1$

Temperature 1 = "normal boiling point" therefore $T_1 = 113.7\ ℃ = 386.85\ K$

At the normal boiling point, $a_{I_{2(g)}} = \frac{101.3\ kPa}{1\ bar} \times \frac{1\ bar}{100\ kPa} = 1.013$

Therefore, $K_1 = \frac{a_{I_{2(g)}}}{a_{I_{2(l)}}} = \frac{1.013}{1} = 1.013$

Temperature 2 = "5 bar boiling point" therefore $T_2 = ???$

At the normal boiling point, $a_{I_{2(g)}} = \frac{5.000\ bar}{1\ bar} = 5.000$

Therefore, $K_2 = \frac{a_{I_{2(g)}}}{a_{I_{2(l)}}} = \frac{5.000}{1} = 5.000$

Crunch Numbers:

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

$$\frac{1}{T_2} = \frac{1}{386.85\ K} - \frac{\left(8.314462 \frac{J}{mol \cdot K}\right)}{\left(20.752 \frac{kJ}{mol}\right)\left(\frac{1000\ J}{1\ kJ}\right)} ln\left(\frac{5.065}{1.013}\right)$$

$$\frac{1}{T_2} = (0.002585\ K^{-1}) - (0.00040066\ K^{-1}) ln(5.000)$$

$$\frac{1}{T_2} = (0.002585\ K^{-1}) - (0.00040066\ K^{-1})(1.609)$$

$$\frac{1}{T_2} = (0.002585\ K^{-1}) - (0.0006448 K^{-1})$$

$$\frac{1}{T_2} = 0.001940\ K^{-1}$$

$$T_2 = \frac{1}{0.001940\ K^{-1}}$$

$$T_2 = 515\ K$$

$$T_2 = 242\ ℃$$

5. The standard entropy for $F^-_{(aq)}$ is $-13.8\ \frac{J}{mol \cdot K}$. **[4+2 marks]**

The standard entropy for $Mg^{2+}_{(aq)}$ is $-137\ \frac{J}{mol \cdot K}$.

(a) The vast majority of standard entropy values are positive. With reference to the 3rd Law of Thermodynamics, explain why this is the case. *[2 marks]*

The 3rd Law of Thermodynamics states that the entropy of a perfect crystal at $0\ K$ is zero.

For a substance to have a negative absolute entropy, it would therefore need to be more highly ordered than a perfect crystal at $0\ K$. Effectively, it would need to have less than one accessible microstate. This is impossible.

(b) How is it possible for these ions to have negative values for standard entropy? *[2 marks]*

Standard entropies for ions are not absolute values. They are measured relative to the standard entropy for $H^+_{(aq)}$ - which has had its standard entropy defined as zero. *This is because it's impossible to look at an ion in isolation without considering the counterion.*

As such, if the hydration sphere around a particular ion is more highly ordered than the hydration sphere around $H^+_{(aq)}$, that information can be represented as a negative standard entropy of the ions.

BONUS *(2 marks)*

Propose a valid reason why the magnitude of the standard entropy for $Mg^{2+}_{(aq)}$ might be so much larger than the magnitude of the standard entropy for $F^-_{(aq)}$. Briefly explain your logic.

Because the magnitude of charge of $Mg^{2+}_{(aq)}$ is larger than the magnitude of charge of $F^-_{(aq)}$, it is reasonable to conclude that the water molecules around $Mg^{2+}_{(aq)}$ will be more strongly attracted to it and that $Mg^{2+}_{(aq)}$ will therefore have a more highly ordered hydration sphere (potentially with more layers of water being "organized" due to their attraction to the strong positive charge of the cation).