Winter 2025 **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 7 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) Marks will be deducted for improper use of significant figures and for missing or incorrect units. Show units in every step of all calculations. Significant figures will only be checked in final answers. If a question has subparts (a, b, c, etc.), the answer to each subpart is considered a "final answer".
9) You have 90 minutes to complete this test.

Question Breakdown

Q1	**Q2**	**Q3**	**Q4**	**Q5**									**Total**
/ 12	/ 7	/ 15	/ 14	/ 12									/ 60

1. The following data were obtained for carbon dioxide (CO_2). **[12 marks]**

	temperature (°C)	pressure (bar)
triple point	-56.60	5.18
critical point	31.98	73.74

(a) Define the term "triple point". *[1 mark]*

temperature and pressure at which solid, liquid and gas phases coexist in equilibrium

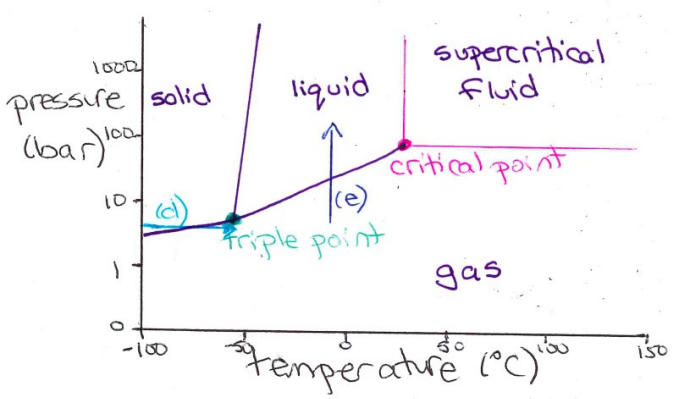
(b) Define the term "critical point". *[1 mark]*

highest temperature and pressure at which there is a distinction between gas and liquid phases; above the critical point, there is supercritical fluid

(c) Sketch a phase diagram for carbon dioxide. On your diagram, you must label: *[4 marks]*

- both axes
- the triple point and critical point
- 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.



(d) On your phase diagram, draw a line of constant pressure (arrow labeled (d)) where only sublimation occurs. Over what temperature range is this possible? *[2 marks]*

see turquoise arrow on diagram above

This is possible at temperatures below the triple point ($-56.60°C$)

(e) On your phase diagram, draw a line of constant temperature (arrow labeled (e)) where condensation occurs. Over what temperature range is this possible? *[2 marks]*

see dark blue arrow on diagram above

This is possible at temperatures above the triple point ($-56.60°C$) but below the critical point ($73.74°C$)

(f) Is pressure-induced melting possible for carbon dioxide? Why or why not? *[2 marks]*

No. The slope of the solid-liquid equilibrium curve is positive, so compressing a liquid may give a solid but compressing a solid can never give a liquid.

2. Predict the sign of the entropy change for each of the following reactions. Justify your answer, and state whether you expect the entropy change to be large or small. **[7 marks]**

(a) $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$ *[2 marks]*

$\Delta S > 0$

One product is a gas while no reactants are gases. Since gases can have a much larger number of positional microstates than either solids or liquids, the products will have a much larger entropy than the reactants.

(b) $Hg_{(l)} \rightarrow Hg_{(s)}$ *[2 marks]*

$\Delta S < 0$

In this reaction, a liquid freezes to a solid. Solids and liquids have similar densities so we expect the entropy change to be smaller than any reaction involving production or consumption of a gas. Solids are more ordered than liquids, so the solid will have fewer microstates and therefore a smaller entropy than the liquid.

(c) $HF_{(g)} + H_2O_{(l)} \rightarrow H^+_{(aq)} + F^-_{(aq)} + H_2O_{(l)}$ *[3 marks]*

For full marks, your answer must address two factors affecting the entropy change and identify which of the two factors will dominate.

$\Delta S < 0$

One reactant is a gas while no products are gases. Since gases can have a much larger number of positional microstates than either solids or liquids, the reactants will have a much larger entropy than the products.

The fluoride ion also has a negative standard entropy value (see data sheet). That means that it must organize the water molecules around it. This further increases the order of the products and therefore makes ΔS even more negative by a small amount.

3. Consider the following phase change: **[15 marks]**

$$H_2O_{(l)} \rightarrow H_2O_{(g)}$$

(a) Calculate the standard Gibbs free energy change for this phase change at 25 °C. *[6 marks]*

Step 1: Calculate $\Delta_r H°$ from standard enthalpies of formation

$$\Delta_r H° = \sum \Delta_f H°(products) - \sum \Delta_f H°(reactants)$$

$$\Delta_r H° = \Delta_f H°\left(H_2O_{(g)}\right) - \Delta_f H°\left(H_2O_{(l)}\right)$$

$$\Delta_r H° = \left(-241.8 \frac{kJ}{mol}\right) - \left(-285.8 \frac{kJ}{mol}\right)$$

$$\Delta_r H° = 44.0 \frac{kJ}{mol}$$

Step 2: Calculate $\Delta_r S°$ from standard entropies

$$\Delta_r S° = \sum \Delta_f S°(products) - \sum \Delta_f S°(reactants)$$

$$\Delta_r S° = S°\left(H_2O_{(g)}\right) - S°\left(H_2O_{(l)}\right)$$

$$\Delta_r S° = \left(188.8 \frac{J}{mol \cdot K}\right) - \left(69.91 \frac{J}{mol \cdot K}\right)$$

$$\Delta_r S° = 118.9 \frac{J}{mol \cdot K}$$

Step 3: Calculate $\Delta_r G°$ from $\Delta_r H°$, $\Delta_r S°$ and temperature

$$\Delta_r G° = \Delta_r H° - T\Delta_r S°$$

$$\Delta_r G° = \left(44.0 \frac{kJ}{mol}\right) - (298.15\ K)\left(118.9 \frac{J}{mol \cdot K}\right)\left(\frac{1\ kJ}{1000\ J}\right)$$

$$\Delta_r G° = \left(44.0 \frac{kJ}{mol}\right) - \left(35.45 \frac{kJ}{mol}\right)$$

$$\Delta_r G° = 8.6 \frac{kJ}{mol}$$

(b) Assuming that the enthalpy and entropy change for this process are not very temperature sensitive, use the standard values to calculate a predicted normal boiling point for water. Comment on this value. *[5 marks]*

The Short Way:

At the normal boiling point, equilibrium has been reached for conditions that closely resemble standard conditions.

- $a_{H_2O_{(l)}} = 1$
- by definition, vapour pressure is 1 atm so $a_{H_2O_{(g)}} = \frac{1\ atm}{1\ bar} \times \frac{1.01325\ bar}{1\ atm} = 1.01325 \approx 1$
- therefore, $K = \frac{a_{H_2O_{(g)}}}{a_{H_2O_{(l)}}} = \frac{1.01325}{1} = 1.01325 \approx 1$

Therefore, since neither the forward nor the reverse reaction are thermodynamically favoured at the normal boiling point $\Delta_r G° = 0$

$$\Delta_r G° = \Delta_r H° - T\Delta_r S°$$
$$T\Delta_r S° = \Delta_r H° - \Delta_r G°$$
$$T = \frac{\Delta_r H° - \Delta_r G°}{\Delta_r S°}$$
$$T = \frac{\left(44.0\frac{kJ}{mol}\right) - \left(0\frac{kJ}{mol}\right)}{118.9\frac{J}{mol \cdot K}} \times \frac{1000\ J}{1\ kJ}$$
$$T = 370\ K$$
$$T = 97\ ℃$$

This is close to the actual normal boiling point of water $(100\ ℃ = 373.15\ K)$

The Long Way:

Step 1: Calculate equilibrium constant at 25 ℃ from standard free energy change

$$\Delta_r G° = -RT\ln K$$
$$\ln K = -\frac{\Delta_r G°}{RT}$$
$$\ln K = -\frac{\left(8.6\frac{kJ}{mol}\right)\left(\frac{1000\ J}{1\ kJ}\right)}{\left(8.314\ 462\frac{J}{mol \cdot K}\right)(298.15\ K)}$$
$$\ln K = -3.5$$
$$K = e^{-3.5}$$
$$K = 3.2 \times 10^{-2}$$

Step 2: Organize information:

Reaction Equation: $H_2O_{(l)} \rightarrow H_2O_{(g)}$ $\Delta_r H° = 44.0 \frac{kJ}{mol}$

$K = \frac{a_{H_2O_{(g)}}}{a_{H_2O_{(l)}}}$ by definition, $a_{H_2O_{(l)}} = 1$

Temperature 1 = 25 °C therefore $T_1 = 298.15\ K$
At 25 °C, $K = 3.2 \times 10^{-2}$ therefore $K_1 = 3.2 \times 10^{-2}$

Temperature 2 = "normal boiling point" therefore $T_2 = ???$
At the normal boiling point, $a_{H_2O_{(g)}} = \frac{1\ atm}{1\ bar} \times \frac{1.01325\ bar}{1\ atm} = 1.01325$
Therefore, $K_2 = \frac{a_{H_2O_{(g)}}}{a_{H_2O_{(l)}}} = \frac{1.01325}{1} = 1.01325$

Step 3: 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 $\frac{1}{T_2} = \frac{1}{T_1} - \frac{R}{\Delta_r H°} ln\left(\frac{K_2}{K_1}\right)$

$$\frac{1}{T_2} = \frac{1}{298.15\ K} - \frac{\left(8.314462 \frac{J}{mol \cdot K}\right)}{\left(44.0 \frac{kJ}{mol}\right)\left(\frac{1000\ J}{1\ kJ}\right)} ln\left(\frac{1.01325}{0.032}\right)$$

$$\frac{1}{T_2} = (0.0033540\ K^{-1}) - (0.000189\ K^{-1}) ln(31.9248)$$

$$\frac{1}{T_2} = (0.0033540\ K^{-1}) - (0.000189\ K^{-1})(3.463383)$$

$$\frac{1}{T_2} = (0.0033540\ K^{-1}) - (0.000655 K^{-1})$$

$$\frac{1}{T_2} = 0.002700\ K^{-1}$$

$$T_2 = \frac{1}{0.002700\ K^{-1}}$$

$$T_2 = 370.4\ K$$

$$T_2 = 97.2\ ℃$$

This is close to the actual normal boiling point of water $(100\ ℃ = 373.15\ K)$

(c) Calculate the standard Gibbs free energy change for this phase change at $90\ ℃$. Is the forward reaction thermodynamically favoured at this temperature? Why or why not? *[2 marks]*

$\Delta_r G° = \Delta_r H° - T\Delta_r S°$

$\Delta_r G° = \left(44.0 \frac{kJ}{mol}\right) - (363.15\ K)\left(118.9 \frac{J}{mol \cdot K}\right)\left(\frac{1\ kJ}{1000\ J}\right)$

$\Delta_r G° = \left(44.0 \frac{kJ}{mol}\right) - \left(43.17 \frac{kJ}{mol}\right)$

$\Delta_r G° = +0.8 \frac{kJ}{mol}$

This reaction is **not** thermodynamically favoured in the forward direction at $90\ ℃$ because $\Delta_r G° > 0$

(d) Calculate the standard Gibbs free energy change for this phase change at $110\ ℃$. Is the forward reaction thermodynamically favoured at this temperature? Why or why not? *[2 marks]*

$\Delta_r G° = \Delta_r H° - T\Delta_r S°$

$\Delta_r G° = \left(44.0 \frac{kJ}{mol}\right) - (383.15\ K)\left(118.9 \frac{J}{mol \cdot K}\right)\left(\frac{1\ kJ}{1000\ J}\right)$

$\Delta_r G° = \left(44.0 \frac{kJ}{mol}\right) - \left(45.55 \frac{kJ}{mol}\right)$

$\Delta_r G° = -1.68 \frac{kJ}{mol}$

$\Delta_r G° < 0$ so this reaction is thermodynamically favoured in the forward direction at $110\ ℃$.

4. Consider the following reaction: **[14 marks]**

$$NO_{2(g)} + H_2O_{(l)} \rightarrow HNO_{3(aq)}$$

(a) Calculate the standard Gibbs free energy change for this reaction at 25 °C. *[2 marks]*

$\Delta_r G° = \sum \Delta_f G°(products) - \sum \Delta_f G°(reactants)$

$\Delta_r G° = \Delta_f G°(HNO_{(aq)}) - [\Delta_f G°(NO_{2(g)}) + \Delta_f G°(H_2O_{(l)})]$

$\Delta_r G° = \left(-111.25 \frac{kJ}{mol}\right) - \left[\left(51.31 \frac{kJ}{mol}\right) + \left(-237.1 \frac{kJ}{mol}\right)\right]$

$\Delta_r G° = 74.5 \frac{kJ}{mol}$

(b) Calculate equilibrium constant (K) for this reaction at 25 °C. *[2 marks]*

$\Delta_r G° = -RTlnK$

$lnK = -\frac{\Delta_r G°}{RT}$

$lnK = -\frac{\left(74.5 \frac{kJ}{mol}\right)\left(\frac{1000\ J}{1\ kJ}\right)}{\left(8.314\ 462 \frac{J}{mol \cdot K}\right)(298.15\ K)}$

$lnK = -30.1$

$K = e^{-30.1}$

$K = 9 \times 10^{-14}$

(c) Write the reaction quotient (Q) expression for this reaction. *[1 mark]*

$Q = \frac{(a_{HNO_3})}{(a_{NO_2})(a_{H_2O})}$

(d) Calculate the Gibbs free energy change for this reaction at 25 °C when $P_{NO_{2(g)}} = 5.00\ bar$ and $[HNO_{3(aq)}] = 0.0100\ M$? *[4 marks]*

Step 1: Calculate reaction quotient

$Q = \frac{(a_{HNO_3})}{(a_{NO_2})(a_{H_2O})} = \frac{\left(\frac{0.0100\ M}{1\ M}\right)}{\left(\frac{5.00\ bar}{1\ bar}\right)(1)} = \frac{0.0100}{5.00} = 0.00200$

Step 2: Calculate free energy change under these nonstandard conditions

$\Delta_r G = \Delta_r G° + RTlnQ$

$\Delta_r G = \left(74.5 \frac{kJ}{mol}\right) + \left(8.314\ 462 \frac{J}{mol \cdot K}\right)\left(\frac{1\ kJ}{1000\ J}\right)(298.15\ K) ln(0.00200)$

$\Delta_r G = \left(74.5 \frac{kJ}{mol}\right) + \left(-15.41 \frac{kJ}{mol}\right)$

$\Delta_r G = 59.1 \frac{kJ}{mol}$

(e) At what temperature will the equilibrium constant for this reaction be double your answer to part (b)? *[5 marks]*

Step 1: Calculate $\Delta_r H°$ from standard enthalpies of formation

$$\Delta_r H° = \sum \Delta_f H°(products) - \sum \Delta_f H°(reactants)$$

$$\Delta_r H° = \Delta_f H°(HNO_{(aq)}) - [\Delta_f H°(NO_{2(g)}) + \Delta_f H°(H_2O_{(l)})]$$

$$\Delta_r H° = \left(-207.36\,\frac{kJ}{mol}\right) - \left[\left(33.18\,\frac{kJ}{mol}\right) + \left(-285.8\,\frac{kJ}{mol}\right)\right]$$

$$\Delta_r H° = 45.3\,\frac{kJ}{mol}$$

Step 2: Organize information:

Reaction Equation: $NO_{2(g)} + H_2O_{(l)} \rightarrow HNO_{3(aq)}$ $\Delta_r H° = 45.3\,\frac{kJ}{mol}$

Temperature 1 = 25 ℃ therefore $T_1 = 298.15\ K$ and $K_1 = 9 \times 10^{-14}$ (answer to part (b))

Temperature 2 = "unknown" therefore $T_2 = ???$ and $K_2 = 2K_1$
(you can calculate a numerical value for K_2 but it's easier not to)

Step 3: 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 $\frac{1}{T_2} = \frac{1}{T_1} - \frac{R}{\Delta_r H°} ln\left(\frac{K_2}{K_1}\right)$

$$\frac{1}{T_2} = \frac{1}{298.15\ K} - \frac{\left(8.314462\frac{J}{mol \cdot K}\right)}{\left(45.3\frac{kJ}{mol}\right)\left(\frac{1000\ J}{1\ kJ}\right)} ln\left(\frac{2\ K_1}{K_1}\right)$$

$$\frac{1}{T_2} = (0.0033540\ K^{-1}) - (0.000184\ K^{-1}) ln(2)$$

$$\frac{1}{T_2} = (0.0033540\ K^{-1}) - (0.000184\ K^{-1})(0.693147)$$

$$\frac{1}{T_2} = (0.0033540\ K^{-1}) - (0.000127 K^{-1})$$

$$\frac{1}{T_2} = 0.003227\ K^{-1}$$

$$T_2 = \frac{1}{0.003227\ K^{-1}}$$

$$T_2 = 309.9\ K$$

$$T_2 = 36.8\ ℃$$

5. For the following electrochemical cell, $E° = -0.5768\ V$ at 25 °C. **[12 marks]**

$$Ag(s)\ |\ Ag^{+}(aq)\ 1.00\ M\ \|\ Cl^{-}(aq)\ 1.00\ M\ |AgCl\ (s), Ag(s)$$

(a) Identify the cathode **and** write a balanced equation for its half-reaction. *[2 marks]*

Cathode is $AgCl_{(s)}$

$$AgCl_{(s)} + e^{-} \rightarrow Ag_{(s)} + Cl^{-}_{(aq)}$$

(b) Identify the anode **and** write a balanced equation for its half-reaction. *[2 marks]*

Cathode is $Ag_{(s)}$

$$Ag_{(s)} \rightarrow Ag^{+}_{(aq)} + e^{-}$$

(c) Write a balanced chemical equation for the overall reaction occurring in this electrochemical cell **and** provide a numerical value for υ_e. *[2 marks]*

$$AgCl_{(s)} \rightarrow Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$$

$$\upsilon_e = 1$$

(d) Write a balanced chemical equation for the dissolution of solid $AgCl$ in water **and** write the equilibrium constant expression for this reaction (K_{sp} expression for $AgCl$). *[2 marks]*

$$AgCl_{(s)} \rightarrow Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$$

$$K_{sp} = \frac{(a_{Ag^+})(a_{Cl^-})}{a_{AgCl}} \text{ or, since } a_{AgCl} = 1,\ K_{sp} = (a_{Ag^+})(a_{Cl^-})$$

(e) Calculate a numerical value for the K_{sp} of $AgCl$ at 25 °C. *[4 marks]*

Note that equations in (c) and (d) are the same. For a similar question, see Practice Test Questions 9 #18.

Step 1: Calculate standard free energy change from standard potential

$$\Delta_r G° = -\upsilon_e F E°$$

$$\Delta_r G° = -(1)\left(96\,485\,\frac{C}{mol}\right)\left(-0.5768\,\frac{J}{C}\right)$$

$$\Delta_r G° = 5.565 \times 10^{4}\,\frac{J}{mol}$$

Step 2: Calculate equilibrium constant from standard free energy change

$$\Delta_r G° = -RT\ln K$$

$$\ln K = -\frac{\Delta_r G°}{RT}$$

$$\ln K = -\frac{\left(5.565\times10^{4}\frac{J}{mol}\right)}{\left(8.314\,462\frac{J}{mol\cdot K}\right)(298.15\ K)}$$

$$\ln K = -22.45$$

$$K = e^{-22.45}$$

$$K = 1.8 \times 10^{-10}$$