Grading policy: One point is given for each numbered equation shown in the solution, or for written statements and/or equations to the same effect. The total score for this problem set is 24 points plus a maximum of 1 bonus point.

Note. PAQ means ‘Please answer the question.’ This means that either part of the question was unanswered (comes with a caret ∧) or the answer given did not completely answer the question.

1. (22-23). Derive

\[
\left( \frac{\partial (A/T)}{\partial T} \right)_V = -\frac{U}{T^2}
\]  

[4 points]

Solution. Apply the quotient rule to the derivative given to obtain

\[
\left( \frac{\partial (A/T)}{\partial T} \right)_V = \frac{T \left( \frac{\partial A}{\partial T} \right)_V - A}{T^2}
\]  

(2)

From the differential form of \( dA \) we have

\[ dA = -SdT - VdP \]

(3)

where the necessary derivative is seen to be

\[
\left( \frac{\partial A}{\partial T} \right)_V = -S
\]

(4)

The result follows straightaway:

\[
\left( \frac{\partial (A/T)}{\partial T} \right)_V = -\frac{ST - A}{T^2} = -\frac{U}{T^2}
\]

(5)

2. (23-1). Sketch the phase diagram for oxygen using the following data: triple point, 54.3 K and 1.14 torr; critical point, 154.6 K and 37828 torr; normal melting point, \(-218.4^\circ\)C; and normal boiling point, \(-182.9^\circ\)C. Does oxygen melt under an applied pressure as water does? [5 points]

Solution. [One point for each correctly labelled point]
The slope of the liquid-solid coexistent curve is positive [1 point]; therefore, oxygen does not melt under applied pressure.

**Note.** Points cannot be ordered, so it is meaningless to say that point B is higher than point A. However the individual components can be ordered so it is right to say, for example, that the temperature of the critical point (i.e. the value of the horizontal co-ordinate) is higher than the temperature of the triple point.

**Note.** Don’t forget the critical point.

3. (23-2). Sketch the phase diagram for I₂ using the following data: triple point, 113°C and 0.12 atm; critical point, 512°C and 116 atm; normal melting point, 114°C; and normal boiling point, 184°C. [4 points]

**Solution.** [One point for each correctly labelled point]
4. (23-20). Determine the value of \( \frac{dT}{dP} \) for water at its normal boiling point of 373.15 K given that the molar enthalpy of vaporization is 40.65 kJ mol\(^{-1}\), and the densities of the liquid and vapor are 0.9584 g\cdot mL\(^{-1}\) and 0.6010 g\cdot L\(^{-1}\), respectively. Estimate the boiling point of water at 2 atm. [7 points]

**Solution.** Apply the Clapeyron equation (23.10)

\[
\frac{dP}{dT} = \frac{\Delta_v \overline{H}}{T \Delta_v \overline{V}}
\]

(6)

to get, when inverted:

\[
\frac{dT}{dP} = \frac{T \Delta_v \overline{V}}{\Delta_v \overline{H}} = \frac{T (V_f - V_i)}{T m \left( \frac{1}{\rho_f} - \frac{1}{\rho_i} \right)}
\]

(7)

(8)

where \( m \) is the molar mass and \( \rho \) is the (mass) density. (The subscripts are \( f \) for final state and \( i \) for initial state) Its value is

\[
\frac{dT}{dP} = \frac{(373.2 \text{ K})(18.02 \text{ g} \cdot \text{mol}^{-1})}{40.65 \text{ kJ} \cdot \text{mol}^{-1}} \left( \frac{1}{0.6010 \text{ g} \cdot \text{dm}^{-3}} - \frac{1}{958.4 \text{ g} \cdot \text{dm}^{-3}} \right)
\]

(9)

\[
= 0.2750 \text{ K} \cdot \text{L} \cdot \text{kJ}^{-1} = 27.50 \text{ K} \cdot \text{bar}^{-1} = 27.12 \text{ K} \cdot \text{atm}^{-1}
\]

(10)

Making the very crude assumption that

\[
\frac{dT}{dP} \approx \frac{\Delta T}{\Delta P} \Rightarrow \Delta T = \frac{dT}{dP} \Delta P
\]

(11)

\[
T + \Delta T \approx 373.15 \text{ K} + (27.12 \text{ K} \cdot \text{atm}^{-1}) (1 \text{ atm}) = 400.27 \text{ K} = 127.12 ^\circ \text{C}
\]

(12)

**Note.** The change in pressure is only one atmosphere.
5. (23-27) The molar enthalpy of vaporization of water is 40.65 kJ·mol\(^{-1}\) at its normal boiling point. Use the Clausius-Clapeyron equation to calculate the vapor pressure of water at 110°\(\text{C}\). The experimental value is 1075 torr. [4 + 1 points]

\textbf{Solution.} Assuming that the enthalpy change of vaporization is constant over the temperature range considered, the Clausius-Clapeyron equation can be integrated [1 bonus point]

\[
\int_{P_1}^{P_2} d\ln P = \frac{\Delta_v \overline{H}}{RT^2} \int_{T_1}^{T_2} \frac{dT}{T^2}
\]

(13)

to get the integrated form

\[
\ln \frac{P_2}{P_1} = \frac{\Delta_v \overline{H}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

(14)

Rearranging the equation, the answer can be computed to be

\[
P_2 = P_1 e^{\frac{\Delta_v \overline{H}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)}
\]

(15)

\[
= (760 \text{ torr}) e^{\frac{40.65 \text{ kJ mol}^{-1}}{8.315 \text{ J mol}^{-1} \cdot \text{K}^{-1}} \left( \frac{1}{373.15 \text{ K}} - \frac{1}{283.15 \text{ K}} \right)}
\]

(16)

\[
= 1070 \text{ torr}
\]

(17)

which is in excellent agreement with the experimental value, with an agreement to within 0.5%.