IMPORTANT: Write clearly and neatly. Make sure that you give some reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a brief justification or explanation.

Give units for all quantities!   **YOUR NAME** ___SOLUTIONS___

Some data: $R = 8.314 \, J \, K^{-1} \, mol^{-1}$ 1 atm = 101325 Pa $N_A = 6.022 \times 10^{23} \, mol^{-1}$ $\gamma = C_p/C_v$

$C_p - C_v = nR$ $dU = dq + dw$ $dS = dq/T$ $H = U + pV$ $G = H - TS$

$A = U - TS$

(1)   *35 points*

i)   Starting with an expression for the differential of G, prove that $(\partial V/\partial T)_p = -(\partial S/\partial p)_T$. *Show work and any results you rely on.*

ii)   Use this result to find ΔS for the isothermal expansion of 1 mol of a real gas from a pressure p_1 to p_2, where the equation of state is $pV = (R+a)T$ where a is a constant.

i) $dG = dH - TdS - SdT$; $dH = dU + pdV + Vdp$; $dU = dq + dw$

$= TdS - pdV$

so $dG = TdS - pdV + pdV + Vdp - TdS - SdT$

$= Vdp - SdT$.

Consider $G(p,T)$: $dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$.

By comparing terms, $\left(\frac{\partial G}{\partial T}\right)_p = -S$ and $\left(\frac{\partial G}{\partial p}\right)_T = V$.

Second derivatives are equal, $\frac{\partial^2 G}{\partial T \partial p} = -\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$.

ii) $V = (R+a)\frac{T}{p}$ $\therefore \left(\frac{\partial V}{\partial T}\right)_p = \frac{R+a}{p}$.

isothermal $\Delta S = \int dS = \int_{p_1}^{p_2} \left(\frac{\partial S}{\partial p}\right)_T dp = -(R+a)\int_{p_1}^{p_2} \frac{1}{p} dp$

$= (R+a) \ln(p_1/p_2)$.

(2)   *35 points*

Consider the gas-phase dissociation reaction $I_2 \rightarrow 2\,I$ where, at 1000 K, $\Delta_f G(\text{I atom}) = +24$ kJ mol^{-1}.

Calculate the degree of dissociation α for I_2 at 1000 K when the total equilibrium pressure is 10^4 Pa. *Do not assume α is small!*

For $I_2 \longrightarrow 2I$, $\Delta G^{\ominus} = +48 \text{ kJ mol}^{-1} = -RT \ln K$

$\therefore K = \exp \dfrac{-48000}{8.314 \times 1000} = 3.109 \times 10^{-3}$.

$$I_2 \longrightarrow 2\,I$$

	I_2	$2I$
initial pressure	p	0
equil. pressure	$p(1-\alpha)$	$2p\alpha$
activity	$\dfrac{p}{p^{\ominus}}(1-\alpha)$	$\dfrac{2p\alpha}{p^{\ominus}}$

Note total pressure $P_{TOT} = p(1+\alpha)$.

$$K = \left(\frac{2p\alpha}{p^{\ominus}}\right)^2 \bigg/ \frac{p}{p^{\ominus}}(1-\alpha) = \frac{p}{p^{\ominus}}\frac{4\alpha^2}{1-\alpha} = \frac{p(1+\alpha)}{p^{\ominus}(1+\alpha)(1-\alpha)}4\alpha^2 = \frac{P_{TOT}}{p^{\ominus}}\frac{4\alpha^2}{1-\alpha^2}$$

$$K \cdot \frac{p^{\ominus}}{P_{TOT}} = 3.109 \times 10^{-3} \times \frac{10^5 \text{ Pa}}{10^4 \text{ Pa}} = 0.03109 = \frac{4x}{1-x} \quad \text{where } x = \alpha^2$$

$$\therefore x = 0.007713 \quad \text{so } \alpha = \sqrt{x} = 0.0878.$$

If you prefer to use mole fractions,

$$I_2 \longrightarrow 2I$$

	I_2	$2I$
initial amount	n	0
equil. amount	$n(1-\alpha)$	$2n\alpha$
mole fraction	$\dfrac{n(1-\alpha)}{n(1+\alpha)}$	$\dfrac{2n\alpha}{n(1+\alpha)}$
activity	$\dfrac{1-\alpha}{1+\alpha}\dfrac{P_{TOT}}{P^{\ominus}}$	$\dfrac{2\alpha}{1+\alpha}\dfrac{P_{TOT}}{p^{\ominus}}$

total $= n(1+\alpha)$

$$K = \frac{4\alpha^2}{(1+\alpha)^2}\frac{P_{TOT}^2}{p^{\ominus 2}} \cdot \frac{p^{\ominus}}{P_{TOT}}\frac{1+\alpha}{1-\alpha} = \frac{4\alpha^2}{1-\alpha^2}\frac{P_{TOT}}{p^{\ominus}} \quad \text{as before.}$$

(3)   *30 points*

Here is a plot of ln p vs 1/T where p is vapor pressure of a liquid (in Pa). Derive the boiling temperature, and enthalpy and entropy of vaporization from this graph. *Show work.* You may assume these quantities do not vary with temperature.
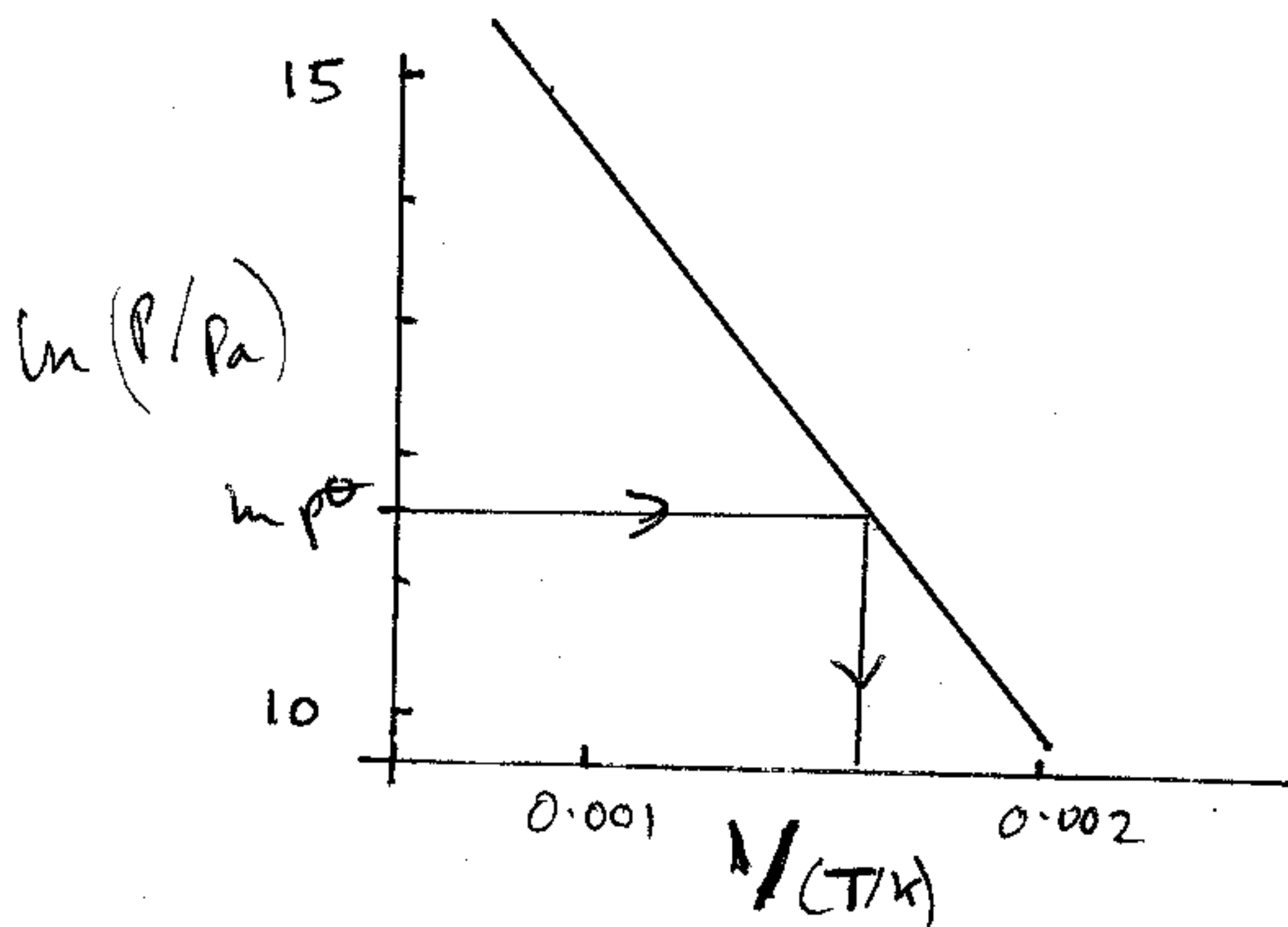
The boiling temp T_b is when $p = p^\ominus = 10^5 Pa$ $\therefore \ln p = 11.51$.

From the graph, $\frac{1}{T_b} \approx 0.0016$ $\therefore T_b \approx 625 K$.

Clausius-Clapeyron tells us $\frac{d \ln p}{d \frac{1}{T}} = \frac{-\Delta_{vap}H}{R}$.

Slope $\approx \frac{-5}{0.001 K^{-1}} = -5000 K$ from the plot $= -\frac{\Delta_{vap}H}{R}$

$\therefore \Delta_{vap}H \approx 42 \ kJ \ mol^{-1}$.

At T_b, $0 = \Delta G = \Delta H - T\Delta S$ $\therefore \Delta S = \frac{\Delta H}{T} = 67 \ JK^{-1} mol^{-1}$.