

EXAM 3
12 November 2004

*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: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ $1 \text{ atm} = 101325 \text{ Pa}$ $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ $\gamma = C_p/C_v$
 $C_p - C_v = nR$ $dU = dq + dw$ $dS = dq/T$ $H = U + pV$ $G = H - TS$
 $A = U - TS$ Trouton's constant = $85 \text{ J K}^{-1} \text{ mol}^{-1}$

(1) 36 points

- i) Starting with a general 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 change in pressure of 1 mol of a non-ideal gas from a pressure p_1 to pressure p_2 , where the equation of state for 1 mol is $pV = RT + a p^2/(RT)$. a is a constant.

$$G = H - TS = U + pV - TS ; \quad dG = dU + pdV + Vdp - TdS - SdT$$

and $dU = dq + dw = TdS - pdV$

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

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

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

$$\Delta S = \int dS = \int_{p_1}^{p_2} \left(\frac{\partial S}{\partial p}\right)_T dp = - \int_{p_1}^{p_2} \left(\frac{\partial V}{\partial T}\right)_p dp.$$

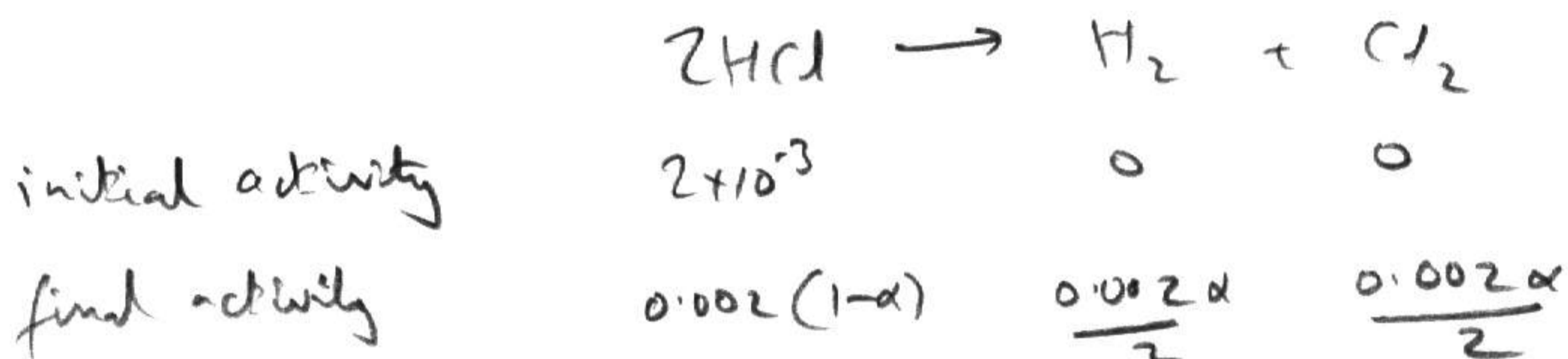
$$V = \frac{RT}{p} + \frac{ap}{RT} \quad \therefore \left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p} - \frac{ap}{RT^2} \quad \therefore \Delta S = - \int_{p_1}^{p_2} \left(\frac{R}{p} - \frac{ap}{RT^2}\right) dp$$

$$= - \left[R \ln p - \frac{ap^2}{2RT^2} \right]_{p_1}^{p_2} = R \ln \left(\frac{p_1}{p_2}\right) + \frac{a}{2RT^2} (p_2^2 - p_1^2).$$

(2) 34 points

For the reaction $2 \text{HCl(g)} \rightarrow \text{H}_2\text{(g)} + \text{Cl}_2\text{(g)}$

at 1300 K, $\Delta G^\circ = +80 \text{ kJ mol}^{-1}$. In a sealed, rigid container the pressure of initially pure HCl is $2.0 \times 10^5 \text{ Pa}$. What will be the equilibrium degree of dissociation of HCl (it is not very small), and the final pressure of H_2 ?



$$K = \frac{\left(\frac{0.002\alpha}{2}\right)^2}{\left(0.002(1-\alpha)\right)^2} = \frac{1}{4} \frac{\alpha^2}{(1-\alpha)^2} = e^{-\frac{\Delta G}{RT}} = 6.107 \times 10^{-4}$$

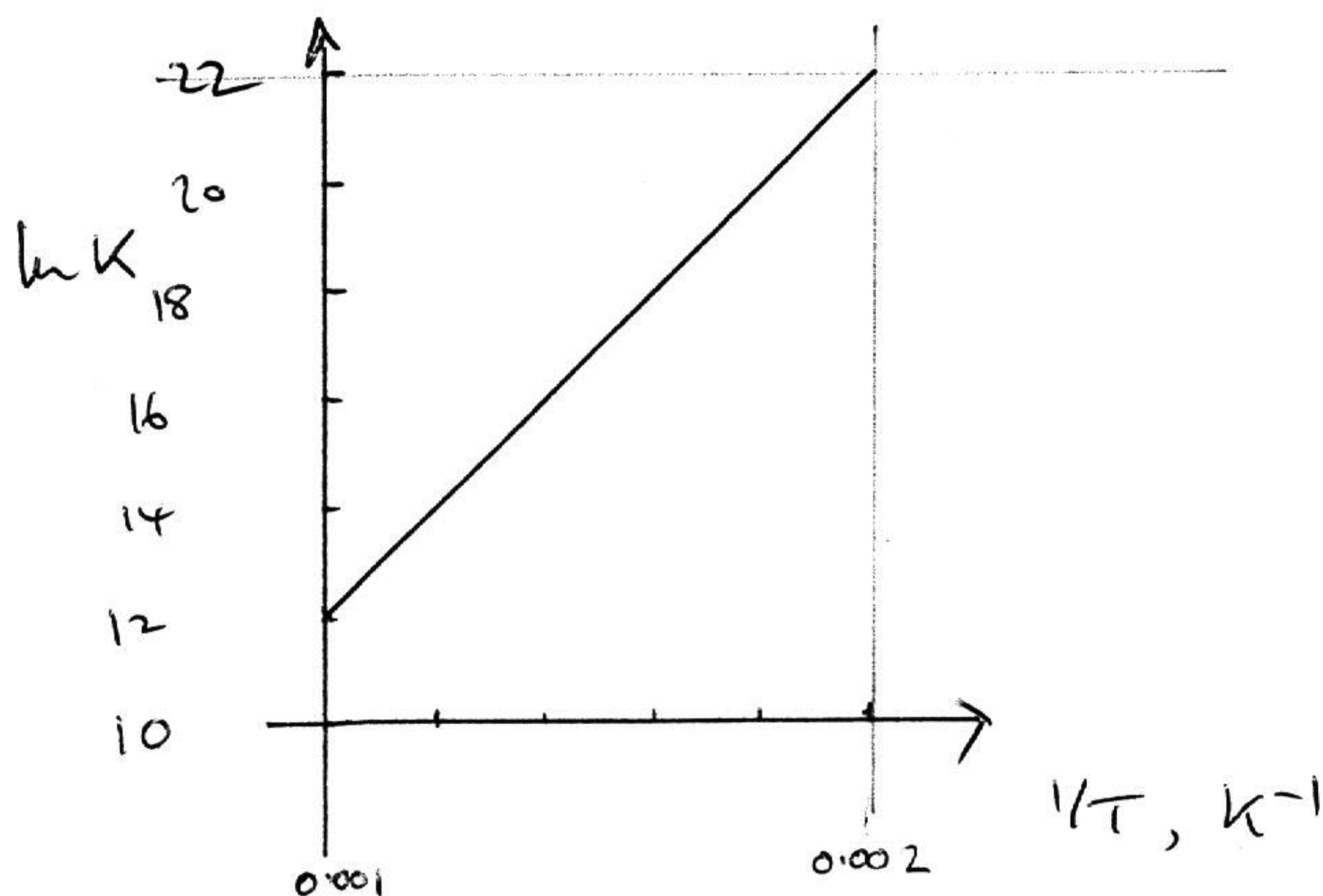
$$\therefore \frac{\alpha^2}{(1-\alpha)^2} = 0.00244 \quad \therefore \frac{\alpha}{1-\alpha} = \sqrt{0.00244} = 0.0494$$

$$\therefore \alpha = \underline{0.0471}$$

$$P_{\text{H}_2} = a_{\text{H}_2} \times p^\ominus = \frac{0.002\alpha}{2} \times 10^5 \text{ Pa} = \underline{4.7 \text{ Pa}}$$

(3) 30 points

Here is a plot of the temperature dependence of an equilibrium constant, in the form $\ln K$ vs $1/T$. Derive the standard enthalpy and entropy changes from this graph. Show work and give units. You may assume these quantities do not vary with temperature.



$$\text{Slope} = -\frac{\Delta H}{R} = \frac{10}{0.001 \text{ K}^{-1}} = 10^4 \text{ K}^{-1} \therefore \Delta H = \underline{\underline{-8.31 \times 10^4 \text{ J mol}^{-1}}}$$

Pick any point, say when $1/T = 0.002 \text{ K}^{-1}$ i.e. $T = 500 \text{ K}$.

$$\ln K = 22 \text{ so } \Delta G = -RT \ln K = -91454 \text{ J} = \Delta H - T\Delta S$$

$$\therefore \Delta S = \frac{\Delta H - \Delta G}{T} = \underline{\underline{16.7 \text{ J K}^{-1} \text{ mol}^{-1}}}$$