

### EXAM 3

9 November 1999

*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) 25 points

- Starting with an expression for the differential of  $A$ , derive the result  $(\partial p/\partial T)_V = (\partial S/\partial V)_T$ .
- Use this result to find  $\Delta S$  for the isothermal expansion of 1 mol of a real gas from  $V_1$  to  $V_2$ , where the equation of state is  $pV^x = RT$  where  $x$  is a constant ( $x \neq 1$ ).

$$dA = dU - Tds - SdT = (\tau ds - pdV) - Tds - SdT \\ = -pdV - SdT$$

$$\text{also } dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT \therefore -p = \left(\frac{\partial A}{\partial V}\right)_T \text{ and } -S = \left(\frac{\partial A}{\partial T}\right)_V$$

$$p = RTV^{-x} \therefore \left(\frac{\partial p}{\partial T}\right)_V = RV^{-x}$$

$$\Delta S = \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V}\right)_T dV = R \int_{V_1}^{V_2} V^{-x} dV = \frac{R}{1-x} \left[ V^{1-x} \right]_{V_1}^{V_2} \\ = \frac{R}{1-x} (V_2^{1-x} - V_1^{1-x})$$

(2) 15 points.

An organic compound has a normal boiling point of 400 K and  $\Delta_{\text{vap}}H = 25 \text{ kJ mol}^{-1}$ . Estimate the temperature at which its vapor pressure is  $10^4 \text{ Pa}$ .

$$\ln p = \text{const} - \frac{\Delta_{\text{vap}}H}{R} \cdot \frac{1}{T}$$

When  $T = 400 \text{ K}$ ,  $p = 10^5 \text{ Pa}$   $\therefore$

$$\ln 10^5 = \text{const} - \frac{25000}{8.314} \cdot \frac{1}{400}$$

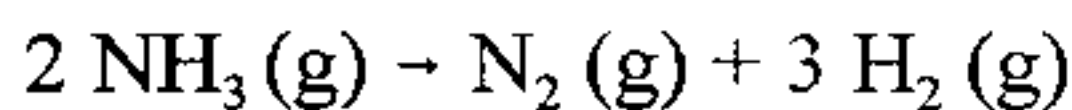
$$\therefore \text{const} = 19.03$$

$$\ln 10^4 = 19.03 - \frac{\Delta_{\text{vap}}H}{R} \cdot \frac{1}{T}$$

$$\therefore 9.21 = 19.03 - \frac{3007}{T} \quad \therefore \underline{\underline{T = 306 \text{ K}}}$$

(3) 30 points

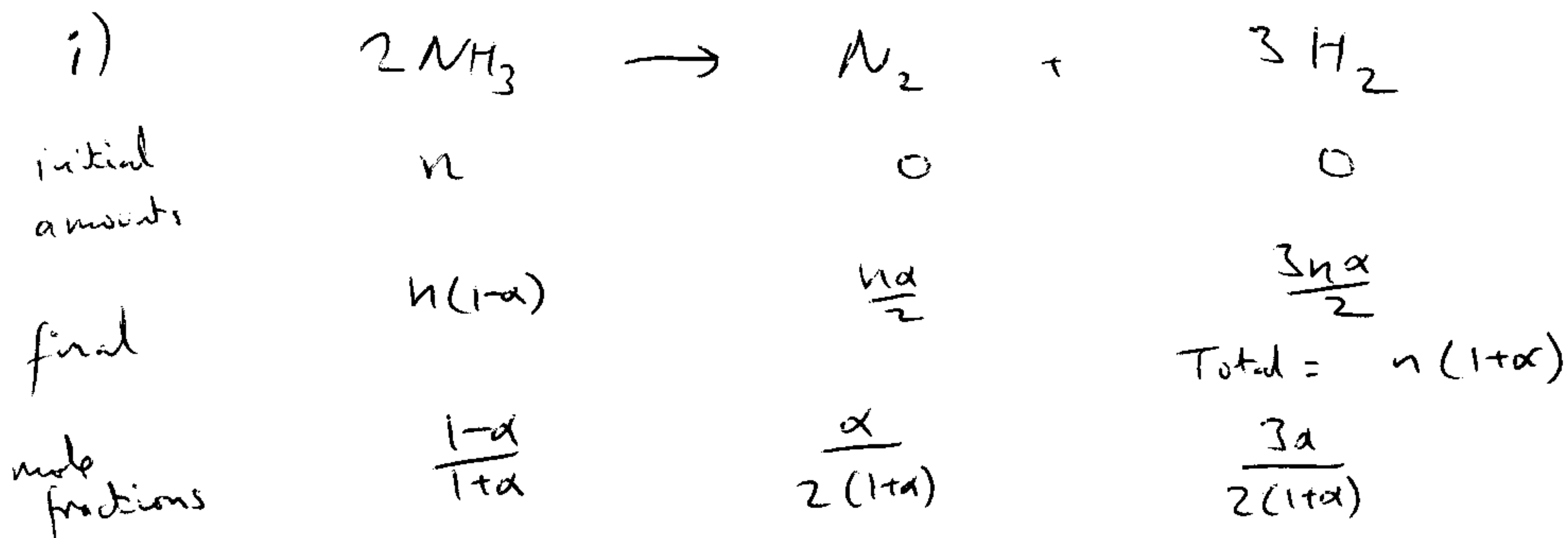
Consider the reaction



Starting with pure  $\text{NH}_3$  at 700 K, a fraction  $\alpha$  dissociates and the total pressure at equilibrium is  $10^5$  Pa.

(i) Find the equilibrium constant  $K$  in terms of  $\alpha$ .

(ii) The container is expanded and the total pressure drops. Qualitatively, explain briefly if you expect the following quantities to decrease, stay the same, or increase: (a)  $K$  (b)  $\alpha$ .



= activity in this case, because  $p/p^\ominus = 1$  here.

$$K = \frac{a_{\text{N}_2} a_{\text{H}_2}^3}{a_{\text{NH}_3}^2} = \frac{\frac{\alpha}{2} \cdot \left(\frac{3\alpha}{2}\right)^3 \frac{1}{(1+\alpha)^4}}{(1-\alpha)^2 \frac{1}{(1+\alpha)^2}} = \frac{27}{16} \frac{\alpha^4}{(1-\alpha)^2 (1+\alpha)^2}$$
$$= \frac{27}{16} \frac{\alpha^4}{(1-\alpha^2)^2} = \frac{27}{16} \frac{1}{\left(\frac{1}{\alpha^2} - 1\right)^2}$$

ii) By Le Chatelier's principle: low  $p \Rightarrow$  more dissociation because that gives more particles i.e. tends to raise the pressure.  
 $\alpha$  goes up.  $K$  remains the same.

(4) 30 points

An equilibrium constant  $K$  is found to obey

$$\ln K = -2.7 + 1500/T - 10^6/T^2$$

over the temperature range 250 - 400 K. Calculate  $\Delta H$ , then  $\Delta G$ , then  $\Delta S$ , all at 298 K. Give units.

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H}{R} \quad \text{Write } x = \frac{1}{T}, \text{ so } \ln K = -2.7 + 1500x - 10^6 x^2.$$

$$\begin{aligned} \frac{d \ln K}{d(1/T)} &= \frac{d \ln K}{dx} = 1500 - 2 \times 10^6 x = 1500 - \frac{2 \times 10^6}{T} = -5211 \text{ at } 298 \text{ K} \\ &= -\frac{\Delta H}{R} \therefore \Delta H_{298} = +43.3 \text{ kJ mol}^{-1}. \end{aligned}$$

$$T = 298 \text{ K} \Rightarrow \ln K = -8.927.$$

$$\Delta G_{298} = -RT \ln K = +22.12 \text{ kJ mol}^{-1}.$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} = +71.1 \text{ J K}^{-1} \text{ mol}^{-1}.$$