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

(1) *25 points*

i) Starting with an expression for the differential of A, derive the result $(\partial p/\partial T)_V = (\partial S/\partial V)_T$.

ii) Use this result to find ΔS 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 ($x \neq 1$).

$$dA = dU - TdS - SdT = (TdS - pdV) - TdS - SdT$$
$$= -pdV - SdT$$

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

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

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

$$= \frac{R}{1-x}\left(V_2^{1-x} - V_1^{1-x}\right).$$

(2) *15 points.*

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

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

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

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

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

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

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

(3) *30 points*

Consider the reaction $2\ NH_3\ (g) \rightarrow N_2\ (g) + 3\ H_2\ (g)$

Starting with pure NH_3 at 700 K, a fraction α dissociates and the total pressure at equilibrium is 10^5 Pa.

(i) Find the equilibrium constant K in terms of α.

(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) α.

i)

	$2NH_3$	$\rightarrow N_2$	$+ 3H_2$
initial amounts	n	0	0
final	$n(1-\alpha)$	$\frac{n\alpha}{2}$	$\frac{3n\alpha}{2}$
			Total = $n(1+\alpha)$
mole fractions	$\frac{1-\alpha}{1+\alpha}$	$\frac{\alpha}{2(1+\alpha)}$	$\frac{3\alpha}{2(1+\alpha)}$

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

$$K = \frac{a_{N_2}\, a_{H_2}^3}{a_{NH_3}^2} = \frac{\frac{\alpha}{2} \cdot \left(\frac{3\alpha}{2}\right)^3 \frac{1}{(1+\alpha)^4}}{(1-\alpha)^2 \frac{1}{(1+\alpha)^2}} = \frac{27}{16} \frac{\alpha^4}{(1-\alpha)^2(1+\alpha)^2}$$

$$= \frac{27}{16} \frac{\alpha^4}{(1-\alpha^2)^2} = \frac{27}{16} \frac{1}{\left(\frac{1}{\alpha^2}-1\right)^2}.$$

ii) By Le Chatelier's principle: Low $p \Rightarrow$ more dissociation because that gives more particles i.e. tends to raise the pressure.

α 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 ΔH, then ΔG, then ΔS, all at 298 K. Give units.

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

$$\frac{d \ln K}{d\, {}^1/_T} = \frac{d \ln K}{dx} = 1500 - 2\times10^6 x = 1500 - \frac{2\times10^6}{T} = -5211 \text{ at } 298\,K$$

$$= -\frac{\Delta H}{R} \therefore \quad \Delta H_{298} = +43.3 \text{ kJ mol}^{-1}.$$

$T = 298K \Rightarrow \quad \ln K = -8.927.$

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

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