EXAM 3

4 November 2002

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) *35 points*

i) Starting with a general expression for the differential of A, prove that $(\partial p/\partial T)_V = (\partial S/\partial V)_T$. *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 volume V_1 to V_2, where the equation of state is $pV = R(T + aT^2 + bT^3)$ where a and b are constants.

i) $dA = d(U - TS) = dq + dw - TdS - SdT = \cancel{TdS} - pdV - \cancel{TdS} - SdT$

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

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

ii) $$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V}\left(1 + 2aT + 3bT^2\right)$$

$$\Delta S = \int_{V_1}^{V_2} dS = \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V}\right)_T dV = R\left(1 + 2aT + 3bT^2\right)\ln\left(\frac{V_2}{V_1}\right) .$$

(2) *40 points*

For the reaction $2\ A(g) \rightarrow B(g) + C(g)$

the standard Gibbs energy change in J mol^{-1} is given by $\Delta G = 93\ T - (1.8 \times 10^9/T^2) - 2.5 \times 10^{-4}\ T^2$ where T is in kelvin.

i) Deduce ΔH and ΔS at 500 K.

ii) Initially pure A at 3×10^5 Pa and 500 K comes to equilibrium. The temperature and total pressure is held constant. What is the equilibrium partial pressure of B in Pa, and what is the degree of dissociation α of A? *Do not assume α is small!*

i) Could use $\Delta H = \dfrac{\partial\ \Delta G/T}{\partial\ 1/T}$ or alternatively

$$\ln K = \frac{-\Delta G}{RT} = \frac{-93}{R} + \frac{1.8\times10^9}{RT^3} + \frac{2.5\times10^{-4}}{R}T .$$

$$-\frac{\Delta H}{R} = \frac{d\ \ln K}{d\ 1/T} = \frac{d\ \ln K}{dT}\Big/\frac{d\ 1/T}{dT} = \frac{3\times 1.8\times10^9}{RT^2} - \frac{2.5\times10^{-4}\ T^2}{R}$$

$\therefore \Delta H = -21600 + 62.5 \approx -21540$ J mol^{-1} at 500 K.

$\Delta G = 46500 - 7200 - 62.5 \approx 39240$ J mol^{-1}.

$\Delta S = (\Delta H - \Delta G)/T = -121.6$ J K^{-1} mol^{-1}.

ii)

	$2A \longrightarrow$	$B\ +$	C
initial activity	3	0	0
equilibrium activity	$3-2x$	x	x

$a = p/p^\circ$

stoichiometry keeps amount + pressure constant, conveniently.

$$K = \frac{x^2}{(3-2x)^2} = e^{-\Delta G/RT} = 7.95\times10^{-5} \therefore \frac{x}{3-2x} = \sqrt{K}$$

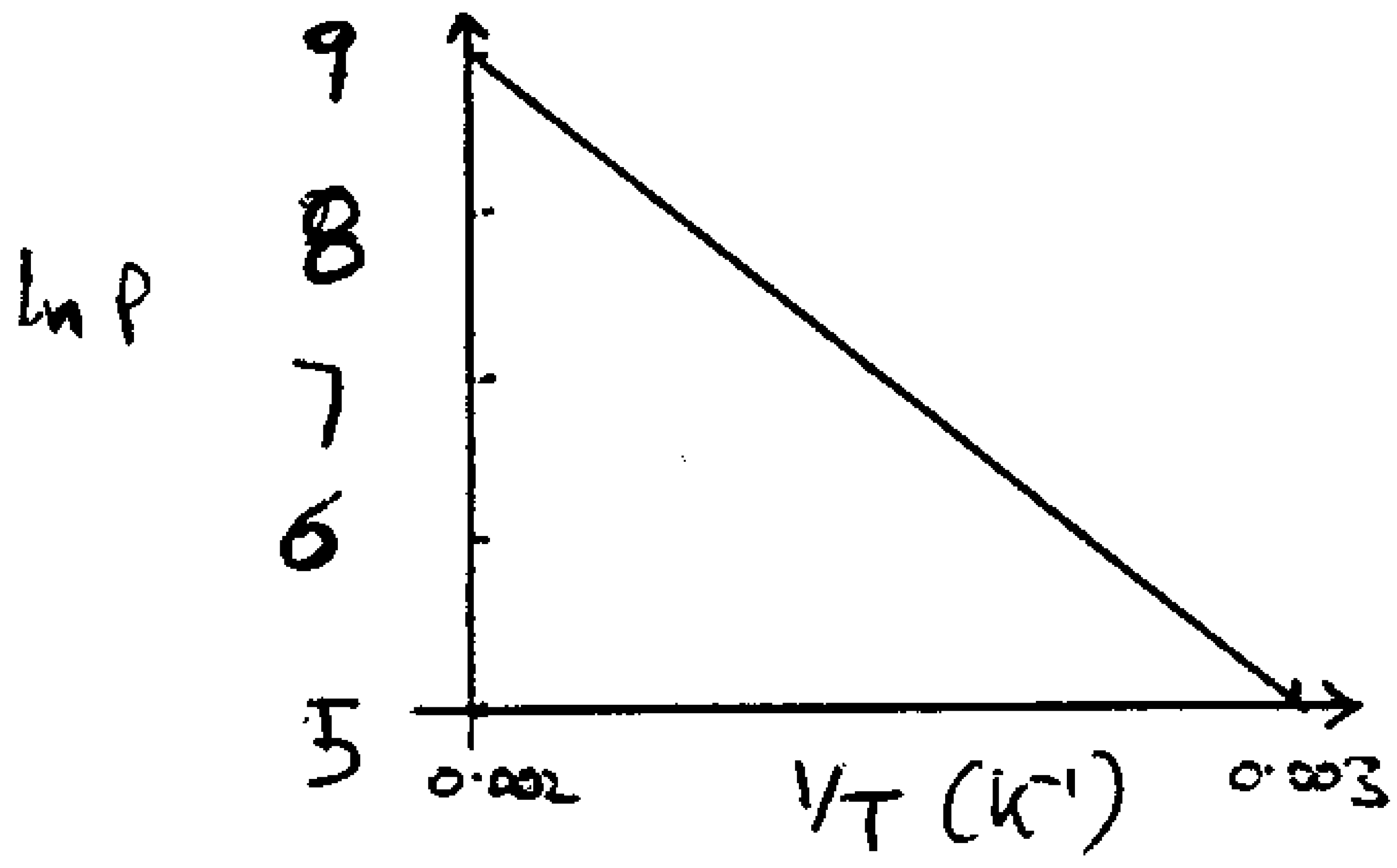
$\therefore x = 0.0262$,

$p_B = 0.0262 \times p^\circ = 2.62\times10^3$ Pa .

equilibrium activity of A also equals $3(1-\alpha)$ where α is the degree of dissociation, so $3\alpha = 2x$ and $\alpha = 0.0175$.

(3) *25 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.



general straight line $y = mx + c$.

slope $m = \dfrac{-(9-5)}{0.003 - 0.002\ \text{K}^{-1}} = -4000\ \text{K}$

$= -\dfrac{\Delta H}{R} \quad \therefore \Delta H = 33.3\ \text{kJ mol}^{-1}$.

Pick any point on the line, such as $\frac{1}{T} = 0.002\ \text{K}^{-1}$ with $\ln p = 9$:

$y = mx + c$ so $9 = -4000 \times 0.002 + c \quad \therefore c = 17$.

At the boiling point $y = \ln 10^5 = 11.51 \quad \therefore x = \dfrac{y-c}{m}$

$= \dfrac{11.51 - 17}{-4000\ \text{K}} = 1.372 \times 10^{-3}\ \text{K}^{-1}$

$T_b = 1/x = 729\ \text{K}$.

At T_b, $\Delta G = 0$ so $\Delta S = \dfrac{\Delta H}{T_b} = 45.6\ \text{J K}^{-1}\text{mol}^{-1}$.