

EXAM 4

20 November 2003

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) 34 points

Consider the reaction



Initially 0.1 mol of pure NOBr is confined in a container whose volume is $2 \times 10^{-3} \text{ m}^3$. At 500 K the degree of dissociation of NOBr is found to be 0.2, and rises to 0.6 at 600 K. Deduce the enthalpy and entropy change for the dissociation reaction given above. You may assume these two quantities do not vary with temperature, and that all the gases behave ideally.

	2NOBr	\rightarrow	2NO	$+$	Br_2
Initial activity	a_0		0		0
Equilibrium activity	$a_0(1-\alpha)$		$a_0\alpha$		$a_0\alpha/2$

$$K = \frac{(a_0\alpha)^2 a_0\alpha}{2 a_0^2 (1-\alpha)^2} = \frac{a_0}{2} \frac{\alpha^3}{(1-\alpha)^2}$$

At 500K, initial $p = \frac{nRT}{V} = \frac{0.1 \times 8.314 \times 500}{2 \times 10^{-3}} \text{ Pa} = 2.08 \times 10^5 \text{ Pa}$
 $\therefore a_0 = 2.08$

At 600K, $p = 2.49 \times 10^5 \text{ Pa}$ so $a_0 = 2.49$, $\therefore K = 0.013$
 $K = 1.68$

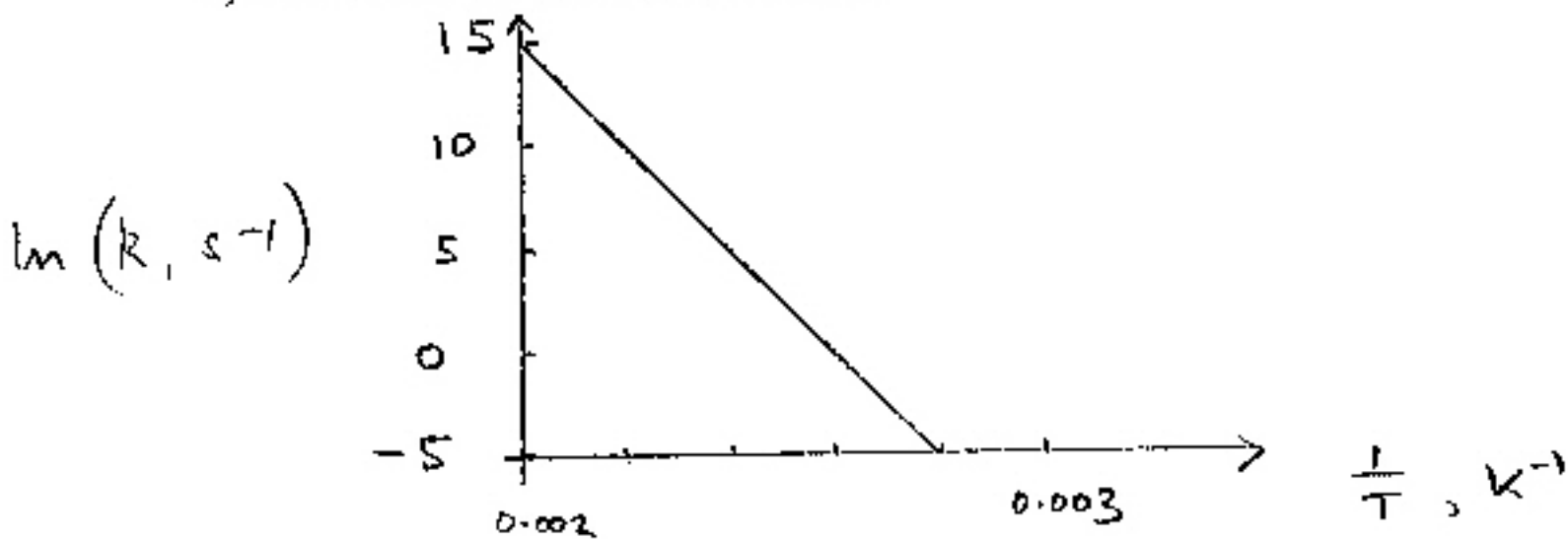
$$\ln\left(\frac{K_1}{K_2}\right) = -\frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \therefore \Delta H = 121 \text{ kJ mol}^{-1}$$

at 500K, $\Delta G = -RT \ln K = 18.1 \text{ kJ mol}^{-1} = \Delta H - T\Delta S$
 $\therefore \Delta S = \frac{\Delta H - \Delta G}{T} = 207 \text{ J K}^{-1} \text{ mol}^{-1}$

(2) 33 points.

Here is an Arrhenius plot of the rate constant for the reaction given in Question 1. Use it to

- Define the order of the reaction.
- Derive the Arrhenius parameters. Give units.
- Predict the rate constant at 1000 K.



a) Units of k are s^{-1} so it is **FIRST ORDER**.

b) Slope = $-\frac{E_a}{R} = \frac{15 - (-5)}{0.002 - 0.0028} = -25 \times 10^3 \text{ K}$

$\therefore E_a = 208 \text{ kJ mol}^{-1}$

$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T}$ $\therefore 15 = \ln A - 25 \times 10^3 \times 0.002$
 $\therefore \ln A = 65$ and $A = 1.7 \times 10^{28} \text{ s}^{-1}$

c) $k(1000\text{K}) = A e^{-\frac{E_a}{RT}} = 1.7 \times 10^{28} \text{ s}^{-1} \times e^{-\frac{25000}{1000}}$
 $= 2.4 \times 10^{17} \text{ s}^{-1}$

(3) 33 points

The reaction $2A + B \rightarrow 3C + 2D$ is found to be 0.5 order in A and zero order in B.

a) Write out the rate law to show the reaction rate v in terms of $[A]$ (no work needed for this step).

b) Through consideration of $d[A]/dt$, integrate this rate law and find the half-life $t_{1/2}$ of A. You may assume that initially the concentration of A is $[A]_0$.

$$a) \quad v = k [A]^{0.5}$$

$$b) \quad \frac{d[A]}{dt} = -2v = -2k [A]^{0.5}$$

↑
stoichiometry

$$\therefore \int [A]^{-0.5} d[A] = \int -2k dt$$

$$\therefore 2 [A]^{0.5} = -2kt + \text{const.}$$

When $t=0$, $[A] = [A]_0$ so

$$2 [A]_0^{0.5} = -2kt + 2 [A]_0^{0.5}$$

$$\text{or } kt = [A]_0^{0.5} - [A]^{0.5}$$

When $t = t_{1/2}$, $[A] = [A]_0 / 2$ so

$$kt_{1/2} = [A]_0^{0.5} - \left(\frac{[A]_0}{2}\right)^{0.5}$$

$$t_{1/2} = \frac{[A]_0^{0.5}}{k} \left(1 - \frac{1}{\sqrt{2}}\right)$$