EXAM 4

30 November 2000

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) *33 points*

Consider the reaction $2A \rightarrow B$ with rate law $v = k[A]^3$.

i) What is the order of the reaction?

ii) Assuming there is initially pure A with concentration $[A]_0$, find the concentration of A at a general time t.

iii) Derive an expression for the half life in terms of k and $[A]_0$.

i) Third order.

ii) $v = -\frac{1}{2}\frac{d[A]}{dt} = k[A]^3 \quad \therefore \quad \frac{d[A]}{dt} = -2k[A]^3$

$\therefore \int [A]^{-3} d[A] = -2kt + \text{const} = -\frac{1}{2}[A]^{-2}$.

$t=0,\ [A]=[A]_0 \quad \therefore \quad \text{const.} = -\frac{1}{2}[A]_0^{-2}$

$\therefore \quad [A]^{-2} = 4kt + [A]_0^{-2} \quad \therefore \quad [A] = \frac{1}{\sqrt{4kt + [A]_0^{-2}}}$

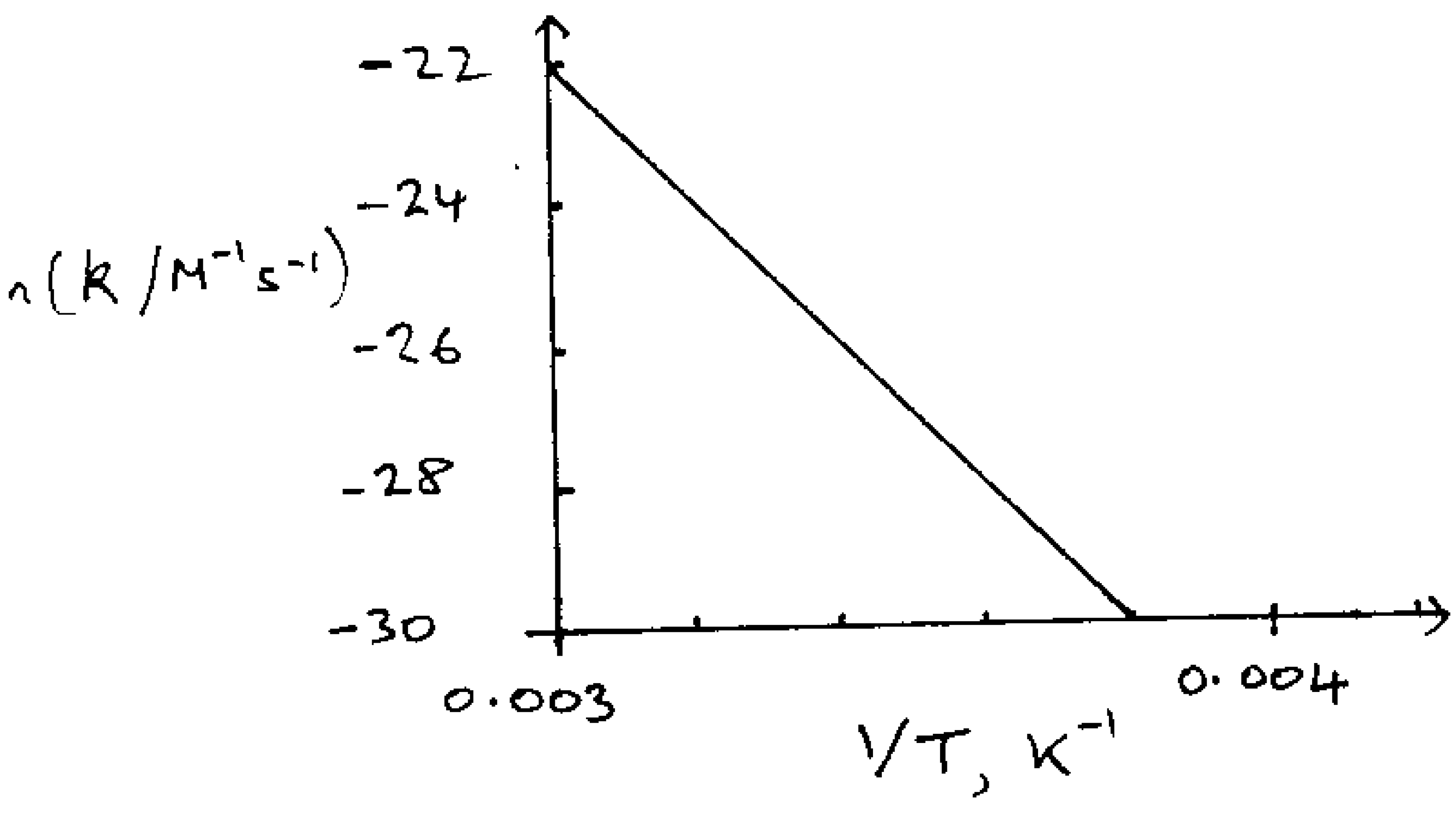
iii) $t = t_{1/2}$ when $[A] = [A]_0/2 \quad \therefore \quad -\frac{1}{2}\left(\frac{[A]_0}{2}\right)^{-2} = -2kt_{1/2} - \frac{1}{2}[A]_0^{-2}$

$\therefore \quad \frac{4}{[A]_0^2} - \frac{1}{[A]_0^2} = 4kt_{1/2}$

$\therefore \quad t_{1/2} = \frac{1}{4k} \cdot \frac{3}{[A]_0^2}$.

(2) *33 points.*

Here is an Arrhenius plot for a reaction. Find the Arrhenius parameters.



$$\text{slope} = -\frac{E_a}{R} = \frac{-22+30}{0.0030 - 0.0038\ K^{-1}} = -10000\ K$$

$$\therefore E_a = \underline{83.14\ kJ\,mol^{-1}}.$$

$$\ln K = \ln A - \frac{E_a}{RT}$$

$$\therefore -22 = \ln A - 10000 \times 0.0030$$

$$= \ln A - 30$$

$$\therefore \ln A = 8 \quad \therefore A = e^{8}\ s^{-1}M^{-1} = \underline{2980\ M^{-1}s^{-1}}.$$

(3) *34 points*

Here is a possible mechanism for the global gas-phase reaction $2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$:

$N_2O_5 \rightarrow NO_2 + NO_3$	rate constant k_1
$NO_2 + NO_3 \rightarrow N_2O_5$	rate constant k_{-1}
$NO_2 + NO_3 \rightarrow NO_2 + NO + O_2$	rate constant k_2
$NO + N_2O_5 \rightarrow 3\ NO_2$	rate constant k_3

Assuming that the concentrations of NO and NO_3 are in steady state, find the rate law implied by the mechanism in terms of elementary rate constants and concentrations of major species.

$$0 = \frac{d[NO]}{dt} = k_2[NO_2][NO_3] - k_3[NO][N_2O_5]$$

$$0 = \frac{d[NO_3]}{dt} = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - k_2[NO_2][NO_3]$$

$$\therefore\ k_1[N_2O_5] = (k_{-1}+k_2)[NO_2][NO_3]$$

$$\therefore\ [NO_3] = \frac{k_1[N_2O_5]}{(k_{-1}+k_2)[NO_2]}.$$

$$v = \text{rate of reaction} = \frac{d[O_2]}{dt} = k_2[NO_2][NO_3] = \frac{k_2 k_1 [N_2O_5]}{(k_{-1}+k_2)}.$$

Alternatively, $v = -\frac{d[N_2O_5]}{dt} = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] + k_3[NO][N_2O_5]$

$$= [N_2O_5]\left\{k_1 - k_{-1}\frac{k_1}{(k_{-1}+k_2)} + \frac{k_2 k_1}{(k_{-1}+k_2)}\right\}$$

$$= [N_2O_5]\left\{\frac{k_1(k_{-1}+k_2) - k_{-1}k_1 + k_2 k_1}{k_{-1}+k_2}\right\}$$

which is the same as above.