

EXAM 4

30 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

Consider the reaction $3A \rightarrow B$ with rate law $v = k [A]^{5/2}$.

- What is the order of the reaction?
- Assuming there is initially pure A with concentration $[A]_0$, find the concentration of A at a general time t .
- Derive an expression for the half life in terms of k and $[A]_0$.

i) 5/2
 ii) $v = -\frac{1}{3} \frac{d[A]}{dt} = k [A]^{5/2} \therefore \int [A]^{-5/2} d[A] = \int -3k dt$
 $\therefore -\frac{2}{3} [A]^{-3/2} = -3kt + \text{const.}$ When $t=0$, $[A] = [A]_0$, so
 $\frac{2}{3} [A]^{-3/2} = +3kt + \frac{2}{3} [A]_0^{-3/2}$
 $\therefore [A] = \left(\frac{9}{2} kt + [A]_0^{-3/2} \right)^{-2/3}$

iii) Substitute $[A] = [A]_0/2$ into $\left(\frac{9}{2} kt + [A]_0^{-3/2} \right)^{-2/3}$ to get

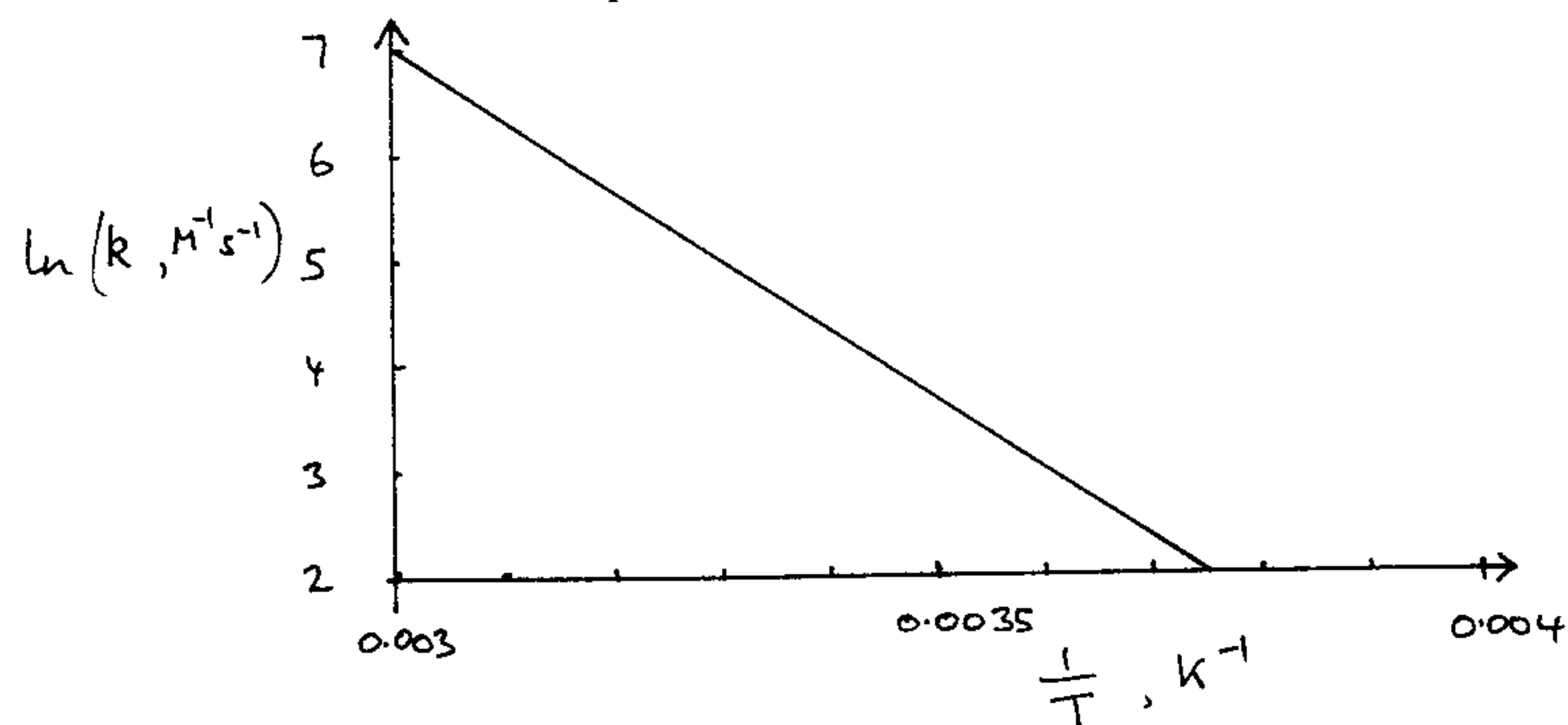
$$\left(\frac{[A]_0}{2} \right)^{-3/2} - [A]_0^{-3/2} = \frac{9}{2} k t_{1/2}$$

$$\therefore t_{1/2} = \frac{2}{9k} [A]_0^{-3/2} (2^{3/2} - 1)$$

$$\left(\approx \frac{0.406}{k} [A]_0^{-3/2} \right)$$

(2) 25 points.

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



$$k = A e^{-E_a/RT} \quad \text{so} \quad \ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T}$$

$$\text{slope} = \frac{7-2}{0.003 - 0.00375} = -6667 = -\frac{E_a}{R}$$

$$\therefore E_a = 55.4 \text{ kJ mol}^{-1}$$

Pick one point, e.g., when $\frac{1}{T} = 0.003$:

$$\ln k = 7 = \ln A - 6667 \times 0.003 = \ln A - 20$$

$$\therefore A = e^{27} = 5.3 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$$

(same units as k)

(3) 25 points

Consider the Michaelis-Menten mechanism for enzyme catalysis of $S \rightarrow P$:



By putting $[ES]$ into steady-state and making use of the relation $[E] + [ES] = [E]_0$

i) Derive the rate law for formation of P as a function of $[S]$, $[E]_0$ and elementary rate constants.

ii) What is/are the reaction order(s) in the limits as $[S]$ tends to zero and $[S]$ tends to infinity?

$$i) \quad [E] = [E]_0 - [ES] \quad \text{and} \quad 0 = \frac{d[ES]}{dt} = k_1 [E][S] - (k_2 + k_3)[ES]$$

$$\therefore k_1 [S]([E]_0 - [ES]) = (k_2 + k_3)[ES]$$

$$\therefore k_1 [E]_0 [S] = [ES] \{k_2 + k_3 + k_1 [S]\}$$

$$\therefore [ES] = \frac{k_1 [E]_0 [S]}{k_2 + k_3 + k_1 [S]}$$

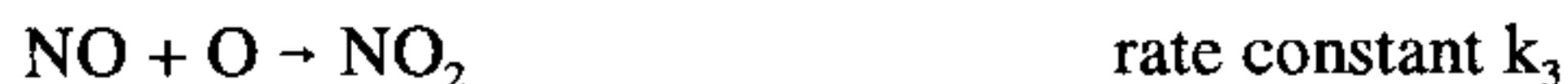
$$\text{Rate} = \frac{d[P]}{dt} = k_3 [ES] = \frac{k_1 k_3 [E]_0 [S]}{k_2 + k_3 + k_1 [S]}$$

$$ii) \quad \text{As } [S] \rightarrow 0, \text{ rate} \rightarrow \frac{k_1 k_3 [E]_0 [S]}{k_2 + k_3} \quad \text{i.e. second order,}$$

$$\text{As } [S] \rightarrow \infty, \text{ rate} \rightarrow k_3 [E]_0 \quad \text{i.e. first order,}$$

(4) 25 points

Here is a possible mechanism for the global gas-phase reaction $2 \text{NO}_2 \rightarrow 2 \text{NO} + \text{O}_2$:



Assuming that the concentration of O is in steady state, find the rate law implied by the mechanism in terms of elementary rate constants and concentrations of major species (HINT: use the rate of formation of a product).

$$0 = \frac{d[\text{O}]}{dt} = k_1 [\text{NO}_2] - k_2 [\text{NO}_2][\text{O}] - k_3 [\text{NO}][\text{O}]$$

$$\therefore [\text{O}] = \frac{k_1 [\text{NO}_2]}{k_2 [\text{NO}_2] + k_3 [\text{NO}]}$$

NO is involved in many steps, O₂ in only one.

$$\frac{d[\text{O}_2]}{dt} = k_2 [\text{O}][\text{NO}_2] = \frac{k_1 k_2 [\text{NO}_2]^2}{k_2 [\text{NO}_2] + k_3 [\text{NO}]}$$