

EXAM 4

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

(1) 34 points

Consider the reaction $A \rightleftharpoons B$ initially at equilibrium. The system is now perturbed in a temperature jump experiment and the concentration of A is displaced down by x . At the new temperature the kinetics are first order in both directions, with forward rate constant k_1 and reverse rate constant k_2 , and the equilibrium constant is K .

- i) Show that with x_0 as the initial value of the displacement, $x = x_0 \exp(-t/\tau)$ where the relaxation constant $\tau = 1/(k_1 + k_2)$.
- ii) $\tau = 10^{-6} \text{ s}$ and $K = 10^5$. Derive k_1 and k_2 .

$$\begin{aligned}
 [A] &= [A]_{eq} - x & \frac{d[A]}{dt} &= -\frac{dx}{dt} = -k_1[A] + k_2[B] \\
 [B] &= [B]_{eq} + x & &= -k_1[A]_{eq} + k_1x + k_2[B]_{eq} + k_2x
 \end{aligned}$$

Now $k_1[A]_{eq} = k_2[B]_{eq} \therefore \frac{dx}{dt} = -(k_1 + k_2)x$

$\therefore x = x_0 e^{-(k_1 + k_2)t}$

$$\begin{aligned}
 k_1 + k_2 &= 10^6 \text{ s}^{-1} & K = k_1/k_2 = 10^5 & \therefore k_1 = 10^5 k_2 \\
 k_2(1 + 10^5) &= 10^6 \text{ s}^{-1} & \therefore k_2 &\approx 10 \text{ s}^{-1} \text{ and } k_1 \approx 10^6 \text{ s}^{-1}
 \end{aligned}$$

(2) 33 points.

Consider the following mechanism for $A + B \rightarrow C$, where X^* is an energized intermediate whose concentration can be assumed to be in steady state.

i) What is the rate law for product (C) formation.

ii) What is the overall reaction order when $[B]$ is very high?

iii) What is the overall reaction order when $[B]$ is very small?



$$1) \quad v = \frac{d[C]}{dt} = k_2 [X^*][B]$$

$$\text{ss: } 0 = \frac{d[X^*]}{dt} = k_1 [A][B] - k_{-1} [X^*] - k_2 [X^*][B]$$

$$\therefore [X^*] = \frac{k_1 [A][B]}{k_{-1} + k_2 [B]}$$

$$\therefore v = \frac{k_1 k_2 [A][B]^2}{k_{-1} + k_2 [B]}$$

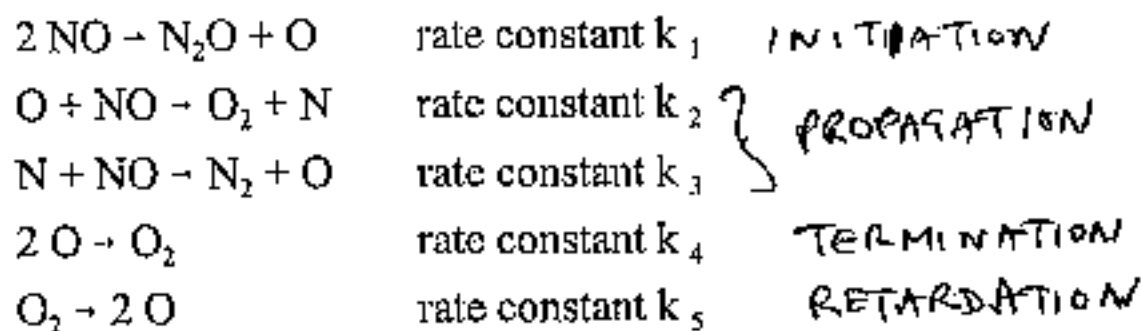
$$\text{ii) } [B] \text{ large} \Rightarrow v \approx \frac{k_1 k_2 [A][B]^2}{k_2 [B]} = k_1 [A][B] \quad \text{2}^{\text{nd}} \text{ order}$$

$$\text{iii) } [B] \text{ small} \Rightarrow v \approx \frac{k_1 k_2 [A][B]^2}{k_{-1}} \quad \text{3}^{\text{rd}} \text{ order}$$

(3) 33 points

Here is a possible mechanism for the thermal decomposition of NO to N₂ plus O₂. Identify initiation, propagation, retardation and/or termination steps. What is the rate law for formation of N₂?

Assume that the concentrations of N and O are in steady states.



$$\phi = \frac{d[\text{O}]}{dt} = k_1 [\text{NO}]^2 - k_2 [\text{O}][\text{NO}] + k_3 [\text{N}][\text{NO}] - 2k_4 [\text{O}]^2 + 2k_5 [\text{O}_2] \quad (1)$$

$$\phi = \frac{d[\text{N}]}{dt} = -k_3 [\text{N}][\text{NO}] + k_2 [\text{O}][\text{NO}] \quad (2)$$

$$v = \frac{d[\text{N}_2]}{dt} = k_3 [\text{N}][\text{NO}] = k_2 [\text{O}][\text{NO}] \quad \text{by (2)}$$

$$\text{Add (1) and (2)} \quad k_1 [\text{NO}]^2 - 2k_4 [\text{O}]^2 + 2k_5 [\text{O}_2] = 0$$

$$[\text{O}] = \sqrt{\frac{k_1 [\text{NO}]^2 + 2k_5 [\text{O}_2]}{2k_4}}$$

$$\therefore v = k_2 [\text{NO}] \sqrt{\frac{k_1 [\text{NO}]^2 + 2k_5 [\text{O}_2]}{2k_4}}$$