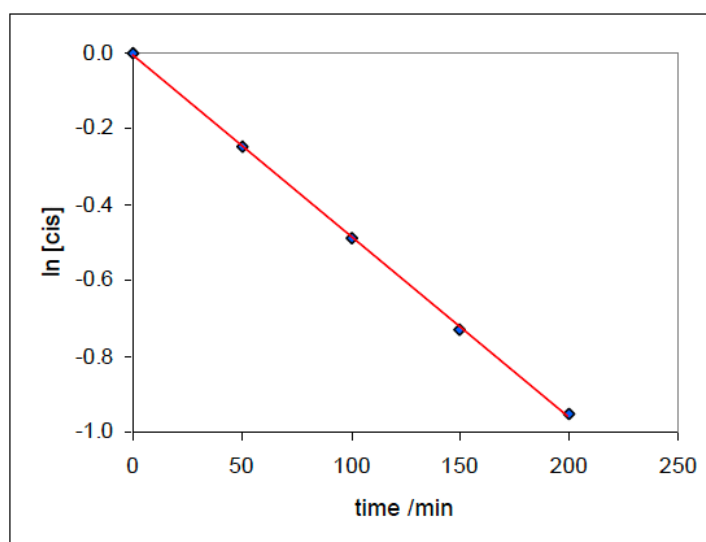


1. Stilbene (Ph-CH=CH-Ph) exists in both *cis* and *trans* forms. A sample of stilbene, initially 100% *cis*, is gradually transformed to a mixture of both isomers as shown in the table. Calculate the equilibrium constant and the rate constants for the forward and reverse reactions

t/min	% cis	[cis]	ln [cis]
0	100	1.00	0.000
50	82	0.78	-0.244
100	68	0.61	-0.487
150	57	0.48	-0.730
200	49	0.39	-0.953
inf.	17	0.00	

0.5 point
for plot



$$\text{slope} = -(k_1 + k_2) = -4.783 \times 10^{-3} \text{ min}^{-1}$$

$$(k_1 + k_2) = 0.287 \text{ s}^{-1}$$

$$\frac{k_1}{k_2} = K = \frac{[\text{trans}]_{\text{eq}}}{[\text{cis}]_{\text{eq}}} = \frac{1 - 0.17}{0.17} = 4.88$$

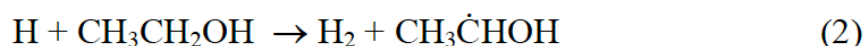
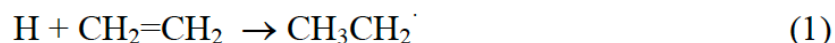
1 point

$$\underline{\underline{k_f = 0.24 \text{ s}^{-1}}}$$

$$\underline{\underline{k_b = 0.049 \text{ s}^{-1}}}$$

1 point

2. In a pulse radiolysis experiment H atoms are suddenly created in liquid ethanol (density 0.79 g cm^{-3}) containing 12 mM ethene. The initial concentration of H atoms falls to half its value in 1.5 ns. Two different radical products are detected by ESR, $\text{CH}_3\text{CH}_2\cdot$ and $\text{CH}_3\dot{\text{C}}\text{HOH}$, in the ratio 1:2.



Calculate the pseudo-first-order rate constant for H decay, and thence determine the second-order rate constants for reactions (1) and (2).

$$t_{1/2} = (\ln 2)/\lambda_{\text{H}} = 1.5 \text{ ns}$$

0.5 points

So pseudo-first-order rate constant, $\lambda_{\text{H}} = \underline{4.62 \times 10^8 \text{ s}^{-1}}$

$\lambda_{\text{H}} = \lambda_1 + \lambda_2$, the sum of the parallel reaction paths

$$\lambda_1/\lambda_2 = [\text{CH}_3\text{CH}_2\cdot]/[\text{CH}_3\dot{\text{C}}\text{HOH}] = 1/2 = 0.5$$

$$\text{Hence, } \lambda_{\text{H}} = 3.5\lambda_1$$

$$\lambda_1 = 1.54 \times 10^8 \text{ s}^{-1}$$

$$\lambda_2 = 3.08 \times 10^8 \text{ s}^{-1}$$

$$\text{But } \lambda_1 = k_1[\text{CH}_2=\text{CH}_2] = 0.012 k_1$$

$$\therefore \underline{k_1 = 1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}}$$

1 points

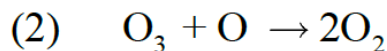
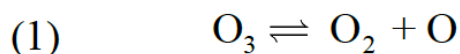
$$\text{Similarly, } \lambda_2 = k_2[\text{CH}_3\text{CH}_2\text{OH}]$$

$$\text{Since } [\text{CH}_3\text{CH}_2\text{OH}] = 0.79 \text{ g cm}^{-3} = 790/46 = 17.2 \text{ M,}$$

$$\underline{k_2 = 1.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}}$$

1 points

3. Consider the following mechanism for the decomposition of ozone into oxygen:



(a) Derive the rate equation for $-d[\text{O}_3]/dt$ in terms of $[\text{O}_2]$ and $[\text{O}_3]$.

Apply the steady-state approximation to $[\text{O}]$

$$\frac{d[\text{O}]}{dt} = k_1[\text{O}_3] - k_{-1}[\text{O}_2][\text{O}] - k_2[\text{O}_3][\text{O}] = 0$$

$$[\text{O}] = \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]}$$

$$-\frac{d[\text{O}_3]}{dt} = k_1[\text{O}_3] - k_{-1}[\text{O}_2][\text{O}] + k_2[\text{O}_3][\text{O}] = 2k_2[\text{O}_3][\text{O}]$$

$$\underline{\underline{-\frac{d[\text{O}_3]}{dt} = \frac{2k_1k_2[\text{O}_3]^2}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]}}}$$

2 points

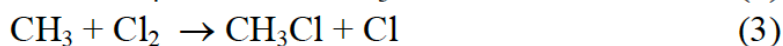
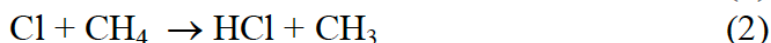
(b) Under what condition will the reaction be first order with respect to ozone? Show how the rate equation reduces in this situation.

At **low** $[\text{O}_2]$, where $k_{-1}[\text{O}_2] \ll k_2[\text{O}_3]$,

$$\underline{\underline{-\frac{d[\text{O}_3]}{dt} = 2k_1[\text{O}_3]}}$$

0.5 points

4. Consider the following free radical chain mechanism:



(a) Identify the reactants, products and intermediates, and write down the overall reaction.

reactants: Cl_2, CH_4

products: $\text{HCl}, \text{CH}_3\text{Cl}$

intermediates: Cl, CH_3

0.5 points

overall reaction: $\text{Cl}_2 + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3\text{Cl}$

(b) Derive the rate law for the overall reaction.

$$\text{SSA for Cl:} \quad 2R_1 - R_2 + R_3 - 2R_4 = 0$$

$$\text{SSA for CH}_3: \quad R_2 - R_3 = 0$$

$$\therefore R_2 = R_3 \quad \text{and} \quad R_1 = R_4$$

$$\begin{aligned} \text{where} \quad R_1 &= k_1[\text{Cl}_2] \\ R_2 &= k_2[\text{Cl}][\text{CH}_4] \\ R_3 &= k_3[\text{CH}_3][\text{Cl}_2] \\ R_4 &= k_4[\text{Cl}]^2 \end{aligned}$$

2 points

$$k_1[\text{Cl}_2] = k_4[\text{Cl}]^2 \quad \text{gives} \quad [\text{Cl}] = (k_1/k_4)^{1/2}[\text{Cl}_2]^{1/2}$$

$$\therefore \text{Rate of reaction} = R_3 = R_2 = (k_1/k_4)^{1/2}k_2[\text{Cl}_2]^{1/2}[\text{CH}_4]$$