Exercise: Reaction Rates, Reaction Orders, Rate Laws

Q1: $D \xrightarrow{k_1} A \xrightarrow{k_2} \emptyset$. Calculate $\frac{d[A]}{dt}$

$$\boxed{\frac{d[A]}{dt} = \underbrace{k_1[D]}_{\text{production}} - \underbrace{k_2[A]}_{\text{degradation}}}$$

Q2: $A + B \xrightarrow{k} C$. Assume elementary reaction. Calculate $\frac{d[A]}{dt}$

$$V = \underbrace{-\frac{d[A]}{dt}}_{\text{differential form}} = \underbrace{k[A][B]}_{\text{rate law}} \quad \text{(simple rate law)}$$

$$\therefore \boxed{\frac{d[A]}{dt} = -k[A][B]}$$

Q3: $nA + mB \xrightarrow{k} C$. Assume simple rate law. Calculate $\frac{d[A]}{dt}$

$$V = -\frac{1}{n}\frac{d[A]}{dt} = k[A]^n[B]^m \qquad \therefore \boxed{\frac{d[A]}{dt} = -nk[A]^n[B]^m}$$

Q4: $\underbrace{A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C}_{\text{fast}} \underbrace{\xrightarrow{k_2} D}_{\text{very slow}}$ Calculate reaction rate $V = \frac{d[D]}{dt} = ?$

Assume: fast, very slow

Based on assumption, $k_{-1} \gg k_2$. So we neglect the slight perturbation by C slowly leaking away to form D $\Rightarrow$ to simplify problem

$$\begin{cases} A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C & \text{(fast)} \\ C \xrightarrow{k_2} D & \text{(very slow)} \end{cases}$$

Then, at equilibrium: $k_1[A][B] = k_{-1}[C]$

$$\Rightarrow [C] = \frac{k_1}{k_{-1}}[A][B]$$

$$\boxed{\therefore V = \frac{d[D]}{dt} = k_2[C] = \frac{k_1 k_2}{k_{-1}}[A][B]}$$

Exercise: Reaction Half-Life

Q 5: Derive the half-life of 1st-order reaction.

Integrated rate law: $\ln[A] = \ln[A_0] - kt$

Answer: Plug in $[A] = \frac{1}{2}[A_0]$ and solve for t.

$$\ln[A] - \ln[A_0] = -kt$$

$$\ln\frac{[A]}{[A_0]} = \ln\frac{\frac{1}{2}[A_0]}{[A_0]} = \ln\frac{1}{2} = -\ln 2 = -kt$$

$$\therefore \boxed{t = \frac{\ln 2}{k}}$$

Q6: Derive the half-life of 2nd-order reaction.

Integrated rate law: $\frac{1}{[A]} = \frac{1}{[A_0]} + 2kt$

Answer: Plug in $[A] = \frac{1}{2}[A_0]$ and solve for t.

$$\frac{1}{\frac{1}{2}[A_0]} = \frac{1}{[A_0]} + 2kt$$

$$\frac{2}{[A_0]} - \frac{1}{[A_0]} = 2kt$$

$$\frac{1}{[A_0]} = 2kt$$

$$\therefore \boxed{t = \frac{1}{2k[A_0]}}$$

Note: The proper definition for 2^{nd}-order integrated rate law

$$A + A \xrightarrow{k} P \qquad (\text{or } 2A \xrightarrow{k} P)$$

should be :

$$\boxed{\frac{1}{[A_t]} = \frac{1}{[A_0]} + \underline{\underline{2}}kt}$$

Some text may have incorrectly neglected the '2' here!

Derivation: For $2A \xrightarrow{k} P$, we have

$$\begin{cases} v = -\frac{1}{2}\frac{d[A]}{dt} = \frac{d[P]}{dt} & (\text{differential form}) \\ v = k[A]^2 & (\text{rate law}) \end{cases}$$

Therefore : $-\frac{1}{2}\frac{d[A]}{dt} = k[A]^2$ → To get integrated rate law : We rearrange the equation as shown on the left

$$-\frac{1}{2}\frac{d[A]}{[A]^2} = k\,dt$$

$$\int_{[A_0]}^{[A_t]}\left(-\frac{1}{2}\cdot\frac{1}{[A]^2}\right)d[A] = \int_{t_0}^{t} k\,dt$$

$$\cancel{-}\frac{1}{2}\cdot(\cancel{-}A^{-1})\Big|_{[A_0]}^{[A_t]} = k(t-\cancel{t_0}^{\,0})$$

↓

$$\frac{1}{2}\left(\frac{1}{[A_t]} - \frac{1}{[A_0]}\right) = k(t-0) = kt$$

$$\therefore \frac{1}{[A_t]} - \frac{1}{[A_0]} = 2kt \Rightarrow \boxed{\frac{1}{[A_t]} = \frac{1}{[A_0]} + \underline{\underline{2}}kt}$$