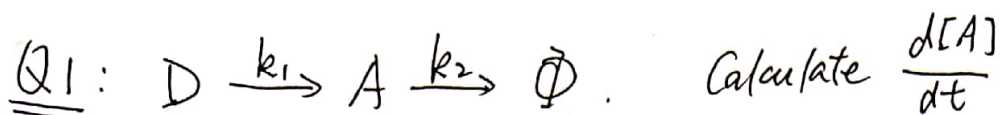
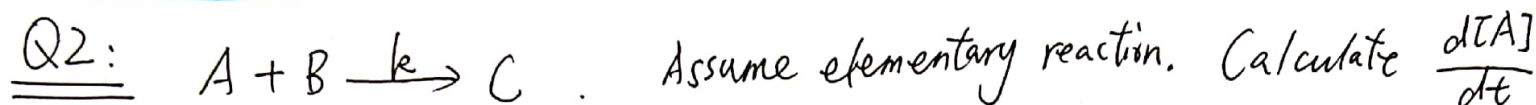


Exercise: Reaction Rates, Reaction Orders, Rate Laws

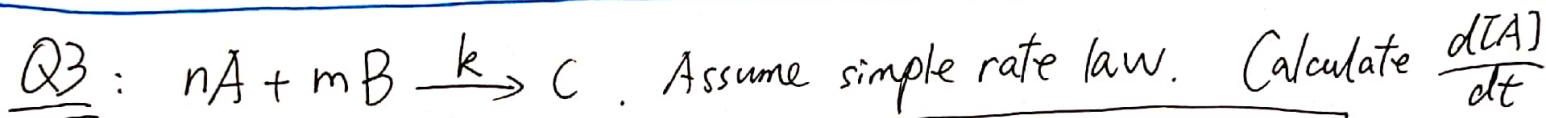


$$\frac{d[A]}{dt} = \underbrace{k_1[D]}_{\text{production}} - \underbrace{k_2[A]}_{\text{degradation}}$$

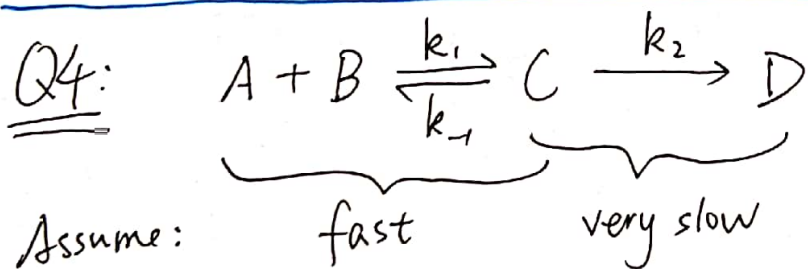


$$v = \underbrace{-\frac{d[A]}{dt}}_{\text{differential form}} = \underbrace{k[A][B]}_{\text{rate law}} \quad (\text{simple rate law})$$

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

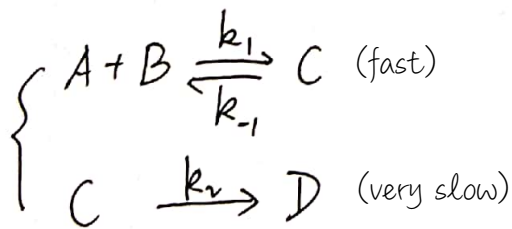


$$v = -\frac{1}{n} \frac{d[A]}{dt} = k[A]^n[B]^m \quad \therefore \boxed{\frac{d[A]}{dt} = -nk[A]^n[B]^m}$$



Calculate reaction rate $v = \frac{d[D]}{dt} = ?$

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



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

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

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

Exercise: Reaction Half-Life

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

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

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

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

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

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

Q 6: Derive the half-life of 2nd-order reaction.

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

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 2nd-order integrated rate law



should be :

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

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: $-\frac{1}{2} \frac{d[A]}{dt} = k[A]^2 \rightarrow$ To get integrated rate law :

$$-\frac{1}{2} \frac{d[A]}{[A]^2} = k dt \quad \leftarrow \text{we rearrange the equation as shown on the left}$$

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

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

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

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