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Chemical Kinetics

10^4 yrs $\longrightarrow$ sec

10^{-18} sec

$$\nu_A A + \nu_B B \longrightarrow \nu_C C + \nu_D D$$

$t = 0$ $\quad n_A(0) \quad n_B(0) \quad n_C(0) \quad n_D(0)$

$t = t$? $\quad n_A(t) = n_A(0) - \nu_A \xi(t)$

$$n_B(t) = n_B(0) - \nu_B \xi(t)$$

$$n_C(t) = n_C(0) + \nu_C \xi(t)$$

$$n_D(t) = n_D(0) + \nu_D \xi(t)$$

$$2\ H_2 + O_2 \longrightarrow 2\ H_2O$$

$-100 \qquad -50 \qquad +100$

$$\frac{dn_A}{dt} = -\nu_A \frac{d\xi}{dt}$$

$$\frac{dn_C}{dt} = (+\nu_C) \frac{d\xi}{dt}$$

(1)

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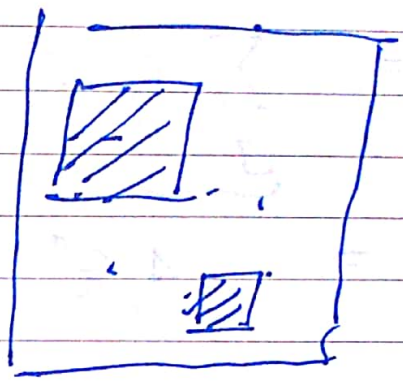
$$-\frac{1}{\nu_A}\frac{dn_A}{dt} = \frac{d\xi}{dt}$$

$$+\frac{1}{\nu_C}\frac{dn_C}{dt} = \frac{d\xi}{dt}$$



$$-\frac{1}{\nu_A}\frac{dn_A/V}{dt} \equiv -\frac{1}{\nu_A}\frac{d[A]}{dt} = \frac{1}{V}\frac{d\xi}{dt}$$

$$+\frac{1}{\nu_C}\frac{dn_C/V}{dt} \equiv +\frac{1}{\nu_C}\frac{d[C]}{dt} = \frac{1}{V}\frac{d\xi}{dt}$$

Rate / velocity $\equiv v \equiv \frac{1}{V}\frac{d\xi}{dt} = -\frac{1}{\nu_A}\frac{d[A]}{dt}$

$$= -\frac{1}{\nu_B}\frac{d[B]}{dt}$$

$$= +\frac{1}{\nu_C}\frac{d[C]}{dt}$$

$$= +\frac{1}{\nu_D}\frac{d[D]}{dt}$$

$$-\frac{1}{\nu_A}\frac{d[A]}{dt} = ?$$

$$= k[A]^3[B]^2$$

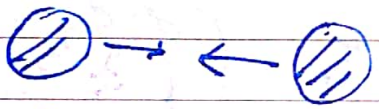
Rate equation

(2)

$H_2 + I_2 \longrightarrow 2HI \quad v = k[H_2][I_2]$

$H_2 + Br_2 \longrightarrow 2HBr$

$$v = \frac{k'[H_2][Br_2]^{3/2}}{1 + k''[HBr][Br_2]^{-1}}$$



$H_2 \qquad I_2 / Br_2$

$NO_2 + CO \longrightarrow CO_2 + NO$

$v = k[NO_2]^2$

$H_2 \longrightarrow H + H$

$Br_2 \longrightarrow Br + Br$

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$$v \propto [A]^m [B]^n$$

$$= k [A]^m [B]^n$$

k → rate constant

$$v = k'[A]$$

$$= -\frac{1}{\nu_A}\frac{d[A]}{dt}$$

$$-\frac{1}{\nu_A}\frac{d[A]}{dt} = k'[A]$$

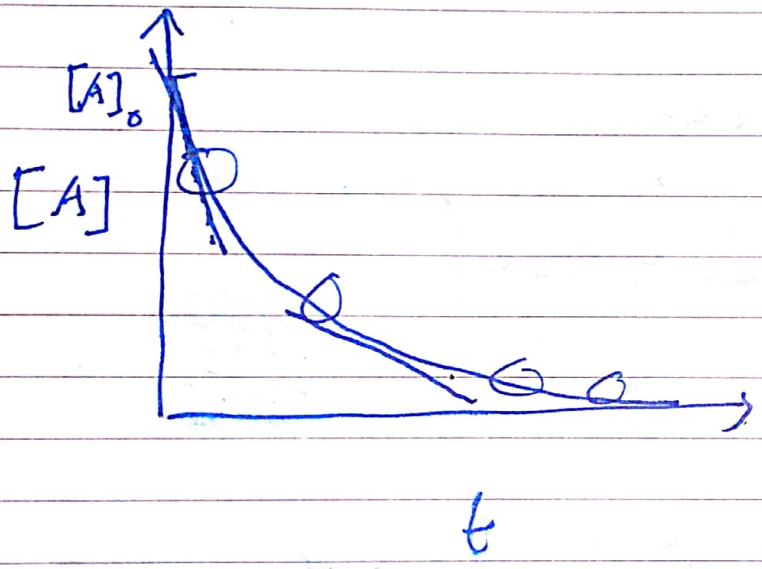
$$-\frac{d[A]}{dt} = k[A]^m \quad | k = k'\nu_A$$

$$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = \int_0^t k\,dt$$

$$\ln \frac{[A]}{[A]_0} = -kt$$

$$[A] = [A]_0 e^{-kt}$$

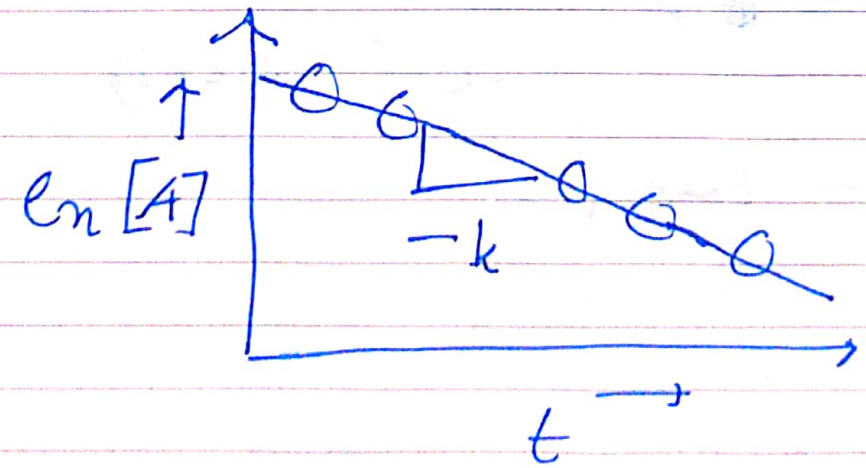
Int. rate law



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

$[A](t) \rightarrow$ ⌐ ⌐ ⌐

$(t) \rightarrow$ ⌐ ⌐ ⌐ ⌐



$$\ln[A] - \ln[A]_0 = -kt$$

$$y - y_0 = mx$$

$$m = -k$$

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At $t = t_{1/2}$

$$[A](t) = \frac{1}{2}[A]_0$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

$t_{1/2}$ ∝ $\frac{1}{k}$

$[A]_0 \rightarrow [A]_{0/2}$ — $t_{1/2}$ = 1 hr

$[A]'_0 \rightarrow [A]'_{0/2}$ — 1 hr

$$\frac{d[A]}{dt} = -k[A]^n \quad \Big| \quad -k[A]^2 \quad -k[A][B]$$

$t_{1/2} = ?$ $\qquad n \neq 1$