KINETICS

$$^{14}C \rightarrow {}^{14}N + \beta$$

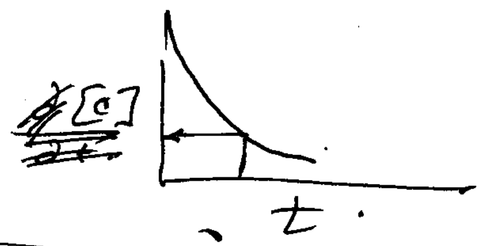
$$\frac{\#\beta}{t} \Rightarrow RATE = \frac{\Delta[N]}{\Delta t} = \frac{-\Delta[C]}{\Delta t} \Rightarrow -\frac{\partial[C]}{\partial t}$$

POSITIVE #.

$$RATE \Rightarrow -\frac{\partial[C]}{\partial t} \propto [C]$$

$$\underbrace{RATE}_{\frac{mol}{L-s}} = -\frac{\partial[C]}{\partial t} = \underbrace{k}_{\frac{1}{s} \text{ or } s^{-1}}\underbrace{[C]}_{\frac{mol}{l}}$$

RATE LAW.



$$-\frac{\partial[C]}{\partial t} = k[C]$$

$$+\int_{[C]_0}^{[C]} \frac{\partial[C]}{[C]} = \int_0^t -k\,\partial t$$

$$\ln[C]\Big|_{[C]_0}^{[C]} = -kt\Big|_0^t$$

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

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

$$\frac{[C]}{[C]_0} = e^{-kt}$$

integrated rate law

$$\boxed{[C] = [C]_0 e^{-kt}}$$

half life

$t_{1/2}$ $\qquad [C]_t = \frac{1}{2}[C]_0$

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

$$\ln\left(\frac{1\,\cancel{[C]_0}}{2\,\cancel{[C]_0}}\right) = -k t_{1/2}$$

$$-\ln\left(\tfrac{1}{2}\right) = +k t_{1/2}$$

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

$$8H^+ + 5Fe^{2+} + MnO_4^- \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

overall reaction

made of $\underbrace{\text{elementary reaction steps}}_{\text{reaction mechanism}}$.

<u>Stoichiometry does not allow prediction of reaction mechanism!</u>

$$aA + bB \rightarrow cC + dD$$

$$\text{RATE} = \frac{\partial[C]}{c\,\partial t} = \frac{\partial[D]}{d\,\partial t} = \frac{-\partial[A]}{a\,\partial t} = \frac{-\partial[B]}{b\,\partial t}$$

$$X + Y \rightarrow Z$$

$$\underbrace{\text{Rate} = k\,[X]^m[Y]^n}_{\text{RATE LAW}}$$

n, m ← order of reax.

k ← rate const.

$m + n \equiv$ <u>overall</u> order of reaction.

We can have zero order. ("pseudo-zero order")

" " " fractional "

How to determine order of reaction!

$$A + B \xrightarrow{k} C$$

Method of initial rates.

expts	[A] ($\underline{M}$)	[B] ($\underline{M}$)	Rate. (M/l-s)
1	1×10^{-5}	1×10^{-5}	7.6×10^{-7}
2	2×10^{-5}	1×10^{-5}	1.5×10^{-6}
3	2×10^{-5}	2×10^{-5}	6.1×10^{-6}

$$\frac{\text{rate}_{2}}{\text{rate}_{1}} = \frac{1.5\times10^{-6}}{7.6\times10^{-7}} = \frac{\cancel{k}\,[A]_{2}^m\,\cancel{[B]_{2}^n}}{\cancel{k}\,[A]_{1}^m\,\cancel{[B]_{1}^n}}$$

$$= 2 = \left(\frac{2\times10^{-5}}{1\times10^{-5}}\right)^m = (2)^m \rightarrow m = 1$$

for [A] held constant: expt ② & ③

$$\frac{③}{②} = \frac{6.1\times10^{-6}}{1.5\times10^{-6}} = \left(\frac{2\times10^{-5}}{1\times10^{-5}}\right)^n = (2)^n .$$

$$4 \Longrightarrow n = 2 .$$

$$\text{Rate} = k[A][B]^2$$

$$\frac{\text{rate}③}{\text{rate}②} = \left(\frac{[B]_③}{[B]_②}\right)^m .$$

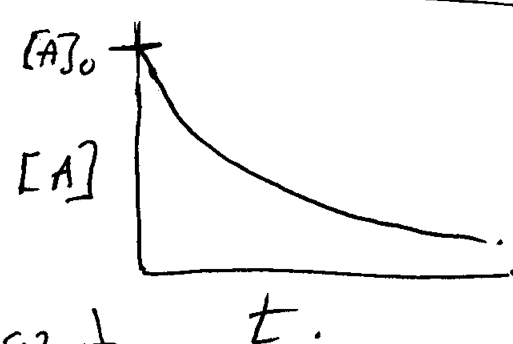
$$\ln\left(\frac{\text{rate}③}{\text{rate}(2)}\right) = m \ln\left(\frac{[B]_③}{[B]_②}\right).$$

solve for m!

$$A \rightarrow B .$$

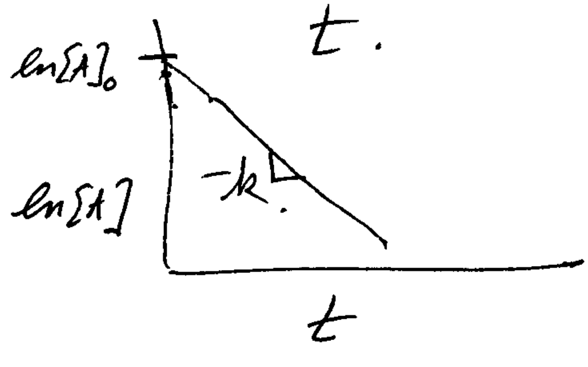
$$\text{Rate} = \frac{-\partial[A]}{\partial t} = k[A]$$

$$[A] = A_0 e^{-kt} .$$



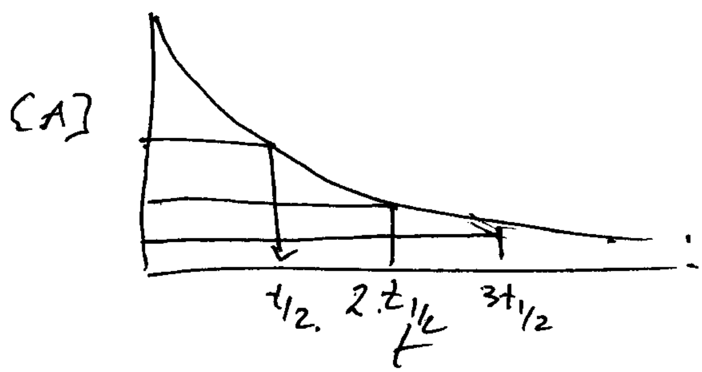
$$\ln[A] = \ln[A]_0 - kt$$

$$y = b + mx$$



HALF LIFE

$$t_{1/2} = \frac{\ln 2}{k} \quad (1^{ST} \text{ order reaction}).$$



2ND ORDER.

$C_2H_6 \rightarrow CH_3$.

$R = k[C_2H_6]^2$

$$\cancel{2}W \rightarrow Q$$

$$\text{Rate} = k[W]^2. \qquad k: \frac{l}{mol\text{-}s}.$$

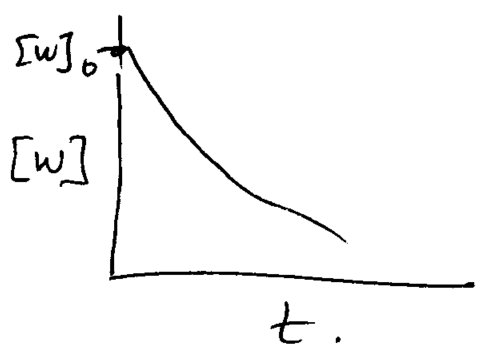
$$\Downarrow$$

$$-\frac{\partial[W]}{\partial t} = k[W]^2.$$

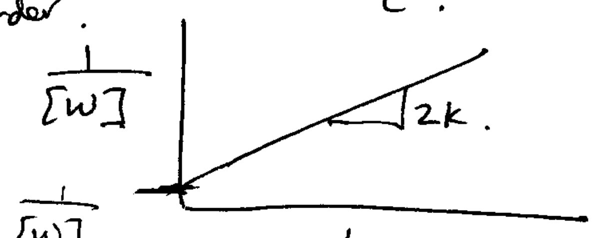
$$-\frac{\partial[W]}{[W]^2} = k\,\partial t.$$

$$+\frac{1}{2[W]}\Bigg|_{[W]_0}^{[W]} = kt\Bigg|_0^t.$$

$$\boxed{\frac{1}{[W]} - \frac{1}{[W]_0} = 2kt.}$$



2nd order.



zero order.

$$P \rightarrow Q$$

$$\text{Rate} = k.$$