First order Reactions

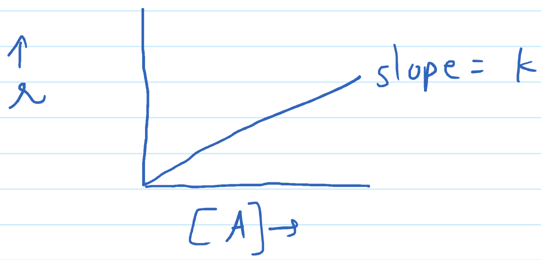
Consider a first order reaction $A \rightarrow B$, let a_0 be initial concentration of A. a_t and b_t be the concentrations of A and B at time t. Let x be change in concentration of A in time t.

	A $\longrightarrow$	B
$t=0$	a_0	
$t=t$	$a_t = a_0 - x$	$b_t = x$

For first order reaction rate law expression is given as:

$$r = k[A] = k a_t = k(a_0 - x) \quad - I$$

For first order reaction, rate of reaction increases linearly with concentration of reactants.



Also for any general reaction $A \longrightarrow B$, $r = -\frac{dA}{dt} = \frac{dB}{dt}$

$$-\frac{dA}{dt} = \frac{-d(a_t - a_0)}{dt} = -\frac{d(a_0 - x - a_0)}{dt} = \frac{dx}{dt}$$

$$\frac{dB}{dt} = \frac{d}{dt}(b_t - 0) = \frac{dx}{dt}$$

Thus $r = \frac{dx}{dt} \quad - II$

Equate I and II

$$k(a_0 - x) = \frac{dx}{dt}$$

$$\frac{dx}{a_0 - x} = k\,dt$$

Integrate both sides

$$\int_0^x \frac{dx}{a_0 - x} = k \int_0^t dt$$

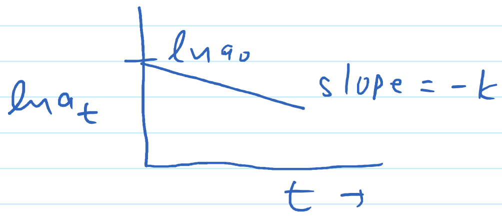
$$\left. \frac{\ln(a_0 - x)}{-1} \right|_0^x = k \; t \Big|_0^t \qquad \int \frac{1}{a+bx} dx = \frac{1}{b} \ln(a+bx)$$

$$\frac{\ln(a_0 - x) - \ln a_0}{-1} = k(t-0)$$

$$\ln a_0 - \ln(a_0 - x) = kt \qquad \left(\ln a_t = -kt + \ln a_0 \right)$$

$$\ln a_0 - \ln a_t = kt$$

$$\ln \frac{a_0}{a_t} = kt$$



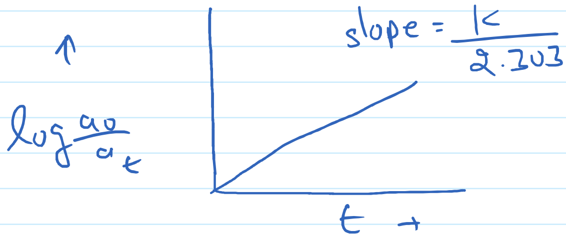
$$2.303 \log \frac{a_0}{a_t} = kt \quad ✓$$

$$k = \frac{2.303}{t} \log \frac{a_0}{a_t}$$

$\ln = \log_e$

$\log_{10}$

$\log_e = 2.303 \log_{10}$



Concentration of Reactants at time t

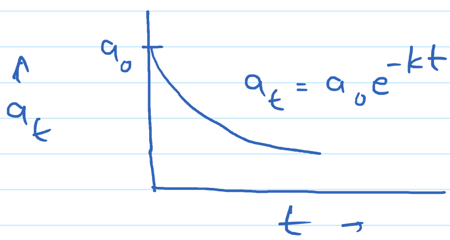
$$\ln \frac{a_0}{a_t} = kt$$

$$\frac{a_0}{a_t} = e^{kt}$$

$$a_t = a_0 e^{-kt}$$

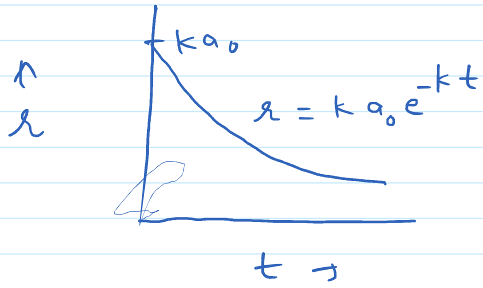
$\log_e(a) = b$

$a = e^b$



Thus concentration of reactants decrease exponentially with time

$$r = k a_t = k(a_0 e^{-kt})$$



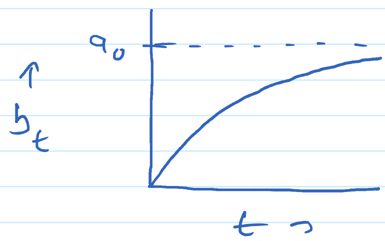
Concentration of products at time t

$$a_t = a_0 e^{-kt}$$

$$a_0 - x = a_0 e^{-kt}$$

$$x = a_0 - a_0 e^{-kt}$$

$$b_t = a_0 (1 - e^{-kt})$$



$$e^{-\infty} = 0$$

Life time of reaction

Time of completion of reaction is called life time of reaction (t_{LT}). When reaction is completed

$$a_t = 0$$

$$a_0 e^{-kt} = 0$$

$$e^{-kt} = 0$$

$$t = \infty$$

Thus a first order reaction gets completed in infinite time interval. In other words a first order reaction never gets completed. When first order reaction is 99.9% complete it is assumed to be complete

Half life time of reaction

Time in which 50% reaction is completed is called half life time of reaction ($t_{1/2}$). when reaction is half complete.

$$a_t = \frac{a_0}{2}$$

$$a_0 e^{-kt_{1/2}} = \frac{a_0}{2}$$

$$e^{-kt_{1/2}} = \frac{1}{2}$$

$$e^{kt_{1/2}} = 2$$

$$kt_{1/2} = \ln 2$$

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

$kt = \log_e 2$

$e^{kt} = 2$

Thus for first order reaction half life time is independent of concentration of reactants.

Examples of first order reactions

1) Hydrogenation of ethene.

2) All natural and artificial radioactive decay of unstable nuclei.

3) Decomposition of N_2O_5 and N_2O.

eg: $2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$

$10M$ N_2O_5 $\xrightarrow{10\ min}$ $5M$ $\xrightarrow{10\ min}$ 2.5 $\xrightarrow{10\ min}$ 1.25

$20M$ $\xrightarrow{10\ min}$ $10\ M$