Chem

Chemical Kinetics

Mishu
090092

Chemical kinetics:

The branch of physical chemistry which deals with the rate of reactions is called chemical kinetics.

Rate of reaction:

The rate of a reaction tells as to what speed the reaction occurs. Let us consider a simple reaction

$A \rightarrow P$

C_0 0 when $t=0$

$C=C_0-x$ x when $t=t$

The concentration of the reactant A decreases and that of P increases as time passes. The rate of reaction is defined as the change in concentration of any reactant or products per unit time. When t is equal to zero, the concentration of reactant is C_0 and product is zero. when t is equal to t, then the concentration of reactant is $C = C_0 - x$ and product is x

Rate of reaction = rate of disappearance of A
= rate of appearance of B

$$rate = -\frac{d[A]}{dt} = +\frac{d[P]}{dt}$$

$$= -\frac{d[C]}{dt} = +\frac{dx}{dt}$$

[ ] represents the concentration in mole per litre.

Rate laws / laws of chemical kinetics:

At a fixed temperature the rate of a given reaction depends on concentration of reactants. "The rate of reaction is directly proportional to the reactant concentration, each concentration being raised to some power."

$$\begin{array}{lll} A \longrightarrow & P & \\ C_0 & 0 & , t=0 \\ c=C_0-x & x & , t=t \end{array}$$

When $t=0$ ∴ the concentration of reactant is C_0 and produc P is zero. After a time t the concentration of reactant A is $c=C_0-x$ and product P is x.

The rate of reaction $-\frac{dc}{dt} \propto c^n$

$$-\frac{dc}{dt} = Kc^n$$

K= Velocity constant

Nao, the rate of reaction,

$$-\frac{dc}{dt} = kc^{n}$$

$n=0$, $$-\frac{dc}{dt} = kc^{0} = k.1 = K$$

$$-dc = Kdt \quad -①$$

Integrating the equation ① we get,

$$-\int_{c_0}^{c} dc = K\int_{0}^{t} dt$$

$$-[c]_{c_0}^{c} = K[t]_{0}^{t}$$

$$-[c-c_0] = K[t-0] \longrightarrow C_0 - C = Kt$$

$$\boxed{C = C_0 - Kt} \quad -(iv)$$

$$\boxed{C_0 = C + Kt} \quad -(v)$$

$$-(c-c_0) = Kt \quad -(iii)$$

$$\boxed{x = Kt} \quad [x = C_0 - C]$$

The rate constant is equal to the rate of reaction at all concentration.

Now, the rate of reaction,

$$-\frac{dc}{dt} = kc^n$$

for first order reaction, n=1.

$$-\frac{dc}{dt} = kc^1$$

$$-\frac{dc}{dt} = kc$$

$$-\frac{dc}{c} = kdt$$

Integrating,
$$-\int_{c_0}^{c}\frac{dc}{c} = k\int_{0}^{t}dt$$

$$-[\ln c]_{c_0}^{c} = k[t]_0^t$$

$$-[\ln c - \ln c_0] = k[t-0]$$

$$-\ln\frac{c}{c_0} = kt$$

$$\ln\frac{c_0}{c} = kt$$

$$\ln\frac{c_0}{c_0-x} = kt \quad \text{—①}$$

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Order of a reaction:

The order of a reaction is defined as the sum of the powers of concentrations in the rate law.

$$rate = K[A]^m[B]^n \quad — ①$$

The order of such a reaction is $(m+n)$

Rate law	Reaction order
$rate = K[N_2O_5]$	1
$rate = K[H_2][I_2]$	$1+1 = 2$
$rate = K[NO_2]^2$	2
$rate = K[H_2][NO]^2$	$1+2 = 3$
$rate = K[CHCl_3][Cl_2]^{1/2}$	$1+\frac{1}{2} = 1\frac{1}{2}$

Reactions may be classified according to the order.

If, $m+n = 1$, 1st order reaction

$m+n = 2$, 2nd order reaction

$m+n = 3$, 3rd order reaction

☐ Zero order reaction

A zero order reaction is one whose rate is independent of concentration. For example, the rate law for the reaction

$$NO_2 + CO \rightarrow NO + CO_2$$

at 200°c

$$\text{rate} = K[NO_2]^2$$

Here the rate does not depend on [CO], so this is not in ded in the rate law and the power of [CO] is understood to be zero. The reaction is zeroth order with respect to [CO] The reaction is second order with respect to $[NO_2]$. The overall reaction order is 0+2=2.

Difference between order and molecularity.

Order	Molecularity
① It is the sum of the powers of the concentration terms in the rate law expression.	① It is the number of reacting species undergoing simultaneous collision in the elementary or simple reaction.
② It is an experimentally determined value.	② It is a theoretical concept.
③ It can have fraction value.	③ It is always a whole number.
④ It can assume zero value.	④ It can not have zero value

1st order reaction

Let,

$$\begin{array}{ccc} A \longrightarrow & B & t \\ C_0 & 0 & t=0 \\ C=C_0-x & x & t=t \end{array}$$

Suppose that when $t=0$, the concentration of reactant A is C_0 and product B is zero. After a time t, the concentration of reactant A is C_0-x and product is x

(iii) **Termolecular reaction** (molecularity = 3)

$A + B + C \rightarrow P$

$2A + B \rightarrow P$

$2A + C \rightarrow P$

Example:

$2NO + O_2 \rightarrow 2NO_2$

$2NO + Cl_2 \rightarrow 2NOCl$

Complex reaction

Most chemical reactions are complex reactions. These occur in a series of steps. Each step is an elementary reaction.

The decomposition of N_2O_5,

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

is an example of chemical reaction. It occurs by the follo steps.

Step 01 $2N_2O_5 \longrightarrow 2NO_2 + 2NO_3$ (slow)

Step 02 $NO_2 + NO_3 \longrightarrow NO + NO_2 + O_2$ (slow)

Step 03 $NO + NO_3 \longrightarrow 2NO_2$ (fast)

$\longrightarrow t$ $\longrightarrow t$ $\longrightarrow t$

$y = c - mx$ $y = mx$ $y = mx + c$

Unit of zeroth order reaction

For a zero order reaction the rate constant K is given,

$$K = \frac{d[A]}{dt} = \frac{mole}{Litre} \times \frac{1}{time}$$

Thus the unit of K are $mole\,L^{-1}\,t^{-1}$

Molecularity of reaction

A **Elementary reaction**

The moleculanty of an elementary reaction is defined a the number of reactant molecules involved in a reaction. Based on the number of molecule of reactant, 'Elementary reaction are 3 types.

① Monomolecular reaction./unimolecular reaction.

(ii) Bimolecular reaction.

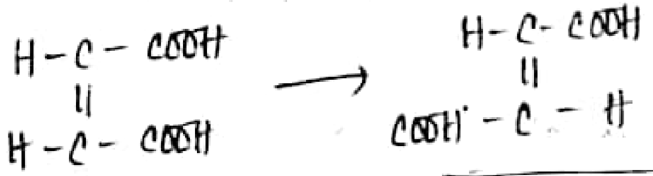
(iii) Termolecular reaction.

① **Unimolecular reaction:** (molecularity = 1)

$A \longrightarrow P$ (product)

$Br_2 \longrightarrow 2Br$

Example



maleic acid

fumaric acid

(ii) **Bimolecular reaction** (molecularity = 2)

$A + B \longrightarrow P$

$A + A \longrightarrow P$

Example ① $CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$

(ii) $2HI \rightarrow H_2 + I_2$

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$$-\left[\frac{c^{-2+1}}{-2+1}\right]_{c_0}^{c} = K[t]_0^t$$

$$\left[\frac{1}{c}\right]_{c_0}^{c} = K[t-0]$$

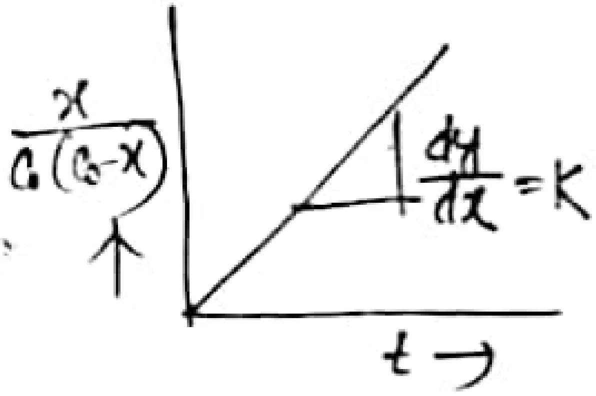
$$\frac{1}{c} - \frac{1}{c_0} = kt$$

$$c = c_0 - x$$

$$\boxed{x = c_0 - c}$$

$$\frac{c_0 - c}{cc_0} = kt$$

$$\boxed{\frac{x}{(c_0-x)c_0} = kt}$$



Properties

① **Unit**: The rate constant for a second order reaction is expressed

$$K = \frac{1}{t} \times \frac{x}{c_0(c_0-x)}$$

$$= \frac{1}{\text{time}} \times \frac{\text{concentration}}{\text{concentration} \times \text{concentration}}$$

$$= \frac{1}{\text{time}} \times \frac{1}{\text{mol/litre}}.$$

Property of nth order reaction:

① **Half life:** when $t = t_{1/2}$, $x = \frac{1}{2}C_0$

$$\frac{1}{n-1}\left[\frac{1}{\left(C_0-\frac{C_0}{2}\right)^{n-1}} - \frac{1}{C_0^{\,n-1}}\right] = k t_{1/2}$$

$$k t_{1/2} = \frac{1}{n-1}\left[\frac{1}{\left(\frac{C_0}{2}\right)^{n-1}} - \frac{1}{C_0^{\,n-1}}\right]$$

$$k t_{1/2} = \frac{1}{n-1}\left[\frac{2}{C_0^{\,n-1}} - \frac{1}{C_0^{\,n-1}}\right]$$

$$k t_{1/2} = \frac{1}{n-1}\times\frac{1}{C_0^{\,n-1}}$$

$$t_{1/2} = \frac{1}{k}\times\frac{1}{n-1}\times\frac{1}{C_0^{\,n-1}}$$

$$\boxed{t_{1/2}\propto\frac{1}{C_0^{\,n-1}}}$$

Half life for a 1st order reaction is not depend on the initial concentration. It is inversely proportional to K; the velocity of rate constant.

⑭ The 1st order reaction is not over in whole life

We know, $\ln \frac{C_0}{C} = Kt$ — ①

$\boxed{\text{after a time } t', \text{ the ratio of } \frac{C_0}{C} \text{ is equal to } C_0}$

$\boxed{\ln C_0 = Kt'}$

$$\ln \frac{C_0}{0} = Kt$$

$$\ln \alpha = Kt$$

$$Kt = \alpha$$

$$t = \frac{\alpha}{K} = \alpha$$

We can see the following equation the 1st order reaction is continuously occurred. And it is never over.

2nd order reaction:

$$2NO_2 \longrightarrow N_2O_4$$

$$2A \longrightarrow P$$

$C_0 \quad 0 \quad t=0$

$C(C_0-x) \quad x \quad t=t$

suppose that ....

For a second order reaction, rate of reaction is proportional to the square of the concentration of the reactant. Thus,

$$-\frac{dc}{dt} = kc^n$$

for 2nd order reaction, $n=2$

$$-\frac{dc}{dt} = kc^2$$

$$-\frac{dc}{c^2} = kdt$$

Integrating the equation ① we get,

$$-\int \frac{dc}{c^2} = k\int dt$$

when, to $t=0$, $c=c_0$, when $t=t$, $c=c$

$$-\int_{c_0}^{c} \frac{dc}{c^2} = k\int_0^t dt$$

$$-\int_{c_0}^{c} c^{-2}dc = k\int_0^t dt$$

④ **Half life:**

$$\boxed{x = \frac{C_0}{2}}, \quad \boxed{t = t_{1/2}}$$

$$\frac{\frac{C_0}{2}}{C_0\left(C_0 - \frac{C_0}{2}\right)} = k t_{1/2}$$

$$\frac{C_0}{2} \times \frac{2}{C_0^2} = k t_{1/2}$$

$$t_{1/2} = \frac{1}{k} \cdot \frac{1}{C_0}$$

$$\boxed{t_{1/2} \propto \frac{1}{C_0}}$$

Half life is inversely proportional to initial concentration.

* উৎপাদ এবং বিক্রিয়কের ঘনমাত্রার নির্দিষ্ট সময় পর্যায়ে মাপলে K এর মান change হলো.

$$A + B \longrightarrow P$$

$$\begin{array}{cccc} a & b & 0 & t=0 \\ (a-x) & (b-x) & x & t=t \end{array}$$

$$\frac{dx}{dt} \propto (a-x)(b-x)$$

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

Properties of a 1st order reaction

① **Unit**: The rate constant of a 1st order reaction is

$$K = \frac{2.303}{t}\log\frac{[C_0]}{[C]}$$

We can see that the rate constant for a first order reaction is independent of the concentration. So the unit of the rate constant of a 1st order reaction is $\boxed{time^{-1}}$

(II) **Half life**: The half life of a reaction can be defined as the time required for the concentration of a reactant to decrease to half of its initial value.

The rate constant of a 1st order reaction

$$K = \frac{2.303}{t}\log\frac{[C_0]}{[C]}$$

where, $[C_0]$ is initial concentration and $[C]$ is the concentration at any time t.

when $t = t_{1/2}$, $C = \frac{C_0}{2}$

$$K = \frac{2.303}{t_{1/2}}\log\frac{C_0}{\frac{C_0}{2}} = \frac{2.303}{t_{1/2}}\log 2$$

?

Determination of order of reaction using Half life:

$A \rightarrow P$

$C_{01} \rightarrow (t_{1/2})_1 = l_1$ l_1 means 1st half life

$C_{02} \rightarrow (t_{1/2})_2 = l_2$ l_2 means 2nd half life.

From nth order reaction we get,

$$(t_{1/2})_1 = \frac{1}{K} \times \frac{1}{n-1} \times \frac{1}{C_{01}^{n-1}} \quad ①$$

$$(t_{1/2})_2 = \frac{1}{K} \times \frac{1}{n-1} \times \frac{1}{C_{02}^{n-1}} \quad ⑪$$

① ÷ ⑪

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{C_{02}}{C_{01}}\right)^{n-1}$$

$$\log (t_{1/2})_1 - \log (t_{1/2})_2 = (n-1) \log \left(\frac{C_{02}}{C_{01}}\right)$$

$$(n-1) = \frac{\log \left\{\frac{(t_{1/2})_1}{(t_{1/2})_2}\right\}}{\log \left(\frac{C_{02}}{C_{01}}\right)}$$

$$n = 1 + \frac{\log \left\{\frac{(t_{1/2})_1}{(t_{1/2})_2}\right\}}{\log \left(\frac{C_{02}}{C_{01}}\right)}$$

Collision theory of reaction rate:

Theory: A chemical reaction takes place only by collisions between the reacting molecules. But not all collisions are effective. Only a small fraction of the collisions produce a reaction.

Condition: (i) The colliding molecules must possess sufficient kinetic energy to cause a reaction.

(ii) The reacting molecule must collide with proper orientation.

Temperature dependence on reaction rate and Arrhenius equation

Limitations of collision theory:

(I) The theory applies to simple gaseous reaction only.

(II) For reactions involving complex molecules, the experimental rate constants are quite different from the calculated values.

(III) The collision theory is silent on the cleavage and formation of bonds involved in the reaction.

Transition state Theory / Activated complex Theory / Absolut rate Theory

nth order reaction

$$\begin{array}{lll} A \rightarrow & P & \\ C_0 & 0 & t=0 \\ C = C_0 - x & x & t=t \end{array}$$

$$-\frac{dc}{dt} = kc^n$$

$$-\frac{dc}{c^n} = k\,dt$$

Integrating this equation,

$$-\int_{c_0}^{c} \frac{dc}{c^n} = k\int_0^t dt$$

$$-\left[\frac{c^{-n+1}}{-n+1}\right]_{c_0}^{c} = k[t]_0^t$$

$$\frac{1}{n-1}\left[\frac{1}{c^{n-1}}\right]_{c_0}^{c} = k[t-0]$$

$$\frac{1}{n-1}\left[\frac{1}{c^{n-1}} - \frac{1}{c_0^{n-1}}\right] = kt$$

$$\boxed{\frac{1}{n-1}\left[\frac{1}{(c_0-x)^{n-1}} - \frac{1}{c_0^{n-1}}\right] = kt}$$

experimentally determined quantity. Ea is an activation energy R is the gas constant and T is the kelvin temperature.

Taking natural logs ~~of~~ each ~~log~~ sides in equation,

$$\ln K = \ln A + \ln e^{-\frac{Ea}{RT}}$$

$$\ln K = \ln A - \frac{Ea}{RT}$$

$$2.303 \log K = 2.303 \log A - \frac{Ea}{RT}$$

$$\log \cancel{A} K = \log A - \frac{Ea}{2.303R} \times \frac{1}{T}$$

If K_1 and K_2 are the values of rate constant at temperatures T_1 and T_2 respectively,

$$\log k_1 = \log A - \frac{E_A}{2.303R} \times \frac{1}{T_1} \quad \text{—} ①$$

$$\log K_2 = \log A - \frac{Ea}{2.303R} \times \frac{1}{T_2} \quad \text{—} ⑪$$

~~① - ⑪~~

~~log k log k~~

⑪ - ① $\log k_2 - \log K_1 = \frac{Ea}{2.303R} \left[\frac{1}{T_2} - \frac{1}{T_2} \right]$

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The transition state theory may be summerised as follows.

① In a collision, the first approaching reactant molecules (A and B

slow down due to gradual repulsion between their electron clouds. In the process, the kinetic energy of the two molecule is converted into potential energy.

② As the molecules come close, the interpenetration of their electron clouds occurs which allows the rearrangement of valence electrons.

③ A partial bond is formed between the atoms A and B and weakening of B-C bond. This leads to formatio

weakening of B-C bond. The activated com-

☐ $\boxed{\text{3rd order reaction}}$

Let us consider a simple third reaction of the typ

$$3A \longrightarrow P$$

C_0	0	$t=0$
$C = C_0 - x$	x	$t=t$

the rate of reaction,

$$-\frac{dc}{dt} = kc^3$$

$$-\frac{dc}{c^3} = kdt$$

$$-\int_{C_0}^{C} c^{-3}\,dc = k\int_0^t dt$$

$$-\left[\frac{c^{-3+1}}{-3+1}\right]_{C_0}^{C} = kt$$

$$\rightarrow \left[\frac{1}{-2c^2} + \frac{1}{2C_0^2}\right] = kt$$

$\boxed{\text{Half Life}}$

$t = t_{1/2}$, $x = \frac{1}{2}C_0$

$$kt_{1/2} = \frac{1}{2}\left[\frac{1}{(C_0 - \frac{C_0}{2})^2} - \frac{1}{C_0^2}\right]$$

$$= \frac{1}{2}\left[\frac{4}{C_0^2} - \frac{1}{C_0^2}\right]$$

$$= \frac{1}{2} \times \frac{3}{C_0^2}$$

$$t_{1/2} = \frac{3}{2k} \times \frac{1}{C_0^2}$$

$$\propto \frac{1}{C_0}$$

life [$t_{1/2}$] proportional of the

$$\frac{dx}{(a-x)(b-x)} = k\,dt$$

$$\frac{1}{b-a}\left[\frac{1}{a-x} - \frac{1}{b-x}\right]dx = k\,dt$$

After integrating this equation we get,

$$\frac{1}{b-a}\left[-\int_0^x \frac{-dx}{a-x} + \int_0^x \frac{-dx}{b-x}\right] = k\int_0^t dt$$

$$\frac{1}{b-a}\left\{\left[-\ln(a-x)\right]_0^x + \left[\ln(b-x)\right]_0^x\right\} = k\left[t\right]_0^t$$

$$\frac{1}{b-a}\left\{-\ln(a-x) + \ln a + \ln(b-x) - \ln b\right] = kt$$

$$\frac{1}{b-a}\left\{\ln\frac{a}{a-x} + \ln\frac{b-x}{b}\right\} = kt$$

$$-\frac{1}{a-b}\left\{\ln\frac{a(b-x)}{b(a-x)}\right] = kt$$

$$\boxed{\frac{1}{a-b}\ln\frac{b(a-x)}{a(b-x)} = kt} \rightarrow \boxed{\begin{matrix} a \gg b \\ a \gg x \end{matrix}}$$

⑪ **Negative catalyst:**

A catalyst which retards the rate of a chemica reaction is caled negative reaction.