WEST BENGAL STATE UNIVERSITY
SYLLABUS FOR CHEMISTRY (HONOURS) ON PHOTOCHEMISTRY
UNDER CHOICE BASED CREDIT SYSTEM
SEM IH

Chemical kinetics (15 Lectures) **Marks: 14**

Rate law, order and molecularity: Introduction of rate law, Extent of reaction; rate constants, order; Forms of rates of First, second and n-th order reactions; Pseudo first order reactions (example using acid catalyzed hydrolysis of methyl acetate); Determination of order of a reaction by half-life and differential method; Opposing reactions, parallel reactions and consecutive reactions (with explanation of kinetic and thermodynamic control of products; all steps first order) ; Rate equation for the fast reaction

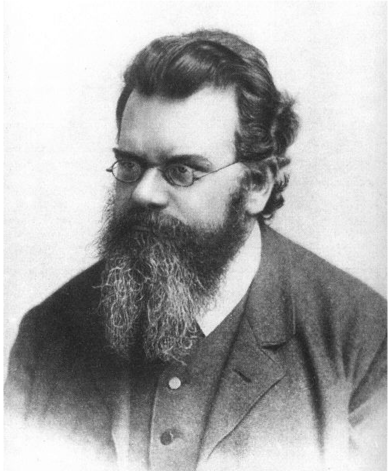
Role of T and theories of reaction rate: Temperature dependence of rate constant; Arrhenius equation, energy of activation; Rate-determining step and steady-state approximation – explanation with suitable examples; Collision theory; Lindemann theory of unimolecular reaction; outline of Transition State theory (classical treatment)

Homogeneous catalysis: Homogeneous catalysis with reference to acid-base catalysis; Primary kinetic salt effect; Enzyme catalysis; Michaelis-Menten equation, Lineweaver Burk plot, turn-over number

Books to follow:

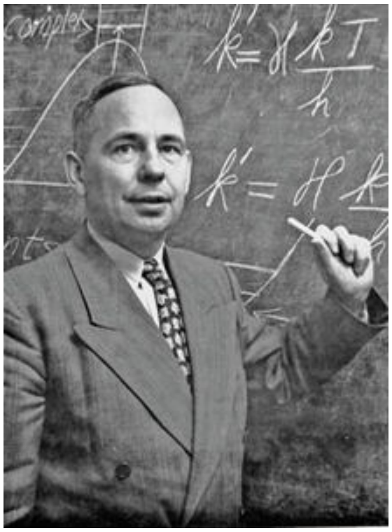
- *McQuarrie, D. A. & Simons, J. D. Physical Chemistry: A Molecular Approach, Viva Press*
- *Atkins, P. W. & Paula, J. de Atkins' Physical Chemistry, Oxford University Press*
- *Rakshit, P.C., Physical Chemistry, Sarat Book House*
- *Laidler, K. J. Chemical Kinetics, Pearson*
- *Castellan, G. W. Physical Chemistry, Narosa*

This course is taught by
Dr. Dipankar Mondal
Assistant Professor, Department of Chemistry,
BKC College, 111/2 B.T. Road, BonHoogly,
Dunlop, Kolkata-700108

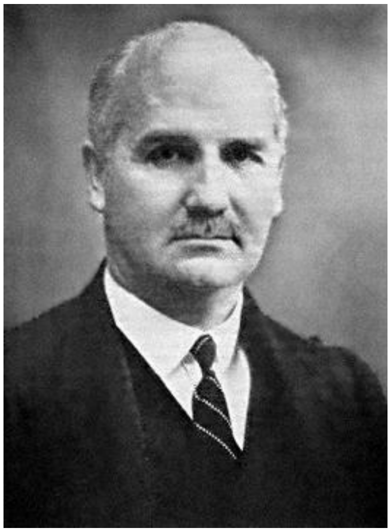


Ludwig Boltzmann (1844-1906)

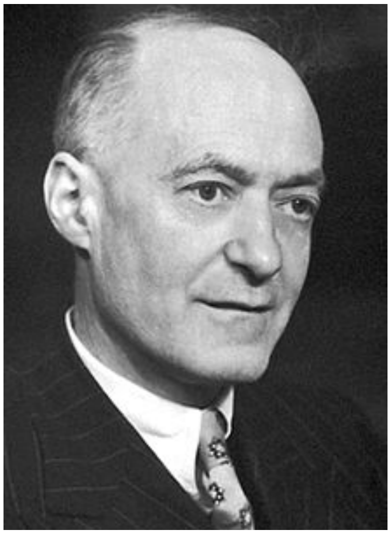
James Clerk Maxwell (1831-1879)



Henry Eyring (1901-1981)



Frederick Lindemann (1886-1957)



Cyril Hinshelwood (1897-1967)

Svante Arrhenius (1859-1927)

- https://en.wikipedia.org

❖ Rate of a Reaction

It is defined as the amount of chemical change occurring per unit time.

The rate of reaction depends on temperature, pressure, the concentration of the reactants and may depends on the concentration of catalyst and inhibitors that may not appear in the overall reaction.

From the kinetics point of view, the reactions are classified into two groups.

(i) **Homogeneous Reactions:** A homogeneous reaction occurs entirely within one phase.

(ii) **Heterogeneous Reaction:** This type of reaction takes place more than one phase; a common type of heterogeneous reaction has a rate which depends on the surface of a catalyst or area of the reaction vessel.

- Rate of the reaction is typically expressed as the decrease in concentration of reactant or as the increase in concentration of the product per unit time.

$$\underset{\text{(Reactant)}}{R} \longrightarrow \underset{\text{(Product)}}{P}$$

The rate of the above reaction can be expressed as

$$-\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

$$Rate\ of\ consumption = Rate\ of\ formation$$

❖ Rate law and Rate Constant

The rate of reaction is often found to be proportional to the concentrations of the reactants raised to a power.

$$A + B \longrightarrow P$$

Rate of the above reaction $v \propto [A][B]$

$$or \quad v = k[A][B]$$

The coefficient k is called the **rate constant** for the reaction. The rate constant is independent of the concentrations but depends on the temperature. An experimentally determined equation of this kind is called the rate law of the reaction.

More formally, a rate law is an equation that expresses the rate of reaction as a function of the concentrations of all the species present in the overall chemical equation for the reaction at some time.

❖ Order of a Reaction

If we consider a reaction of the form

$$\alpha A + \beta B = \gamma C + \delta D$$

Then rate law has the simple form

$$v = k[A]^{\alpha}[B]^{\beta}$$

The constant α is the reaction order with respect to A

The constant β is the reaction order with respect to B

The total or overall order of the reaction is α+β. The order of the reaction is the sum of powers of the concentration terms of reactants in the experimentally determined rate equation for the reaction.

❖ Molecularity

The molecularity of an elementary reaction is the number of molecules coming together to react in an elementary reaction. Elementary reactions that involve one, two or three molecules are termed unimolecular, bimolecular, and termolecular respectively. *A reaction that does not involve any intermediates occurs in a single step and is called an elementary reaction.*

Order	**Molecularity**
(i) The order of reaction is the sum of the powers of concentration terms of all the reactants in the experimentally determined rate equation	(i) The molecularity of an elementary reaction is defined to be the number of reactant molecules involve in the chemical reaction
(ii) The order sometimes be fractional in number	(ii) The molecularity is always an integer number.
(iii) The order of reaction is obtained from the experimental results	(iii) The molecularity is given on the basis of some proposed theoretical mechanism
(iv) All second order reaction are not necessarily bimolecular	(iv) All bimolecular reactions are of the second order

Zero Order Reaction:

A reaction is said to be zero order if the rate of the reaction is independent of concentration of the reactants.

$$\underset{\text{(Reactant)}}{A} \xrightarrow{k} \underset{\text{(Product)}}{P}$$

at t=0	$[A]_0$	0
at time t	$[A]_t$	

Now from basic kinetics law we can write

$$-\frac{d[A]}{dt} = k[A]^0 = k$$

$$d[A] = -kdt$$

$$\int_{[A]_0}^{[A]_t} d[A] = \int_0^t -kdt$$

$$[A]_t - [A]_0 = -kt$$

$$[A]_t = [A]_0 - kt \qquad (a)$$

Half Life of Zero Order Reaction:

The length of time required for half of the reactant to disappear is called half-life of the reaction and is denoted as $t_{1/2}$. Therefore, for zero order reaction it can be represented as

$$\underset{\text{(Reactant)}}{A} \xrightarrow{k} \underset{\text{(Product)}}{P}$$

at t=0	$[A]_0$	0
at time $t_{1/2}$	$\frac{[A]_0}{2}$	

Now, the equation (a) can be written as follows

$$\frac{[A]_0}{2} = [A]_0 - kt_{1/2}$$

$$or \quad kt_{1/2} = [A]_0 - \frac{[A]_0}{2}$$

$$or \quad kt_{1/2} = \frac{[A]_0}{2}$$

$$or \quad t_{1/2} = \frac{[A]_0}{2k}$$

$$\underset{\text{(Reactant)}}{\text{A}} \xrightarrow{k} \underset{\text{(Product)}}{\text{P}}$$

at t=0	a	0
at time t	(a-x)	x

Now from basic kinetics law for zero order reaction we can write

$$\frac{dx}{dt} = k(a-x)^0 = k$$

$$dx = kdt$$

$$\int dx = \int kdt$$

$$x = kt + I.C$$

$$at\ t = 0\ then\ x = 0; therefore\ \mathrm{I.C} = 0$$

$$x = kt$$

$$Therefore; \quad k = \frac{x}{t} = \frac{concentration}{time}$$

$$Unit\ of\ k\ is\ concentration.time^{-1}\ or\ mol.lit^{-1}sec^{-1}$$

First Order Reaction:

$$\underset{\text{(Reactant)}}{\text{A}} \xrightarrow{k} \underset{\text{(Product)}}{\text{P}}$$

at t=0	$[A]_0$	0
at time t	$[A]_t$	

Now from basic kinetics law we can write

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

$$\frac{d[A]}{[A]} = -kdt$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = \int_0^t -kdt$$

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

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

$$[A]_t = [A]_0 e^{-kt} \qquad (b)$$

This is the equation for first order reaction

Half Life of First Order Reaction:

The time required for half of the reactant to change for a first order reaction can be evaluated as follows

$$A \xrightarrow{k} P$$

	(Reactant)	(Product)
at t=0	$[A]_0$	0
at time $t_{1/2}$	$\frac{[A]_0}{2}$	

Therefore, the equation (b) can be written as follows

$$\frac{[A]_0}{2} = [A]_0 e^{-kt_{1/2}}$$

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

$$\text{or} \qquad \ln\left(\frac{1}{2}\right) = -kt_{1/2}$$

$$\text{or} \qquad \ln\ 2 = kt_{1/2}$$

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

	$A \xrightarrow{k}$ (Reactant)	P (Product)
at t=0	a	0
at time t	(a-x)	x

Now from basic kinetics law for first order reaction, we can write

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

$$\frac{dx}{(a-x)} = kdt$$

$$\int \frac{dx}{(a-x)} = \int kdt$$

$$-\ln(a-x) = kt + I.C$$

$$at\ t = o\ then\ x = 0; therefore\ \mathrm{I.C} = \ln a$$

$$-\ln(a-x) = kt + \ln a$$

$$ln\frac{a}{(a-x)} = kt$$

$$k = \frac{1}{t} ln\frac{a}{a-x}$$

$$or \quad k = \frac{2.303}{t} log\frac{a}{a-x}$$

$$Therefore; \quad k = \frac{1}{t} = \frac{1}{time}$$

$$Unit\ of\ k\ is\ time^{-1}\ or\ sec^{-1}$$

Second Order Reaction:

	$2A \xrightarrow{k}$ (Reactant)	P (Product)
at t=0	$[A]_0$	0
at time t	$[A]_t$	

Now from basic kinetics law we can write

$$-\frac{d[A]}{dt} = k[A]^2$$

$$\frac{d[A]}{[A]^2} = -kdt$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = \int_0^t -kdt$$

$$[\frac{1}{[A]}]_{[A]_0}^{[A]_t} = -kt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

This is the equation for second order reaction when the concentration of the two reactants are equal

Half Life of Second Order Reaction:

$$2A \longrightarrow P$$

	(Reactant)	(Product)
at t=0	$[A]_0$	0
at time $t_{1/2}$	$\frac{[A]_0}{2}$	

$$\frac{1}{\frac{[A]_0}{2}} = \frac{1}{[A]_0} + kt_{1/2}$$

$$or \quad \frac{1}{[A]_0} = kt_{1/2}$$

$$t_{1/2} = \frac{1}{[A]_0 k}$$

$$2A \longrightarrow P$$

	(Reactant)	(Product)
at t=0	a	0
at time t	(a-x)	x

Now from basic kinetics law for second order reaction, we can write

$$\frac{dx}{dt} = k(a-x)^2$$

$$\frac{dx}{(a-x)^2} = kdt$$

$$\int \frac{dx}{(a-x)^2} = \int kdt$$

$$\frac{1}{a-x} = kt + I.C$$

$$at\ t = o\ then\ x = 0;\ therefore\ \mathrm{I.C} = \frac{1}{a}$$

$$\frac{1}{a-x} - \frac{1}{a} = kt$$

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

$$k = \frac{1}{t}\frac{x}{a(a-x)}$$

$$Therefore; \quad k = \frac{concentration}{t(concentration)(concentration)} = \frac{1}{time.concentration}$$

$$Unit\ of\ k\ is\ concentration^{-1}time^{-1}\ or\ lit.mol^{-1}sec^{-1}$$

A second order reaction when initial concentration of the two reactants are different

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

(Reactant) (Product)

at t=0	a	b	0
at time t	(a-x)	(b-x)	

Now from basic kinetics law we can write

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

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

$$\frac{1}{(a-b)}\left[\frac{1}{(b-x)} - \frac{1}{(a-x)}\right]dx = kdt$$

$$\frac{1}{(a-b)}\int\left[\frac{1}{(b-x)} - \frac{1}{(a-x)}\right]dx = \int kdt$$

$$\frac{1}{(a-b)}[-\ln(b-x) + \ln(a-x)] = kt + I.C$$

$$at\ t = o\ then\ x = 0; therefore\ \mathrm{I.C} = \frac{1}{a-b}ln\frac{a}{b}$$

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

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

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

❖ Pseudo First Order reaction

There are a number of reactions of various kinds which satisfy the 1st order equation, but actually more than one reactant is involved and except one all are present very excess in quantity in the chemical reaction; such processes are called pseudo-first order reaction.

Example: Hydrolysis of an ester in an acid medium is such an example of this kind. Water and ester participate but the rate of reaction is experimentally observed to depend only on the concentration of ester as water is present in such large excess, that even if the reaction is complete, the concentration of water would remain unaltered.

$$CH_3-CO-OCH_2-CH_3+H_2O \xrightarrow{H^+} CH_3-COOH+CH_3-CH_2-OH$$

$$-\frac{d[CH_3COOC_2H_5]}{dt}=k[CH_3COOC_2H_5][H_2O][H^+]$$

Here, $[H_2O] \gg [CH_3COOC_2H_5]$ and H^+ being the catalyst is constant.

$$Therefore, -\frac{d[CH_3COOC_2H_5]}{dt}=k'[CH_3COOC_2H_5];\ where\ k'=k.[H_2O][H^+]$$

❖ Determination of the Order of a Reaction

(a) Method of integration:

This method is to be determined by an analysis the amount of reactants decomposes after various interval of time and to substitute the data to the equation of the reaction of first order or second order and so on

$$\left.\begin{aligned} k_1 &= \frac{1}{t} ln\frac{a}{a-x} \\ or\ \ k_1 &= \frac{2.303}{t} log\frac{a}{a-x} \end{aligned}\right\} 1st\ order\ reaction$$

$$k_2=\frac{1}{t}(\frac{1}{a-x}-\frac{1}{a})\Big\} 2nd\ order\ reaction$$

$$k_3=\frac{1}{2t}(\frac{1}{(a-x)^2}-\frac{1}{a^2})\Big\} 3rd\ order\ reaction$$

(b) Differential Method:

The rate of the reaction of nth order starting initial concentration with C_1

$$-\frac{dc_1}{dt}=kC_1^n$$

$$\text{or} \ln\left(-\frac{dC_1}{dt}\right) = \ln k + n\ln C_1 \qquad \text{(i)}$$

if we start the same reaction with initial concentration C_2 then we can write

$$-\frac{dC_2}{dt} = kC_2^n$$

$$\text{or} \ln\left(-\frac{dC_2}{dt}\right) = \ln k + n\ln C_2 \qquad \text{(ii)}$$

Now if we do (i) - (ii), we will get

$$\ln\left(-\frac{dC_1}{dt}\right) - \ln\left(\frac{-dC_2}{dt}\right) = n(\ln C_1 - \ln C_2)$$

$$\text{or } n = \frac{\ln\left(\frac{-dC_1}{dt}\Big/\frac{-dC_2}{dt}\right)}{\ln\left(\frac{C_1}{C_2}\right)}$$

(c) Method of Isolation

Consider general chemical equation

$$\alpha A + \beta B = \gamma C + \delta D$$

Let assume the rate law has the form (as we do not know the order of the reaction)

$$r = k[A]^{m_A}[B]^{m_B}$$

Suppose the initial reaction mixture has a large excess of concentration of A. In this case, the concentration of A remains essentially constant as the reaction takes place. Therefore, above equation becomes

$$r = k'[B]^{m_B} \quad ; \qquad \text{where } k' = k[A]^{m_A} = \text{constant}$$

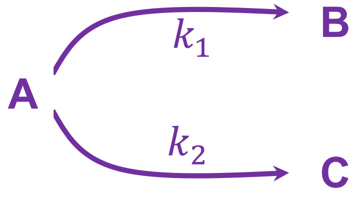
The order of B then be determined by measuring the rate as a function of [B]. The only requirement is that A always be in large excess so that k' remains constant. Likewise, if B is initially present in large excess, then rate of the reaction will be

$$r = k''[A]^{m_A} \quad ; \qquad \text{where } k'' = k[A]^{m_B} = \text{constant}$$

The order of A then be determined by measuring the rate as a function of [A]. In this way method of isolation is used to elucidate order of the reaction.

Mechanism of some complex reactions

❖ Parallel Reaction or Competitive Reactions



The rate of decomposition of reactant A

$$-\frac{d[A]}{dt} = k_1[A] + k_2[A] = (k_1 + k_2)[A]$$

$$-\frac{d[A]}{[A]} = (k_1 + k_2)dt$$

$$\int \frac{-d[A]}{[A]} = \int (k_1 + k_2)dt$$

$$\ln[A] = -(k_1 + k_2)t + I.C$$

$$\text{at time t} = 0 \text{ then } I.C = \ln\,[A]_o$$

Now, $\ln[A] = -(k_1 + k_2)t + \ln\,[A]_o$

$$ln\frac{[A]}{[A]_O} = -(k_1 + k_2)t$$

$$[A] = [A]_O e^{-(k_1+k_2)t}$$

If we want calculate the product concentration, then any moment the formation rate of product B will be

$$\frac{d[B]}{dt} = k_1[A]$$

$$\frac{d[B]}{dt} = k_1[A]_O e^{-(k_1+k_2)t}$$

$$\int d[B] = \int k_1[A]_O e^{-(k_1+k_2)t} dt$$

$$[B] = -\frac{k_1[A]_O}{(k_1+k_2)} e^{-(k_1+k_2)t} + I.C$$

$$\text{at time t} = 0 \text{ then } 0 = -\frac{k_1[A]_O}{(k_1+k_2)} e^{-(k_1+k_2)0} + I.C$$

$$\mathrm{I.C} = \frac{k_1[A]_O}{(k_1+k_2)}$$

$$[B] = -\frac{k_1[A]_O}{(k_1+k_2)} e^{-(k_1+k_2)t} + \frac{k_1[A]_O}{(k_1+k_2)}$$

$$[B] = \frac{k_1[A]_O}{(k_1+k_2)} (1 - e^{-(k_1+k_2)t})$$

Similarly, we can solve the equation $\frac{d[C]}{dt} = k_2[A]$ and will get

$$[C] = \frac{k_2[A]_O}{(k_1+k_2)} (1 - e^{-(k_1+k_2)t})$$

The ratio of the rates is same as the amount of B and C forms at any stage

$$\frac{rate\ of\ formation\ of\ B}{rate\ of\ formation\ of\ C} = \frac{amount\ of\ B\ forms\ at\ any\ moment}{amount\ of\ C\ forms\ at\ any\ moment} = \frac{k_1}{k_2} = Z$$

❖ Opposing Reaction or Reversible Reactions

$$\mathrm{A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{B};\ \text{Equilibrium constant}\quad K = \frac{k_1}{k_2}$$

At t=0	a	0
At time t	(a-x)	x

The rate of formation of B at any time is

$$\frac{dx}{dt} = k_1(a-x) - k_2(x) = k_1 a - (k_1+k_2)x$$

$$\int \frac{dx}{k_1a - (k_1 + k_2)x} = \int dt$$

$$-\frac{1}{k_1 + k_2} ln[k_1a - (k_1 + k_2)x] + I.C = t$$

$$at\ t = 0\ then\ x = 0\ so\ I.C = \frac{1}{k_1 + k_2} ln[k_1a]$$

$$Therefore, t = -\frac{1}{k_1 + k_2} ln[k_1a - (k_1 + k_2)x] + \frac{1}{k_1 + k_2} ln[k_1a]$$

$$or \quad t = \frac{1}{k_1 + k_2} ln\left[\frac{k_1a}{k_1a - (k_1 + k_2)x}\right]$$

$$Now\ replacing\ k_1 = Kk_2$$

$$or \quad t = \frac{1}{Kk_2 + k_2} ln\left[\frac{k_1a}{k_1a - (k_1 + k_2)x}\right]$$

$$or \quad k_2(1 + K) = \frac{1}{t} ln\left[\frac{k_1a}{k_1a - (k_1 + k_2)x}\right]$$

Similarly, k_1 can be obtained from the above equation.

Alternatively, we can also measure rate constant k_1 and k_2 after reaction reach at equilibrium. Suppose x_e is the concentration of B at equilibrium, then

$$\frac{dx}{dt} = k_1(a - x_e) - k_2x_e = 0$$

$$or\ k_2 = \frac{k_1(a - x_e)}{x_e}$$

$$Hence \qquad \frac{dx}{dt} = k_1(a - x) - k_2x = k_1(a - x) - \frac{k_1(a - x_e)}{x_e}x$$

$$or \quad \frac{dx}{dt} = \frac{k_1ax_e - k_1xx_e - k_1ax + k_1xx_e}{x_e}$$

$$or \quad \frac{dx}{dt} = \frac{k_1 a}{x_e}(x_e - x)$$

$$\int \frac{dx}{\frac{k_1 a}{x_e}(x_e - x)} = \int dt$$

$$\frac{x_e}{ak_1}\int_0^{x_e} \frac{dx}{(x_e - x)} = \int_0^t dt$$

$$\frac{x_e}{ak_1}\frac{lnx_e}{(x_e - x)} = t$$

$$k_1 = \frac{x_e}{at}\frac{lnx_e}{(x_e - x)}$$

❖ Consecutive Reaction or Series Reaction

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$

At t=0	A_0	0	0
At time t	[A]	[I]	[P]

The rate of unimolecular decomposition of A is

$$-\frac{d[A]}{dt} = -k_1[A] \qquad (i)$$

and A is not replenished. The intermediate I is formed from A (at a rate k_a[A]) but decays to P (at a rate k_b[I]). The net rate of formation of I is therefore

$$\frac{d[I]}{dt} = k_1[A] - k_2[I] \qquad (ii)$$

The product P is formed by the unimolecular decay of I

$$\frac{d[P]}{dt} = k_2[I] \qquad (iii)$$

We suppose that initially only A is present, and that its concentration is $[A]_0$. The first of the rate laws, eqn (i), is ordinary first-order decay, so we can write

$$[A] = [A]_0 e^{-k_1 t} \qquad (iv)$$

Now the equation (ii) becomes

$$\frac{d[I]}{dt} = k_1[A]_0 e^{-k_1 t} - k_2[I]$$

$$\frac{d[I]}{dt} + k_2[I] = k_1[A]_0 e^{-k_1 t}$$

Now multiplying both side by $e^{k_2 t}$

$$\frac{d[I]}{dt} e^{k_2 t} + k_2[I]e^{k_2 t} = e^{k_2 t} k_1 [A]_0 e^{-k_1 t}$$

$$\frac{d}{dt}([I]e^{k_2 t}) = e^{(k_2 - k_1)t} k_1 [A]_0$$

$$\int d([I]e^{k_2 t}) = \int e^{(k_2 - k_1)t} k_1 [A]_0 dt$$

$$[I]e^{k_2 t} = \frac{k_1}{(k_2 - k_1)} e^{(k_2 - k_1)t} [A]_0 + I.C$$

$$at\ t = 0\ then\ [I] = 0; \qquad I.C = -\frac{k_1}{(k_2 - k_1)} [A]_0$$

$$[I]e^{k_2 t} = \frac{k_1}{(k_2 - k_1)} e^{(k_2 - k_1)t} [A]_0 - \frac{k_1}{(k_2 - k_1)} [A]_0$$

$$[I] = \frac{k_1}{(k_2 - k_1)} e^{-k_1 t} [A]_0 - \frac{k_1}{(k_2 - k_1)} e^{-k_2 t} [A]_0$$

$$[I] = \frac{k_1}{(k_2 - k_1)} [A]_0 (e^{-k_1 t} - e^{-k_2 t})$$

At all times [A] + [I] + [P] = $[A]_0$, so it follows that

$$[P] = [A]_0 - [A] - [I]$$

$$[P] = [A]_0 - [A]_0 e^{-k_1 t} - \frac{k_1}{(k_2 - k_1)} [A]_0 (e^{-k_1 t} - e^{-k_2 t})$$

$$[P] = [A]_0 \{1 - e^{-k_1 t} - \frac{k_1}{(k_2 - k_1)} (e^{-k_1 t} - e^{-k_2 t})\}$$

$$[P] = [A]_0\{1 - \frac{k_2 e^{-k_1 t} - k_1 e^{-k_1 t} + k_1 e^{-k_1 t} - k_1 e^{-k_2 t}}{(k_2 - k_1)}\}$$

$$[P] = [A]_0\{1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{(k_2 - k_1)}\}$$

The concentration of the intermediate I rises to a maximum and then falls to zero. The concentration of the product P rises from zero towards $[A]_0$.

Case I: when $k_2 \gg k_1$

$$Then\ \frac{1}{(k_2 - k_1)} \approx \frac{1}{k_2}\ and\ \ k_1 e^{-k_2 t} - k_2 e^{-k_1 t} \approx k_2 e^{-k_1 t}$$

$$[P] = [A]_0 \left\{1 - \frac{k_2 e^{-k_2 t}}{k_2}\right\}$$

$$= [A]_0\{1 - e^{-k_1 t}\}$$

Case I: when $k_2 \ll k_1$

$$Then\ \frac{1}{(k_2 - k_1)} \approx \frac{1}{-k_1}\ and \quad k_1 e^{-k_2 t} - k_2 e^{-k_1 t} \approx -k_1 e^{-k_2 t}$$

$$[P] = [A]_0 \left\{1 - \frac{k_1 e^{-k_2 t}}{k_1}\right\}$$

$$= [A]_0\{1 - e^{-k_2 t}\}$$

This shows that overall reaction is simple first order reaction and rate of the reaction follow simply the kinetics of the slower process.

❖ The Dependence of Rate of Reaction on Temperature

The most satisfactory method for expressing the influence of temperature on rate of the reaction is by Arrhenius rate equation. This equation is based on J. H. Van’t Hoff equation for the temperature coefficient of the equilibrium constant.

$$R \underset{k_r}{\overset{k_f}{\rightleftharpoons}} P \quad and\ K_{eq} = \frac{k_f}{k_r}$$

Here K_{eq} is the equilibrium constant and k_f and k_r rate constants for forward and backward reaction of the above equation

$$\frac{d\ lnK_{eq}}{dT} = \frac{\Delta H}{RT^2}$$

$$or \quad \frac{d\ ln\frac{k_f}{k_r}}{dT} = \frac{\Delta H}{RT^2}$$

$$\frac{d\ lnk_f}{dT} - \frac{d\ lnk_r}{dT} = \frac{H_2}{RT^2} - \frac{H_1}{RT^2}$$

Where H_1 and H_2 are assumed to be characteristic of forward and backward reaction.

$$\frac{d\ lnk_f}{dT} = \frac{H_2}{RT^2} + C \quad and \quad \frac{d\ lnk_r}{dT} = \frac{H_1}{RT^2} + C$$

It is found experimentally that the temperature variation of the specific rate was best expressed by assuming c to be zero, so that

$$\frac{d\ lnk}{dT} = \frac{E_a}{RT^2}$$

The quantity E_a is called as the activation energy of the reaction.

$$\int d\ lnk = \int \frac{E_a}{RT^2} dt$$

$$lnk = -\frac{E_a}{RT} + \ln A; \quad \ln A\ is\ integration\ constant$$

$$\ln k - \ln A = -\frac{E_a}{RT}$$

$$ln\frac{k}{A} = -\frac{E_a}{RT}$$

$$k = Ae^{-\frac{E_a}{RT}}$$

Here A is called pre-exponential factor or frequency factor. The unit of A is as same as rate constant k. A and E_a are called Arrhenius parameter, nearly independent of temperature of the reaction being study.

❖ The Collision Theory of Reaction Rates

Let consider a bimolecular elementary gas-phase reaction

$$A + B \overset{k}{\rightarrow} Product$$

The rate of the above reaction will be $\upsilon = -\frac{d[A]}{dt} = \mathrm{k[A][B]} \quad (i)$

It is obvious that this reaction cannot occur more often than the number of times molecules A and B collide. Using naive assumption that every collision between the hard spheres A and B yields products then rate of the reaction depends on the frequency with which molecules collide or collision frequency per unit volume

$$\upsilon = -\frac{d\widetilde{N}_A}{dt} = \mathbb{Z}_{AB} = \pi\sigma_{AB}^2\sqrt{\frac{8k_BT}{\pi\mu}}\widetilde{N}_A\widetilde{N}_B \qquad (ii)$$

in which $\sigma_{AB}^2 = \frac{1}{2}(\sigma_A + \sigma_B)$ and $\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}$ where σ_A andσ_B are the molecular diameters, m_A and m_B the molecular masses, $\widetilde{N}_A$ and $\widetilde{N}_B$ the number of molecules of A and B per unit volume. *The reaction clearly indicates that collision frequency is directly proportional to molecular radios, average speed and number density of the reactants.*

However, every collision does not, in fact, result in the reaction of A and B, a collision will be successful only if the kinetic energy exceeds a minimum value, the activation energy, E_a, of the reaction. This requirement suggests that

$$v = -\frac{d\widetilde{N}_A}{dt} = \pi\sigma_{AB}^2\sqrt{\frac{8k_BT}{\pi\mu}}\widetilde{N}_A\widetilde{N}_B e^{-E_a/_{RT}} \qquad (iii)$$

$$-\frac{dN_A[A]}{dt} = \pi\sigma_{AB}^2\sqrt{\frac{8k_BT}{\pi\mu}}N_A[A]N_A[B]e^{-E_a/_{RT}} \qquad (iv)$$

$$-\frac{d[A]}{dt} = \pi\sigma_{AB}^2\sqrt{\frac{8k_BT}{\pi\mu}}N_A[A][B]e^{-E_a/_{RT}} \qquad (v)$$

Here N_A is Avogadro number.

Now equating equation (i) and (v) we will obtain

$$k[A][B] = \pi\sigma_{AB}^2\sqrt{\frac{8k_BT}{\pi\mu}}N_A[A][B]e^{-E_a/_{RT}} \qquad (vi)$$

$$k = N_A\pi\sigma_{AB}^2\sqrt{\frac{8k_BT}{\pi\mu}}e^{-E_a/_{RT}}$$

$$k = N_A Z_{AB} e^{-E_a/_{RT}}; \qquad where\ Z_{AB} = \frac{\mathbb{Z}_{AB}}{\widetilde{N}_A\widetilde{N}_B} \qquad (vii)$$

This equation has the same form as Arrhenius equation, so the collision theory predicts for frequency factor

$$A = N_A Z_{AB} = N_A\pi\sigma_{AB}^2\sqrt{\frac{8k_BT}{\pi\mu}} \qquad (viii)$$

The rates tend to be smaller than the collision theory predicts, in many cases by a factor of 10^5 or more. To account for this, an additional factor P, called the probability factor or the steric factor, is inserted in the expression for k. The idea behind this is that even those collisions having the requisite energy may not produce reaction; originally it was supposed that the molecules had to collide in a particular configuration, hence the name ***steric factor***. The steric factor is normally found to be several orders of magnitude smaller than unity. This idea has some validity, especially since the low rates of reaction are usually observed with complex molecules. Presumably two complex molecules will have less chance of colliding in the correct orientation for reaction than will two simple molecules. Therefore, final expression would be

$$k = N_A P Z_{AB} e^{-E_a/RT}$$

❖ The Lindemann–Hinshelwood Mechanism

In the Lindemann–Hinshelwood mechanism it is supposed that a reactant molecule A becomes energetically excited by collision with another A molecule

$$A + A \overset{k_a}{\rightarrow} A^* + A \qquad (i)$$

$$\frac{d[A^*]}{dt} = k_a[A]^2$$

The energized molecule (A*) might lose its excess energy by collision with another molecule:

$$A^* + A \overset{k'_a}{\rightarrow} A + A \qquad (ii)$$

$$\frac{d[A^*]}{dt} = k'_a[A^*][A]$$

Alternatively, the excited molecule might shake itself apart and form products P. That is, it might undergo the unimolecular decay

$$A^* \overset{k_b}{\rightarrow} P \qquad (iii)$$

$$\frac{d[A^*]}{dt} = -k_b[A^*]$$

If the unimolecular step is slow enough to be the rate-determining step, the overall reaction will have first-order kinetics, as observed. This conclusion can be demonstrated explicitly by applying the steady-state approximation to the net rate of formation of A^*

$$\frac{d[A^*]}{dt} = k_a[A]^2 - k'_a[A^*][A] - k_b[A^*] = 0$$

$$k_a[A]^2 - k'_a[A^*][A] = k_b[A^*]$$

$$[A^*] = \frac{k_a[A]^2}{k_b + k'_a[A]} \qquad (iv)$$

So the rate law for the formation of P is

$$\frac{d[P]}{dt} = k_b[A^*]$$

$$= k_b \frac{k_a[A]^2}{k_b + k'_a[A]} \qquad (v)$$

At this stage the rate law is not first-order. However, if the rate of deactivation by(A*,A) collisions is much greater than the rate of unimolecular decay, in the sense that

$$k'_a[A^*][A] \gg k_b[A^*] \qquad or \quad k'_a[A] \gg k_b$$

Then we can neglect k_b in the denominator and obtain

$$\frac{d[P]}{dt} = k_b \frac{k_a[A]^2}{k'_a[A]}$$

$$\frac{d[P]}{dt} = k[A] \qquad where\ k = k_b \frac{k_a}{k'_a}$$

This is a first-order rate law.

The Lindemann–Hinshelwood mechanism can be tested because it predicts that, as the concentration (and therefore the partial pressure) of A is reduced, the reaction should switch to overall second-order kinetics. Thus, when$k'_a[A^*][A] \ll k_b[A^*]\ or\ \ k'_a[A] \ll k_b$, the rate law in equation

$$\frac{d[P]}{dt} = k[A]^2$$

The physical reason for the change of order is that at low pressures the rate-determining step is the bimolecular formation of A*.

If we also write the full rate law equation then the expression for the effective rate constant, k, can be rearranged to

$$\frac{1}{k} = \frac{k'_a}{k_a k_b} + \frac{1}{k_a[A]}$$

Hence, a test of the theory is to plot $\frac{1}{k}$ against $\frac{1}{[A]}$, and to expect a straight line.

❖ The Transition State Theory (The Eyring Equation)

$$A + B \leftrightharpoons AB^{\neq} \xrightarrow{k_2} Products$$

If the activated complex $\mathrm{AB}^{\neq}$ is in equilibrium with reactants, the equilibrium constant for the formation of complexes is given by

$$K^{\neq} = \frac{[AB^{\neq}]}{[A][B]}$$

$$or \qquad [AB^{\neq}] = K^{\neq}[A][B]$$

According to rate law, the rate of the above reaction

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k_2[A][B] \qquad (i)$$

According to transition state theory, the rate of the above reaction

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = [AB^{\neq}](rate\ of\ passage\ over\ barrier) \quad (ii)$$

The rate of passage over the barrier is equal to the the frequency with which the activated complex decomposes into product (ν).

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = [AB^{\neq}]\nu \qquad (iii)$$

Equation (i)=Equation (iii)

$$k_2[A][B] = [AB^{\neq}]\nu = K^{\neq}[A][B]\nu$$

$$k_2 = K^{\neq}\nu$$

The frequency ν is equal to $\frac{\varepsilon}{h}$ where ε is the average energy of the vibration that leads to decomposition. Since this is by hypothesis a thoroughly excited vibration at the temperature T, it has its classical energy $\varepsilon = k_B T$.

And the corresponding frequency becomes

$$\nu = \frac{k_B T}{h}$$

Therefore, the rate constant can be represented as

$$k_2 = K^{\neq} \frac{k_B T}{h} \qquad (iv)$$

From classical Thermodynamics point of view, we know that standard free energy change of a reaction can be written as

$$\Delta G^O = -RTlnK; where\ K\ is\ equlilibrium\ constant$$

$$\Delta G^{\neq} = -RTlnK^{\neq};\ \Delta G^{\neq}\ is\ free\ energy\ of\ activation$$

$$or \qquad lnK^{\neq} = \frac{-\Delta G^{\neq}}{RT}$$

From Gibbs-Helmholtz relation

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$$

Here, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are called the enthalpy or heat of activation and entropy of activation respectively.

Now the rate constant takes the form

$$k_2 = \frac{k_B T}{h} e^{-\Delta H^{\neq}/_{RT}} e^{\Delta S^{\neq}/_{R}} \qquad (v)$$

Now equation (iii) gives

$$\ln k_2 = ln\left(\frac{k}{h}\right) + lnT + lnK^{\neq}$$

$$\frac{d\ lnk_2}{dT} = \frac{1}{T} + \frac{dlnK^{\neq}}{dT} \qquad (vi)$$

From Arrhenius rate equation, we know $\frac{dlnk_2}{dT} = \frac{E_a}{RT^2}$

Therefore,

$$\frac{E_a}{RT^2} = \frac{1}{T} + \frac{dlnK^{\neq}}{dT} \qquad (vii)$$

We also know that from Van't Hoff isochoric

$$\frac{dlnK^{\neq}}{dT} = \frac{\Delta E^{\neq}}{RT^2}$$

Now the equation (vii) can be written as

$$\frac{E_a}{RT^2} = \frac{1}{T} + \frac{\Delta E^{\neq}}{RT^2}$$

$$or \quad E_a = RT + \Delta E^{\neq} \qquad\qquad (viii)$$

We know $H = E + PV$

$$\Delta H_P^{\neq} = \Delta E^{\neq} + P\Delta V^{\neq}$$

Therefore, equation (viii) can be written as

$$E_a = RT + (\Delta H_P^{\neq} - P\Delta V^{\neq})$$

$$E_a = RT + (\Delta H_P^{\neq} - \Delta n^{\neq} RT)$$

$$E_a = \Delta H_P^{\neq} - RT(\Delta n^{\neq} - 1)$$

$$-\Delta H_P^{\neq} = -E_a - RT(\Delta n^{\neq} - 1)$$

Now the equation (v) will take the form

$$k_2 = \frac{k_B T}{h} e^{{-E_a - RT(\Delta n^{\neq} - 1)}/_{RT}} e^{{\Delta S^{\neq}}/_{R}} \qquad\qquad (ix)$$

$$k_2 = \frac{k_B T}{h} e^{{-E_a}/_{RT}} e^{-(\Delta n^{\neq} - 1)} e^{{\Delta S^{\neq}}/_{R}} \qquad\qquad (ix)$$

Comparing with Arrhenius equation of the form

$$k = Ae^{{-E_a}/_{RT}}$$

We will find

$$A = \frac{k_B T}{h} e^{-(\Delta n^{\neq} - 1)} e^{{\Delta S^{\neq}}/_{R}} \qquad\qquad (x)$$

For unimolecular reaction $\Delta n^{\neq} = 0$ then

$$k_2 = \frac{k_B T}{h} e^{{-E_a}/_{RT}} e^{-(0-1)} \; e^{{\Delta S^{\neq}}/_{R}} = \frac{k_B T}{h} e^{{-E_a}/_{RT}} e \; e^{{\Delta S^{\neq}}/_{R}} \qquad\qquad (ix)$$

For bimolecular reaction $\Delta n^{\neq} = -1$ then

$$k_2 = \frac{k_B T}{h} e^{{-E_a}/_{RT}} \; e^2 \; e^{{\Delta S^{\neq}}/_{R}} \qquad\qquad (ix)$$

Ionic Reaction-Salt effects:

Consider a reaction between two ions, $A^{Z_A}$and B^{Z_B}, Z_A and Z_B being the ionic charges. It proceeds through an activated complex, $(AB)^{Z_A+Z_B}$.

$$A^{Z_A} + B^{Z_B} \rightleftharpoons (AB)^{Z_A+Z_B} \xrightarrow{k_2} Products$$

Example $S_2O_8^{2-} + I^- \rightleftharpoons (S_2O_8 - I)^{\neq} \xrightarrow{k_2} 2SO_4^{2-} + \frac{1}{2}I_2$

The complex is considered to be in equilibrium with reactants, but since we are dealing with ions, it is necessary to express the equilibrium constant in activities rather than concentrations:

$$K^{\neq} = \frac{a^{\neq}}{a_A a_B} = \frac{c^{\neq}}{c_A c_B} . \frac{\gamma^{\neq}}{\gamma_A \gamma_B}$$

The a's and γ's are the activities and activity coefficients.

$$c^{\neq} = c_A c_B K^{\neq} \frac{\gamma_A \gamma_B}{\gamma^{\neq}}$$

The rate of the reaction

$$-\frac{d[A]}{dt} = k_2[A][B] = \frac{k_B T}{h} c^{\neq}$$

Therefore, the rate constant,

$$k_2 = \frac{k_B T}{h} K^{\neq} \frac{\gamma_A \gamma_B}{\gamma^{\neq}}$$

$$\log_{10} k_2 = \log_{10} \frac{k_B T}{h} K^{\neq} + \log_{10} \frac{\gamma_A \gamma_B}{\gamma^{\neq}}$$

In dilute aqueous solution the activity coefficient terms can be estimated from the Debye-Hiickel theory at 25^{O}C in an aqueous solution, as $\log_{10} \gamma_i = -0.509 Z_i^2 \sqrt{I}$, where I is ionic strength

$$\log_{10} k_2 = \log_{10} k_2^O + [-0.509 Z_A^2 - -0.509 Z_B^2 + 1.018(Z_A + Z_B)^2]\sqrt{I}$$

$$\log_{10} k_2 = \log_{10} k_2^O + 1.018 Z_A Z_B \sqrt{I}$$

The BrØnsted equation predicts that the plot of $\log_{10} k_2$ vs. the $\sqrt{I}$ should be a straight line. For a water solution at 25^{O}C the slope is nearly equal to $Z_A Z_B$, the product of the ionic charges. Three special cases can occur:

(1) If Z_A, and Z_B have the same sign, Z_AZ_B is positive, and the rate constant increases with the ionic strength.

(2) If Z_A and Z_A have different signs, Z_AZ_B is negative, and the rate constant decreases with the ionic strength.

(3) If one of the reactants is uncharged, Z_AZ_B is zero and the rate constant is independent of the ionic strength.

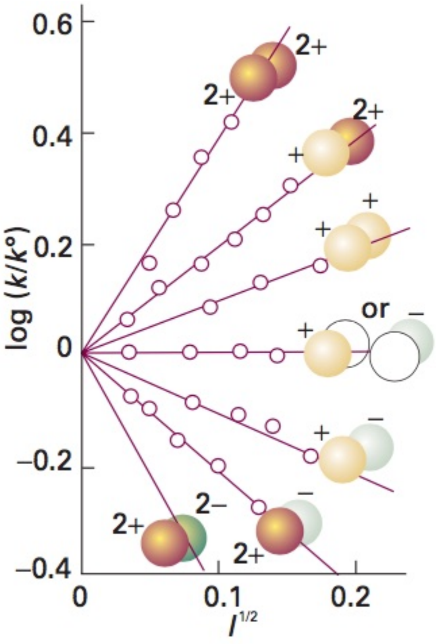


Figure 1: Experimental tests of the kinetic salt effect for reactions in water at 298 K. The ion types are shown as spheres, and the slopes of the lines are those given by the Debye–Hückel limiting law and equation given above

Those theoretical conclusions have been verified in a number of experimental studies. A few examples are illustrated in above figure. This change of k_2 with I is called the ***primary kinetic salt effect***. It should be noted that the ionic strength I is calculated from $\frac{1}{2}\sum_i m_iZ_i^2$ and the summation is extended over all the ionic species present in solution, not merely the reactant ions.