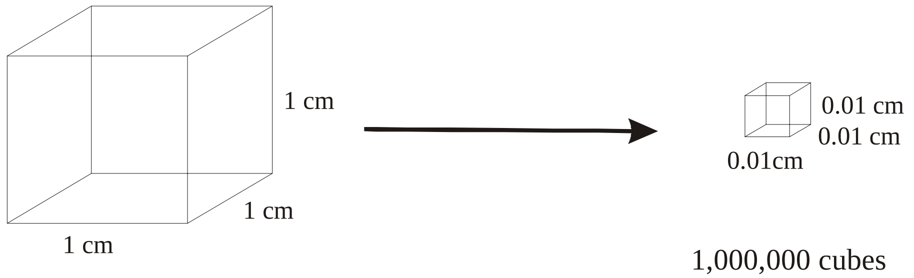
FACTORS AFFECTING RATE OF REACTION

1)Chemical nature of the reactants a freshly exposed metallic sodium surface furnishes almost instantly when explored to air and moisture – very fast reaction . Reaction between iron and moisture (air) to form rust is slow. Reason- iron do not lose electron easily. It depends on the inherent tendencies of atoms ,molecules, or ions to undergo changes in chemical bonds.

2) Ability of the reactants to come in contact with each other. For reaction to occur the reactants must collide with each other:

(a) homogeneous reaction –when reactants are in the same phase, e.g liquid, gas.

(b) heterogeneous reaction –reactant only able to meet at the interface. Rate of reaction dictated by the area of contact between the phases i.e surface area plays an important role.



Total surface area = 6 cm^2

1,000,000 cubes
total surface are = 600 cm^2

3) Concentration of the Reactants

The rates of both homogeneous and heterogeneous reactions are affected by the concentrations of the reactants.

4)Temperature of the system

Chemical reaction will occur faster at higher temperature. e.g chemical metabolism slows down in cooler surrounding.

5) Presence of rate promoting agents or catalysts. Catalysts are substances that increase the rate of reactions without itself being used up. Best example is enzymes.

ZERO –ORDER REACTION

Say our reaction of interest is,

$$aA \quad + \quad bB \quad \rightarrow \quad \text{products}$$

No need to specify the products since order of reaction is defined interms of the reactant concentration.

For zero-order , the rate of reaction is independent of the reactant concentrations.

Rate $= -\frac{1}{a}\frac{d[A]}{dt} = k^{'}[A]^{\circ}[B]^{\circ} = k^{'}$

a is only a coefficient, Thus

$$-\frac{d[A]}{dt} = k \qquad (\text{mol dm}^{-3}\ \text{s}^{-1})$$

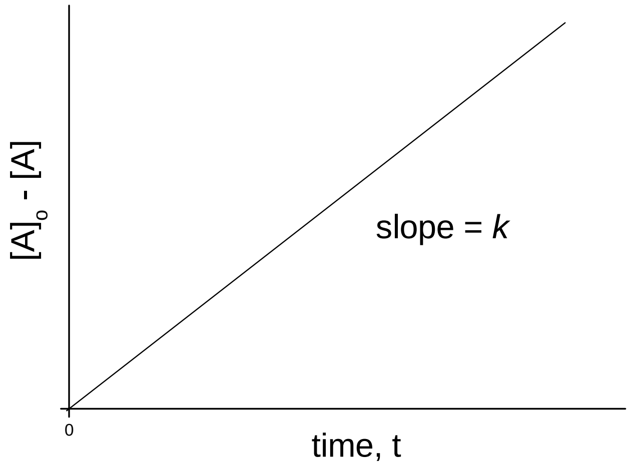
zero-order rate constant $k = ak'$

$$-d[A] = -kdt$$

intergration from t = 0 and t = t gives

$$\int_{[A]_\circ}^{[A]} d[A] = [A] - [A]_\circ = -\int_{t=0}^{t} kdt = -kt$$

or, $[A] = [A]_\circ - kt$



FIRST ORDER REACTION

(Tertib Pertama)

A → products

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

intergration :

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

$$-\int_{[A]_1}^{[A]_2} \frac{1}{[A]} d[A] = k\int_{t_1}^{t_2} dt$$

$$\ln\frac{[A]_1}{[A]_2} = k(t_2 - t_{1)}$$

if $t_1 = 0$ s $\quad \therefore \ln\frac{[A]_\circ}{[A]} = kt$

or
$$\ln[A] = [A]_\circ e^{-kt}$$
$$\ln[A] = \ln[A]_\circ - kt$$

e.g : decomposition of gaseous, N_2O_5,

$$2N_2O_5 \longrightarrow 4NO_2 + O_2 \;:\; aA \longrightarrow \text{products}$$

$$v = -\frac{1}{2}\frac{d[A]}{dt} = k[A]$$

$$\therefore rate = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = k[N_2O_5]$$

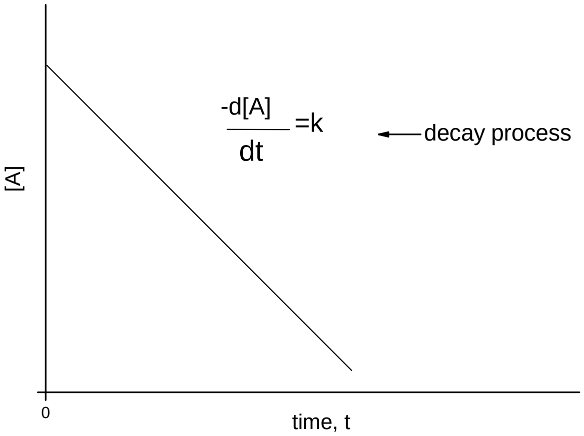
can also write :

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

$$where K_A = ak$$

The plot of ln [A] versus t will give a slope of $-K$ (unit of K, s^{-1})

t = 0 at any point of *t* changes in [A] could be changes in physical properties.



example : radioactive decays

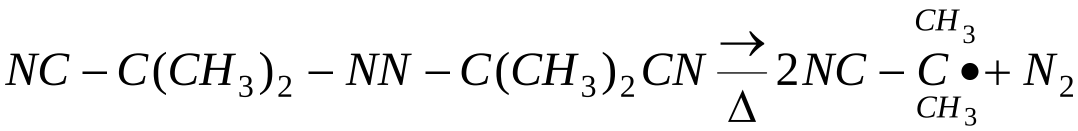
$$^{238}_{92}U \rightarrow ^{4}_{2}He + ^{234}_{90}Th$$

rearrangement of methyl isonitrile to acetonitrile

$$H_3CNC \longrightarrow H_3C - CN$$

Example :

The thermal decomposition of 2,2’- azobisisobutyronitrile (AIBN)



$$NC - C(CH_3)_2 - NN - C(CH_3)_2CN \xrightarrow[\Delta]{} 2NC - \overset{CH_3}{\underset{CH_3}{C}}\bullet + N_2$$

Has been studied in an inert organic solvent at room temperature. The progress of reaction has been monitored by the optical absorption at 350nm. The following data are obtained.

t(s)	0	2000	4000	6000	8000	10000	12000	∞
Abs	1.50	1.26	1.07	0.92	0.81	0.72	0.65	0.40

Assuming the reaction is first order calculate the rate constant.

$$\ln \frac{[AIBN]}{[AIBN]_\circ} = -kt$$

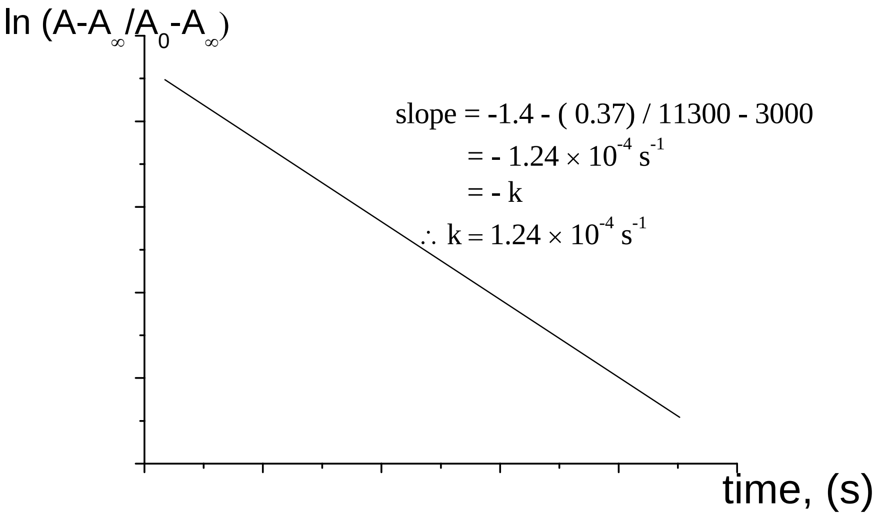
different in the absorbance t= 0 and t = ∞ , $(A_\circ - A_\infty)$ is propotional to [AIBN] initially present in solution. The instantaneous concentration [AIBN]$*$ at time $t \alpha (A - A_\infty)$

Thus,

$$\ln \frac{A - A_\infty}{A_\circ - A_\infty} = -kt$$

since $A_\circ = 1.50$ and $A_\infty = 0$.

t(s)	2000	4000	6000	8000	10000	12000
$\ln\left(\frac{A - A_\infty}{A_\circ - A_\infty}\right)$	-0.246	-0.496	-0.749	-0.987	-1.240	-1.482



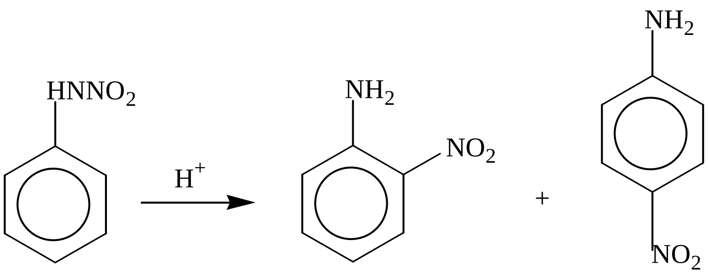
slope = -1.4 - (0.37) / 11300 - 3000

= - 1.24 × 10^{-4} s^{-1}

= - k

∴ k = 1.24 × 10^{-4} s^{-1}

Example 1:



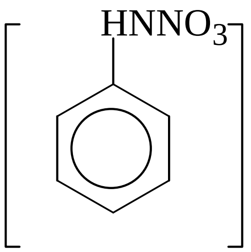
Reaction can be monitored by removing sample at suitable interval, quenching with excess alkali and measure the intensity of yellow color of the products. The following results were obtained

t (s)	0	300	780	1500	2400	3600	∞
Absorbance	0	0.036	0.074	0.120	0.162	0.199	0.249

Show that the reaction is First Order and determine the first order rate constant.

Example 2 :

Say



= a

rate constant for first order reaction, K

$$\therefore kt = 2.303\log_{10}\left(\frac{a}{a-x}\right) or \ln\frac{a}{a-x}$$

where a – concentration of reactant at $t_\circ$

$(a-x)$ is concentration at t

By assuming that the Beer-Lambert Law is obeyed, decadic absorbance.

If $A_\circ$ is the initial absorbance and A_∞ when the reaction is complete, $A_{\infty - A_t} \alpha$ concentration at time, t

$$\therefore kt = \ln \frac{(A_{\infty - A_\circ})}{(A_{\infty - A_t})}$$

for the first order rate constant, $\ln(A_{\infty -} A_t)$ vs t should give a straight line with slope –*k*

ANSWER : k $= 4.42 \times 10^{-4} s^{-1}$

Let,

$$[A] = [A]_\circ - x$$
$$[B] = [B]_\circ - x$$

where x is mol dm^{-3} of A and B consumed in time t

$$-\frac{d[A]}{dt} = -\frac{d[A]_\circ - x}{dt} = \frac{dx}{dt} = k[A][B]$$

$$= \quad k([A]_\circ - x)([B]_\circ - x)$$

$$\frac{dx}{([A]_\circ - x)([B]_\circ - x)} = kdt$$

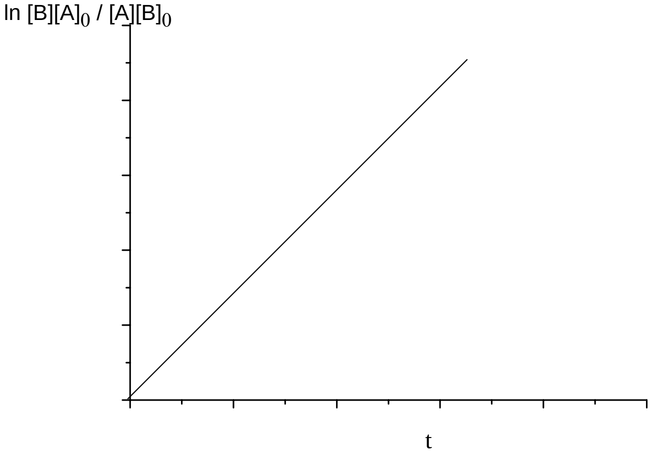
After integration:

$$\frac{1}{[B]_\circ - [A]_\circ} \ln \frac{([B]_\circ - x)}{([A]_\circ - x)} \frac{[A]_\circ}{[B]_\circ} = kt$$

OR

$$\frac{1}{[B]_\circ - [A]_\circ} \ln \frac{[B][A]_\circ}{[A][B]_\circ} = kt$$

assuming a=b=1 and $[A]_\circ \neq [B]_\circ$



SECOND ORDER REACTION

Consider,

aA + bB → product

type-1

$$\text{rate} = -\frac{1}{a}\frac{d[A]}{dt} = k'[A]^2[B]^\circ$$

$$= k'[A]^2$$

The rate is second order w.r.t *A* and zero-order w.r.t *B*

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

Where, $k = ak'$ in (mol dm^{-3})$^{-1}$ s^{-1}

integration:

$$\int_{[A]_\circ}^{[A]} \frac{1}{[A]^2} d[A] = -\int_0^t kdt$$

$$\frac{1}{[A]} - \frac{1}{[A]_\circ} = kt$$

type-2

$$\text{rate} = -\frac{1}{a}\frac{d[A]}{dt} = k'[A][B]$$

first-order w.r.t A and B

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

where $K = ak'$

Second order is most common reactions

Example :

$CH_3COCH_3\,(aq) + H^+\,(aq) \longrightarrow CH_3COHCH_3^+\,(aq)$

$2NO_2\,(g) \longrightarrow 2NO\,(g) + O_2\,(g)$

Example hydrolysis of acetyl chloride

$CH_3COCl + H_2O \longrightarrow CH_3COOH + HCl$

Water in excess compared to acetyl chloride molarity of $H_2O \times 55.5$ mol dm^{-3} the amount of H_2O consumed is almost negligible.

Rate is expressed,

$$-\frac{d[CH_3COCl]}{dt} = k[CH_3COCl][H_2O]$$

$$= k'[CH_3COCl]$$

where $k' = k[H_2O]$. The reaction therefore appears to be First-Order kinetics and is called a pseudo-First-Order reaction.

HALF LIFE

Consider First-order reaction $[A] = \frac{[A]_\circ}{Z}, t = t_{1/2}$

Thus,

$$\ln\frac{[A]_{\circ/2}}{[A]_\circ} = -kt_{1/2}$$

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

SECOND ORDER REACTION

Example :

The reaction between iodoethane and tertiary amine $C_6H_5N(CH_3)_2$ can be followed by titrating the liberated iodide ions with silver nitrate solution.

$C_2H_5I + C_6H_5N(CH_3)_2 \rightleftharpoons C_6H_5N(CH_3)_2C2H_5^+ + I^-$

In an experiment at $25^\circ C$ using equimolar amounts of reactants, the following values of the iodoethana concentration were obtained ;

Time, s	0	89	208	375	625	803	1041	1375	1875
$[C_2H_5I]$ mol dm^{-3}	1.6	1.4	1.2	1.0	0.8	0.7	0.6	0.5	0.4

Determine the order of reaction and the rate constant, k

ANSWER :

If the reaction is second-order, the rate equation,

$$-d\frac{[C_2H_5I]}{dt} = k[C_2H_5I][C_6H_5N(CH_3)_2]$$

Initial concentration for both reactants = $[A]_\circ$

Concentration of each reactant at $t = [A]_t$

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

A plot of $\frac{1}{[A]_t}$ vs t should give a straight line of slope, k

t,s	0	89	208	375	625	803	1041	1375	1875
$\frac{1}{[A]}$	0.625	0.714	0.833	1.0	1.250	1.428	1.667	2.00	2.50

A straight line plot → the reaction is second-order

Slope = $k = 1.00 \times 10^{-3} dm^3 mol^{-1} s^{-1}$

ENERGY of ACTIVATION

Example :

The rate constant k for the first-order decomposition of acetone-dicarboxylic acid in aqueous solution are as follows :

Temp/$^\circ C$	0	10	20	30	40	50	60
$k, 10^5 / s$	2.46	10.8	47.5	163	576	1850	5480

Calculate the energy of activation for the reaction

The Arrhenius equation for the rate constant , k

$$k = A \exp\left(\frac{-Ea}{RT}\right)$$

Taking logarithm,

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

A plot of $\ln k$ vs $\frac{1}{T}$ should give a straight line of slope $-\frac{E_a}{R}$

or $-\frac{E_a}{2.303}$ if in $\log_{10}$

The activation energy ,

$$E_a = 97.3 kJmol^{-1}$$

$\ln k$	-10.613	-9.133	-7.652	-6.420	-5.157	-3.99
T/K	0.00366	0.00353	0.00341	0.0033	0.00319	0.0036

Slope = -11683.2 $\therefore E_a = 11683 \times 8.314$

$\ln(10.8 \times 10^{-5}) = -9.133$ $= 9.713 kJmol^{-1}$

UNIMOLECULAR REACTION

Unimolecular reactions are first-order reactions rate constant independent of pressure above pressure ≈ 1 bar.

Rate constant drops at lower pressure.

An isolated reaction of gas molecules.

Examples :

Isomerization

$CH_3NC \longrightarrow CH_3CN$ $E_a = 160.5 kJmol^{-1}$ at 470-530 K

Dissociation to stable molecules

$C_2H_5Cl \longrightarrow C_2H_4 + HCl$ $E_a = 254 kJmol^{-1}$ at 670-770 K

Dissociation to free radicals

$C_2H_6 \longrightarrow \bullet 2CH_3$ $E_a = 360 kJmol^{-1}$ at 820-1000 K $HNO_3 \longrightarrow \bullet OH + NO_2$ $E_a = 205 kJmol^{-1}$ at 890-1200 K

Where does these high activation energies come from?

First approximation of the answer was provided by Lindemann in 1922.

"When a molecule is excited to a higher energy state by a bimolecular collision, there is a time before decomposition or isomerization."

Decomposition of azomethane at high pressure

$$CH_3N_2CH_3 \longrightarrow C_2H_6 + N_2$$

shows first-order kinetics i.e : rate α $[CH_3N_2CH_3]$

However the rate increases with temperature showing the reactant must surmount an energy barrier, but first-order preclude collisional activation.

Recall, the excited molecule may lose its extra energy in a second bimolecular collision.

The reaction involves a reacting gas A with an excess of inert gas M, the excitation step and de-excitation step.

$$\mathrm{A} + \mathrm{M} \xrightarrow{k_1} \mathrm{A}^* + \mathrm{M}$$

$$\mathrm{A}^* + \mathrm{M} \xrightarrow{k_2} \mathrm{A} + \mathrm{M}$$

$$\mathrm{A}^* \xrightarrow{k_3} \mathrm{B} + \mathrm{C}$$

A is a reactant molecule that can be excited on collision with *M*, which is either another *A* molecule or added diluent (bath) gas molecule in simplified form,

$$\mathrm{A} + \mathrm{M} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^* + \mathrm{M}$$

$$\mathrm{A}^* \longrightarrow \mathrm{P}$$

$$\frac{d[A^*]}{dt} = k_1[A][M] - k_2[A^*][M] - k_3[A^*]$$

formation of A*

removal of A*

Low pressure limit, when k_2[M] << k_3,

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

$A*$ isomerize or dissociate , rate determined by the number of collisions that are sufficiently energetic.

Rate determining step is bimolecular excitation. Once activated (A*) more likely to react than deactivate.

$$k = k_1[M] \qquad \text{remains constant}$$

At very low P, the reaction second-order when the partial pressure of M is changed .

However, the product can also activate or quench so that [M] is constant and the reaction is pseudo first order.

In a unimolecular dissociation, [M] increases but since the products are less efficient in energizing A, k_1 [M] ~ constant.

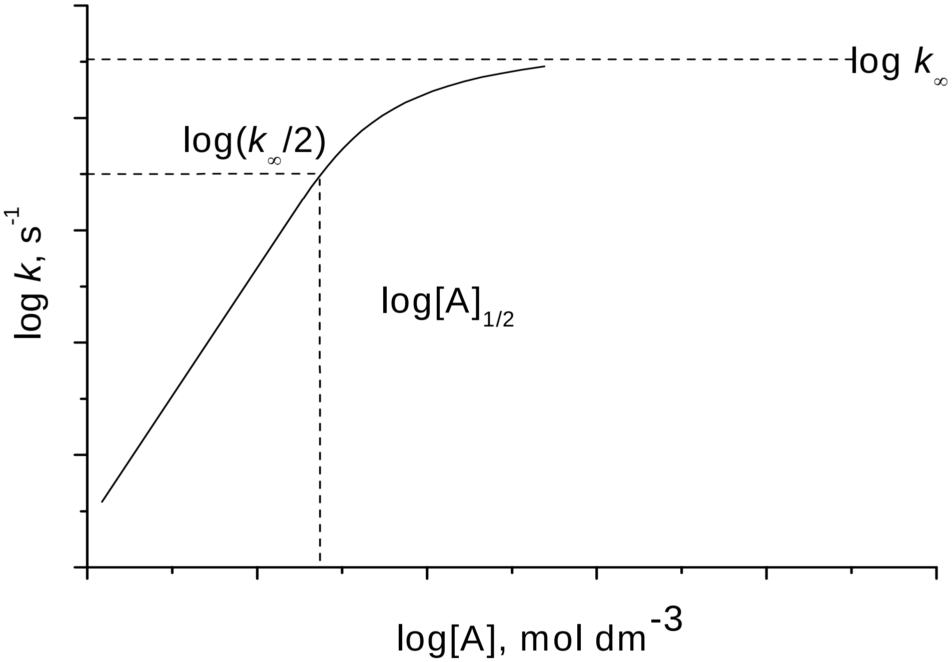
Thus, the reaction pseudo first-order.

At low pressure the rate constant of a unimolecular reaction decreases and the reaction is in the fall off region.

Since $A*$ is never present at a very high concentration after a short build-up period, rate of consumed is the same rate at which it is produced.

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

$$\frac{d[P]}{dt} = -\frac{d[A]}{dt} = k_3[A^*] = \frac{k_1k_3[A][M]}{k_2[M]+k_3} = k[A]$$



The rate constant drops with decreasing pressure for the decomposition of azomethane at 603K

The equation has two limiting forms :

1. High pressure limit, when k_2[M] >> k_3,

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

i.e : Collisional deactivation is much faster than the unimolecular reaction A^*. $k \approx k_3k_1/k_2$ i.e : becomes independent of pressure. The rate determining step is the first-order reaction of A* and the overall kinetics also first-order.

$$-\frac{d[A]}{dt}=\frac{k_1k_3[A][M]}{k_2[M]}$$

$$=\frac{k_1k_3[A]}{k_2}=k'[A]$$

LINDEMANN THEORY

Comparison of $[M]_{1/2}$ for unimolecular reaction.

$$k=k_\infty/(1+k_3/k_2[M]$$

The rate coefficient at high/infinite pressure

$$k_\infty=k_3k_1/k_2$$

If $[M]_{1/2}$ as the third body concentrationat which the experimental rate coefficient falls to half of its high pressure value,

$$[M]_{1/2}=k_\infty/k_1$$

We can estimate $[M]_{1/2}$ from the experimental value k_∞

assuming the collision theory rate coefficient for activation.

$$k_1 = Z\exp(-\frac{Ea}{RT})$$

where Z is collision frequency factor

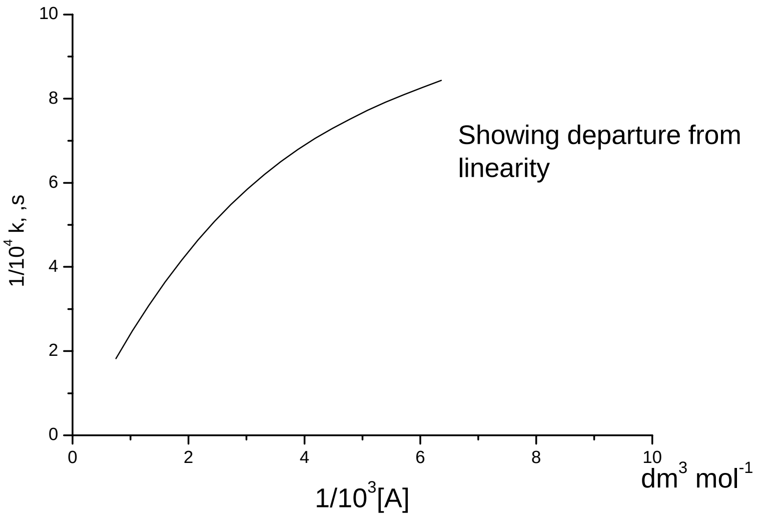
Unimolecular reaction	T/K	E, KJ mol^{-1}	$[M]_{1/2}$ exp M	$[M]_{1/2}$ calc M	K_1, s^{-1}
Cyclopropane → propene	760	275	3×10^{-4}	1.5×10^{4}	3×10^{15}
cyclobutane → 2 ethene	720	267	10^{-5}	2×10^{4}	4×10^{15}
$CH_3NC \longrightarrow CH_3CN$	500	161	4×10^{-4}	2×10^{2}	4×10^{13}
$C_2H_5NC \longrightarrow C_2H_5CN$	500	160	3.5×10^{-5}	3.5×10^{2}	6×10^{13}
$N_2O \longrightarrow N_2 + O$	890	256	0.8	4.0	6×10^{11}

There are discrepancies between experiment and calculated $[M]_{1/2}$

Worse when molecules get larger.

For the reaction

Trans $-C_2H_2D_2 \longrightarrow$ cis $- C_2H_2D_2$ at 794K



$$\frac{1}{k} = \frac{1}{k_1}[M] + \frac{1}{k_\infty}$$

Thus, the plot of 1/k vs [M] should give a straight line.

k_∞ can be determined by extrapolating to $\frac{1}{[M]} = 0$

The plot is far from linearity indicate another problem in Lindemann approach.

Lindemann mechanism provide simplified representation of the physical processes which involved unimolecular reactions. Its failures similar to those in collision theory, fails to take account of real molecular structure.

All subsequent models are built on the foundation of second-order activation to an energized molecule, followed by a first order reaction.

Lindemann Theory : exercise

The following values of the overall rate constant k’ were obtained for the decomposition of dimethyl ether :

J_o/m mol dm^{-3}	1.20	1.89	3.55	5.42	8.18
10^4k’/s^{-1}	2.48	3.26	4.61	5.54	6.29

Use the data to demonstrate the validity of Lindemann theory and obtain the limiting value of *k’* at high pressure

ANSWER:

$$A + A \rightleftharpoons A^* + A$$

$$A^* \xrightarrow{k_3} \text{products}$$

A and A* are normal and energized reactants respectively.

Assuming a steady state of A*

$$\text{Rate} = \frac{k_1 k_3 [A]^2}{k_2 [A] + k_3} = k'[A]$$

k’ is the overall first-order rate constant

therefore,

$$k' = \frac{k_1 k_3 [A]}{k_2 [A] + k_3}$$

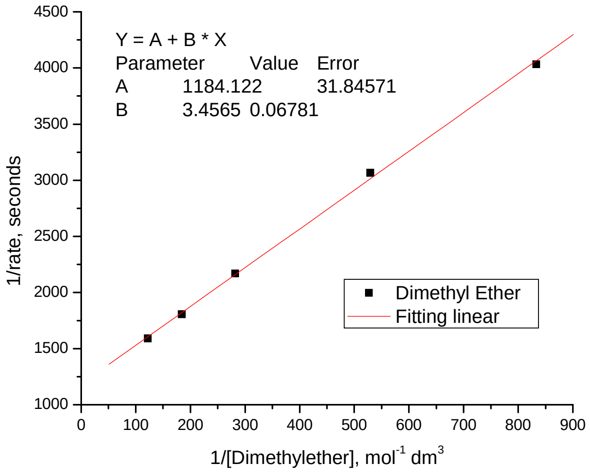
At high pressure k_2 [A]>>k_3, the overall rate constant limits to the value,

$$k_\infty = \frac{k_1 k_3}{k_2}$$

taking the reciprocal in the expression k' gives ,

$$\frac{1}{k'} = \frac{k_2}{k_1 k_3} + \frac{1}{k_1[A]} = \frac{1}{k_\infty} + \frac{1}{k_1[A]}$$

Therefore , the plot of $\frac{1}{k'}$ against $\frac{1}{[A]}$ will gives a straight line of slope $\frac{1}{k_1}$ and intercept $\frac{1}{k_\infty}$.



The graph is a straight line, Lindemann theory is valid for this reaction.

$$\text{Intercept} = \frac{1}{k_\infty} = 01184s$$

$$k_\infty = 8.55 \times 10^{-4} s^{-1}$$

BIMOLECULAR REACTIONS

An elementary reaction that involves two molecules.

e.g : in the gas phase

$$H + H_2 \longrightarrow H_2 + H$$

$$CO + O_2 \longrightarrow CO_2 + O$$

$$K + HBr \longrightarrow KBr + H$$

$$PH_3 + B_2H_6 \longrightarrow PH_3BH_3 + BH_3$$

In solution phase

$$2CH_3COOH \longrightarrow (CH_3COOH)_2 \text{ (non polar solvent)}$$

$$Fe^{3+} + Fe^{2+} \longrightarrow Fe^{2+} + Fe^{3+}$$

The predominant force between two non polar , unchanged molecules is a strong repulsion.

If the molecule can react in an exothermic reaction, the activation energy is a measure of the energy required to deform the electron clouds of the reactants so that the reaction can occur.

E_a for exothermic Bimolecular Reactions

Reaction type	Electronic structure	E_a , $kJmol^{-1}$
Molecule+ molecule	Two closed shells	80-200
Radical +molecule	One closed shell/ one open shell	0-60
Radical + radical	Two open shells	~ 0

Radicals refer to molecules with at least one orbital vacancy in their valence shells and to atoms.

Most reactions in gas phase involve radicals.

Arrhenius parameters for bimolecular reactions

Reaction	Log $\left(\frac{A}{Lmol^{-1}s^{-1}}\right)$	E_a, $kJmol^{-1}$
$Br + H_2 \rightarrow HBr + H$	10.8	76.2
$I + H_2 \rightarrow HI + H$	11.4	143.0
$Cl + H_2 \rightarrow HCl + H$	10.9	23.0
$N + NO \rightarrow N_2 + O$	10.2	0
$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$	8.5	45.2
$2CH_3 \rightarrow C_2H_6$	10.5	0
$CH_3 + NO \rightarrow CH_3NO$	8.8	0

The pre exponential factor involving atoms in the range of $10^{10.5} – 10^{11.5}$ L $mol^{-1}s^{-1}$ but the activation energies differ appreciably.

Some bimolecular reaction are very complex. Some cases the rate of reaction depends on the pressure – indicates the reaction leads to a collision complex. This is a weakly bound molecule that survives for a short time but longer than the characteristic periods of its vibration and rotations.

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{AB} \longrightarrow \text{products}$$

When AB is formed, the reaction is no longer a bimolecular. At low pressure the unimolecular dissociation of AB is in the fall off region, the overall reaction may approach third-order reaction.

Example of such reaction:

$$\mathrm{ClO} + \mathrm{NO} \rightleftharpoons \mathrm{ClONO} \longrightarrow \mathrm{Cl} + \mathrm{NO_2}$$

Rate constant = 6.2×10^{-12} cm3 s^{-1} exp $\left(\frac{294K}{T}\right)$

Example :

$$\mathrm{A} + \mathrm{B} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{AB} \xrightarrow{k_3} \mathrm{C}$$

say a weak complex AB is formed assuming k2 >> k3 , the first step remains in equilibrium . Thus , the rate equation is,

$$\frac{d[C]}{dt} = k_2[AB]$$

$$\therefore \frac{k_1}{k_2} = K_c(c^\circ)^{\Sigma vi} = K_c / c^\circ$$

c° *- a standard concentration in one mole per liter.*

$$K_c = \frac{[AB]c^\circ}{[A][B]}$$

$$\frac{k_1}{k_2} = \frac{[AB]}{[A][B]}$$

We eliminate [AB]

$$\frac{d[C]}{dt} = \frac{k_1k_3}{k_2}[A][B] = k_3(K_c / c^\circ)[A][B]$$

TRIMOLECULAR REACTIONS

Two atoms cannot combine in a bimolecular reaction in the gas phase to form a diatomic molecule because the energy release causes the molecules to dissociate.

Need a third atom to carry away the energy produced.

Atoms recombination reactions are third order in the gas phase.

The third order elementary reaction

$$2A + M \longrightarrow A_2 + M$$

$$A + B + M \longrightarrow AB + M$$

Rate equation :

$$\frac{d[A_2]}{dt} = k[A]^2[M]$$

$$\frac{d[AB]}{dt} = k[A][B][M]$$

Trimolecular reactions by avoiding three – body collision.

$$A + M \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AM$$

M is a polyatomic molecule capable of forming a complex.

AM can dissociate with rate constant k_2 to regenerate A and B or to form A_2 with rate constant k_3

$$AM + A \xrightarrow{k_3} A_2 + M$$

The steady rate equation :

$$\frac{d[A_2]}{dt} = \frac{k_1 k_3 [A]^2 [M]}{k_2 + k_3[A]}$$

The intermediate is short lived. Thus, $k_2 >> k_3 [A]$

$$\frac{d[A_2]}{dt} = \frac{k_1}{k_2} \cdot k_3 [A]^2 [M]$$

since, $\frac{k_1}{k_2} = K_c (c^\circ)^{\Sigma vi}$

where $K_c = \frac{[AM]c^\circ}{[A][M]}$

Now, $\frac{d[A_2]}{dt} = (K_1 / c^\circ) k_3 [A]^2 [M]$

If k_2 follows Arrhenius equation with E_{a2}.

$\therefore$ the activation energy for trimolecular reaction ,

$$E_a = RT^2 \frac{d \ln k_1}{dT} + RT^2 \frac{d \ln k_2}{dT}$$

$$= \Delta H_1^\circ + E_{a2}$$

If the first step is exothermic and the E_a for second step not too large, E_a can be negtive.

If the combination of atom with another atom or diatomic is trimolecular, the reverse reaction is bimolecular, and the

Arrhenius equation for the reverse reaction may be calculated using K_c (see bimolecular reaction).

Reaction	T/K	Log K, $L^2\ mol^{-2}\ s^{-1}$
$H + H + M \longrightarrow H_2 + M$	300	10.0 (H_2)
$O + O + M \longrightarrow O_2 + M$	300	8.9 (O_2)
$O + O_2 + M \longrightarrow O_3 + M$	380	8.1 (O_2)
$O + NO + M \longrightarrow NO_2 + M$	300	10.46 (O_2)
$H + NO + M \longrightarrow HNO + M$	300	10.7 (H_2)

CHAIN REACTIONS

Involving radicals and exothermic

Example:

$$H_2 + Br_2 \rightleftharpoons 2HBr$$

At 500 – 1500 K, typical of unbranched chain reaction.

The empirical rate equation :

$$\text{Rate} = \frac{1}{2}\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{1 + k'[HBr]/[Br_2]}$$

If NO HBr at t= 0 , rate at t= 0

$\alpha[H_2][Br]^{1/2}$

If sufficient HBr is added, k’ [HBr] / [Br_2] >> 1,

Then initial rate, $\frac{\alpha[H_2][Br_2]^{3/2}}{[HBr]}$

The presence of product inhibits the forward reaction.

$2 \times [HBr] \longrightarrow 1/2 \times$ initial rate

At low [HBr] , rate $\alpha[Br_2]^{1/2}$, thus Br_2 dissociates, suggest that Br atom plays role in the mechanism.

IF the dissociation is in equilibrium:

$$[Br] = K^{1/2}[Br_2]^{1/2}$$

Christiansen, Herzfed and Polanyi (1919) :

Br could react with H_2 to start reaction.

Proposed mechanism :

Initiation

$$Br_2 + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Br + M$$

Propagation

$$Br + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HBr + H$$

$$H + Br_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} HBr + Br$$

The carrier gas is M. The net reaction is the sum of step 2 and 3. The reaction is initiated by Br_2 NOT H_2 because bond in bromine is much weaker.

k_2 is endothermic, E_a is high , slower reaction.

k_{-2} is fast , destroys product, inhibition reaction.

Termination $Br^{\cdot} + Br^{\cdot} \rightarrow Br_2$

Chain reaction rapidly reaches steady state when;

$$\frac{d[Br]}{dt} \approx \frac{d[H]}{dt} \approx 0$$

Then , $k_{-3} = 0$

The steady-state rate equation :

$$\frac{1}{2}\frac{d[HBr]}{dt}=\frac{k_2(k_1/k_{-1})^{1/2}[H_2][Br_2]^{1/2}}{1+\dfrac{k_{-2}[HBr]}{k_3[Br_2]}}$$

$\dfrac{k_1}{k_{-1}}$ is the dissociation constant of bromine

$k=k_2(k_1/k_{-1})^{1/2}$

IF k_{-3} is included ,

$$\frac{1}{2}\frac{d[HBr]}{dt}=\frac{k_2(k_1/k_{-1})^{1/2}[H_2][Br_2]^{1/2}}{1+k_{-2}[HBr]/k_3[Br_2]}\left(\frac{1-[HBr]^2}{K[H_2][Br_2]}\right)$$

where , $K=\dfrac{k_2k_3}{k_{-2}k_{-3}}$

The equilibrium constant for the overall reaction.

For low extent of reaction, the steady-state law becomes the rate law for the reverse reaction.

Under condition [HBr] >>K$[H_2][Br_2]^{1/2}$

$$-\frac{1}{2}\frac{d[HBr]}{dt}=k_{-3}\left(\frac{k_1}{k_{-1}}\right)^{1/2}[HBr][Br_2]^{1/2}$$

First order in [HBr] at constant [Br2]

The steady state law at equilibrium is still applicable whether we start from

H_2 + Br OR HBr

PYROLYSIS OF HYDROCARBON

EXAMPLE: Production of ethylene from ethane, cracking process of higher hydrocarbons to produce butadiene, butene and propylene.

Generally heterogeneous reaction with solid catalysts.

Homogeneous reaction of ethane ⟶ ethylene pyrolysis.

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

reaction at 700 – 900K ,P >0.2 bar

Reaction Mechanism :

Initiation : $C_2H_6 \xrightarrow{k_1} 2CH_3$

Chain transfer $CH_3 + C_2H_6 \xrightarrow{k_2} CH_4 + C_2H_5$

propagation $C_2H_5 \xrightarrow{k_3} C_2H_4 + H$

$H + C_2H_5 \xrightarrow{k_4} H_2 + C_2H_5$

Termination $H + C_2H_5 \xrightarrow{k_5} C_2H_6$

The rate of equation of ethane ;

$$\frac{d[C_2H_6]}{dt} = -(k_1 + k_2[CH_3] + k_4[H])[C_2H_6]$$

The rate of formation of ethane in the last step is ignored because termination occurs after long chain of reactions.

In the steady state, the rates of change of the radical concentrations ≈ zero.

$$\frac{d[CH_3]}{dt} = 2k_1[C_2H_6] - k_2[CH_3][C_2H_6] = 0$$

$$\frac{d[C_2H_5]}{dt} = (k_2[CH_3] + k_4[H])[C_2H_6] - (k_3 + k_5[H])[C_2H_5] = 0$$

$$\frac{d[H]}{dt} = k_3[C_2H_5] - k_4[H][C_2H_6] - k_5[H][C_2H_5] = 0$$

Therefore, the steady state concentration of the radicals, $^\bullet$CH3 , $^\bullet C_2H_5$, $^\bullet$H can be obtained from these simultaneous equation.

$$[CH_3] = \frac{2k_1}{k_2}$$

$$[C_2H_5] = \frac{2k_1 + k_4[H]}{k_3 + k_5[H]}[C_2H_6]$$

$$[H] = \frac{2k_1k_5 \pm \sqrt{(2k_1k_5)^5 + 16k_1k_3k_4k_5}}{-4k_4k_5}$$

k_1 is small so that ,

$$[H] = \left(\frac{k_1 k_3}{k_4 k_5} \right)^{1/2}$$

$\therefore$ Rate of reaction of ethane

$$\frac{d[C_2H_6]}{dt} = -\left[3k_1 = k_4 \left(\frac{k_1 k_3}{k_4 k_5} \right)^{1/2} \right] [C_2H_6]$$

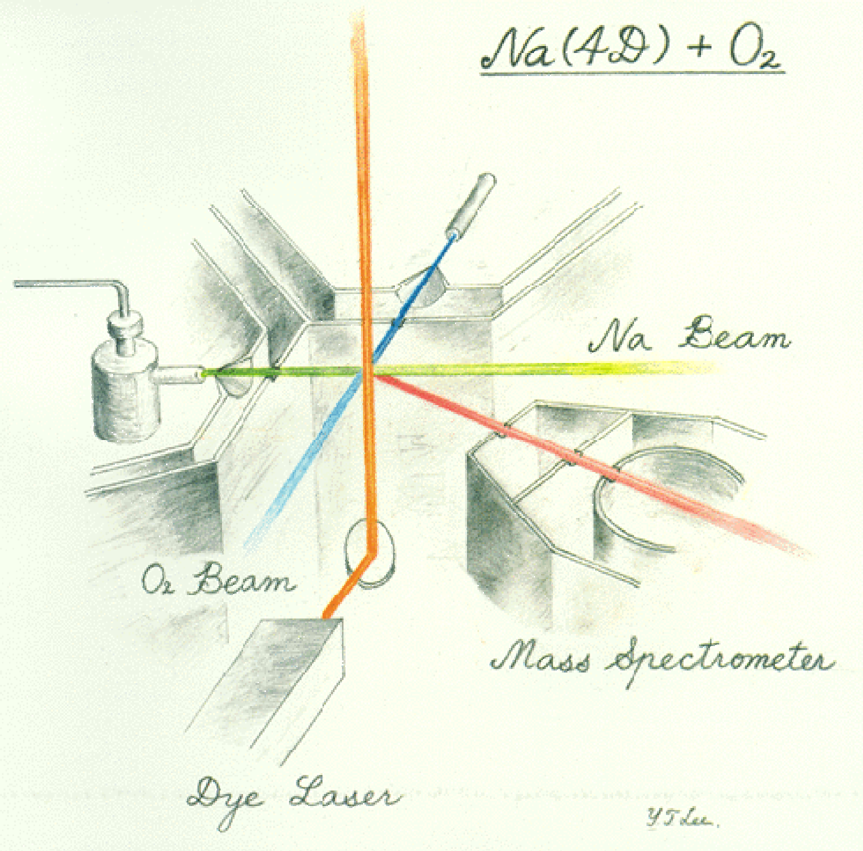
The reaction is first-order!

NOTE: HARPOON REACTION

The Nobel Prize in Chemistry 1986 - "for their contributions concerning the dynamics of chemical elementary processes"

		
Dudley R. Herschbach	**Yuan T. Lee**	**John C. Polanyi**
◔1/3 of the prize	◔1/3 of the prize	◔1/3 of the prize
USA	USA	Canada
Harvard University Cambridge, MA, USA	University of California Berkeley, CA, USA	University of Toronto Toronto, Canada
b. 1932	b. 1936 (in Hsinchu, Taiwan)	b. 1929

Yuan T. Lee's Crossed Molecular Beam Experiment



The above illustration was drawn by Professor Yuan T. Lee, who shared the 1986 Nobel Prize in Chemistry.
The purpose of this experiment was to study the chemical reaction of sodium atoms with oxygen molecules. In the experiment, a beam of sodium atoms (green, chemical symbol Na) and a beam of oxygen molecules (blue, chemical symbol 0_2) intersect in a vacuum. The products of the sodium-oxygen reaction (red) are ionized by laser radiation (orange) aimed at the point of intersection of the two beams so that the products can be detected and measured by the mass spectrometer.

By tuning the wavelength of the laser, specific products of the chemical reaction can be identified and measured. By moving the position of the mass spectrometer, the spatial distribution of the reaction products can be determined. Through control of the sources of the atoms and molecules, reactants in specific can be selected for study, as in the case of the 4D state of the sodium.
Shown in black and white is the variety of devices needed to form and shape the beams. Using instruments such as these, chemists have been able at last to study chemical reactions in great quantitative detail.

DYNAMICS OF CHEMICAL REACTIONS

The benefits of modern chemistry so profoundly affect our daily lives that it is difficult to imagine a world without them. Yet, despite all this progress, man’s basic understanding of the most fundamental aspects of chemical reactions is just beginning to yield to the scientists’ probes.
In 1986, the Nobel Prize in Chemistry was shared by three physical chemists. Two, Dudley R. Herschbach and Yuan T. Lee, were supported in their research by Basic Energy Sciences. The Prize was awarded for discoveries that helped to explain the physical dynamics of chemical reactions.
Specifically, Basic Energy Sciences research revealed how two molecules undergoing a chemical reaction collide, combine and transform themselves, step by step, into very different resultant products. Although the reactions studied were comparatively simple and straightforward, the insights gained revolutionized prevailing thought.
From the point of view of chemical reaction dynamics, the 19th century way of writing down chemical reactions, using arrows and symbols, is misleading. The equations obscure which aspects of chemical reactions are important and which ones are not. If one looks at the reactions in a different light, as did Herschbach and Lee, focusing instead on particular structures of certain atomic electrons and orbitals, the pieces of the puzzle begin to fall into place.
Striking similarities stand out among their experimental data. These form a relatively small number of "rules" which govern chemical reactions and their dynamics. These, in turn, can be generalized to other molecules and other reactions. With this knowledge, it may be possible ultimately to manipulate, using

a variety of control mechanisms, the timing, speed, sequence, extent, and very nature of chemical reactions, attended by virtually unlimited variations and possibilities.

The specifics of the Basic Energy Sciences contribution may be appreciated by visualizing a chemical reaction. Imagine, for a moment, an immensely enlarged, slow motion picture of one atom, potassium (K), and one molecule, methyl iodide (CHJ), hurtling toward each other through the vacuum of a laboratory chamber on a collision course set by the scientists to result in a glancing blow.

In some cases, the expected chemical reaction takes place with the explosive formation of two by-products, potassium iodide (KI) and an incomplete methyl group (CH,), flying off in opposite directions. In other cases, the collision results in no chemical reaction, with the original constituents, called reactants, simply bouncing off each other in a physically expected distribution of random directions.

By varying the velocities and angles of the incoming reactants, and by measuring and determining the distributions of the resulting products, Basic Energy Sciences researchers were able to infer the necessary and sufficient conditions under which the reaction would take place. In the case studied, the incoming potassium atom had to strike the opposing methyl iodide molecule on the iodide end, and then bounce backward.

Over the years, the experimental devices used to analyze the reactions became more sophisticated and the kinds of reactants and reactions studied became more complex. Gradually, the data began to reveal patterns and similarities, even though the molecular structures of the varying reactants appeared to be quite different.

This led to what Herschbach called **the "harpoon" model of reaction dynamics.** One molecule sneaks up on the other, uses a very specific valence electron orbital as its harpoon, spears its target in one selective and vulnerable spot, and hauls it in. Once these mechanisms are known, many of the other potentially obscuring complexities of molecular shapes, bonds, and electron potentials, fall away as being irrelevant.

The experimental technique used in these studies, developed by Herschbach and Lee, is today known as "crossed-molecular beam" research. The facility recently constructed at Lawrence Berkeley Laboratory, under Lee’s direction and with continued support from Basic Energy Sciences, is widely acclaimed as the best molecular beam instrumentation facility in the world.

In recent years, this facility enabled Lee to study more complex molecules, such as those having long hydrocarbon chains. Pioneering exploration was begun in two key areas of pressing national interest-hydrocarbon (oil and natural gas) combustion and atmospheric chemistry.

With these advances, understanding chemistry from first principles is now a practical goal. Its applicability extends beyond fuel burning and ozone depletion. Insights gained using crossed-molecular beam research may yield new models of how catalysts operate in specific chemical reactions. Because the velocities of molecular collisions, which determine reaction potentials, are related to temperature, the nature of reaction rates is now a subject of detailed and quantifiable research.

Perhaps more importantly, crossed-molecular beam research permits a better understanding of reaction intermediates, the short-lived arrangements of atoms and molecules that are the first results of a molecular collision, but which soon decay to some other or more stable forms. Manipulating the reaction intermediates offers one of the best hopes for precisely controlling chemical reactions and, thus, determining the nature of the final reaction products.

For Herschbach and Lee, more than two decades of fundamental research culminated in the Nobel Prize. They envisioned and devised a productive experimental approach, built and perfected the necessary hardware and instruments, gathered data with sufficient variety and scope to yield robust conclusions, and presented the scientific community with a wholly new view of chemistry and the dynamics of reactions.

Crossed-molecular beam research is now firmly established as a fundamental research tool. With continued support from Basic Energy Sciences, it is being used in a growing number of inquiries. With expanding knowledge, focused more on applications, improved understanding of reaction dynamics and, perhaps, the ability to control the reactions themselves, move closer to reality.

Despite all the wondrous advances of modern chemistry, new frontiers remain to be explored. Crossed-molecular beam research lies at the forefront of this endeavor, with great potential for continuing contributions to industry, health, and environment.

HARPOON MECHANISM

Consider the reaction ,

$$K + Br2 \longrightarrow KBr + Br$$

The first stage of the reaction is the transfer of valence electron of the alkali atom to the halogen molecule. Such a transfer is possible even when the reactants are far apart (5 –10 $\overset{\circ}{A}$). Once the transfer takes place, the strongly attractive Coulombic force brings the two oppositely charged ions togethers, followed by the formation of the products.

The metal atom uses its valence electron as a “harpoon” in order to pull in the halogen molecule, employing the coulombic interionic attraction as a “rope” . There are three energy contributions to the charge transfer process.

ionization energy of K, $\longrightarrow$ I

electron affinity of $Br_{2,}$ $\longrightarrow$ E_{ea}

coulombic interaction energy between the ions

$$\longrightarrow -\frac{e_2}{4\pi\varepsilon_\circ R}$$

e = electronic charge

$\varepsilon_\circ$ = permittivity of vacuum

The charge transfer occurs when the difference between I and E_{ea}

Is balanced by the coulombic interaction energy.

i.e :

$$\frac{e^2}{4\pi\varepsilon_\circ R_x} = I - Eea = \Delta E$$

R_x is the critical distance at which charge transfer takes place. By solving the above equation, the value of R_x can be obtained.

From R_x , the collision cross-section can be obtained as, $\sigma^* = \pi R_x^2$

And $P = \frac{\sigma^*}{\sigma}$ substituting the values of e and $\varepsilon_\circ$,

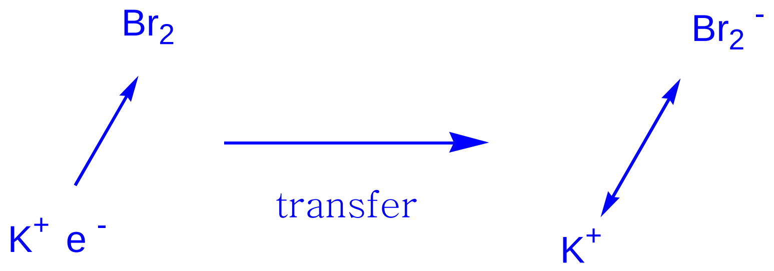
$$R_x = \frac{(1.602\times10^{-19})^2}{4\pi(8.854\times10^{-12})\cdot \Delta E / N_A}$$

$$R_x(in-m) = \frac{2.3066\times10^{-28}\times N_A}{\Delta E(in-J)}$$

$$R_x(in-\overset{\circ}{A}) = \frac{14.4}{\Delta E(in-eV)}$$

Harpoon Mechanism :

e.g $K + Br2 \longrightarrow KBr + Br$



Br_2

K^+ e^-

transfer

Br_2^-

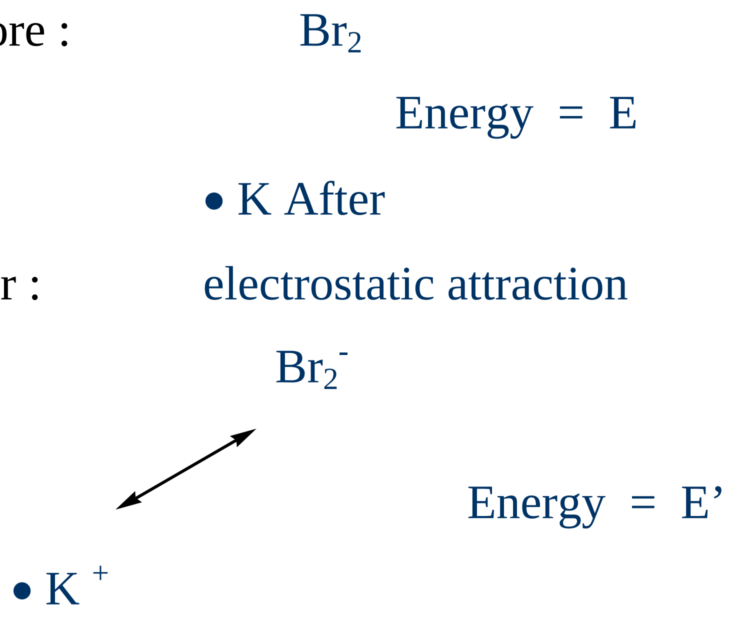
K^+

electron
transfer attraction

now there are electrostatic

The electron is like a harpoon, and the attraction due to coulombic attraction is the line of the harpoon.

The attractive force creates a larger cross-sectional reactive area than predicted by collision theory.



Before : Br_2

Energy = E

• K After

After : electrostatic attraction

Br_2^-

Energy = E’

• K^+

Since energy cannot be created nor destroyed.

Hence,

$$\Delta E' = 0 = I - E_a - \frac{e^2}{4\pi\varepsilon_\circ R_x} = 0$$

or,

$$\Delta E = \frac{e_2}{4\pi\varepsilon_\circ R_x}$$

Harpoon Mechanism Calculation

$\rho = \frac{\sigma *}{\sigma}$ (apparent = $\sigma * / \sigma$ from simple collision theory)

$R^* = R_x$ where d= R (K) + R (Br_2)

$$= \frac{R^{*2}}{d^2} = \left(\frac{e^2}{4\pi\varepsilon_\circ d(I - E_a)} \right)^2$$ (*general formula*)

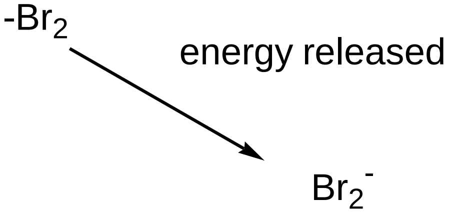
$$\sigma^* = \pi R^{*2}$$

$$P = \frac{\sigma^*}{\sigma} = \frac{R^{*2}}{d^2} = \left(\frac{e^2}{4\pi\varepsilon_\circ d(I - E_a)} \right)^2$$

$$d = R(K) + R(Br_2)$$

$\therefore$ -E_a

because energy has to be put in



= 250kJ mol-1

$\therefore$ -E_a I is +ve because energy has to be put in.

With I = 420 kJ mol^{-1} , Ea = 250kJ mol^{-1}

d= 400pm , P≈12