Chapter 13. Chemical Kinetics

What we will learn:

- The rate of a reaction
- The rate law
- The relation between reactant concentration and time
- Activation energy
- Reaction energy
- Reaction mechanism
- Catalysis

Chemical kinetics:

- *The area of chemistry investigating the speed (rate) of chemical reactions*

Reactants $\longrightarrow$ Products

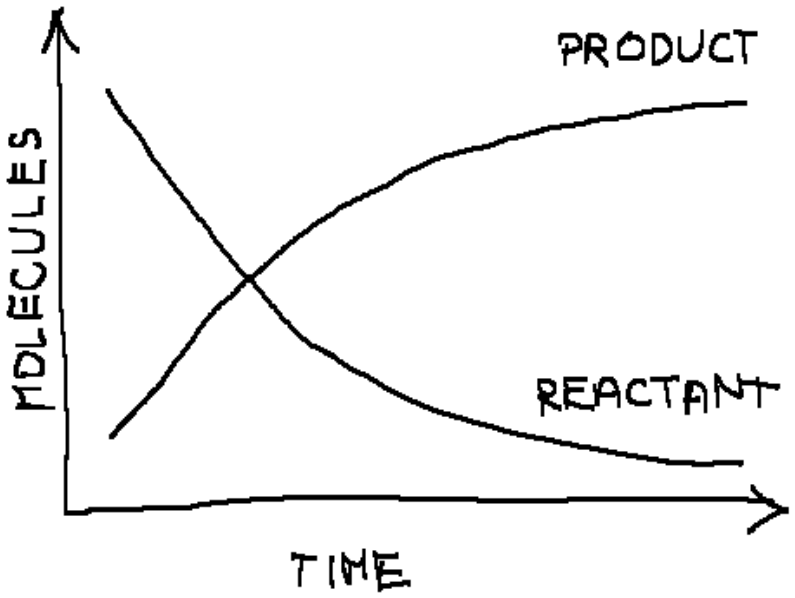
Reaction rate:

The change in the concentration of a reactant or product with time (M/s) M-molarity

During a chemical reaction the concentration of reactants decreases and the concentration of products increases

$$\text{rate} = \frac{\Delta[A]}{\Delta t}$$

$\Delta[A]$	The change in the reactant concentration (molarity)
Δt	The change in time



Reaction between Br_2 and HCOOH:

$$Br_2(aq) + HCOOH(aq) \longrightarrow 2HBr(aq) + CO_2(g)$$

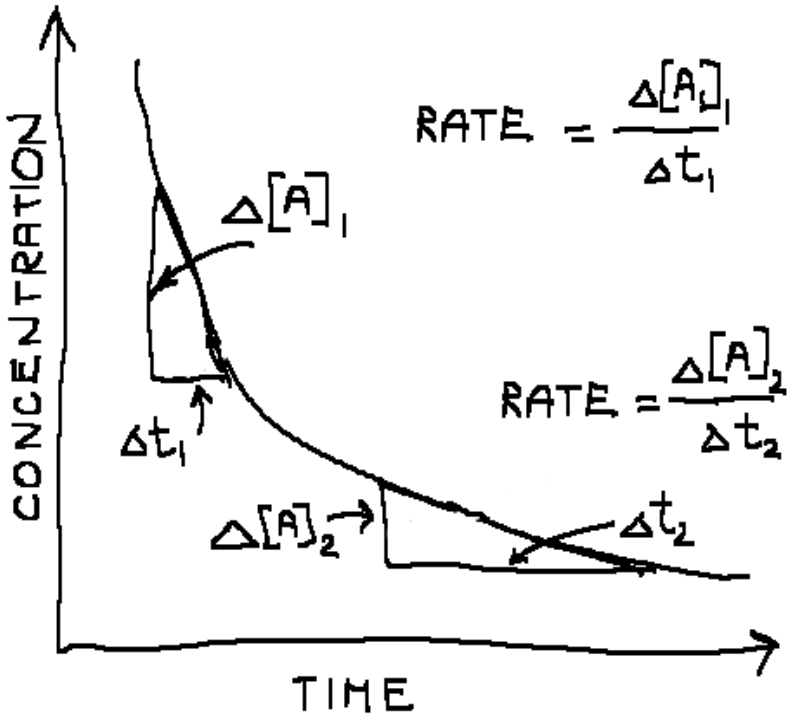
$$\text{average rate} = -\frac{\Delta[Br_2]}{\Delta t}$$

$$= -\frac{[Br_2]_{final} - [Br_2]_{initial}}{t_{final} - t_{initial}}$$

Average rate = the reaction rate averaged at a certain period of time

Instantaneous rate = the reaction rate at a specific instant in time

k_1, k_2 the instantaneous rates



The rate constant:

The rate constant is a constant of proportionality between the reaction rate and the concentration of a reactant

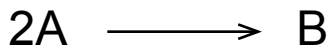
rate = k[A]

k - rate constant

The reaction rate is proportional to the concentration of the reactant. The more reactants, the bigger probability that the reaction occurs

The rate constant “k” is specific for each reaction

Reaction rates and stoichiometry



Two moles of the reactant A disappear, and one mole of the product B is formed at the same time. The reaction rate can be expressed as:

$$rate = -\frac{1}{2}\frac{\Delta[\mathrm{A}]}{\Delta \mathrm{t}}$$

$$rate = \frac{\Delta[\mathrm{B}]}{\Delta \mathrm{t}}$$

General formula

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

$$rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Example

Consider the reaction

$$4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g)$$

At a particular moment of the reaction, O_2 is reacting at the rate 0.024 M/s. At what rate is N_2O_5 forming ?

Data

rate(O_2) = -0.024 M/s (minus sign shows that the concentration of O_2 is decreasing)

Formulas

$$rate = -\frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t}$$

$$-\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t}$$

$$\frac{\Delta[N_2O_5]}{\Delta t} = -2(-0.024\ M/s) = 0.048\ M/s$$

The rate law

The rate law expresses the relationship of the rate of a reaction to the rate constant and the concentration of the reactants

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

The rate law

$$rate = k[A]^x[B]^y$$

where *x* and *y* are numbers taken from **experiment**

Reaction order

The sum of the powers of all reactant concentrations at the reation law

- Rate laws are always determined experimentally
- Reaction order is always defined in terms of reactant concentration
- The order of a reaction is not related to stoichiometric coefficient of the reaction

Example

$$F_2(g) + 2ClO_2(g) \rightarrow 2FClO_2(g)$$

$[F_2]$ (M)	$[ClO_2]$ (M)	Initial Rate (M/s)
0.10	0.010	1.2×10^{-3}
0.10	0.040	4.8×10^{-3}
0.20	0.010	2.4×10^{-3}

Three reaction rate measurments for the $FClO_2$ formation

$$rate = k[F_2]^1[ClO_2]^1$$

The reaction order is 2. The reaction rate constant:

$$k = \frac{rate}{[F_2][ClO_2]}$$

= 1.2 x 10^{-3} / (0.10 M)(0.010 M)

= 1.2 /M s

Reactant concentration and time

First-order reaction

- *A reaction having the rate, which depends on the reaction concentration raised to the first power*

$$A \rightarrow product$$

$$rate = -\frac{\Delta[\mathrm{A}]}{\Delta \mathrm{t}} \qquad k = \frac{rate}{[A]} = \frac{M/s}{M} = 1/s$$

$$rate = k[A]$$

$$-\frac{\Delta[A]}{\Delta t} = k[A]^1$$

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

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

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

$$\int_{[A]0}^{[A]1} \frac{d[A]}{[A]} = -k \int_0^t dt$$

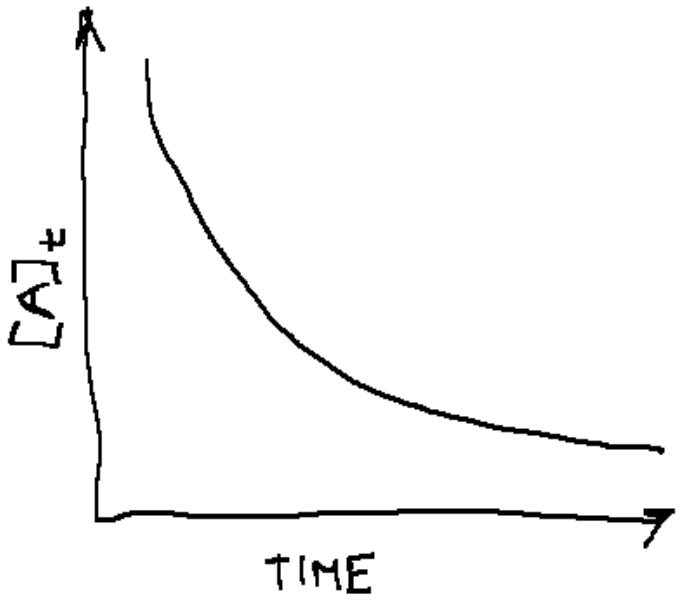
$$\ln[A]_t = -kt + \ln[A]_0$$

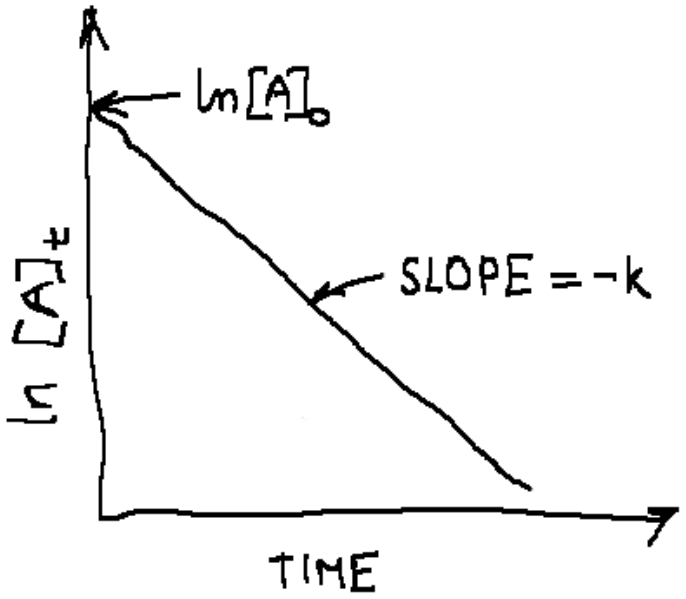
$$-\frac{\Delta[\mathrm{A}]}{\Delta \mathrm{t}} = k[\mathrm{A}]$$

$$\ln \frac{[\mathrm{A}]_\mathrm{t}}{[\mathrm{A}]_0} = -kt$$

$$\ln[\mathrm{A}]_\mathrm{t} = -kt + \ln [A]_0$$

$$y = mx + b$$





Problem

The conversion of cyclopropane to propene is the gas phase is a first order reaction with a rate 6.7 x 10^{-4} s^{-1} at 500 C. The initial concentration of cyclopropane is 0.25 M. What is its concentration after 8.8 min? How it takes that the concentration of cyclopropane decreses to 0.15 M? How long it takes to convert 74 % of the starting material?

Data

k - rate constant = 6.7 x 10^{-4} s^{-1}
$[A]_0$ - initial concentration = 0.25 M
t - time 8.8 min = 528 s

a) Using the equation:

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

$$= -(6.7 \times 10^{-4}\ s^{-1})\ (528\ s) + \ln (0.25)$$

$$= -1.74 \qquad [A]_t = e^{-1.74} = 0.18\ M$$

b) Using the equation:

$$\ln ([A]_t / [A]_0) = -kt$$

$$\ln (0.15\ M / 0.25\ M) = - (6.7 \times 10^{-4}\ s^{-1})\ t$$

$$t = 7.6 \times 10^{2}\ s = 13\ min$$

c) Using the equation:

$$\ln ([A]_t / [A]_0) = -kt$$

$[A]_t$ = ? (26 %)

$[A]_0$ = 0.25 M (100 %)

$$\ln (26 / 100) = - (6.7 \times 10^{-4}\ s^{-1})\ t$$

$$t = 2.0 \times 10^{3}\ s = 33\ min$$

Reaction half-time

- *The time after which the concentration of a reactant decreases to half of its inital concentration*

$$t = \frac{1}{k} ln \frac{[A]_0}{[A]_t}$$

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

$$t_{\frac{1}{2}} = \frac{1}{k} ln2 = \frac{0.693}{k}$$

The half-time of the first order reaction is independent on the initial concentration of a reactant

Example

The decomposition of ethane (C_2H_6) to methyl radicals (CH_3) is a first order reaction with a rate constant 5.36 x 10^{-4} s^{-1} at 700 C

$$C_2H_6(g) \rightarrow 2CH_3(g)$$

Calculate the half-time of the reaction in minutes

Data

k - rate constant = 5.36 x 10^{-4} s^{-1}

Formula

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

Solution

$t_{1/2} = 0.693 / (5.36 \times 10^{-4}\ s^{-1})$

$= 1.29 \times 10^{3}\ s$

$= 21.5\ min$

Second-order reaction

- *A reaction having a rate which depends on the concentration of one reactant raised to the second power of its initial concentration*

$$A \rightarrow product$$

$$rate = -\frac{\Delta[A]}{\Delta t}$$

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

$$-\frac{\Delta[A]}{\Delta t} = k[A]^2$$

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

$$\int_{[A]0}^{[A]1} \frac{d[A]}{[A]^2} = -k\int_0^t dt$$

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

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

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

Second-order reaction

- *A reaction having a rate which depends on the concentration of two different reactants raised to the first power of their initial concentrations*

$$A + B \rightarrow product$$

$$rate \rightarrow k[A][B]$$

Problem

The reaction

$$I(g) + I(g) \rightarrow I_2(g)$$

follows the second-order kinetcs, and has the rate constant 7.0 x 10^9 / M s at 23 C. Calculate the half-time of the reaction if the initial concentration of I is 0.60 M.

Data

k - rate constant = 7.0 x 10^9 / Ms

$[A]_0$ - initial concentration = 0.60 M

Formula

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

Solution

$t = 1 / (7.0 \times 10^{9}\ /Ms)(0.60\ M)$

$= 2.4 \times 10^{-10}\ s$

Zero-order reactions

- *Reaction having the reaction rate which is independent on the concentration of the reactant*

$$A \rightarrow product$$

Zero order reactions are rare. First and second order reactions are common; third order reactions are very complex

$$rate = k[A]^0$$

$$rate = k$$

$$-\frac{\Delta[A]}{\Delta t} = k[A]^0$$

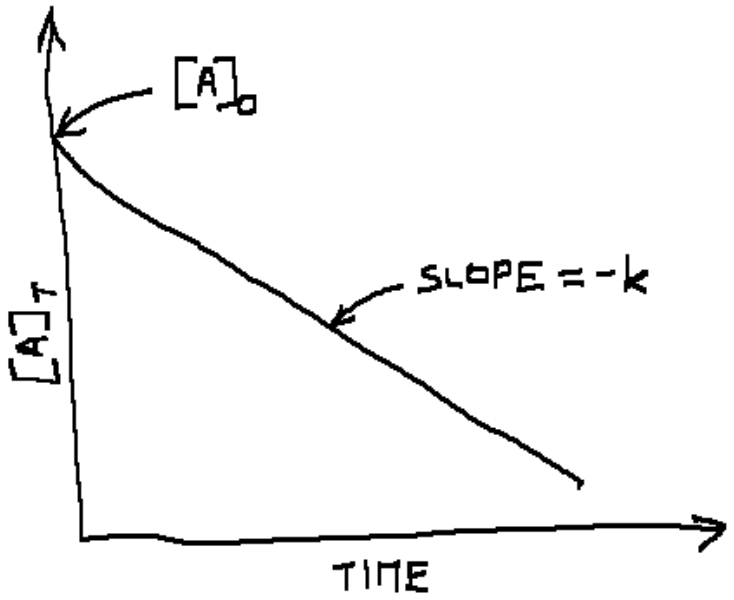
$$-\frac{d[A]}{dt} = k[A]^0$$

$$\int_{[A]0}^{[A]t} d[A] = -k\int_0^t dt$$

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

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

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



Problem

The reaction A ⇆ B is zero order in A with a rate constant of 2.8 x 10^{-2} s^{-1} at 80 C. How long (in seconds) will it take for A to decrease from 0.88 M to 0.14 M ?

Data

k - rate constant = 2.8 x 10^{-2} s^{-1}
$[A]_0$ - initial concentration = 0.88 M
$[A]_1$ - final concentration = 0.14 M

Formula

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

Solution

$$t = \frac{[A]_0 - [A]_t}{k}$$

t = (0.88 M - 0.14 M)/ 2.8 x 10^{-2} s^{-1}

Summary of the reaction

	Zero order	**First order**	**Second order**
Rate law	Rate = k	Rate = k[A]	rate = $k[A]^2$
Integrated rate law	$[A]_t = -kt + [A]_0$	$\ln[A]_t = -kt + \ln[A]_0$	$1/[A]_t = kt + 1/[A]_0$
plot = straight line	$[A]_t$ vs. t	$\ln[A]_t$ vs. t	$1/[A]_t$ vs. t
slope	slope = -k	slope = -k	slope = k
half-life	$t_{½} = [A]_0/2k$	$t_{½} = 0.693/k$	$t_{½} = 1/ k[A]_0$

Activation Energy
Temperature Dependence of Rate Constants

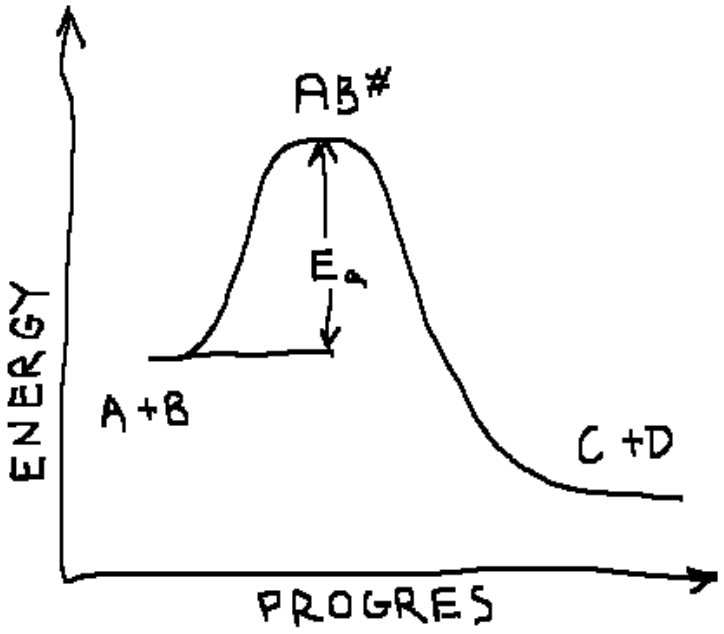
Rates of reactions are faster at higher temperatures, e.g. baking, refrigeration

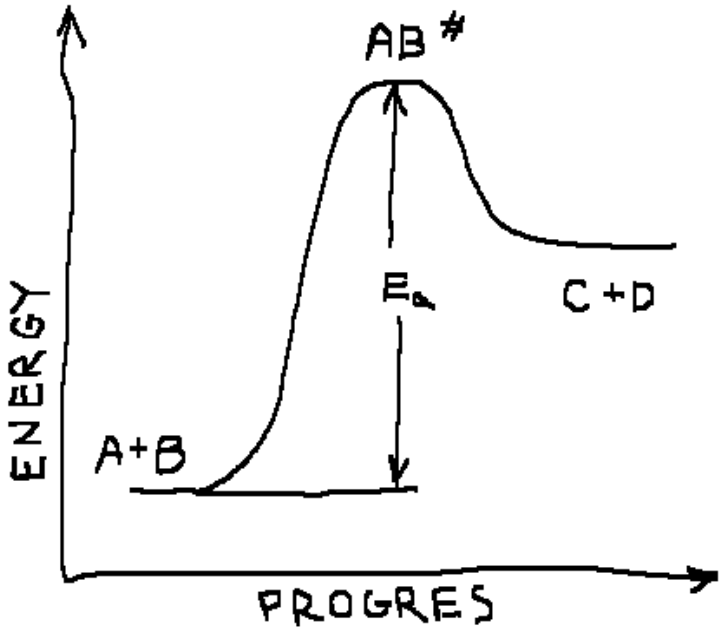
The Collision Theory of Chemical Kinetics

- Rate of a reaction depends on the frequency of effective collisions between the reactant molecules
- To be “effective” collisions must occur with proper orientation and sufficient energy (there is a minimum energy below which no reaction occurs)
- Activation Energy (E_a) - minimum energy required to initiate a reaction
- Activated complex (transition state) - temporary species formed by the reactant molecules when they collide, but before they form products

- E_a energy difference between reactants and the “activated complex” or “transition state”

- E_a may consider this the barrier that keeps molecules without enough energy from reacting. To increase the number of molecules with enough kinetic energy to get over the barrier, the temperature can be raised, making them move faster, i.e., possess more kinetic energy





The Arrhenius Equation

- Measuring the Activation Energy

- Relationship between temperature and rate constant

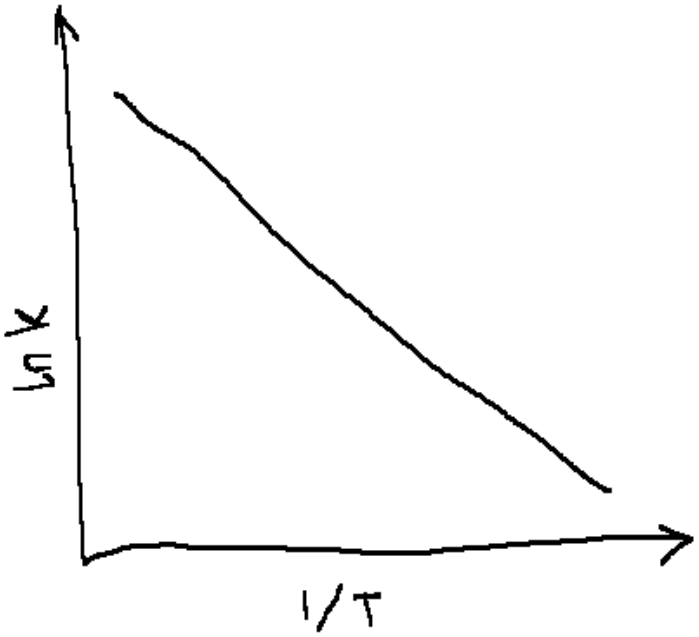
$$k = A\, e^{-Ea / RT}$$

k - rate constant
e - base of the natural logarithm
E_a - activation energy in kJ/mole
R - gas law constant = 8.314 J/K.mole
T - temperature (Kelvin scale)
A - frequency factor (a constant which is proportional to an average number of collisions between reacting molecules, which specifically depends on each molecular system)

Logarithmic form
(equation for straight line)

$$\ln k = \ln A - E_a / RT$$

plot of ln k vs. 1 / T is a straight line with slope = - E_a / R



Useful formulas

$$lnk_1 = lnA - \frac{E_a}{RT_1}$$

$$lnk_2 = lnA - \frac{E_a}{RT_2}$$

$$ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Problem

The reaction

$$2\,NO_2 \rightarrow 2\,NO + O_2$$

has an activation energy of 111 kJ/mole. At 400 C, k = 7.8 L $mole^{-1}s^{-1}$. What is the value of k at 430 C?

Data

k_1 (at 400 C) = 7.8 L $mole^{-1}s^{-1}$
T_1 = 400 + 273 = 673 K
T_2 = 430 + 273 = 703 K
R = 8.314 J/mole K
E_a = 111 kJ/mole = 1.11 x 10^5 J/mole

$$\ln (k_1 / k_2) = (E_a / R)\,(1/T_2 - 1/T_1)$$

$$\ln (7.8\ L\ mol^{-1}s^{-1} / k_2) = (1.11 \times 10^5\ J\ mol^{-1}) / (8.314\ J\ mol^{-1}\ K^{-1})$$

$$. (1 / 703K - 1 / 673K)$$

$$\ln (7.8 / k_2) = (111000 / 8.314) (0.00142 - 0.00148)$$

$$\ln(7.8 / k_2) = -0.80105$$

$$7.8 / k_2 = e^{-0.80105}$$

$$k_2 = 7.8 \times e^{+0.80105} \qquad (e = 2.71828)$$

$$k_2 = (7.8) (2.2278)$$

$$k_2 = 17.377\ L\ mol^{-1}s^{-1}$$

Reaction Mechanisms

Some reactions are a sequence of elementary steps (reactions), and not just a simple reaction from reactants to products. Therefore we propose a reaction mechanism

- Reaction mechanism - a proposed sequence of steps, called elementary processes (individual reactions) by which the reactants are converted into products

- Elementary step (reaction) - a simple reaction being a part of the overall reaction (molecular level)

- Rate-Determining step (reaction) - a slow reaction in the reaction mechanism; determines the overall rate law

Example

Consider the reaction

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

Experiment detects N_2O_2 during the reactions, so this reaction is not simply an NO molecule colliding with an O_2 molecule

Relationship between mechanism and kinetics:

Step 1: $NO + NO \rightarrow N_2O_2$ elementary step

Step 2: $N_2O_2 + O_2 \rightarrow 2\ NO_2$ elementary step

Overal reaction: $2\ NO + N_2O_2 + O_2 \rightarrow N_2O_2 + 2\ NO_2$ overall reaction

N_2O_2 is an intermediate - appears in the steps but not in the overall reaction

Molecularity of reaction

Number of molecules reacting in an elementary step

- **bimolecular** - two molecules
- **unimolecular** - one molecule
- **termolecular** - very rare (more than 2 molecules)

Rate Laws and Elementary Steps

For two-step reactions as shown

Measure rate of reaction → formulate rate law → postulate mechanism

Knowing elementary steps deduce rate law

- A → products unimolecular elementary *rate* = $k[A]$
- A + B → products bimolecular elementary step *rate* = $k[A][B]$
- 2 A → products bimolecular elementary step *rate* = $k[A]^2$

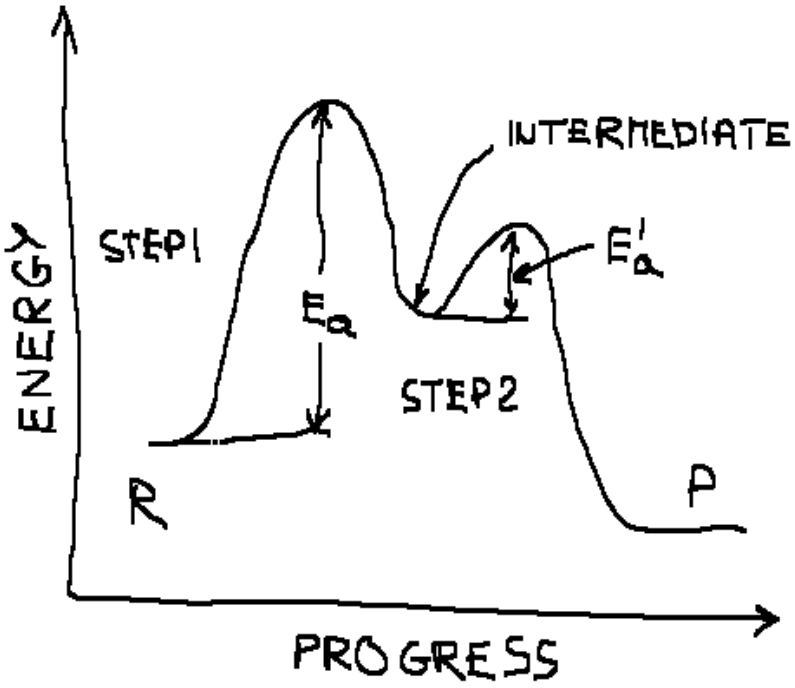
Major points

1. The sum of the elementary steps must give the overall balanced equation for the reaction

2. The rate-determining step should predict the rate law as determined by experiment

3. If the experimentally determined (actual) rate law and the predicted rate laws are the same, then the proposed mechanism is possible

4. For an elementary process, the exponents in the rate expression are equal to the coefficients in the balanced equation for that individual process


ENERGY
STEP1
INTERMEDIATE
E_a
E_a'
STEP2
R
P
PROGRESS

Problem

The gas-phase decomposition of nitrous oxide (N_2O) occurs via two elementary steps:

Step 1: $N_2O \rightarrow N_2 + O$

Step 2: $N_2O + O \rightarrow N_2 + O_2$

The rate law (experimentally) is rate = k[N_2O]. Write the overal reaction. Identify intermediates.

$$N_2O \rightarrow N_2 + O$$

$$N_2O + O \rightarrow N_2 + O_2$$

$$2\,N_2O + O \rightarrow 2N_2 + O_2 + O$$

Because O is produced in the first elementary step and it does not appear in the overall balanced equation, it is an intermediate.

If we assume that step 1 is the rate-determining step, then the rate of the overal reaction is given by

$$\text{rate} = k_1[N_2O]$$

and $k = k_1$, which is confirmed by the experimental rate

If we assume that step 2 is the rate-determining step, then the rate of the overal reaction is given by

$$\text{rate} = k_2[N_2O][O]$$

which is not confirmed by the experimental rate

Problem

For the overall reaction

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

The following mechanism is proposed

Slow: $NO_2 + NO_2 \rightarrow NO + NO_3$

Fast: $NO_3 + CO \rightarrow NO_2 + CO_2$

Net: $NO_3 + NO_2 + CO \rightarrow NO + CO_2 + NO_3$

The slow step, predicts: $rate = k\,[NO_2]^2$

The actual experimental rate law: $rate = k\,[NO_2]^2$

This is a possible mechanism !

What about an alternate, one-step mechanism?

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

This would predict: $rate = k\,[NO_2]\,[CO]$

which is not observed experimentally

This is not a possible mechanism !

Problem

The rate law for the reaction is given by *rate* = $k[NO][Cl_2]$

$$2\ NO(g) + Cl_2\ (g) \rightarrow 2\ NOCl\ (g)$$

A mechanism involving the following steps has been proposed for the reaction

Step1 $NO + Cl_2 \rightarrow NOCl_2$

Step2 $NOCl_2 + NO \rightarrow 2\ NOCl$

If this mechanism is correct, what does it imply about the relative rates of these two steps?

Step1 $NO + Cl_2 \rightarrow NOCl_2$

Step2 $NOCl_2 + NO \rightarrow 2\ NOCl$

Overall $NO + Cl_2 + NOCl_2 + NO \rightarrow NOCl_2 + 2\ NOCl$

$$2\ NO + Cl_2 \rightarrow 2\ NOCl$$

The rate of the first step is $rate = k[NO][Cl_2]$

The rate of the second step is $rate = k[NO][NOCl_2]$

Experimentally $rate = k[NO][Cl_2]$

Ther step 1 is slow, and it is determining the rate of the overall reaction

Example

Decomposition of hydrogen peroxide (faciliated by iodide ions)

$$2\,H_2O_2\,(aq) \rightarrow 2H_2O\,(l) + O_2(g)$$

Experimentally

$$rate = k\,[H_2O_2]\,[I^-]$$

The reaction is first order with respect to both H_2O_2 and I^- , therefore decomposition of H_2O_2 does not occur in a single elementary step.

Proposed mechanism:

Step 1: $H_2O_2 + I^- \rightarrow H_2O + IO^-$

Step 2: $H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-$

Overall: $2\,H_2O_2 \rightarrow 2\,H_2O + O_2$

If we assume that the step 1 is the rate-determining step then

$$rate = k_1 [H_2O_2] [I^-]$$

which agrees with the experment.

Note: IO^- ion is an intermediate because it does not appear in the overall balanced equation, the I^- ion also does not appear in the overall equation, however the presence of the I^- ion is required to speed up the reaction.

A compound which speeds up a reaction is called a **catalyst**

Catalysis

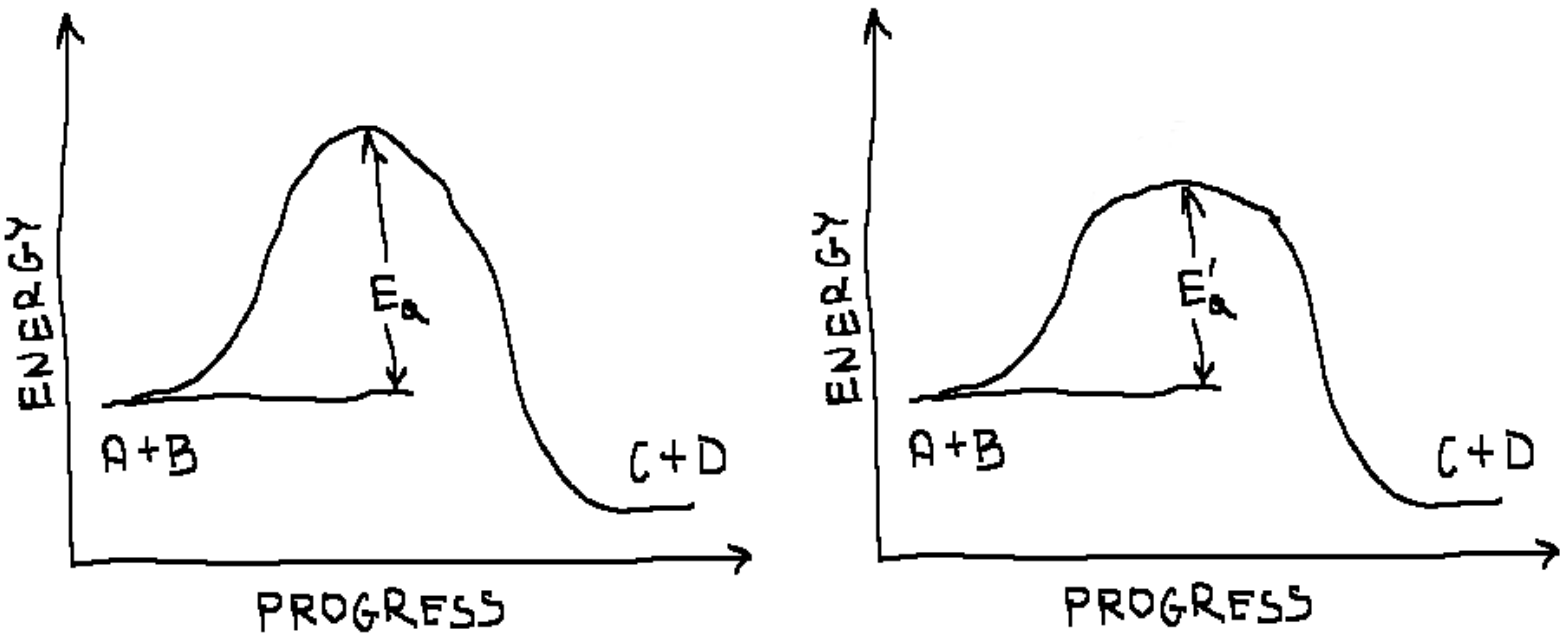
A catalyst is a substance that increases the rate of a reaction without itself being consumed.

Mode of action:

- Catalyst alters the reaction mechanism by providing a lower energy (smaller E_a) pathway for the reaction.

Two types:

- **Homogeneous** (in same phase as reactants)
- **Heterogeneous** (different phase)



A catalyst assists reaction by either

- activating (weaken) one or more bonds in the reactants and/or
- helping to properly orient the reacting molecules (especially on surface of heterogeneous catalysts)

Examples

Catalytic converters in automobiles (2 heterogeneous stages)

- oxidizes CO and unburned hydrocarbons

- converts NO (formed from $N_2 + O_2 \rightarrow 2\ NO$ which occurs in hot engines under pressure) to N_2 and O_2

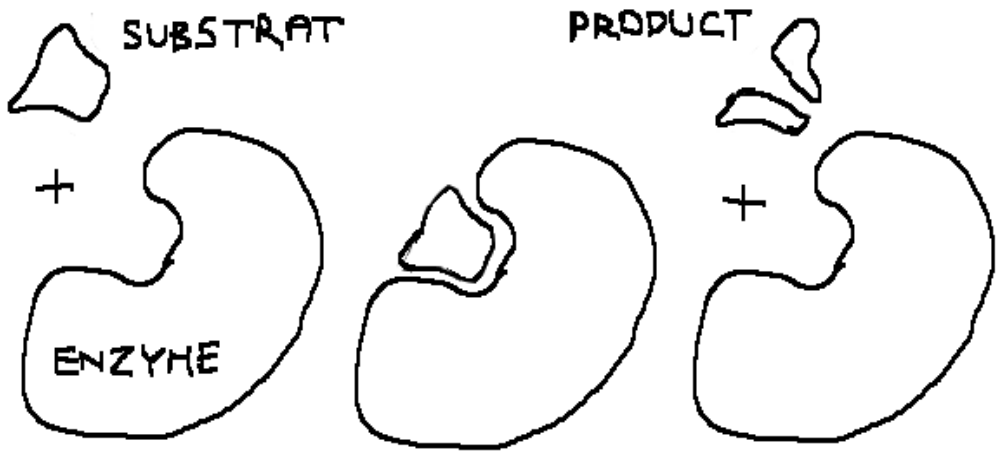
Enzymes (homogeneous) – biological catalysts

- increases rates by millions of times
- very specific
- average cell may have 3000 enzymes
- large proteins with active sites that bind only certain molecules

Enzyme catalyzed reaction for two-step mechanism

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES$$

$$ES \overset{k_2}{\rightarrow} E + P$$


SUBSTRAT
PRODUCT
ENZYME

Problem

Consider the following reaction

$$E + S \underset{k_{-1}}{\overset{k_1}{\leftrightarrows}} ES \qquad \text{(fast reactions, forward and reverse)}$$

$$ES \xrightarrow{k_2} E + P \qquad \text{(slow reaction)}$$

Derive an expression for the rate law of the reaction in terms of the concentration E and S. Assume that the rate of the forward reaction forming ES is equal to the rate of the reverse reaction

The rate law for the second step is

$$rate = k_2[ES]$$

The equilibrium relation is

$$rate_{(forward)} = k_1 [E] [S]$$

$$rate_{(reverse)} = k_{-1} [ES]$$

$$rate_{(forward)} = rate_{(reverse)}$$

$$k_1 [E] [S] = k_{-1} [ES]$$

$$[ES] / [E] [S] = k_1 / k_{-1}$$

$$[ES] = k_1 / k_{-1} [E] [S]$$

$$rate = k_2 k_1 / k_{-1} [E] [S]$$