

CHEMICAL KINETICS/RATE OF CHEMICAL REACTION

- ▶ Branch of physical chemistry that deals with rate of reaction
- ▶ Also known as reaction kinetics
- ▶ Deals with the study of the speeds of reactions and the nanoscale pathways or rearrangement by which atoms and molecules are transformed from reactants to products
- ▶ Includes:
 - ▶ Rate of reaction
 - ▶ Mechanism/sequence of steps by which a reaction occurs
 - ▶ Factors influencing the rate of reaction
- ▶ The rate or speed of reaction is the change in concentration of a reactant or product per unit time (the time can be seconds, minutes, hours, days etc)



where Δ = change, t = time, A = reactant, B = product

▶ DIFFERENT TYPES OF RATE

- ▶ **Average rate:** It is rate over a period of time

$$R = \frac{\Delta \text{Concentration}}{\Delta \text{time}} = - \frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

- ▶ **Instantaneous rate:** this is the slope of a line tangent to the curve of concentration versus time at a particular point of given time

- ▶ **Initial rate:** It is the rate of reaction between time zero (that is initial time when $t = 0$) and a given time. It is given as $R = \frac{\text{Conc at given time} - \text{Conc at time zero}}{\text{Given time}}$

CLASSWORK

Considering a reaction $\text{CO}_{(g)} + \text{NO}_{2(g)} \longrightarrow \text{CO}_{2(g)} + \text{NO}_{(g)}$ with the following data

[CO] mol/dm ³	0.100	0.067	0.050	0.040	0.033
Time (S)	0	10	20	30	40

Calculate the initial rate after (i) 10S (ii) 20S (iii) 30S and the average rate between (i) 10S and 20S (ii) 20S and 40S.

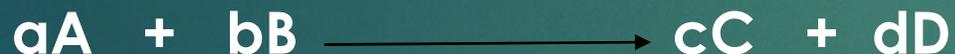
FACTORS AFFECTING RATE OF CHEMICAL REACTIONS

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- ▶ Concentration
- ▶ Physical State/ Surface Area
- ▶ Temperature
- ▶ Catalyst/Enzymes
- ▶ Pressure
- ▶ Visible Light/ Radiation

REACTION RATES, ORDER OF REACTION AND MOLECULARITY CONCEPT

Consider a reaction:



- ▶ Rate of reaction can be given in terms of decrease in the amount of reactant that occur in some interval of time $R = -1/a \frac{d[A]}{dt} = -1/b \frac{d[B]}{dt}$
- ▶ Rate of reaction can be given in terms of increase in the amount of product that occur in some interval of time $R = 1/c \frac{d[C]}{dt} = 1/d \frac{d[D]}{dt}$
- ▶ Rate can be expressed in terms of reactant concentrations as $R = k [A]^x [B]^y$
- ▶ The above reaction helps in defining order of reaction. The reaction is x order wrt A and y order wrt B. Thus the reaction has an overall order of (x + y)

ORDER OF REACTION

- ▶ This is the sum of the power of concentration terms in the differential rate equation
- ▶ $R = k [A]^m [B]^n$ Order of reaction is $m + n$
 - when order of reaction is 0 (zero), it is zero order
 - when order of reaction is 1 (one), it is first order
 - when order of reaction is 2 (two), it is second order
 - when order of reaction is 3 (three), it is third order
- ▶ $R = k$ or $R = k[A]^0$ or $R = k [B]^0$ zero order reaction wrt A or B; Rate is independent of concentration
- ▶ $R = k [A]$ first order reaction wrt [A]
- ▶ $R = k [A][B]$ second order reaction wrt [A] and [B]
- ▶ $R = k[A][B]^2$ third order reaction wrt [A] and [B]²

DETERMINATION OF ORDER OF REACTION

There are four common methods for determining the order of a reaction

- (a) Integration method (b) Half life method © Differential method
(d) Isolation method

▶ CLASSWORK:

The initial rate of decomposition of ethanal $\text{CH}_3\text{CHO}_{(g)} \longrightarrow \text{CH}_4(g) + \text{CO}_2(g)$ was measured at a series of different concentration with the following results

$[\text{CH}_3\text{CHO}]$ (mol/dm ³)	0.10	0.20	0.30	0.40
Rate (mol/dm ³ S)	0.020	0.081	0.182	0.318

Using this data to (i) determine the order of reaction with respect to ethanal (ii) determine the rate constant for the reaction (iii) determine the rate of reaction at a concentration of ethanal of 0.15 mol/dm³

MOLECULARITY OF A REACTION

▶ This is the number of reactant molecules involved in a reaction or number of molecules (atoms or ions) which react together in the rate determining step (slow step) of the reaction

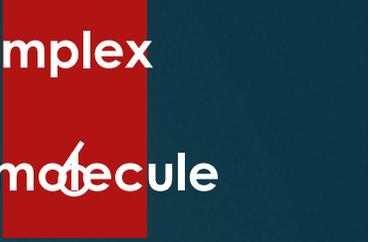
▶ Consider the equation $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{I}^- \longrightarrow 2\text{H}_2\text{O} + \text{I}_2$

▶ The possible mechanisms are as follows:

(i) $\text{H}_2\text{O}_2 + 2\text{I}^- \longrightarrow \text{H}_2\text{O} + \text{OI}^-$ (Slow) This is rate determining step (bimolecular)

(ii) $\text{OI}^- + \text{H}^+ \longrightarrow \text{HOI}$ (Fast) bimolecular

(iii) $\text{HOI} + \text{H}^+ + \text{I}^- \longrightarrow \text{H}_2\text{O} + \text{I}_2$ (Fast) trimolecular

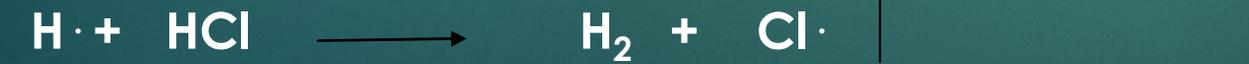


- ▶ Molecularity is applied only to elementary reactions or elementary stages of more complex reactions
- ▶ Elementary reaction is unimolecular if the activated complex is formed from a single molecule
- ▶ It is bimolecular if it is formed from two molecules
- ▶ Elementary reaction may have molecularity 1, 2 and 3
- ▶ Molecularity is obtained from proposal of reaction mechanism and not from experimental work as in the case of order of reaction
- ▶ Summation of elementary steps gives the overall reaction

SIMPLE REACTION MECHANISM

- ▶ Reaction mechanism is the pathway or elementary process/step in a reaction from reactant(s) to product(s)

▶ In a reaction $H_2 + Cl_2 \longrightarrow 2HCl$ has the following elementary process or pathway



- ▶ These elementary processes/steps in a reaction when taken together are known as the mechanism of the reaction.
- ▶ SEE PAGES 10 AND 11 OF THE NOTE FOR DETAILS OF REACTION PROFILE AND MECHANISM

INTEGRATED RATE LAWS/EQUATIONS

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- ▶ This is an expression which shows how the reaction rate is related to concentration
- ▶ It is an approach to experimental determination of the rate law and rate constant for a reaction using calculus
- ▶ Rate equations/laws express the rate as a function of reactant concentrations, product concentration and temperature
- ▶ Consider a reaction $aA + bB \longrightarrow cC + dD$
- ▶ Rate of reaction can be given in terms of decrease in the amount of reactant that occur in some interval of time $R = -1/a \frac{d[A]}{dt} = -1/b \frac{d[B]}{dt}$
- ▶ Rate of reaction can be given in terms of increase in the amount of product that occur in some interval of time $R = 1/c \frac{d[C]}{dt} = 1/d \frac{d[D]}{dt}$
- ▶ Rate can be expressed in terms of reactant concentrations as $R \propto [A]^x[B]^y = k [A]^x[B]^y$
- ▶ The proportionality constant k is called the rate constant and it is specific at a given temperature
- ▶ The exponents x and y are called reaction orders and define how the rate is affected by reactant concentration

CLASSWORK

An experiment is conducted on the rate of decomposition of dinitrogenpentaoxide



The following data are found

[N ₂ O ₅] mol/L	2.4×10^{-3}	7.20×10^{-3}	1.44×10^{-3}
Rate of reaction mol/L S	4.02×10^{-5}	1.21×10^{-4}	2.41×10^{-4}

Calculate the complete rate law of the reaction

ZERO ORDER REACTION

- ▶ This is a reaction whose rate is independent of concentration (i.e. initial concentration)
- ▶ A product
- ▶ Rate equation in differential form is $R = -d[A]/dt = k[A]^0 = k$
- ▶ Rate equation in integrated form is $[A] = [A]_0 - kt$ (plot the graph of [A] vs t)
- ▶ Its half life $t_{1/2} = [A]_0 / 2K$

► FIRST ORDER REACTION

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A reaction of first order can be represented by



$$R = -d[A]/dt = k [A]^1$$

Using calculus, the above expression can be transformed to the integrated first order rate law as follows:

$$-d[A]/dt = k [A]^1$$

$$-d[A]/[A]^1 = k dt$$

If at time $t=0$, $A = [A]_0$ and at time $t=t$, $A = [A]$; then integrate between $t = 0$ and $t=t$

$$\ln [A]/[A]_0 = -kt \quad \text{or} \quad [A]/[A]_0 = e^{-kt} \equiv \ln[A] - \ln [A]_0 = -kt$$

$$\ln [A]_0/[A] = kt \quad \text{or} \quad [A]_0/[A] = e^{kt} \quad \equiv \ln[A]_0 - \ln [A] = kt$$

Since $\ln [A] = 2.303 \log[A]$ therefore $\log[A] = \log [A]_0 - kt/2.303$ (plot a graph of $\log[A]$ vs t and interpret the graph by comparing it with straight line equation)

Note: any of the above equations can be graphically used to illustrate first order reaction

FIRST ORDER REACTION IN TERMS OF HALF LIFE

- Half life is the time required for concentration or amount of a reactant to decompose or decrease to half of its original value i.e. $t=t_{1/2}$, $[A] = [A]_0/2 \longrightarrow [A]/[A]_0 = 1/2$
- Recall $\ln [A]/[A]_0 = -kt_{1/2}$
- $\ln 1/2 = -kt_{1/2} \longrightarrow t_{1/2} = 0.693/k$ (note that $\ln 1/2 = -0.693$)
- Half life of a first order reaction is highly independent on the initial concentration

- ▶ The reaction $A \longrightarrow B + C$ is a first order in $[A]$ and has a half life of 30min. Calculate the specific rate constant if $[A]$ is initially 0.10mol/L. What will be its value after (a) 1.0 hour and (b) 24.0 hour?

SECOND ORDER RATE LAW

- ▶ Considering the reaction: $A + A \longrightarrow \text{product}$ or $aA \longrightarrow \text{product}$
If rate is proportional to the concentration of 2A, then



$$\text{Rate} = -1/a \, d[A]/dt = k[A]^2$$

$$d[A]/dt = -ak[A]^2$$

$$d[A]/[A]^2 = -akdt$$

If at time $t=0$, $A = [A]_0$ and at time $t=t$, $A = [A]_t$; then integrate between $t = 0$ and $t=t$

$$\left(-1/[A]\right) \text{ from limits } [A]_0 \longrightarrow [A]_t = -akt$$

$$-1/[A]_t + 1/[A]_0 = -akt$$

$$1/[A]_t = 1/[A]_0 + akt \quad \text{where } a \text{ is the coefficient of reactant in the balanced overall equation}$$

Plot a graph of $1/[A]$ vs t and interpret the graphical representation

▶ SECOND ORDER REACTION IN TERMS OF HALF LIFE

▶ Recall the second order rate equation $1/[A]_t = 1/[A]_0 + akt$

At half life $t_{1/2}$, $[A]_{t_{1/2}} = [A]_0/2$

$$2/[A]_0 = 1/[A]_0 + akt_{1/2}$$

$$1/[A]_0 = akt_{1/2}$$

$$t_{1/2} = 1/ak[A]_0 \quad \text{Where } a \text{ is coefficient of reactant A in the balanced overall equation}$$

CLASSWORK:

Compounds A and B react to form C and D in a reaction that was found to be second order overall and second order in A. The rate constant at 30°C is 0.622 litre per mole per minute. What is the half life of A when 4.10×10^{-2} M of A is mixed with excess B?

Solution:



As long as some B is present, only the concentration of A affects the rate because the reaction is second order in [A] and second order overall.

$$k = 0.622 \text{ L/mole minute}, [A]_0 = 4.10 \times 10^{-2} \text{ M}, a = 1$$

$$t_{1/2} = 1/ak[A]_0 = 1/1 \times 0.622 \times 4.10 \times 10^{-2} = 39.2 \text{ minutes.}$$

ACTIVATION ENERGY

- ▶ It is the minimum energy required for a reaction to take place
- ▶ It is being altered by applying temperature and catalyst to a chemical reaction
- ▶ The effect of temperature and catalyst either decrease or increase the activation energy of a reaction and thus affect the rate of such chemical reaction.
- ▶ Almost every reaction goes faster when the temperature is raised
- ▶ The rate of reaction is speeded up according to Arrhenius equation when catalyst is used and thereby lowers the activation energy.

ARRHENIUS EQUATION

$$K = A e^{-E_a/RT}$$

Where k = Rate constant, A = Proportionality constant, E_a = Activation Energy, T = Temperature, R = Gas constant

Suppose a value of the rate constant of k_1 at temperature T_1 and k_2 at temperature T_2 then Arrhenius equation can be written thus:

$$K_1 = A e^{-E_a/RT_1} \quad \text{and} \quad K_2 = A e^{-E_a/RT_2}$$

$$\ln K_1 = \ln A - E_a/RT_1 \quad \text{and} \quad \ln K_2 = \ln A - E_a/RT_2$$

$$\log k_1 = \log A - E_a/2.303RT_1 \quad \text{and} \quad \log k_2 = \log A - E_a/2.303RT_2 \quad \text{Subtracting the two equations}$$

$$\log k_2 - \log k_1 = (-E_a/2.303RT_2) - (-E_a/2.303RT_1)$$

$$\log k_2/k_1 = E_a/2.303R (1/T_1 - 1/T_2) = \log \text{Rate}_2/\text{Rate}_1$$

APPLICATIONS OF ARRHENIUS EQUATION TO ILLUSTRATE THE EFFECTS OF TEMPERATURE AND CATALYST

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- (i) The following data are found for a reaction as the temperature is changed, concentration being kept constant

Temperature	20°C	30°C
Rate	1.5mol/LS	2.4mol/LS

Calculate the activation energy, what will the rate at 50°C, other things being kept the same?

- (ii) A catalyst lowers the activation energy for a certain reaction from 75 to 20KJ/mol. What will be the effect on the rate of the reaction at 20°C other things being equal?