Chemical kinetics:

The branch of chemistry which deals with the study of speeds of the rates of a chemical reaction, the factors affecting the rates of the reactions and the mechanism by which the reactions proceed is known as chemical kinetics.

Rate of a Chemical Rkn:-

Rate of reaction is the change in the concentration of any one of the reactants or products per unit time.

To be more specific -

(i) the rate of decrease in concentration of any one of the prod reactants.

ii) the rate of increase in concentration of anyone of the products.

Consider a hypothetical reaction, assuming that the volm of the ~~sys~~ system remains constant.

$$R \rightarrow P$$

One mole of reactant R produces one mole of product P. If $[R]_1$ and $[P]_1$ are the concentrations of R and P respectively at time t_1 and $[R]_2$ and $[P]_2$ are their concentrations at time t_2, then,

$$\Delta t = t_2 - t_1$$

$$\Delta[R] = [R]_2 - [R]_1$$

$$\Delta[P] = [P]_2 - [P]_1.$$

The square bracket means molar concentration.

Rate of disappearance of R -

$$= \frac{\text{Decrease in concentration of } R}{\text{Time taken}} = \frac{-\Delta[R]}{\Delta t}$$

Rate of appearance of P :-

$$= \frac{\text{Increase in concentration of } P}{\text{Time taken}} = \frac{+\Delta[P]}{\Delta t}$$

Since, $\Delta[R]$ is a negative quantity (as concn of reactants is decreasing), it is multiplied with -1 to make the rate of the reaction a positive quantity.

Average rate depends upon the change in concentration of reactants or products and the time taken for that change to occur.

For eg, Consider the reaction:

$$PCl_5 \rightarrow PCl_3 + Cl_2$$

Rate of reaction $= -\frac{\Delta[PCl_5]}{\Delta t} = +\frac{\Delta[PCl_3]}{\Delta t} = +\frac{\Delta[Cl_2]}{\Delta t}$

Average rate

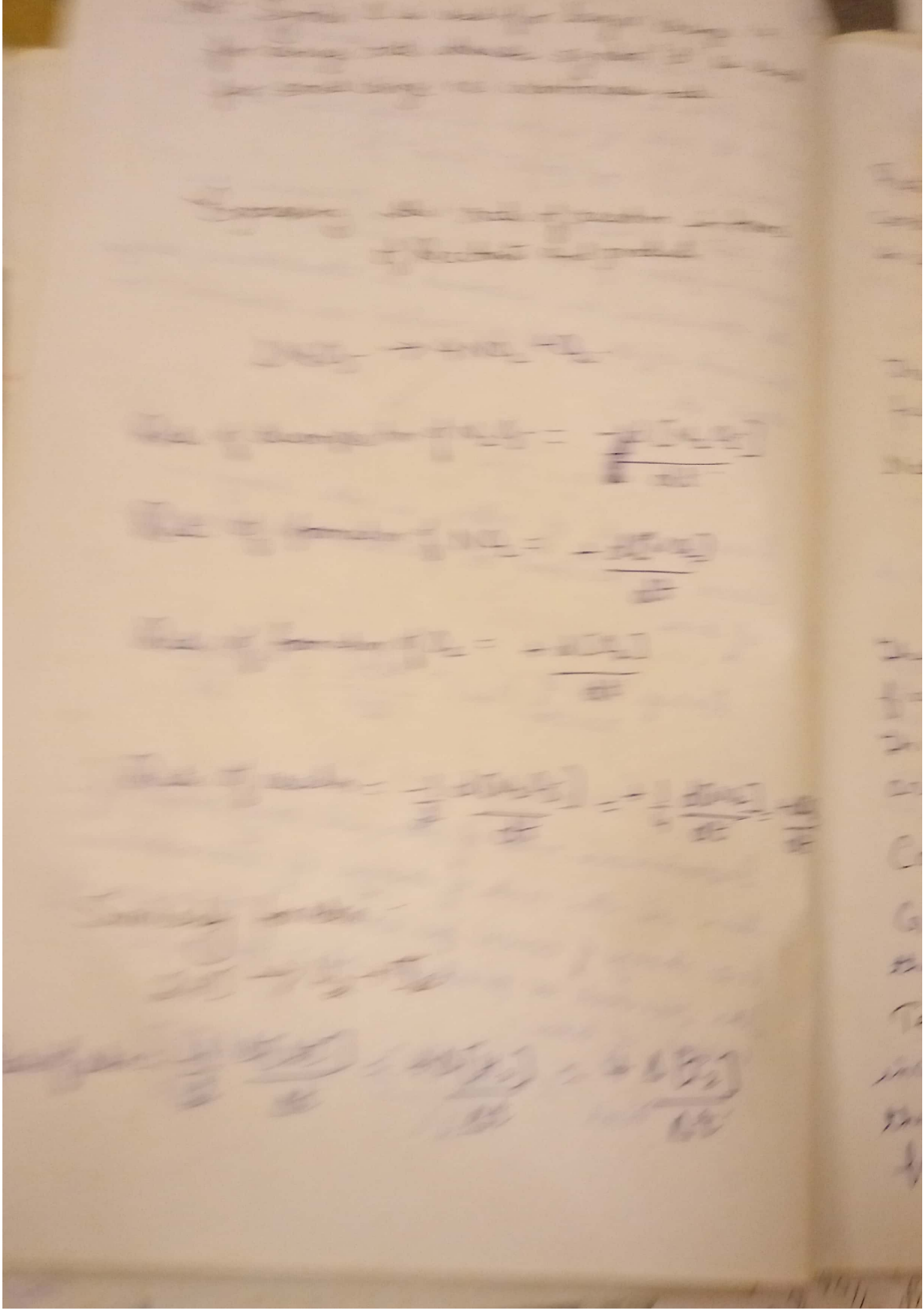
Average rate of ... in the ... of concn of reactant or product ... of time

Average rate of reaction $(r_{av}) = \frac{-\Delta[R]}{\Delta t} = \frac{-\Delta[P]}{\Delta t}$

Instantaneous Rate

Instantaneous rate of ... at any ... time is the rate of ... (i.e change of concn per unit ... of ... the reactants or products at a particular instant of time

Rate $= \frac{d[R]}{dt}$



Factors Influencing the Rate of Reaction:-

Rate of reaction depends upon experimental conditions such as concentration of reactants (pressure in case of gases), temp and catalyst.

Dependence of Rate on Concentration:-

The rate of any reaction depends on following factors:-

Nature of reactants:-

Consider the following 2 reactions:-

$2NO + O_2 \rightarrow 2NO_2$ (fast).

$2CO + O_2 \rightarrow 2CO_2$ (slow).

These reactions appear to be similar but the first is fast while the second is slow. This is because different amount of energies are reqd. for breaking of different bonds.

Concentration (conc) of reactants:-

Greater the concn of reactants, faster is the reaction and vice versa.

Temp:- Rate of rxn increases with increase of temp. In most of the cases the rate of reaction becomes double for 10° rise of temp.

Presence of catalyst:- If it is a positive catalyst it increases the rate of reaction and if it is a negative catalyst it decreases the rate of reaction.

Surface area of reactants:- For a reaction involving solid reactant or catalyst, the smaller is the particle size i.e. the greater is the surface area, the faster is reaction.

Rate Law Expression and Rate constant:-

The representation of rate of reaction in terms of concentration of the reactants is known as the rate law. It is also called as rate equation or rate expression.

Rate of reaction decreases with the passage of time as the concn of reactants decreases. Conversely, rates generally increase when reactants concn increases. So rate of reaction depends upon the concentration of reactants.

Consider a general reaction:-

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

where a, b, c and d are stoichiometric coefficients of reactants and products.

The rate expression for this reaction is:-

$$\text{Rate} \propto [A]^x [B]^y$$

where exponents x and y may or may not be equal to the stoichiometric coefficients (a and b) of the reactants. Above equation can also be written as:-

$$\text{Rate} = k[A]^x [B]^y \quad \text{— (i)}$$

$$-\frac{d[R]}{dt} = k[A]^x[B]^y \quad \text{— (ii)}$$

Eqn (ii) is known as differential rate equation, where k is a proportionality constant called as rate constant

"Rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as stoichiometric coefficient of the reacting species in a balanced chemical equation.

~~For eg:- $2NO + O_2 \rightarrow 2NO_2$.~~

"Rate constant may be defined as the rate of the reaction when the molar concentration of each reactant is taken as unity. That is why rate constant is also called specific reaction rate."

Characteristics rate Constant:-

Some important characteristics of rate constant are:-

(i) Rate constant is a measure of rate of reaction. Greater is the value of rate constant, faster is the reaction

(ii) Each reaction has a definite value of rate constant at a particular temp.

(iii) The value of the rate constant for the same reaction changes with temp.

Order of Reaction:-

In the rate eqn:-

$$\text{Rate} = k[A]^x[B]^y$$

$x+y$ will give the order of reaction.

Hence the sum of powers of the concentration of the reactants in the rate law expression is called as the order of that chemical reaction.

Order of reaction can be 0, 1, 2, 3. and even a fraction.

A zero order reaction means that the rate of reaction is independent of concn of reactant.

A reaction taking place in one step are called elementary reactions.

When sequence of elementary reaction give us a product, the reactions are called complex reactions.

Units for Rate Constant:

For a general reaction,

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

$$\text{Rate} = k[A]^x[B]^y$$

where $x + y = n$ = order of reaction.

$$k = \frac{\text{Rate}}{[A]^x[B]^y}$$

$$= \frac{\text{concn}}{\text{time}} \times \frac{1}{[\text{concn}]^n}$$

Taking SI units of concn, mol L^{-1} and time, s, the units of k for different reaction order are listed:

Rkn	Order	Unit of rate constant
Zero order	0	$\frac{mol\,L^{-1}}{s} \times \frac{1}{(mol\,L^{-1})^0}$ $= mol\,L^{-1}s^{-1}$
First order	1	$\frac{mol\,L^{-1}}{s} \times \frac{1}{(mol\,L^{-1})^1}$ $= s^{-1}$
Second order	2	$\frac{mol\,L^{-1}}{s} \times \frac{1}{(mol\,L^{-1})^2}$ $= mol^{-1}\,L\,s^{-1}$

Molecularity of Rkn:-

* It helps in understanding mechanism of the rkn.

* The number of reacting species (atoms, ions or molecules) taking part in an elementary rkn, which must collide simultaneously

The reaction can be unimolecular when one reacting species is involved, for eg decomposition of ammonium nitrate –

$$NH_4NO_2 \rightarrow N_2 + 2H_2O.$$

Bimolecular reactions involve simultaneous collision betⁿ 2 species, for eg, dissociation of hydrogen iodide –

$$2HI \rightarrow H_2 + I_2.$$

Trimolecular or termolecular reactions involve simultaneous collision betⁿ 3 reacting species, for example,

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

The probablity that more than 3 molecules can collide and react simultaneously is very small. Hence molecularity greater than 3 is not observed.

Molecularity of Rkn:-

ORDER of Rkn

Order of Rxn	Molecularity of Rxn.
1) It is the sum of exponents of the molar concentrations in the rate law equation.	It is the no of atoms ions or molecules that must collide with one another simultaneously so as to result in a chemical reaction.
2) It need not be a whole no i.e. it can be fractional as well as zero.	It is always a whole number. It cannot be zero or fractional
3) It can be determined experimentally only and cannot be calculated.	It can be calculated by simply adding the molecules.
4) Order is applicable to elementary as well as complex rxn	Molecularity is only valid for elementary reactions

Integrated Rate Equation:-

We have already discussed that for the general reaction, $aA + bB \rightarrow cC + dD$.

$$\text{Rate} = \frac{-d[R]}{dt} = k[A]^{\alpha}[B]^{\beta}$$

This form of equation is called differential rate equation. This form is not convenient determine rate law and hence order of rxn.

Moreover, this lacks accuracy.

To overcome this difficulty we integrate the differential equation for the reaction of any order:-

Integrated rate equation for Zero order Rxn:-

Zero order rxn means rate of reaction is proportional to zero power of concentration of reactants.

Consider the general reaction:-

$$R \rightarrow P$$

If it is a reaction of zero order,

$$\text{Rate} = \frac{-d[R]}{dt} = k[R]^0$$

As any quantity raised to power 0 is unity.

$$\text{Rate} = \frac{-d[R]}{dt} = k \times 1$$

$$d[R] = -k \cdot dt$$

Integrating both sides we get:-

$$[R] = -kt + I \quad \text{---} (1)$$

where I = constant of integration.

At $t = 0$, the concentration of $= [R]_0$
where $[R]_0$ is initial concentration of reactant.

Substituting in eqn (1) -

$$[R]_0 = -k \times 0 + I.$$

$$[R]_0 = I. \quad \text{—— (2)}$$

Now substitute (2) in eq (1) -

$$[R] = -kt + [R]_0. \quad \text{— (3)}$$

Comparing eqn (3) with eqn of straight line, $y = mx + c$, if we plot $[R]$ against t, we get a straight line with slope $= -k$ and intercept equal to $[R]_0$.