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An Initiative by अमर उजाला

CHEMICAL KINETICS

PHYSICAL CHEMISTRY

JEE/NEET-2020

NEET- JEE Syllabus

Rates of Chemical reactions, Order of reactions, Rate constant, Effect of concentration and Temperature, Kinetics of first–order reactions, Arrhenius Equation, Kinetics of radioactive disintegrations.

1. Introduction

Chemical Kinetics is the branch of science that deals with rate of reaction, factors affecting the rate of reaction and reaction mechanism.

Different reactions occur at different rate. In fact a chemical reaction involves redistribution of bonds — breaking of bond(s) in the reactant molecule(s) and making of bonds in the product molecule(s). On the basis of rate, reactions are classified as.

i) Instantaneous or extremely fast reactions i.e. reactions with half-life of the order of fraction of second.

ii) Extremely slow reactions i.e. reactions with half-life of the order of years.

iii) Reactions of moderate or measurable rate.

Ionic reactions are instantaneous.

For example $Na^+ + Cl^- + Ag^+ + NO_3^- \longrightarrow AgCl\downarrow + Na^+ + NO_3^-$

There are some molecular reactions which are known to be extremely slow. Their half-lives are of the order of several years.

For example $4Fe + xH_2O + 3O_2 \longrightarrow 2Fe_2O_3.xH_2O$

Note that the reaction given above is called —rusting of iron‖. The half-life of this reaction is in years.

Most molecular reactions especially organic reactions occur at measurable rate. The half-life of such reactions are of the order of minutes, hours, days. Examples of such reactions are numerous. Some of these are given below.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

$$\underset{\text{(Sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{(Glucose)}}{C_6H_{12}O_6} + \underset{\text{(Fructose)}}{C_6H_{12}O_6}$$

$$H_2O_2\,(aq) \longrightarrow H_2O + \frac{1}{2}O_2\uparrow$$

$$2N_2O_5 \longrightarrow 4NO_2 + O_2\uparrow$$

$$NH_4NO_2\,(aq) \longrightarrow 2H_2O + N_2\uparrow$$

In Chemical Kinetics we deal with the rates of only those reactions which occur with measurable rate i.e. which are neither too fast nor too slow. These days rates of fast reactions are also determined using lasers.

Reaction Rates

What is the reaction rate?

- Rates of reactions can be determined by monitoring the change in concentration of either reactants or products as a function of time.

Example 1: For a reaction A → B

$$\text{Average rate} = \frac{\text{change in number of moles of B}}{\text{change in time}}$$

$$= \frac{\Delta(\text{moles of B})}{\Delta t}$$

Note: Rate is positive since it is (moles B_{final} minus moles B_{initial})

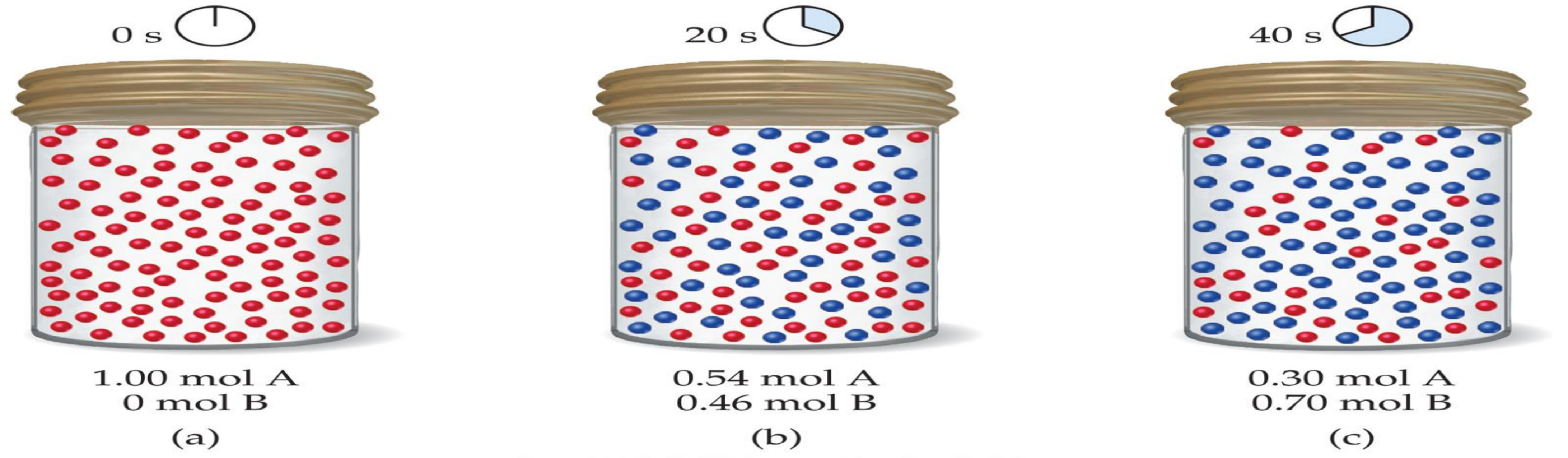
Reaction Rates

For a reaction A → B

$$\text{Average rate with respect to A} = -\frac{\Delta(\text{moles of A})}{\Delta t}$$

Note: minus added to make Rate positive since moles B $_{\text{final}}$ minus moles B $_{\text{initial})}$ gives negative value but made positive because of negative at the beginning for disappearance of reactant. Rates are always expressed as positive.

Suppose A reacts to form B. Let us begin with 1.00 mol A.



Reaction Rates

- At *t* = 0 (time zero) there is 1.00 mol A (100 red spheres) and no B present.
- At *t* = 20 min, there is 0.54 mol A and 0.46 mol B.
- At *t* = 40 min, there is 0.30 mol A and 0.70 mol B.
- Calculating,

$$\text{Average rate} = \frac{\Delta(\text{moles of B})}{\Delta t}$$

$$= \frac{(\text{moles of B at } t = 20) - (\text{moles of B at } t = 0)}{20\text{ min} - 0\text{ min}}$$

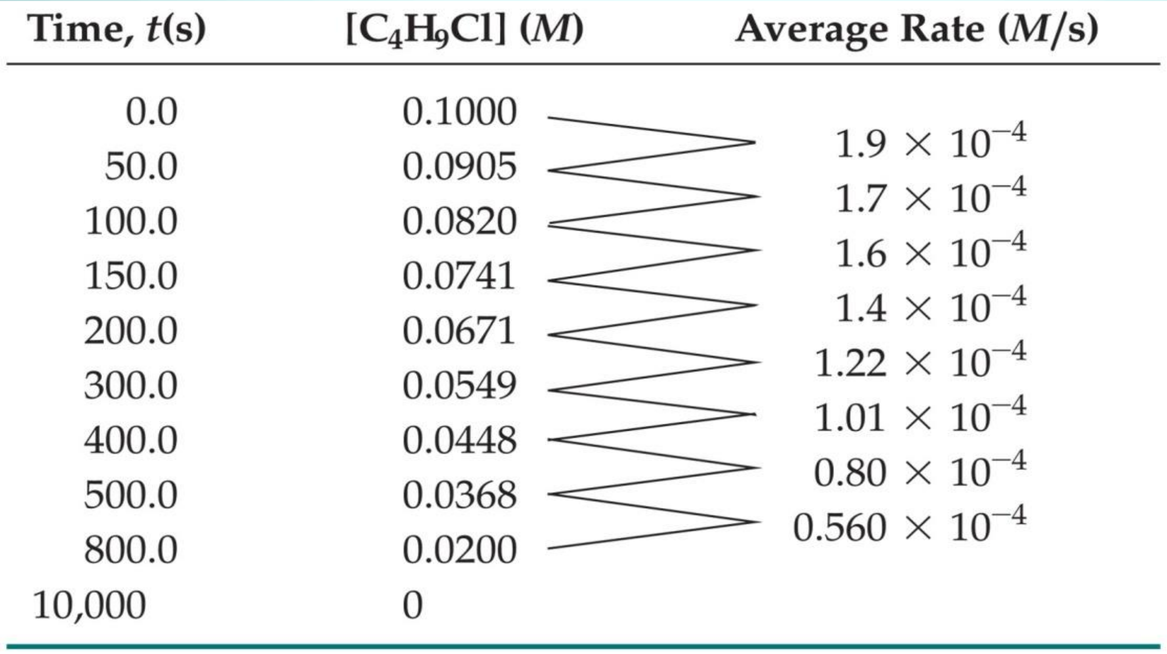
$$= \frac{0.46\text{ mol} - 0\text{ mol}}{20\text{ min} - 0\text{ min}} = 0.023\text{ mol/min}$$

Reaction Rates

$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$$

The average rate of the reaction over each interval is the change in concentration divided by the change in time:

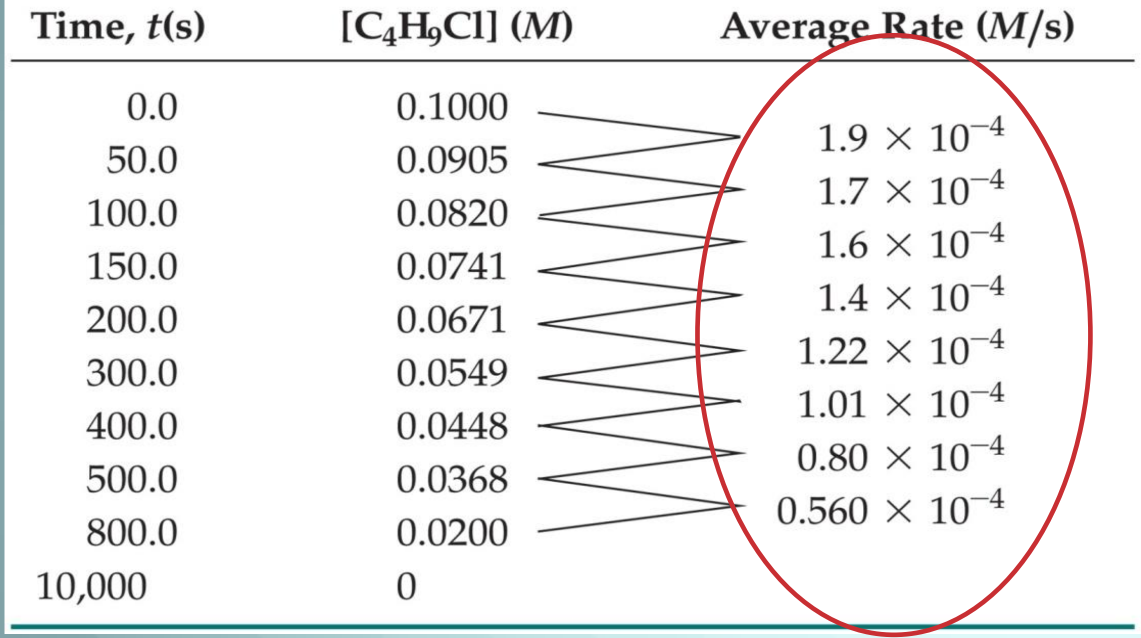
$$\text{Average rate} = \frac{\Delta[C_4H_9Cl]}{\Delta t}$$



Time, *t*(s)	**$[C_4H_9Cl]$ (*M*)**	**Average Rate (*M*/s)**
0.0	0.1000	
		1.9×10^{-4}
50.0	0.0905	
		1.7×10^{-4}
100.0	0.0820	
		1.6×10^{-4}
150.0	0.0741	
		1.4×10^{-4}
200.0	0.0671	
		1.22×10^{-4}
300.0	0.0549	
		1.01×10^{-4}
400.0	0.0448	
		0.80×10^{-4}
500.0	0.0368	
		0.560×10^{-4}
800.0	0.0200	
10,000	0	

Reaction Rates

$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$$



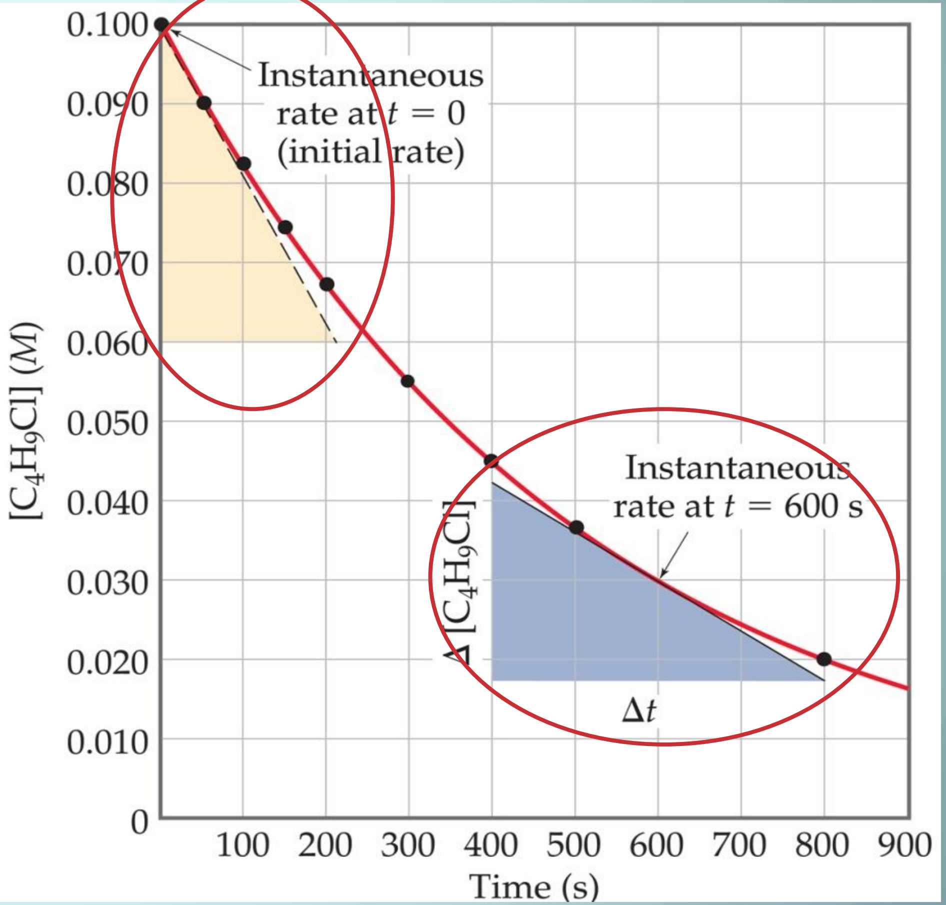
Time, t(s)	$[C_4H_9Cl]$ (M)	Average Rate (M/s)
0.0	0.1000	1.9×10^{-4}
50.0	0.0905	1.7×10^{-4}
100.0	0.0820	1.6×10^{-4}
150.0	0.0741	1.4×10^{-4}
200.0	0.0671	1.22×10^{-4}
300.0	0.0549	1.01×10^{-4}
400.0	0.0448	0.80×10^{-4}
500.0	0.0368	0.560×10^{-4}
800.0	0.0200	
10,000	0	

- ➢Note that the average rate decreases as the reaction proceeds.
- ➢This is because as the reaction goes forward, there are fewer collisions between reactant molecules.

Reaction Rates

$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$

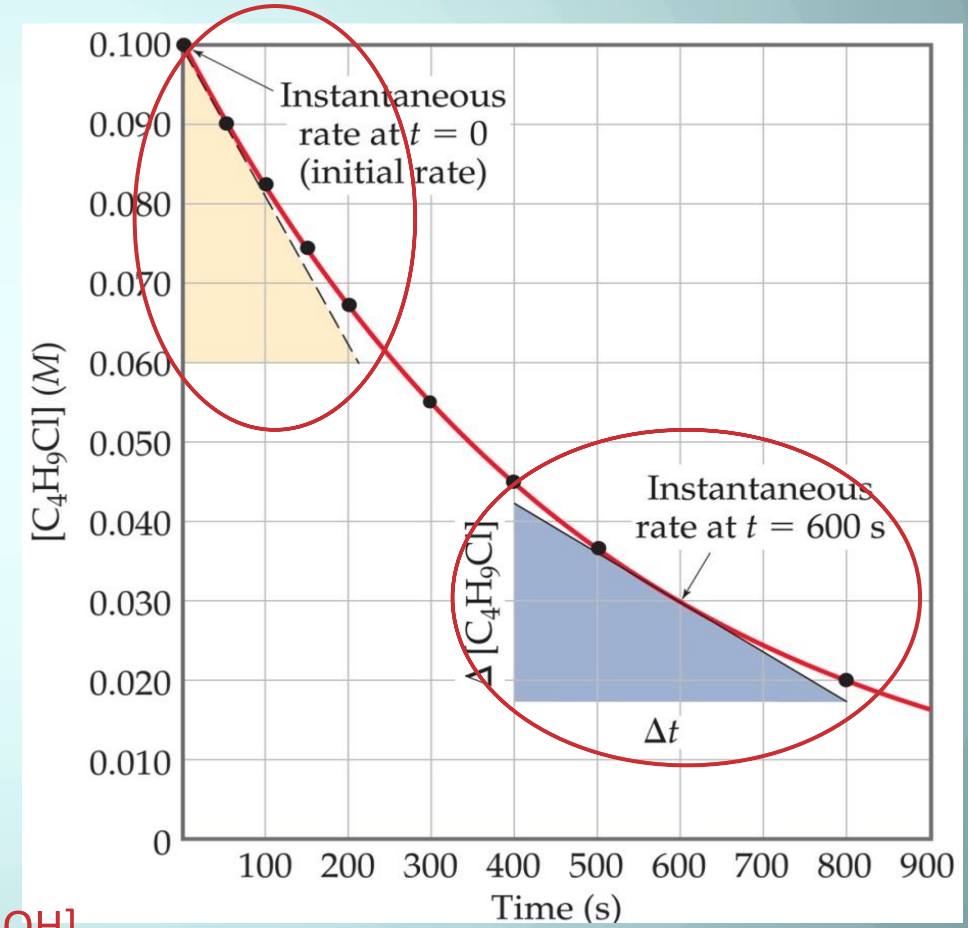
- All reactions slow down over time.
- Therefore, the best indicator of the rate of a reaction is the instantaneous rate near the beginning.



Reaction Rates and Stoichiometry

$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$$

- In this reaction, the ratio of C_4H_9Cl to C_4H_9OH is 1:1.
- Thus, the rate of disappearance of C_4H_9Cl is the same as the rate of appearance of C_4H_9OH.



$$\text{Rate} = \frac{-\Delta[C_4H_9Cl]}{\Delta t} = \frac{\Delta[C_4H_9OH]}{\Delta t}$$

Reaction Rates and Stoichiometry

$$2\,HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$$

- Therefore,

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$$

- To generalize, then, for the reaction

$$aA + bB \longrightarrow cC + dD$$

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

PRACTICE EXERCISE

The decomposition of N_2O_5 proceeds according to the following equation:

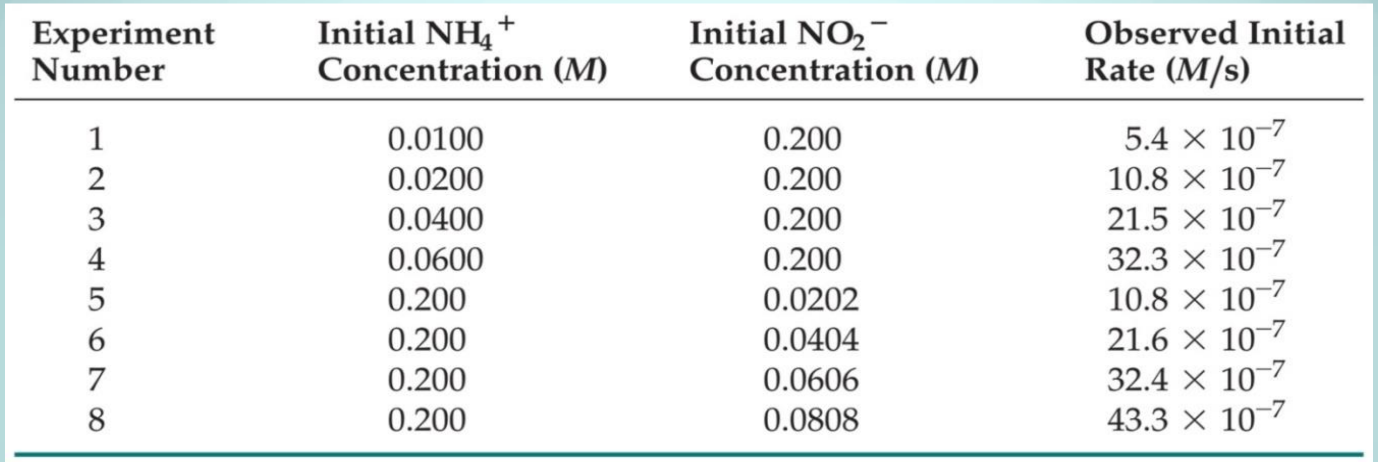
$$2\,N_2O_5(g) \longrightarrow 4\,NO_2(g) + O_2(g)$$

If the rate of decomposition of N_2O_5 at a particular instant in a reaction vessel is 4.2×10^{-7} *M*/s, what is the rate of appearance of (a) NO_2, (b) O_2?

Answers: **(a)** 8.4×10^{-7} *M*/s, **(b)** 2.1×10^{-7} *M*/s

Concentration and Rate

- One can gain information about the rate of a reaction by seeing how the rate changes with changes in concentration.

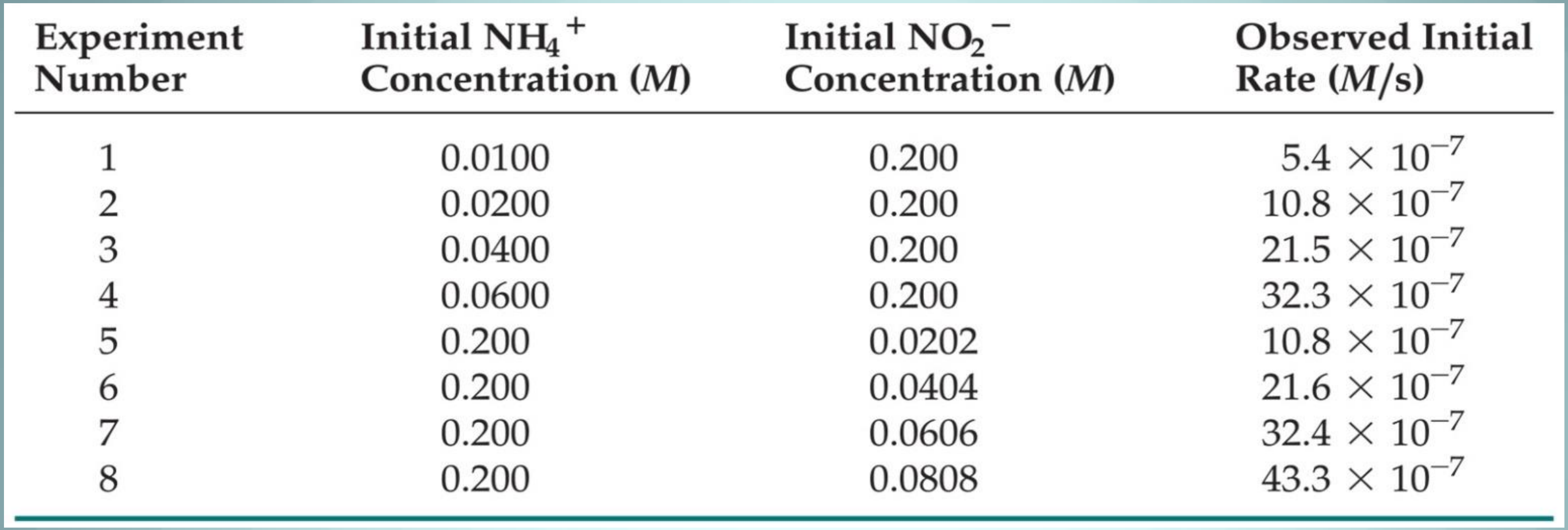


Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

$$NH_4^+{}_{(aq)} + NO_2^-{}_{(aq)} \longrightarrow N_{2(g)} + 2\ H_2O_{(l)}$$

- Comparing Experiments 1 and 2, when $[NH_4^+]$ doubles, the initial rate doubles.

Concentration and Rate



Experiment Number	Initial NH_4^+ Concentration (*M*)	Initial NO_2^- Concentration (*M*)	Observed Initial Rate (*M*/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

$$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2\ H_2O(l)$$

- Likewise, comparing Experiments 5 and 6, when $[NO_2^-]$ doubles, the initial rate doubles.

Concentration and Rate

- This means
  - **Rate $\propto [NH_4^+]$**
  - **Rate $\propto [NO_2^-]$**

Therefore: **Rate $\propto [NH^+] [NO_2^-]$**

or

Rate = $k\,[NH_4^+] [NO_2^-]$

- This equation is called the rate law, and *k* is the rate constant.
  - Rate constant (k) is dependent on temperature

2. RATE OF REACTION

2.1 Average rate of reaction

Rate = $\pm\frac{\Delta C}{\Delta t}$

(–ve sign applies in the case of reactant whose concentration goes on decreasing with time and +ve sign applies in the case of product whose concentration goes on increasing with time).

For Example: $PCl_5 \rightarrow PCl_3 + Cl_2$

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

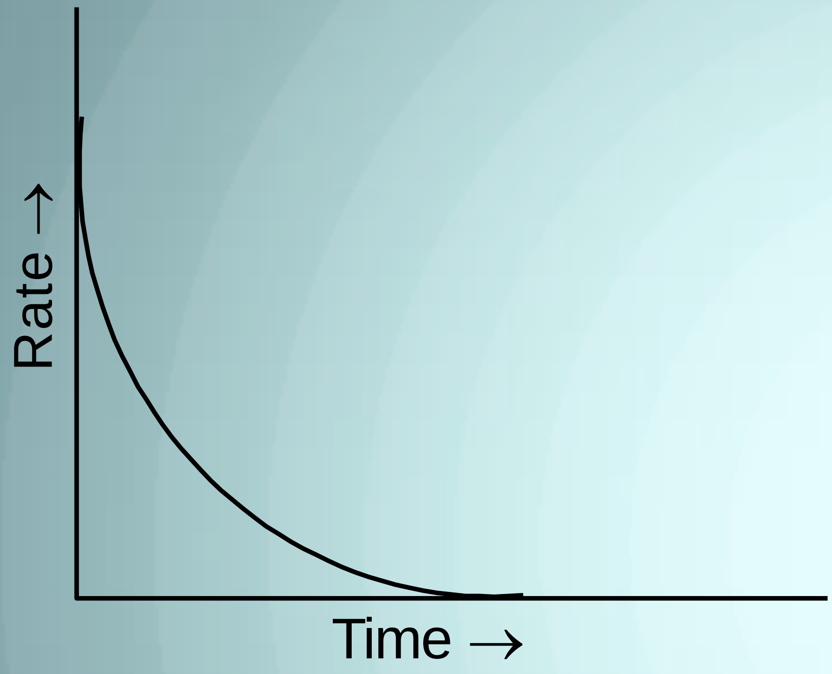
In general, for any reaction of the type

$$A + B \rightarrow C + D$$

Then,

Average of reaction = $\frac{-\Delta[A]}{\Delta t} = \frac{-\Delta[B]}{\Delta t} = \frac{\Delta[C]}{\Delta t} = \frac{\Delta[D]}{\Delta t}$

2.2 Instantaneous rate of reaction



Rate varies from moment to moment so rate of reaction has to be specified at a given instant of time. It is called instantaneous rate or rate at any time t. This is defined as.

$$r_{inst} \text{ or } r_t = \pm \frac{dc}{dt}$$

For the reaction: $2N_2O_5 \longrightarrow 4NO_2 + O_2$

The rate of reaction at any time t may be expressed by one of the following.

$$\frac{-d[N_2O_5]}{dt}, +\frac{d[NO_2]}{dt} \text{ or } +\frac{d[O_2]}{dt}$$

$$+\frac{d[NO_2]}{dt} = 2\left\{-\frac{d[N_2O_5]}{dt}\right\} = 4\left\{+\frac{d[O_2]}{dt}\right\}$$

$$\frac{1}{2}\left\{-\frac{d[N_2O_5]}{dt}\right\} = \frac{1}{4}\left\{+\frac{d[NO_2]}{dt}\right\} = +\frac{d[O_2]}{dt}$$

.

Thus, for a reaction represented by the general equation

$$aA + bB \longrightarrow cC + dD$$

$$\frac{1}{a}\left\{-\frac{dC_A}{dt}\right\} = \frac{1}{b}\left\{-\frac{dC_B}{dt}\right\} = \frac{1}{c}\left\{+\frac{dC_C}{dt}\right\} = \frac{1}{d}\left\{+\frac{dC_D}{dt}\right\}$$

2.3 *Rate law*

$2N_2O_5 \longrightarrow 4NO_2 + O_2\uparrow$

Rate $\propto [N_2O_5]$ or Rate = k $[N_2O_5]$

$$-\frac{d[N_2O_5]}{dt} = k'[N_2O_5]$$

$$+\frac{d[NO_2]}{dt} = k''[N_2O_5]$$

$$+\frac{d[O_2]}{dt} = k'''[N_2O_5]$$

when k′, k″ and k‴ are the rate constants of the reaction. These three rate constants are inter-related.

$$\Rightarrow \frac{k'}{2} = \frac{k'}{4} = k'' \quad as, rate = \frac{1}{2}\left\{-\frac{d[N_2O_5]}{dt}\right\} = \frac{1}{4}\left\{+\frac{d[NO_2]}{dt}\right\} = +\frac{d[O_2]}{dt}$$

Thus, for a reaction represented by the general equation

$aA + bB \longrightarrow cC + dD$

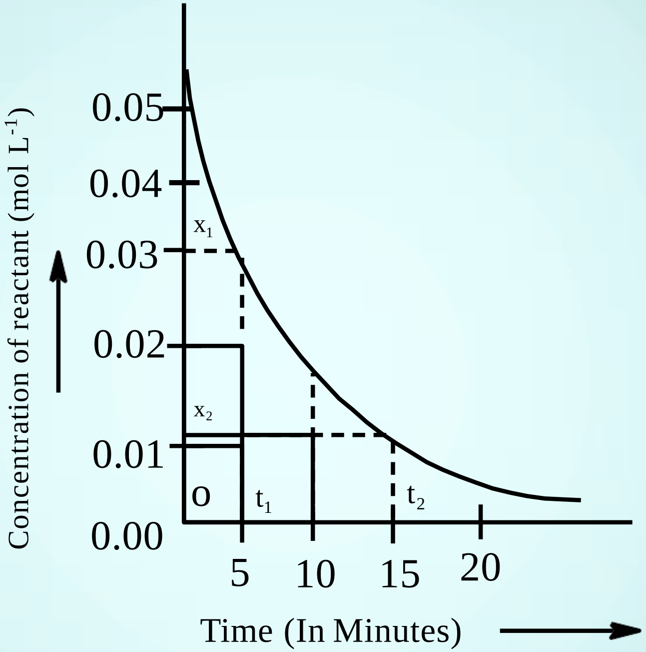
$$\frac{1}{a}\left\{-\frac{dC_A}{dt}\right\} = \frac{1}{b}\left\{-\frac{dC_B}{dt}\right\} = \frac{1}{c}\left\{+\frac{dC_C}{dt}\right\} = \frac{1}{d}\left\{+\frac{dC_D}{dt}\right\}$$

We have, $\frac{k^{I}}{a} = \frac{k^{II}}{b} = \frac{k^{III}}{c} = \frac{k^{IV}}{d}$

Where k^{I}, k^{II}, k^{III} and k^{IV} are the rate constants of the reaction when its rate is expressed in terms A, B, C and D, respectively.

2.4 ***Measurement of rate of reaction by graphs***

(A) MEASUREMENT OF AVERAGE RATE OF REACTION



Average rate of reaction = $\dfrac{X_2 - X_1}{t_2 - t_1}$

For example, from the figure below between the time interval 5 to 15 minutes,

Average rate = $\dfrac{0.03-0.012}{15-5} = \dfrac{0.018}{10} = 0.0018$ mol L^{-1} min^{-1}

(**B**) MEASUREMENT OF INSTANTANEOUS RATE OF REACTION

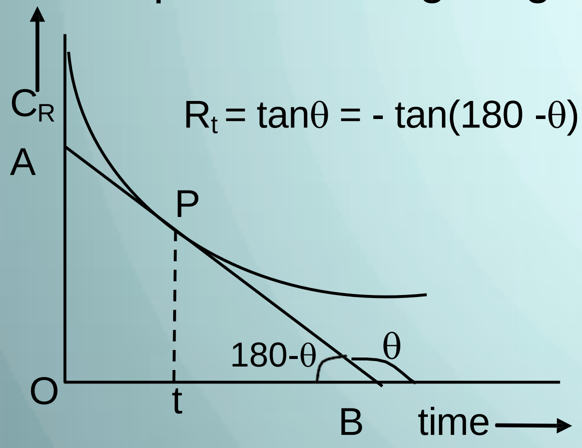
The rate of reaction at any time t is determined in the following way,

i) Concentration of any of the reactants or products which ever may be convenient is determined at various time intervals.

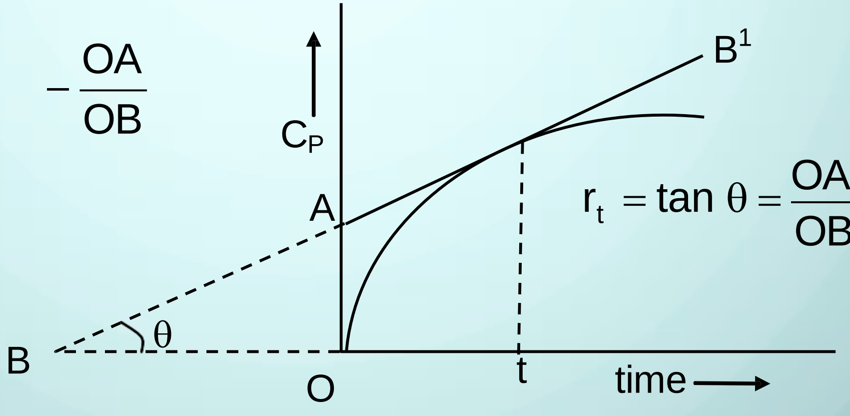
ii) Then concentration vs time curve is drawn.

iii)A tangent is drawn at the point p of the curve which corresponds to the time t at which rate is to be determined.

iv) The slope of the tangent gives the rate of reaction at the required time as shown below.



$R_t = \tan\theta = -\tan(180 - \theta) = -\frac{OA}{OB}$



$r_t = \tan\theta = \frac{OA}{OB}$

(C_R and C_P denote concentration of reactant and product respectively)

UNIT OF RATE OF REACTION:

Unit of rate = $\frac{\text{Unit of concentration}}{\text{Unit of time}}$ = Concentration time^{-1} i.e. mole $l^{-1}s^{-1}$

For gaseous state it is also expressed in atm s^{-1} i.e. change in pressure per unit time

2.5 ***Factors affecting the rate of reaction***

1. **Concentration**
2. **Temperature**
3. **Catalyst**
4. **Surface area of the reactants**
5. **Presence of light**

Example 1: In a reaction 2A Product, the concentration of A decreases form 0.5 mole/litre to 0.4 mole/litre in 10 minutes. Calculate the rate during this interval.

Solution: Rate = rate of disappearance of A

$$= -\frac{1}{2}\frac{\Delta[\mathrm{A}]}{\Delta\,\mathrm{t}} = -\frac{1}{2}\frac{(0.4-0.5)}{10} = 0.005.$$

The negative sign simply indicates the fall in concentration of A. The rate of the reaction is 0.005 $\mathrm{mole\ lit^{-1}min^{-1}}$.

Example 2: The reaction, $2N_2O_5 \longrightarrow 4NO_2 + O_2$, is forming NO_2, at the rate of 0.0072 mole$L^{-1}s^{-1}$ at some time.

(a) What is the rate of change of $[O_2]$ at this time?

(b) What is the rate of change of $[N_2O_5]$ at this time?

(c) What is the rate of reaction at this time?

Solution: The rate of reaction is expressed as

Rate = $-\frac{1}{2}\frac{d[N_2O_5]}{dt} = +\frac{1}{4}\frac{d[NO_2]}{dt} = +\frac{d[O_2]}{dt}$ And given that $\frac{d[NO_2]}{dt} = 0.0072 \text{ mole lit}^{-1}s^{-1}$.

(a) Rate of appearance of $O_2 = \frac{1}{4} \times$ rate of appearance of NO_2

$$\frac{d[O_2]}{dt} = \frac{1}{4} \times \frac{d[NO_2]}{dt} = \frac{1}{4} \times 0.0072 = 0.0018 \text{mole lit}^{-1}s^{-1}.$$

(b) Rate of disappearance of $N_2O_5 = \frac{1}{2} \times$ rate of appearance of NO_2

$$-\frac{d[N_2O_5]}{dt} = \frac{1}{2} \times \frac{d[NO_2]}{dt}$$

$$-\frac{d[N_2O_5]}{dt} = \frac{1}{2} \times 0.0072 = 0.0036 \text{mole lit}^{-1}s^{-1}.$$

(c)Rate of reaction $= \frac{1}{4} \times \frac{d\left[NO_2\right]}{dt}$

$$= \frac{1}{4} \times 0.0072 = 0.0018\,\text{mole lit}^{-1}\text{s}^{-1}.$$

Example 3: In a reaction $H_2+I_2 \longrightarrow 2HI$ the rate of disappearance of I_2 is found to the 10^{-6} mole per litre per second. What would be the corresponding rate of appearance of HI?

Solution: In the given reaction

rate = rate of disappearance of H_2

= rate of disappearance of I_2

= $\frac{1}{2}\times$ rate of appearance of HI

$$\therefore \quad -\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt} = +\frac{1}{2}\times\frac{d[HI]}{dt} = 10^{-6}$$

$$\therefore \quad \frac{d[HI]}{dt} = 2\times10^{-6}\ \text{moleL}^{-1}\text{s}^{-1}$$

Example 4: In the following reaction

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

rate of formation of O_2 is 36 g min^{-1}.

(a) What is rate of formation of H_2O?

(b) What is rate of disappearance of H_2O_2?

Solution : Caution : take amount in mol or mol L^{-1}.

When 2 moles H_2O_2 (68g) decompose, 2 mol H_2O(36g) and 1 mol O_2 (32g) are formed.

$$36gO_2 = \frac{36}{32} = 1.125 mol \min^{-1}$$

$$-\frac{1}{2}\frac{d[H_2O_2]}{dt} = \frac{1}{2}\frac{d[H_2O]}{dt} = \frac{d[O_2]}{dt}$$

(a) $$\frac{d[H_2O]}{dt} = 2\frac{d[O_2]}{dt} = 2.250 \text{ mol min}^{-1}$$

(a) $$-\frac{d[H_2O_2]}{dt} = \frac{2\,d[O_2]}{dt} = 2.250 \text{ mol min}^{-1}$$

3. MOLECULARITY AND ORDER OF REACTION

3.1 ***Molecularity***

A chemical reaction that takes place in one and only one step is called elementary reaction

while a chemical reaction occurring in the sequence of two or more steps is called complicated reaction.

The sequence of steps through which a complicated reaction takes place is called reaction – mechanism.

Each step in a mechanism is an elementary step reaction.

The molecularity of an elementary reaction is defined as the minimum number of molecules, atoms or ions of the reactants(s) required for the reaction to occur and is equal to the sum of the stoichiometric coefficients of the reactants in the chemical equation of the reaction.

Elementary reactions	**Molecularity**
$PCl_5 \rightleftharpoons PCl_3 + Cl_2$	1
$H_2 + I_2 \rightleftharpoons 2HI$	1 + 1 = 2

In general for any elementary reaction

$aA + bB \longrightarrow Product$ Molecularity = a + b

Reactions with molecularity equal to one, two, three etc., are called unimolecular, bimolecular, trimolecular, etc., respectively.

3.2 *Order of reaction*

$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O\ (g)$

Kinetic experiment carried out at 1100 K upon this reaction has shown following rate data.

Expt. No.	[NO] (mole dm^{-3})	$[H_2]$ (mole dm^{-3})	Rate (mole $dm^{-3}s^{-1}$)
1.	5×10^{-3}	2.5×10^{-3}	3×10^{-5}
2.	1.0×10^{-2}	2.5×10^{-3}	1.2×10^{-4}
3.	1.0×10^{-2}	5.0×10^{-3}	2.4×10^{-4}

Rate $\propto [NO]^2$ when $[H_2]$ is constant again from Expt. No.2 and 3, it is evident that when concentration of H_2 is doubled keeping the concentration of NO constant, the rate is just doubled i.e.

Rate $\propto [H_2]$ when [NO] is constant

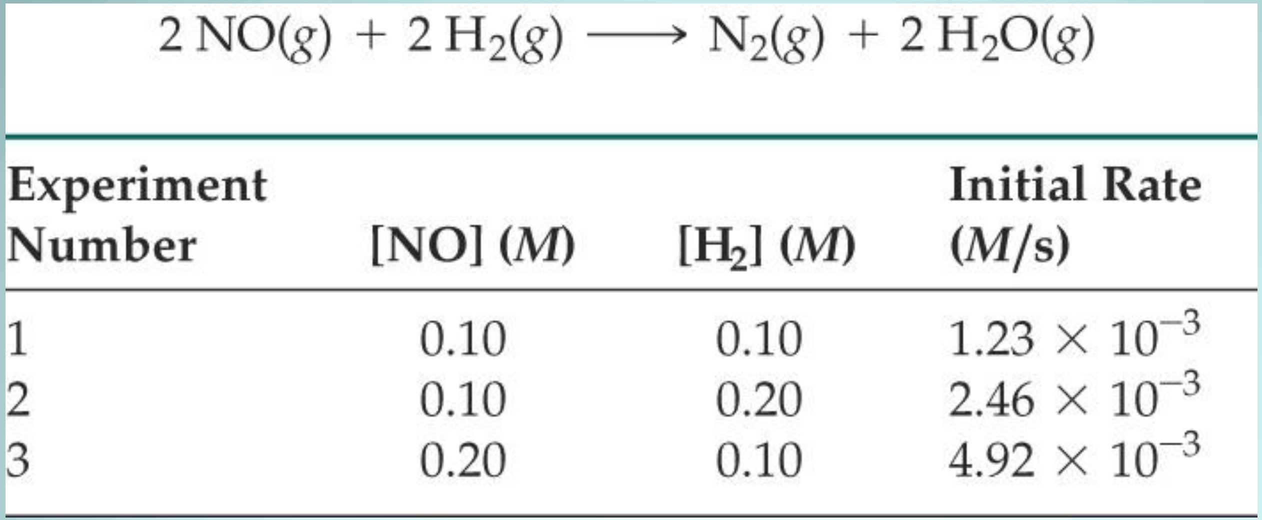
From Expt. (1) and Expt. (3), the rate increases 8-fold when concentrations of both NO and H_2 are doubled simultaneously i.e.

Rate $\propto [NO]^2\ [H_2]$

This is the rate-law of reaction as observed experimentally. So, order of reaction w.r.t. NO is 2 and that w.r.t. H_2 is 1 and overall order is 2 + 1 i.e. 3.

PRACTICE EXERCISE

The following data were measured for the reaction of nitric oxide with hydrogen:



$$2\,NO(g) + 2\,H_2(g) \longrightarrow N_2(g) + 2\,H_2O(g)$$

Experiment Number	[NO] (M)	[H_2] (M)	Initial Rate (M/s)
1	0.10	0.10	1.23×10^{-3}
2	0.10	0.20	2.46×10^{-3}
3	0.20	0.10	4.92×10^{-3}

(a) Determine the rate law for this reaction. **(b)** Calculate the rate constant. **(c)** Calculate the rate when [NO] = 0.050 M and [H_2] = 0.150 M.

Answers: **(a)** rate = $k[NO]^2[H_2]$; **(b)** $k = 1.2\ M^{-2}s^{-1}$; **(c)** rate = $4.5 \times 10^{-4}\ M/s$

3.3 ***Difference between Order and Molecularity***

i)Order is an experimental property while molecularity is the theoretical property.

ii) Order may be any number, fractional, integral zero or even negative whereas molecularity is always aninteger excepting zero.

Example 5:

Reactions	**Rate Law**	**Order**
$CH_3CHO \longrightarrow CH_4 + CO$	Rate $\propto [CH_3CHO]^{3/2}$	1.5
$NH_3 \longrightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2$	Rate $\propto [NH_3]^0$	0
$2HI \longrightarrow H_2 + I_2$	Rate $\propto [HI]^0$ i.e. Rate = k	0

Note that a zero order reaction is one in which rate of change in concentration of reactant remains constant and as such rate of reaction remains throughout constant equal to the rate constant.

iii)Order may change with change in experimental condition while molecularity can‘t.

Example 6:

This reaction follows 1st order kinetics at high gas pressure and 2nd order kinetics at low gas pressure of cyclopropane.

Unit of rate constant

The differential rate expression for nth order reaction is as follows.

$$\frac{dx}{dt} = k(a-x)^n \quad \text{or} \qquad k = \frac{dx}{(a-x)^n dt} = \frac{\text{concentration}}{(\text{concentration})^n\ \text{time}} = \text{conc.}^{1-n}.\text{time}^{-1}$$

If concentration be expressed in mole L^{-1} and time in minute, then k = (mole $L^{-1})^{1-n}$ min^{-1}

For zero order reaction: n = 0 and hence k = mole L^{-1} min^{-1}

For 1st order reaction: n = 1 and hence k = (mole $L^{-1})^0$ $\text{min}^{-1} = \text{min}^{-1}$

For 2nd order reaction: n = 2 and hence k = (mole $L^{-1})^{-1}$ min^{-1} = $\text{mole}^{-1}L\ \text{min}^{-1}$

Example 7:

The experimental rate law for the reaction:

$$2\,NO_2^- + 4\,H^+ + 2\,I^- \rightarrow I_2 + 2\,NO + 2\,H_2O$$

Rate = $k\left[NO_2^-\right]\left[H^+\right]^2\left[I^-\right]$

How the rate of the reaction would be altered if:

(a)$[H^+]$ and $[I^-]$ were kept constant but $[NO_2^-]$ was doubled?

(b)$[I^-]$ and $[NO_2^-]$ were kept constant but $[H^+]$ doubled?

(c)$[I^-]$ and $[NO_2^-]$ were kept constant and pH was increased by one unit?

(d)All the concentrations were doubled?

Solution:

Rate law is , R = $k\left[NO_2^-\right]\left[H^+\right]^2\left[I^-\right]$

By general rule, if concentration is made m times, rate becomes m^n times (n=order)

Order = 1 w.r.t. NO_2^-

= 2 w.r.t. H^+

= 1 w.r.t. I^-

m = 2, n=1, hence, $2^1 = 2$, hence, rate is doubled

m = 2, n = 2, hence, $2^2 = 4$, hence, rate becomes four times,

$m = \frac{1}{10}$, n=2, hence, $\left(\frac{1}{10}\right)^2 = \frac{1}{100}$

Hence rate becomes $\frac{1}{100}$ time

As $[H^+] = 10^{-pH}$

If pH increases by 1 unit, $[H^+]$ becomes $\frac{1}{10}$ times.

m = 2, n = 1 + 2 + 1 = 4

$\therefore$ hence, $m^n = 2^4 = 16$

Hence, rate becomes 16 times.

4. Integrated rate law

4.1 *Zero order reaction*

In a zero order reaction, rate is independent of the concentration of the reactants.

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

or $$-\frac{d(a-x)}{dt} = +\frac{dx}{dt} = k_0 (a-x)^0 = k_0$$

On integrating, we get the integrated rate law as

$$k_0 = \frac{x}{t} or, x = k_0 t$$

or $$k_0 t = a - (a-x)$$

Where k_0 is the rate constant of a zero order reaction, the unit of which is concentration per time. In zero order reactions, the rate constant is equal to the rate of the reaction at all concentrations.