Molecularity

The number of molecules/atoms of reactant taking part in an elementary (single step) reaction is called molecularity of reaction

Note: (i) Molecularity is defined only for elementary (single step) Reaction

(ii) For Complex Reaction (more than one step) Molecularity is not defined [NCERT]

· Elementary Reactions ⟶ Order = Molecularity (Mostly)

(i) $A + B \longrightarrow C$

rate $= K[A]^1[B]^1$ (experimentally)

for elementary reaction, rate law has reactant terms with powers = Stochiometric coeffecient

Molecularity $= 1+1 = 2$
order $= 2$

(ii) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

rate $= K[NH_4NO_2]^1$ (experimentally)
Molecularity $= 1 \Rightarrow$ Unimolecular
order $= 1$

"Molecularity is Actually the number of reactant molecules/atoms that collides simultaneously to bring a chemical change"

(iii) $2HI \longrightarrow H_2 + I_2$

$$rate = K[HI]^2$$ (experimentally)

Molecularity = 2 ⇒ BiMolecular

order $\simeq$ 2

(iv) $2NO + O_2 \longrightarrow 2NO_2$

$$rate = K[NO]^2[O_2]^1$$

Molecularity = 2+1 = 3 Termolecular

order $\simeq$ 3

So, we can see for elementary reaction
order = Molecularity (mostly)

imp
(vi) $CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$

Hydrolysis of ester

$$rate = K[CH_3COOC_2H_5][H_2O]$$

Here water is taken in excess (solvent)
So conc of water nearly remains
Constant throughout the reaction

$$\Rightarrow rate = K'[CH_3COOC_2H_5]^1$$

Order = 1
Molecularity = 2 (as reaction is still elementary)

One molecule of $CH_3COOC_2H_5$ will collide with One molecule of H_2O ⇒ Molecularity is 2

Here, in elementery reaction only order ≠ molecularity.

<u>This reaction is called pseudo First Order</u>

(vii) $C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

$$rate = K[C_{12}H_{22}O_{11}][H_2O]$$

again water is solvent & in excess so concentration of water is so large that it remains constant throughout the reaction

$$rate = K'[C_{12}H_{22}O_{11}]^1$$

Order = 1
Molecularity = 2 Order ≠ Molecularity

Pseudo First Order Reaction

(viii) $2A + \underset{(excess)}{B} \longrightarrow C$

$$rate = K[A]^2[B]_{\to cost}$$

$$rate = K'[A]^2$$

order = 2
Molecularity = 3

Pseudo Second order Reaction

Let us study Complex Reactions Now (Multi-Step)

→ In such reactions, rate law contains terms from the slowest step only

(i) $NO_2 + CO \longrightarrow NO + CO_2$ (Complex)

rate $= K[NO_2]^2$ (experimentally)
Order $= 2$
Molecularity = Not defined for Complex reaction

(ii) $CH_3CHO \longrightarrow CH_4 + CO$ (Complex)

rate $= K[CH_3CHO]^{3/2}$ experimentally
Order $= \frac{3}{2}$

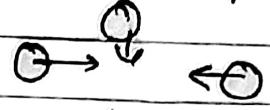
Molecularity = Not Defined for Complex Reactions

(iii) $2NO_2 + F_2 \longrightarrow 2NO_2F$ (Complex)

rate $= K[NO_2][F_2]$ (Experimentally)
order $= 2$
Molecularity = Not Defined for Complex Reactions

Molecularity ≤ 3

The chances of simultaneous collision of 3 molecules with 'proper orientation' & proper 'Energy factor' is rare.



So Molecularity > 3 is not observed.

$$KClO_3 + 6FeSO_4 + 3H_2SO_4 \longrightarrow KCl + 2Fe_2(SO_4)_3 + 3H_2O$$

Molecularity = 10 (X wrong)

Order of Reaction	Molecularity of Reaction
i) experimentally determined	i) theoretically determined
ii) Defined for elementary & complex reaction	ii) Defined only for elementary reaction
iii) Can be −ve, 0, +ve or fractional	iii) Can only be +ve Integers
iv) Can be greater than 3	iv) Cannot be greater than 3.