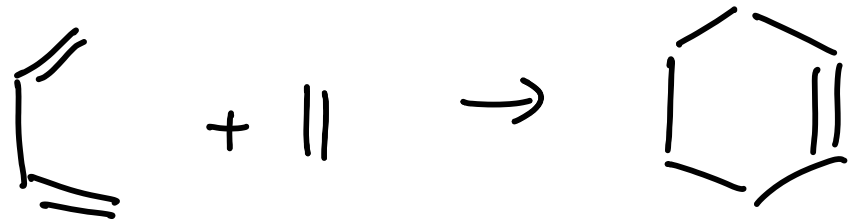
Nobody, I suppose, could devote many years to the study of chemical kinetics without being deeply conscious of the fascination of time and change: this is something that goes outside science into poetry; but science, subject to the rigid necessity of always seeking closer approximations to the truth, itself contains many poetical elements.

Sir Cyril Hinshelwood

$2H_2 + O_2 \rightarrow 2H_2O$ (many steps)



(single step)

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all Chemical reactions may be written as $0 = \sum \nu_i A_i$

ν_i → stoichiometric numbers

$0 = 2H_2O - 2H_2 - 1O_2$

ν_{H_2O}, ν_{H_2}, ν_{O_2} +ve for products, -ve reactants

ξ is the Extent / Advancement of the reaction "xi"

$n_i = n_i^0 + \nu_i \xi$ → extent of the reaction → has units of moles

<u>Consider an example</u>

Start with 4 mols of H_2 & $\frac{1}{2}O_2$

$n_{H_2}(t) = 4 - 2\xi$ / $n_{O_2}(t) = \frac{1}{2} - \xi$

Rate of the reaction $\frac{d\xi}{dt}$ (Extensive)

Other extensive properties → V, U, H, etc

Example of Intensive properties — P, T, density

Rate of the reaction $= V f(T, P, n_i)$ ← homogeneous

$+ A_1 g(T, P, n_i)$ ← heterogeneous

Interested here only in homogeneous reactions

$$\left[\frac{d\xi}{dt} \propto V f(T, P, n_i)\right]$$

$\Rightarrow A g(T, P, n_i)$ ignore

$$n_i = n_i^0 + \nu_i \xi$$

$$\frac{d\xi}{dt} = \frac{1}{\nu_i}\frac{dn_i}{dt}$$

Example:

CY P100 expt

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

conc of H^+

$KMnO_4$ (violet) + olefin

Reaction followed by measuring a property Z

$$Z(n_1, n_2, n_3 \ldots)$$

$\frac{1}{\nu_i}\frac{dn_i}{dt}$ may be related to $\frac{dZ}{dt}$

$$\frac{dz}{dt} = \frac{\partial z}{\partial n_1}\frac{\partial n_1}{\partial t} + \frac{\partial z}{\partial n_2}\frac{\partial n_2}{\partial t} + \cdots$$

$$\frac{\partial n_i}{\partial t} = \nu_i \frac{d\xi}{dt}$$

Rate ← $\frac{dz}{dt} = \frac{d\xi}{dt}\left(\nu_1 \frac{\partial z}{\partial n_1} + \nu_2 \frac{\partial z}{\partial n_2} + \cdots\right)$

$\frac{d\xi}{dt} = \frac{1}{\nu_i}\frac{dn_i}{dt}$ → extensive

Specific Rate of the reaction = $\frac{1}{\nu_i}\frac{d(n_i/V)}{dt}$ → Intensive quantity

Take V to be constant, then

$\frac{n_i}{V} = C_i$

Specific rate $\left(\frac{1}{\nu_i}\frac{dC_i}{dt}\right) \propto C_i^{\alpha} C_j^{\beta} \cdots$

Experimental Rate law → Rate $= k\, C_i^{\alpha} C_j^{\beta} \cdots$] often holds

k → specific rate constant

α → order of the reaction

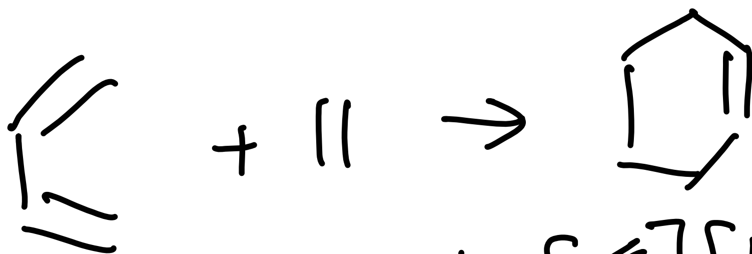
Total order $= \alpha + \beta + \cdots$

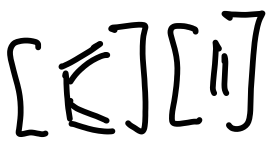
α — order with respect to i

$$2H_2 + O_2 \rightarrow 2H_2O$$

Mechanism is the steps that make up the rxn – elementary steps

Order = molecularity



Rate = k 

$$H + H_2 \rightarrow H_2 + H$$

Integrated Rate law

$A \rightarrow$ products

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^n$$

Consider $n = 1$

$n = 1$, $[A](t) = [A]_0 e^{-kt}$