

Chemical Kinetics

The branch of physical chemistry which deals with the study of reaction rates and their mechanisms is called chemical kinetics (kinesis in Greek means movement)

The factors such as concentration, temperature, pressure and catalyst affect the rate of a reaction. Kinetics study helps in describing the conditions by which the reaction rates can be altered.

Types of reactions on the basis of rate

i) Very fast reaction

These get complete within fraction of seconds, eg: ionic reaction



Ionic reactions just involve exchange of ions, there is no breaking/making of bonds, hence these reactions are very fast.

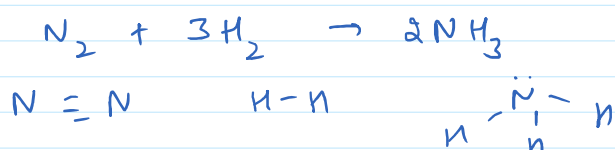
ii) very slow reaction

These require many years for completion. There is no practical importance to study rate of these reactions.

Eg: Making of petroleum

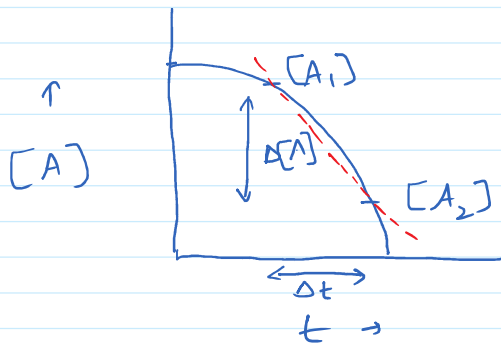
iii) Molecular reactions

These get completed in finite time. Rate of these reactions is studied. these involve making/braking of bonds.



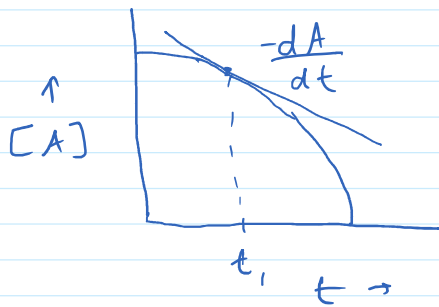
Rate of reactants

Change in concentration / pressure of reactants w.r.t time



rate of reaction = $-\frac{\Delta[A]}{\Delta t}$
 (Average rate)

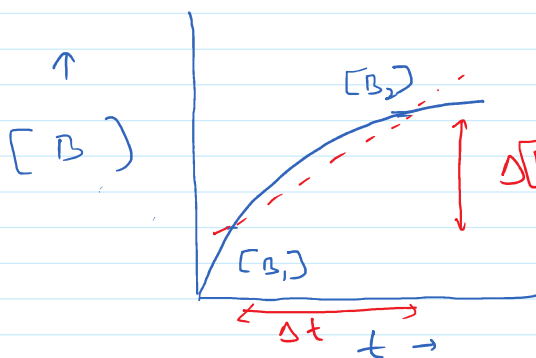
$$= -\left(\frac{[A_2] - [A_1]}{\Delta t}\right)$$



instantaneous rate = $-\frac{dA}{dt}$

Rate of product

Change in concentration / pressure of products w.r.t time.

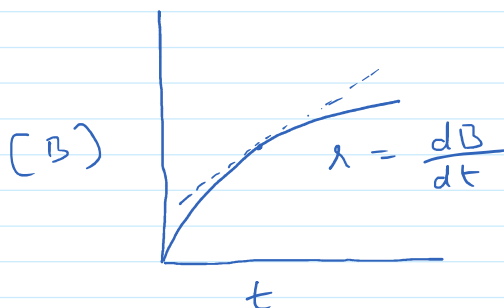


$$\Delta[B] = [B_2] - [B_1]$$

rate of product (average rate)

$$= \frac{\Delta[B]}{\Delta t}$$

$$= \frac{[B_2] - [B_1]}{\Delta t}$$



instantaneous rate = $\frac{dB}{dt}$

Rate of reaction

Rate of reaction is defined as rate of disappearance of reactants / rate of appearance of products divided by their respective stoichiometric coefficients.



$$\text{rate of reaction} = \frac{1}{a} \left(-\frac{dA}{dt} \right) = \frac{1}{b} \left(-\frac{dB}{dt} \right) = \frac{1}{c} \frac{dC}{dt} = \frac{1}{d} \frac{dD}{dt}$$

Average rate:

Rate expressed over a finite interval of time

Instantaneous rate

Rate expressed at a particular moment of time.

Example:



$$t=0 \quad a_0 \quad 0$$

$$t=t \quad a_0 - 2x \quad 3x$$

$$\begin{aligned} \text{rate of A} &= -\frac{dA}{dt} = -\frac{d(a_0 - 2x - a_0)}{dt} = -\frac{d(-2x)}{dt} \\ &= 2\frac{dx}{dt} \end{aligned}$$

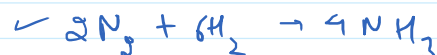
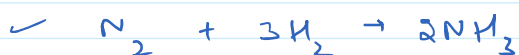
$$\frac{dx}{dt} = -\frac{1}{2} \frac{dA}{dt}$$

$$\text{rate of B} = \frac{dB}{dt} = \frac{d(3x - 0)}{dt} = \frac{d(3x)}{dt} = 3\frac{dx}{dt}$$

$$\frac{dx}{dt} = \frac{1}{3} \frac{dB}{dt}$$

$$\text{rate of reaction, } \frac{dx}{dt} = -\frac{1}{2} \frac{dA}{dt} = \frac{1}{3} \frac{dB}{dt}$$

→ To define rate of reaction, balanced chemical equation must be given.



Units of rate

$$\text{rate} = \frac{\text{change in concentration}}{\text{time}}$$

$$= \frac{\text{mol}}{\text{L s}}$$

in general concentration (time)⁻¹

for gases unit can also be pressure (time)⁻¹

eg: atm s⁻¹