



CHEMISTRY • CLASS 12

CHAPTER 3

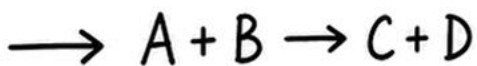
Chemical Kinetics

CHAPTER NOTES

CHEMICAL KINETICS: SCOPE & IMPORTANCE

WHAT DOES IT STUDY?

Chemical kinetics studies reaction rates, the factors affecting them and the pathways by which reactions occur.

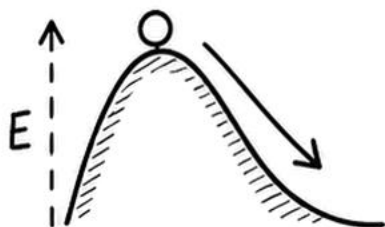


THERMODYNAMICS vs KINETICS

$\Delta G < 0 \longrightarrow$ thermodynamically feasible

Thermodynamics predicts feasibility and extent; it does not tell us how fast.

Kinetics tells the speed and mechanism.



vs



WHY IT MATTERS

A feasible reaction may still be extremely slow.

diamond $\longrightarrow$ graphite

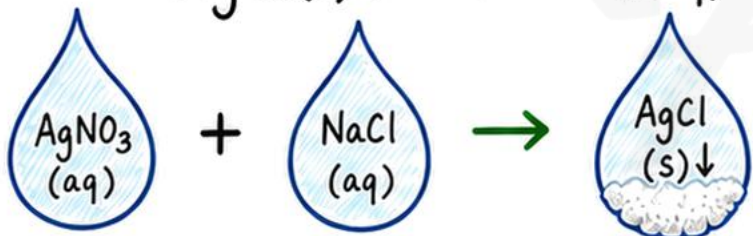
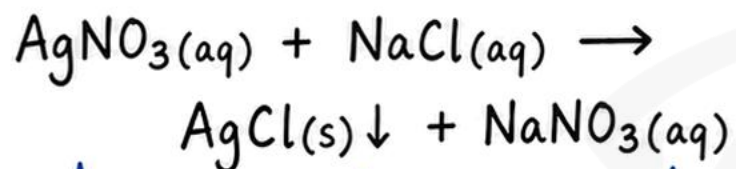
Thermodynamically favoured under ordinary conditions, but kinetically extremely slow.

NATURE OF RATE $\longrightarrow$ RATE LAW $\longrightarrow$ INTEGRATED LAWS $\longrightarrow$ TEMPERATURE & CATALYST $\longrightarrow$ COLLISION THEORY

REACTION RATE: FAST, SLOW & MODERATE PROCESSES

FAST / NEAR-INSTANTANEOUS

Ionic precipitation may occur as soon as solutions mix.



MODERATE

- Inversion of cane sugar
- Hydrolysis of starch



VERY SLOW

Rusting of iron needs air, moisture and a long time.

qualitative process:

iron + oxygen + water $\rightarrow$
rust (hydrated iron(III) oxide)



reaction time increases $\rightarrow$

Rate of reaction = change in concentration of a reactant or product per unit time.

$$\text{rate} \propto \frac{\text{concentration change}}{\text{time interval}}$$

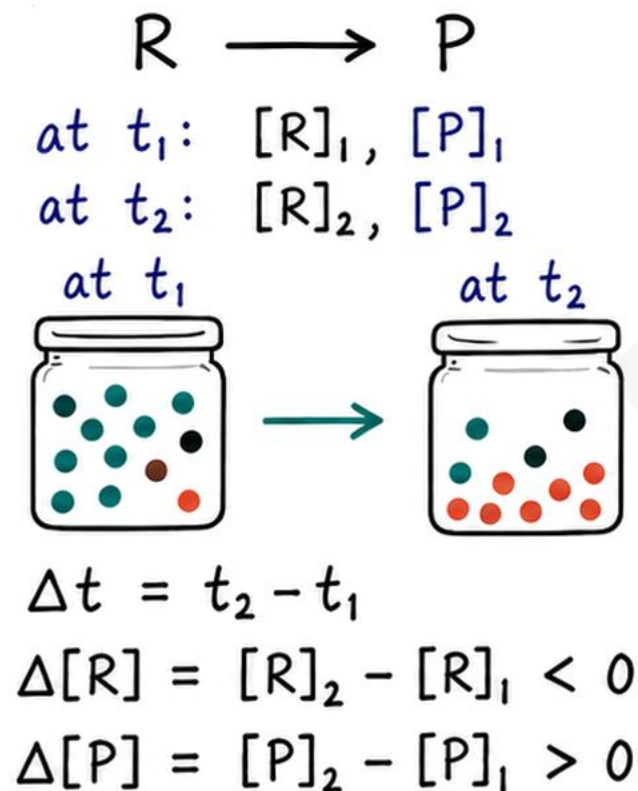
Analogy only:



$$\text{speed} = \frac{\text{distance change}}{\text{time}}$$

AVERAGE RATE: SIGN CONVENTION & UNITS

SET-UP



AVERAGE RATE

$$\text{rate of disappearance of } R = -\frac{\Delta[R]}{\Delta t}$$

$$\text{rate of appearance of } P = +\frac{\Delta[P]}{\Delta t}$$

$$r_{\text{avg}} = \frac{-\Delta[R]}{\Delta t} = +\frac{\Delta[P]}{\Delta t}$$

The minus sign converts the negative reactant concentration change into a positive reaction rate.

UNITS

$$[\text{rate}] = \text{concentration} \times \text{time}^{-1}$$

$$\text{mol L}^{-1} \text{s}^{-1}$$

when concentration
is molarity

$$\text{atm s}^{-1}$$

when a gas is
followed by
partial pressure

- Reactant decreases $\longrightarrow \Delta[R]$ is negative $\longrightarrow \frac{-\Delta[R]}{\Delta t}$ is positive.
- Product increases $\longrightarrow \Delta[P]$ is positive $\longrightarrow \frac{+\Delta[P]}{\Delta t}$ is positive.

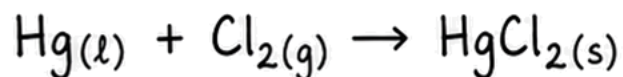
STOICHIOMETRIC RATE OF REACTION



$$r = -\left(\frac{1}{a}\right) \frac{d[A]}{dt} = -\left(\frac{1}{b}\right) \frac{d[B]}{dt} = +\left(\frac{1}{c}\right) \frac{d[C]}{dt} = +\left(\frac{1}{d}\right) \frac{d[D]}{dt}$$

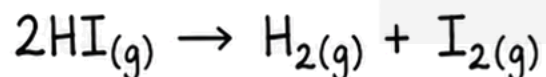
Divide each concentration-change rate by its stoichiometric coefficient so every expression describes the same reaction progress.

EQUAL COEFFICIENTS:



$$r = -\frac{d[\text{Hg}]}{dt} = -\frac{d[\text{Cl}_2]}{dt} = \frac{d[\text{HgCl}_2]}{dt}$$

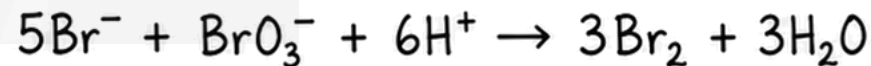
NORMALISE 2HI:



$$r = -\left(\frac{1}{2}\right) \frac{d[\text{HI}]}{dt} = \frac{d[\text{H}_2]}{dt} = \frac{d[\text{I}_2]}{dt}$$

HI disappears twice as fast.

UNEQUAL COEFFICIENTS:



$$\begin{aligned} r &= -\left(\frac{1}{5}\right) \frac{d[\text{Br}^-]}{dt} = -\frac{d[\text{BrO}_3^-]}{dt} = -\left(\frac{1}{6}\right) \frac{d[\text{H}^+]}{dt} \\ &= +\left(\frac{1}{3}\right) \frac{d[\text{Br}_2]}{dt} = +\left(\frac{1}{3}\right) \frac{d[\text{H}_2\text{O}]}{dt} \end{aligned}$$

For a gaseous reaction at constant temperature, rate may also be expressed using partial-pressure change.

rate unit example: atm s^{-1}



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