

how fast a reaction runs, and why: rate laws, integrated equations, collisions and the barrier a catalyst lowers

Rate of reaction

$$-\frac{d[A]}{dt}$$

how fast a reactant is consumed or a product forms, per unit time

→ measured as

Rate law

$$\text{rate} = k[A]^x[B]^y$$

found experimentally; x, y need NOT match the balanced equation's coefficients

→ measured as

Rate constant k

independent of concentration, depends on temperature via the Arrhenius equation

and back: from k at two temperatures you get the activation energy, the height of the barrier the rate law never shows

Rate of Reaction, General Form

for $aA + bB \rightarrow cC + dD$, all four expressions equal the same rate

$$\text{rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

average rate over an interval

$$\text{avg rate} = \frac{\Delta[A]}{\Delta t}$$

instantaneous rate is the SLOPE (tangent) of the concentration-vs-time curve at one instant, dc/dt ; average rate is the same slope taken between two finite points. Units of rate: $\text{mol dm}^{-3} \text{s}^{-1}$

Q. For $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$, N_2O_5 disappears at $0.02 \text{ mol dm}^{-3} \text{s}^{-1}$. Find the rate of formation of NO_2 and O_2 , and the overall rate of reaction.

$$\textcircled{1} \text{ rate} = -\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{4} \frac{d[\text{NO}_2]}{dt} = \frac{d[\text{O}_2]}{dt}$$

$$\textcircled{2} \text{ rate} = \frac{1}{2} \times 0.02 = 0.01 \text{ mol dm}^{-3} \text{s}^{-1}$$

$$\textcircled{3} \frac{d[\text{NO}_2]}{dt} = 4 \times \text{rate} = 0.04 \text{ mol dm}^{-3} \text{s}^{-1};$$

$$\frac{d[\text{O}_2]}{dt} = \text{rate} = 0.01 \text{ mol dm}^{-3} \text{s}^{-1}$$



N_2O_5 decomposes to NO_2 and O_2 in a 2:4:1 mole ratio, which sets the rate-expression coefficients

Answer

rate = 0.01, NO_2 forms at 0.04, O_2 at 0.01 $\text{mol dm}^{-3} \text{s}^{-1}$

Rate Law, Order and Molecularity *

- rate law $\text{rate} = k[A]^x[B]^y$ is found EXPERIMENTALLY, not from the balanced equation
- exponents x, y can be integers, zero, or even fractional
- order of reaction: x+y, the sum of exponents in the rate law
- order can be zero, fractional, or rarely higher than 3
- molecularity: reactant molecules colliding in ONE elementary step, always a small whole number
- it is a theoretical count, not an experimental one
- single elementary step: order and molecularity often equal
- multi-step reaction: usually unequal, rate law reflects only the RATE-DETERMINING step