

Kinetics

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Reaction Rates

For a given reaction $R \rightarrow P$ the **instantaneous rate of consumption** and the **instantaneous rate of formation** are both defined respectively in terms of derivatives below.

$$-\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

Therefor it follows that for a reaction $A + 2B \rightarrow 3C + D$ has rates:

$$\frac{d[D]}{dt} = \frac{1}{3} \frac{d[C]}{dt} = -\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt}$$

By introducing a parameter for **Extent of reaction** (ξ) the rate of reaction can be described with a single rate. For each species J in reaction, the change in amount of J dn_J is given by:

$$dn_J = v_J d\xi$$

where v_J is the stoichiometric number of the species, and negative for reactant species. From that the rate of reaction ν is defined as:

$$\nu = \frac{1}{V} \frac{d\xi}{dt}$$

where V is the volume of the system. For any species J in the system, since $d\xi = dn_J/v_J$ its rate is given by:

$$\nu = \frac{1}{v_J} \times \frac{1}{V} \frac{dn_J}{dt}$$

In the case of a homogenous constant volume reaction the volume is taken into the derivative giving $\frac{d[J]}{dt}$

Rate Laws

Rates of reaction are often proportional to the concentrations of the reactants raised to a power times a proportionality constant. An experimentally determined equation of this kind is the **Rate Law**. Many reaction have rate laws of the form $\nu = k_r[A]^a[B]^b$ where a and b are the orders. The sum of the orders of the individual reactants is the **overall order**. Rate laws must be determined with experimental data.