



# Order of reaction and half-life

## RATE EXPRESSIONS

The rate of reaction between two reactants, A and B, can be followed experimentally. The rate will be found to be proportional to the concentration of A raised to some power and also to the concentration of B raised to a power. If square brackets are used to denote concentration this can be written as  $\text{rate} \propto [A]^x$  and  $\text{rate} \propto [B]^y$ . They can be combined to give the rate expression:

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

where  $k$  is the constant of proportionality and is known as the **rate constant**.

$x$  is known as the **order of the reaction** with respect to A.

$y$  is known as the order of the reaction with respect to B.

The overall order of the reaction =  $x + y$ .

Note: the order of the reaction and the rate expression can only be determined experimentally. They cannot be deduced from the balanced equation for the reaction.

## UNITS OF RATE CONSTANT

The units of the rate constant depend on the overall order of the reaction.

**First order:**  $\text{rate} = k[A]$

$$k = \frac{\text{rate}}{[A]} = \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{\text{mol dm}^{-3}} = \text{s}^{-1}$$

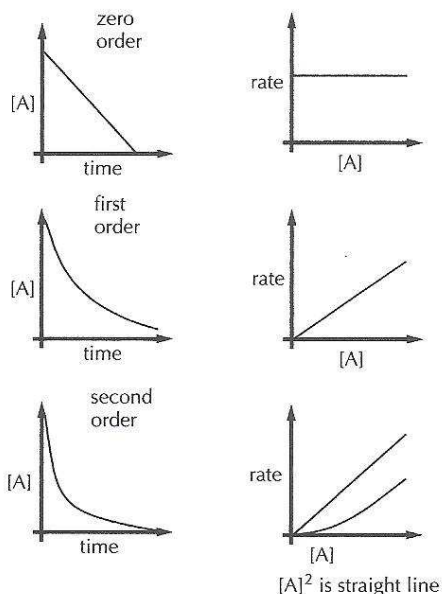
**Second order:**  $\text{rate} = k[A]^2$  or  $k = [A][B]$

$$k = \frac{\text{rate}}{[A]^2} = \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{(\text{mol dm}^{-3})^2} = \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

**Third order:**  $\text{rate} = k[A]^2[B]$  or  $\text{rate} = k[A][B]^2$

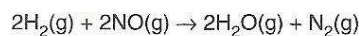
$$k = \frac{\text{rate}}{[A]^2[B]} = \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{(\text{mol dm}^{-3})^3} = \text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

## GRAPHICAL REPRESENTATIONS OF REACTIONS



## DERIVING A RATE EXPRESSION BY INSPECTION OF DATA

Experimental data obtained from the reaction between hydrogen and nitrogen monoxide at 1073 K:



Experiment	Initial concentration of $\text{H}_2(\text{g})$ / $\text{mol dm}^{-3}$	Initial concentration of $\text{NO}(\text{g})$ / $\text{mol dm}^{-3}$	Initial rate of formation of $\text{N}_2(\text{g})$ / $\text{mol dm}^{-3} \text{ s}^{-1}$
1	$1 \times 10^{-3}$	$6 \times 10^{-3}$	$3 \times 10^{-3}$
2	$2 \times 10^{-3}$	$6 \times 10^{-3}$	$6 \times 10^{-3}$
3	$6 \times 10^{-3}$	$1 \times 10^{-3}$	$0.5 \times 10^{-3}$
4	$6 \times 10^{-3}$	$2 \times 10^{-3}$	$2.0 \times 10^{-3}$

From experiments 1 and 2 doubling  $[\text{H}_2]$  doubles the rate so  $\text{rate} \propto [\text{H}_2]$ .

From experiments 3 and 4 doubling  $[\text{NO}]$  quadruples the rate so  $\text{rate} \propto [\text{NO}]^2$ .

Rate expression given by  $\text{rate} = k[\text{H}_2][\text{NO}]^2$ .

The rate is first order with respect to hydrogen, second order with respect to nitrogen monoxide, and third order overall. The value of  $k$  can be found by substituting the values from any one of the four experiments:

$$k = \frac{\text{rate}}{[\text{H}_2][\text{NO}]^2} = 8.33 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

## HALF-LIFE $t_{1/2}$

For a first order reaction the rate of change of concentration of A is equal to  $k[A]$ . This can be expressed as  $\frac{d[A]}{dt} = k[A]$ .

If this expression is integrated then  $kt = \ln [A]_0 - \ln [A]$  where  $[A]_0$  is the initial concentration and  $[A]$  is the concentration at time  $t$ . This expression is known as the integrated form of the rate equation.

The half-life is defined as the time taken for the concentration of a reactant to fall to half of its initial value.

At  $t_{1/2}$   $[A] = \frac{1}{2}[A]_0$  the integrated rate expression then becomes  $kt_{1/2} = \ln [A]_0 - \ln \frac{1}{2}[A]_0 = \ln 2$  since  $\ln 2 = 0.693$  this simplifies to  $t_{1/2} = \frac{0.693}{k}$

From this expression it can be seen that the half-life of a first order reaction is independent of the original concentration of A, i.e. first order reactions have a constant half-life.

