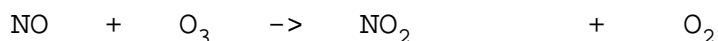# KINETICS

The rate of a reaction depends on the frequency of the collisions between the reacting particles. The rate therefore depends on the concentration of the reactants.

Reaction Order

Example 1

NO   + O_3 -> NO_2 + O_2

This reaction occurs in one step. Its rate depends on the frequency of collisions between NO and O_3 and is therefore proportional to the concentration of NO and O_3.

rate $\propto$ $[NO][O_3]$

$\Rightarrow$ rate = k $[NO][O_3]$ where k = **rate constant**

$\Rightarrow$ rate = k $[NO]^1[O_3]^1$ where the indices (1) are known as
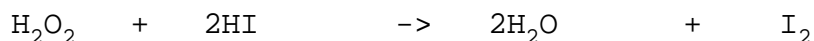   the '**orders**'

This reaction is first order with respect to NO and first order with respect to O_3.

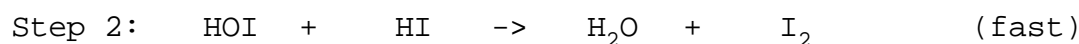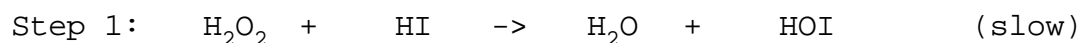The overall order of the reaction is the sum of the indices. The above reaction is therefore second order (1+1).

Example 2

The reaction in example 1 occurred in one step.

Most reactions, however, occur in a series of steps e.g.

H_2O_2 +   2HI   -> $2H_2O$ + I_2

Experiments show that this reaction occurs in two steps:

Step 1: H_2O_2 +   HI   -> H_2O +   HOI   (slow)

Step 2:   HOI +   HI   -> H_2O + I_2 (fast)

Step 2 cannot occur until the HOI from step 1 becomes available. The slow step therefore controls the rate of the whole reaction and is known as the **rate determining step**. The rate of the overall reaction is therefore the rate of step 1:

rate = k $[H_2O_2][HI]$

The following experimental results confirm the above rate equation:

Exp.	Initial $[H_2O_2]$ mol l^{-1}	Initial [HI] mol l^{-1}	Initial rate of formation of I_2 mol l^{-1} s^{-1}
1	4×10^{-5}	2×10^{-5}	1.4×10^{-10}
2	8×10^{-5}	2×10^{-5}	2.8×10^{-10}
3	4×10^{-5}	4×10^{-5}	2.8×10^{-10}

Compare Exps.1 and 2:

If we double $[H_2O_2]$ the rate is also doubled.

Compare Exps.1 and 3:

If we double [HI] the rate is also doubled.

i.e. rate $=$ k $[H_2O_2]$[HI]

Problem

Find k for the above reaction.

Using the results from Exp.1,

$$k = \frac{rate}{[H_2O_2][HI]}$$

$$= \frac{1.4 \times 10^{-10}}{[4 \times 10^{-5}][2 \times 10^{-5}]} \qquad \frac{\{mol\ l^{-1}\ s^{-1}\}}{\{mol\ l^{-1}\}\{mol\ l^{-1}\}}$$

$$= \underline{0.175\ mol^{-1}\ l\ s^{-1}}$$

Example 3

2HI   -> H_2 + I_2

Experiment	Initial [HI] mol l^{-1}	Initial rate of formation of H_2 mol l^{-1} s^{-1}
1	1×10^{-4}	4.5×10^{-10}
2	2×10^{-4}	18.0×10^{-10}
3	3×10^{-4}	40.5×10^{-10}

If we double [HI] the rate increases four times.

If we triple [HI] the rate increases nine times.

i.e. rate $=$ k [HI]^2

This reaction therefore occurs in one step. It is second order with respect to HI and second order overall.

Problem

Find k for the above reaction.   [Ans $= 0.045\ mol^{-1}\ l\ s^{-1}$]
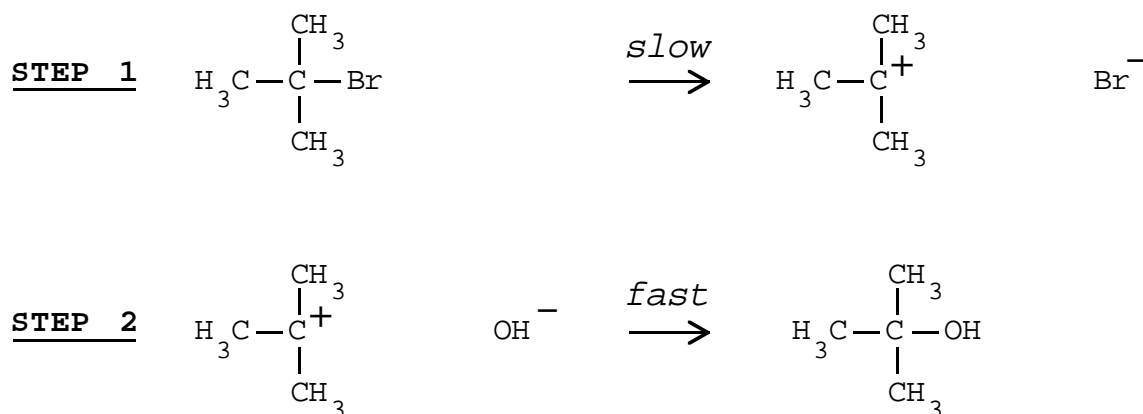
Example 4

The reaction:

$(CH_3)_3CBr$ + OH^- -> $(CH_3)_3COH$ + Br^-

is found, by experiment, to follow the rate equation:

rate = $k[(CH_3)_3CBr]$

The rate does **NOT** depend on the concentration of OH^- !

The reason becomes clear when we consider the mechanism:

STEP 1

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br \xrightarrow{\ slow\ } H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{}^+ \qquad Br^-$$

STEP 2

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{}^+ \qquad OH^- \xrightarrow{\ fast\ } H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$

Step 1 is the rate determining step. It does not involve the hydroxide ion. The rate of step 1,

rate = $k[(CH_3)_3CBr]$,

is therefore the rate of the overall reaction.

N.B. Experimentally determined rate equations can provide evidence for a proposed reaction mechanism but cannot provide proof as other possible reaction mechanisms may also give the same rate equation.