Topic 1 – Kinetics
Revision Notes

1)   Introduction

- Kinetics is the study of reaction rates
- Rate of reaction is defined as the rate of change of concentration of reactants or products (usual units are mol dm^{-3} s^{-1})

2)   Rate equations

- A chemical reaction has a symbol equation e.g. **A + B → C**
- The reaction also has a rate equation, which **cannot** be worked out from the symbol equation. The rate equation can only be determined by experiment
- An example of a rate equation is:

$$\textbf{Rate = k[A]}^2 \qquad \text{where} \quad k = \text{rate constant,}$$
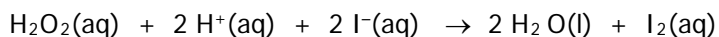$$[A] = \text{concentration of A in mol dm}^{-3}$$

- An order of reaction is defined as the power of a reactant's concentration in the rate equation. In the above example, the order with respect to A is 2
- The overall order of reaction is the sum of the powers of concentration terms in the rate equation
- The rate constant is the constant of proportionality, k, in the rate equation

3)   Deducing the order and constructing the rate equation and

- The initial rate is the rate at the start of the reaction
- Initial rates can be used to determine the order with respect to a reactant
- The order can only be 0, 1 or 2 (for reactions studied at A level)
- If the order is 0, changing the concentration has no effect on the rate
- If the order is 1, doubling the concentration doubles the initial rate
- If the order is 2, doubling the concentration increases the initial rate by a factor of 4
- Once the orders have been determined, the rate equation can be written
- Re-arranging the rate equation and substituting experimental values allows the rate constant to be calculated
- The units for the rate constant can be determined by substituting and cancelling
- There is a worked example on the next page

Example

When hydrogen peroxide solution reacts with iodide ions in aqueous acid, iodine is liberated.

$$H_2O_2(aq) \ + \ 2\,H^+(aq) \ + \ 2\,I^-(aq) \ \rightarrow \ 2\,H_2O(l) \ + \ I_2(aq)$$

The following table gives some experimental results for the reaction.

Experiment	Initial concentration (mol dm^{-3})			Initial reaction rate (mol dm^{-3} s^{-1})
	$[H_2O_2]$	$[I^-]$	$[H^+]$	
1	0.010	0.010	0.10	1.75 x 10^{-6}
2	0.020	0.010	0.10	3.50 x 10^{-6}
3	0.030	0.010	0.10	5.25 x 10^{-6}
4	0.030	0.020	0.10	1.05 x 10^{-5}
5	0.030	0.020	0.20	1.05 x 10^{-5}

a) Experiments 1 and 2 can be used to determine the order with respect to $H_2O_2(aq)$ as $[I^-]$ and $[H^+]$ are unchanged

   Doubling the concentration (0.010 to 0.020) doubles the rate (1.75 x 10^{-6} to 3.50 x 10^{-6}). Order is 1 with respect to H_2O_2

b) Experiments 3 and 4 can be used to determine the order with respect to I^- as $[H_2O_2]$ and $[H^+]$ are unchanged

   Doubling the concentration (0.010 to 0.020) doubles the rate (5.25 x 10^{-6} to 1.05 x 10^{-5}). Order is 1 with respect to I^-

c) Experiments 4 and 5 can be used to determine the order with respect to H^+ as $[H_2O_2]$ and $[I^-]$ are unchanged

   Doubling the concentration (0.10 to 0.20) has no effect on the rate (1.05 x 10^{-5} to 1.05 x 10^{-5}). Order is 0 with respect to H^+

d) The overall order is 2 (1 + 1 + 0)

e) The rate equation for the reaction is: **Rate = k[H$_2$O$_2$][I$^-$]**

f) The rate constant can be calculated using the values from any of the experiments. Using the figures from experiment 1:
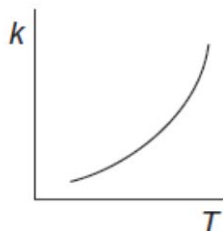
   k = rate/($[H_2O_2][I^-]$)
       = 1.75 x 10^{-6}/(0.010 x 0.010)
       = 0.0175

   units for k: = mol dm^{-3} s^{-1}/(mol dm^{-3} x mol dm^{-3})
              = mol^{-1} dm^3 s^{-1}

4) <u>Effect of temperature on the rate constant</u>

- As temperature increases, the value of k increases (so the reaction rate increases)
- The converse applies to reducing the temperature

5) <u>The rate-determining step</u>

- Most reactions proceed via a series of steps e.g. in the example used above the steps are:

    - $H_2O_2 + I^- \rightarrow H_2O + IO^-$ (slow)

    - $H^+ + IO^- \rightarrow HIO$ (fast)

    - $HIO + H^+ + I^- \rightarrow I_2 + H_2O$ (fast)

- The rate-determining step is the slowest of these steps i.e. the first one in our example
- The reactants in the rate-determining step give the species and orders in the rate equation
- In the example: **Rate = k[H_2O_2][I⁻]**