

## Topic 2 – How fast? Revision Notes

### 1) Introduction

- A chemical reaction has a symbol equation e.g.  $A + B \rightarrow C$
- 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:

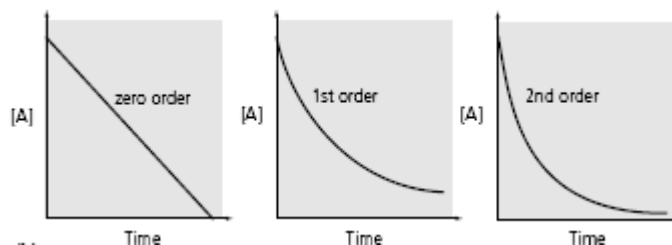
$$\text{Rate} = k[A]^2 \quad \text{where } k = \text{rate constant,}$$

$[A] = \text{concentration of A in mol dm}^{-3}$   
order with respect to A is 2

- Rate is measured in  $\text{mol dm}^{-3} \text{ s}^{-1}$
- The definitions sheet for this module explains the terms: rate of reaction, order, rate constant, half-life and rate-determining step
- The study of reaction rates is sometimes called kinetics

### 2) Concentration-time graphs

- Recall that the concentration of a reactant decreases as the reaction proceeds and the concentration of a product increases as the reaction proceeds
- A concentration time graph can be used to deduce the rate of a reaction at any particular instant. The graph can also be used to deduce the half-life of a reaction (the time taken for the concentration to halve)
- To determine the rate at a particular time, draw a tangent to the curve at the appropriate point and then find the gradient of the tangent (y-difference/x-difference)
- To determine half-lives, use the graph to work out the time taken for the concentration to fall to half of its initial value e.g. 1.0 to 0.5  $\text{mol dm}^{-3}$ .
- The half-lives of a first-order reaction are the same. Three values are needed to show that the half-life is constant e.g. 0.8 to 0.4  $\text{mol dm}^{-3}$ , 0.6 to 0.3  $\text{mol dm}^{-3}$  and 0.4 to 0.2  $\text{mol dm}^{-3}$ . The half-lives may not be identical but will be close enough to say that they are constant e.g. 52s, 49s and 50s
- The shape of the graph for a zero order reaction is different from the other two, so a zero order reaction could be picked out from the shape of the concentration-time graph

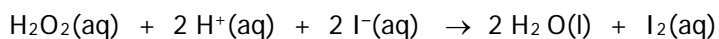


### 3) Deducing the order, constructing the rate equation and calculating the rate constant

- 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
- This procedure is best illustrated using an example

#### Example

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



The following table gives some experimental results for the reaction.

Experiment	Initial concentration (mol dm <sup>-3</sup> )			Initial reaction rate (mol dm <sup>-3</sup> s <sup>-1</sup> )
	[H <sub>2</sub> O <sub>2</sub> ]	[I <sup>-</sup> ]	[H <sup>+</sup> ]	
1	0.010	0.010	0.10	1.75 x 10 <sup>-6</sup>
2	0.020	0.010	0.10	3.50 x 10 <sup>-6</sup>
3	0.030	0.010	0.10	5.25 x 10 <sup>-6</sup>
4	0.030	0.020	0.10	1.05 x 10 <sup>-5</sup>
5	0.030	0.020	0.20	1.05 x 10 <sup>-5</sup>

- a) Experiments 1 and 2 can be used to determine the order with respect to H<sub>2</sub>O<sub>2</sub>(aq) as [I<sup>-</sup>] and [H<sup>+</sup>] are unchanged

Doubling the concentration (0.010 to 0.020) doubles the rate (1.75 x 10<sup>-6</sup> to 3.50 x 10<sup>-6</sup>). Order is 1 with respect to H<sub>2</sub>O<sub>2</sub>

- b) Experiments 3 and 4 can be used to determine the order with respect to I<sup>-</sup> as [H<sub>2</sub>O<sub>2</sub>] and [H<sup>+</sup>] are unchanged

Doubling the concentration (0.010 to 0.020) doubles the rate (5.25 x 10<sup>-6</sup> to 1.05 x 10<sup>-5</sup>). Order is 1 with respect to I<sup>-</sup>

- c) Experiments 4 and 5 can be used to determine the order with respect to H<sup>+</sup> as [H<sub>2</sub>O<sub>2</sub>] and [I<sup>-</sup>] are unchanged

Doubling the concentration (0.10 to 0.20) has no effect on the rate (1.05 x 10<sup>-5</sup> to 1.05 x 10<sup>-5</sup>). Order is 0 with respect to H<sup>+</sup>

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

e) The rate equation for the reaction is: **Rate = k[H<sub>2</sub>O<sub>2</sub>][I<sup>-</sup>]**

f) The rate constant can be calculated using the values from any of the experiments. Using the figures from experiment 1:

$$\begin{aligned}k &= \text{rate}/([\text{H}_2\text{O}_2][\text{I}^-]) \\ &= 1.75 \times 10^{-6}/(0.010 \times 0.010) \\ &= 0.0175\end{aligned}$$

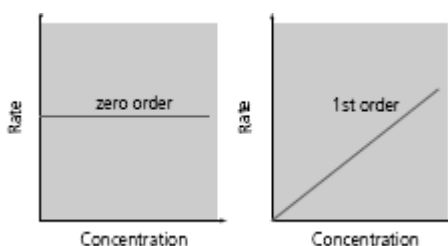
units:

$$\begin{aligned}&= \text{mol dm}^{-3} \text{ s}^{-1}/(\text{mol dm}^{-3} \times \text{mol dm}^{-3}) \\ &= \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}\end{aligned}$$

Source: <http://www.chemsheets.co.uk/>

#### 4) Rate-concentration graphs

- Orders can also be deduced from rate-concentration graphs
- If the graph is a horizontal line, rate is unaffected by changing concentration so the order is 0
- If the graph is a sloping straight line through the origin, rate is directly proportional to concentration so the order is 1
- If the graph is a curve the order is 2 (as far as we are concerned)



#### 5) Effect of temperature on the rate constant

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

#### 6) The rate-determining step

- Most reactions proceed via a series of steps e.g. in the example used above the steps are:
  - $\text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{H}_2\text{O} + \text{IO}^-$  (slow)
  - $\text{H}^+ + \text{IO}^- \rightarrow \text{HIO}$  (fast)
  - $\text{HIO} + \text{H}^+ + \text{I}^- \rightarrow \text{I}_2 + \text{H}_2\text{O}$  (fast)
- The rate-determining step is the slowest of these steps i.e. the first one in our example

- The rate equation can be predicted if the rate-determining step is known. In the example, a molecule of  $\text{H}_2\text{O}_2$  needs to collide with an iodide ion. The rate equation can be expected to be:  $\text{Rate} = k[\text{H}_2\text{O}_2][\text{I}^-]$ . This matches the answer found from the experimental results
- This can be done in reverse i.e. a rate equation can be used to propose a rate-determining step

## 7) Summary of Methods for working out an order of reaction

### a) Zero order

- Concentration-time graph is descending straight line
- Rate-concentration graph is horizontal straight line
- Doubling concentration has no effect on rate (from table of concentrations and rates)

### b) First order

- Concentration-time graph shows equal half-lives (at least two, preferably three)
- Rate-concentration graph is sloping straight line through origin
- Doubling concentration doubles rate (from table of concentrations and rates)

### c) Second order

- Rate-concentration graph is a curve
- Doubling concentration quadruples rate (from table of concentrations and rates)

### d) Graphical method

- Plot  $\log(1/\text{time})$  against  $\log(\text{concentration})$  or  $\log(\text{volume})$
- Draw straight line of best fit
- Gradient gives order (y-difference over x-difference)