Chem Factsheet

January 2003 Number 44

Rate Expression Orders and Experimental Procedures

To succeed with this topic you need to:
- ensure you are fully competent in writing rate expressions from the experimental data provided (Factsheet No.43 (Kinetics II)).

After working through this Factsheet you will be able to:
- recognise which experimental techniques are available to provide 'initial rate' data for rates of reactions;
- know how particular graph plots provide information about orders of reactions;
- use the data from first order reactions to find half-lives.

You need to know three experimental methods for measuring rates
1. Gas syringe - for reactions involving gases
2. Colorimetry - for reactions involving a colour change
3. Sampling methods

Exam Hint : - *To be able to answer questions in the examination and experimental procedures you need to be able to do the following things:*
*(1) use **state symbols** from the chemical equation provided*
*(2) use your own knowledge from your laboratory work about some chemicals (**colours** particularly)*
(3) remember the procedures that are given below

Experimental methods for rates of reactions

1. Reactions producing gases

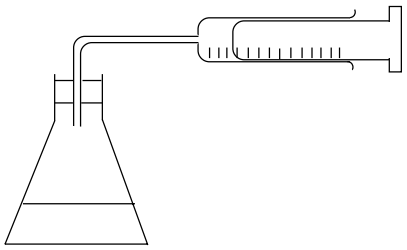
Examples are:

$CaCO_3(aq) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$

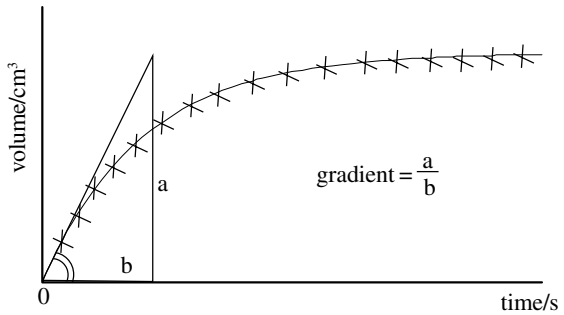
$2H_2O_2\ (aq) \rightarrow 2H_2O(l) + O_2(g)$

$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

Equipment – gas syringe
Volume of gas collected in the syringe is measured at set time intervals



Graph produced
The gradient at zero time is the initial rate



2. Reactions where there is a colour change

Examples are,

$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$

(the purple colour of potassium manganate (VII) disappears to form a colourless solution)

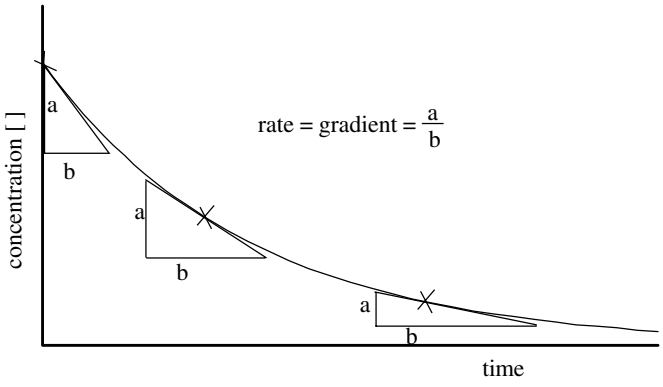
$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_2I\ COCH_3(aq) + HI(aq)$

(the brown/orange colour of iodine solution disappears to form a colourless solution)

Equipment – colorimeter which gives a reading of the light intensity of the solution as it changes.

The readings are taken at set times or connected to a data logger or computer which plots the graph.

Graph produced



Tangents are taken and gradients measured to produce **rates** at **various concentrations** (see later)

3. Sampling techniques using titrations
The first two methods involve starting the reaction and taking readings as the reaction proceeds.

This method involves:
(a) starting the reaction mixture
(b) at fixed times removing a fixed volume of the mixture
(c) stopping the samples from reacting any further by putting them into a liquid that 'quenches' or 'freezes' the reaction
(d) titrating the samples and calculating the concentration of the substance

Examples are:
$CH_3CO_2CH_3(aq) + NaOH(aq) \rightarrow CH_3CO_2Na(aq) + CH_3OH(aq)$

(NaOH concentration found by titrating with HCl (aq))

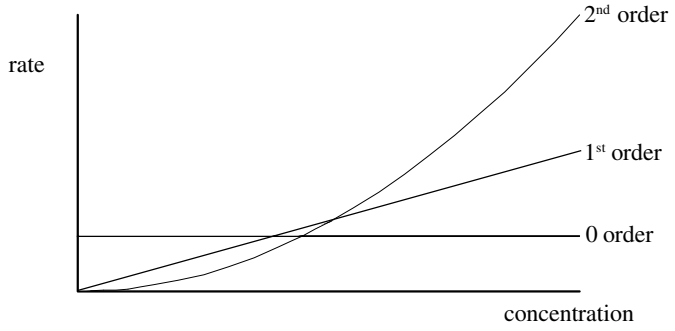
$CH_3COCH_3\ (aq) + I_2(aq) \rightarrow CH_2ICOCH_3(aq) + HI(aq))$

(I_2 concentration found by titrating with sodium thiosulphate solution, $Na_2S_2O_3(aq)$)

This method is sometimes called **'batch sampling'**.

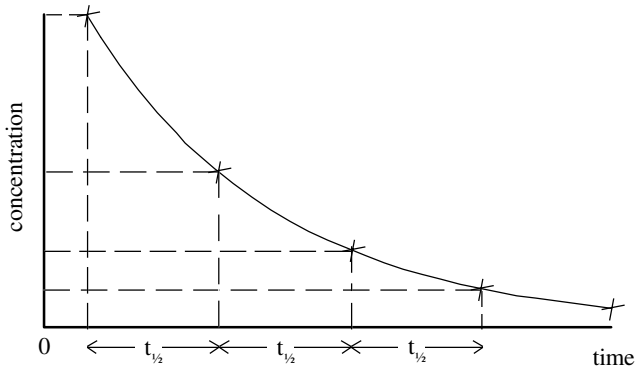
The graph produced will look the same as for Method (2) and the tangents/ gradients found in the same way.

Graphs and orders
A plot of **concentration** against **rate** from any of the results of the experiment procedures above (finding **gradients** which are the **rates**), enables you to find the **order** – as shown below



First order reations and half life ($t_{½}$)
First order reactions are **exponential** when you plot **concentration** against **time**.

This means when the **concentration drops by half** the time taken **every time** for this is the **same** i.e. the half life, $t_{½}$



Exam Hint : - *Questions on 1st order/$t_{½}$ fall into two categories:*
(1) "Show this reaction is 1st order by plotting the results below" *(**Method** – plot concentration against time. **Show** that $t_{½}$ are the **same** so must therefore be 1st order).*

(2) "What is the half life for this reaction?" *(**Method** – plot graph and find $t_{½}$ by method of concentrations going down by half)*

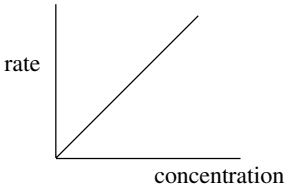
Questions

1. What experimental method(s) could be used to follow the rate of reaction of each of the following reactions? (More than one method may apply to each reaction).
   (a) $CH_3CO_2CH_3\ (aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + CH_3COH(aq)$
   (b) $CH_3Br(aq) + NaOH(aq) \rightarrow CH_3OH(aq) + NaBr(aq)$
   (c) $Zn(s) + 2HNO_3(aq) \rightarrow Zn(NO_3)_2(aq) + H_2(g)$
   (d) $IO_4^-(aq) + 7I^-(aq) + 8H^+(aq) \rightarrow 4I_2(aq) + 4H_2O(l)$
2. Show by graph plot that the following data for a reaction is 1st order.

initial rate / mol $dm^{-3}s^{-1}$	concentration / mol dm^{-3}
3.6×10^{-2}	0.5
7.3×10^{-2}	1.0
14.8×10^{-2}	2.0
22.9×10^{-2}	3.0

Answers

1. (a) 'Quenching' and titrating the CH_3CO_2H with alkali (NaOH
   (b) 'Quenching' and titrating the NAOH with acid (HCl)
   (c) 'Quenching' and titrating the HNO_3 with alkali (NaOH) **OR** collecting H_2 in a gas syringe
   (d) (i) 'Quench' - titrate H^+ with alkali (NaOH)
   (ii) 'Quench' - titrate I_2 with sodium thiosulphate
   (iii) Colorimeter – measure intensity of light as colour changes to orange / brown due to formation of I_2
2. Plot should show that it is of this form.



Acknowledgements:
This Factsheet was researched and written by Sam Goodman
Curriculum Press, Unit 305B, The Big Peg, 120 Vyse Street, Birmingham, B18 6NF