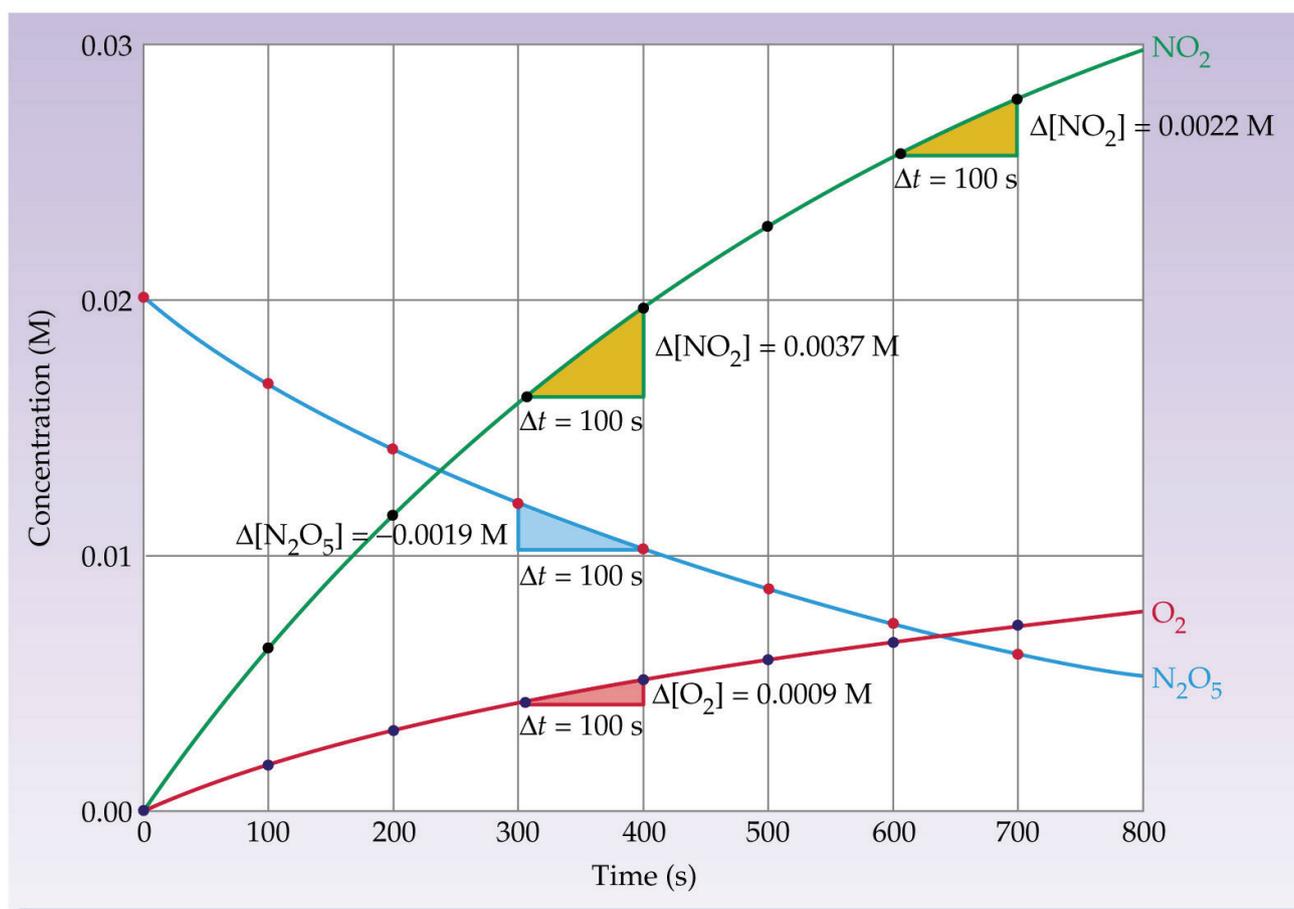


# Unit 2 - Physical Chemistry

## *KINETICS*



*Pupil Notes*

*Learning Outcomes*

*Questions & Answers*

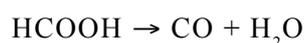


## KINETICS

Chemical kinetics is the study of the speed of chemical reactions. From Standard Grade, Intermediate and Higher Chemistry it is already known that the speed or rate of a chemical reaction depends on factors such as temperature, concentration of the reactants, particle size and whether a catalyst is present or not. It is also known that all reactions have an activation energy and that an activated complex is formed.

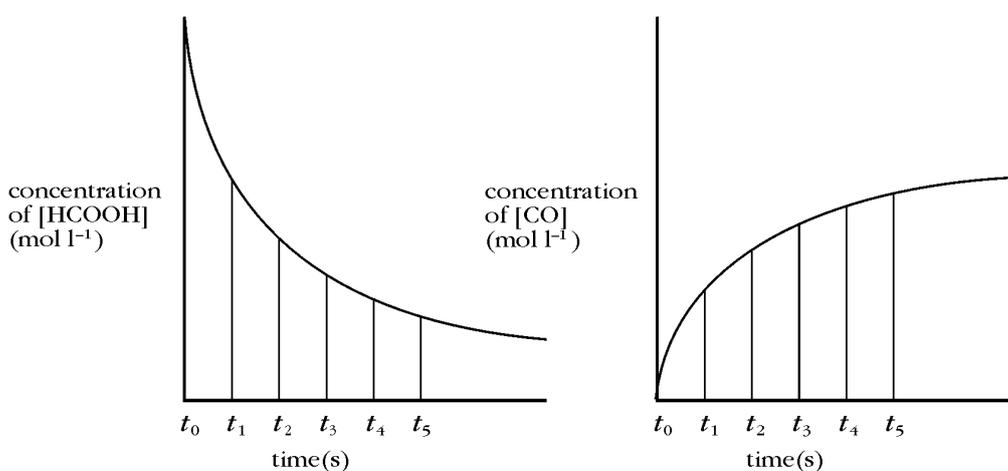
In this section, we are now concerned with the development of these ideas on a more quantitative basis, in which mathematical models are used to state precisely how the concentration of reactants influences the speed of a chemical reaction. We are also interested in how such information can be used to gain an insight into the pathway by which the reaction takes place.

It is customary when dealing with reaction rates to express the rate as a change in concentration of reactant or product in unit time. Expressed in this way, the rate is independent of the size of the sample under consideration. For example, in the decomposition of methanoic acid:



we can determine the reaction rate by following either the decrease in concentration of the acid or the increase in carbon monoxide concentration with time (Figure 25).

**Figure 25**



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The average reaction rate is the change in concentration of either reactants or products divided by the elapsed time. For example, over the time interval  $t_1$  to  $t_2$ :

$$\text{average reaction rate} = \frac{([\text{HCOOH}]_2 - [\text{HCOOH}]_1)}{(t_2 - t_1)}$$

or

$$\text{average reaction rate} = \frac{+([\text{CO}]_2 - [\text{CO}]_1)}{(t_2 - t_1)}$$

(Note that the negative sign is used if we are dealing with reactant concentrations since their concentrations decrease with time.)

It should be clear from the graphs in Figure 25 that, as is the case with most reactions, the rate decreases as the reaction proceeds.

We need to make the elapsed time interval as short as possible, and in effect measure the instantaneous rate, i.e. as  $\Delta t$  approaches zero.

We can write, for a very small time interval,  $dt$ , that the instantaneous rate is:

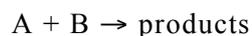
$$\frac{-d[\text{HCOOH}]}{dt} \quad \text{or} \quad \frac{+d[\text{CO}]}{dt}$$

Thus, the rate, at any particular time  $t$ , is given by the gradient of the tangent to the curve at time  $t$ . This will have a maximum value at time  $t = 0$  and it is therefore usual to determine initial rates of reaction and to use these values in the determination of other kinetic parameters.

### Reaction rates and concentration

The qualitative dependence of reaction rate on concentration can be readily demonstrated using a large number of reactions, e.g. the iodine clock reaction, or by measuring the volume of hydrogen produced when magnesium reacts with different concentrations of dilute hydrochloric acid.

If we consider a very simple reaction:



the rate of the forward reaction at any time depends on the concentration of A and B at that time and can be expressed as follows:

$$\begin{aligned} \text{rate} &\propto [A][B] \\ \text{rate} &= k[A][B] \\ \text{where } k &\text{ is the rate constant.} \end{aligned}$$

In more general terms, for a simple reaction:



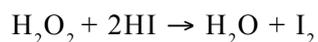
This equation is the rate law.

The quantities  $n$  and  $m$  are termed the orders with respect to the reactants A and B respectively. The overall order of reaction is given as the sum of the powers of the concentration terms that occur in the rate equation, i.e. in the above example the overall order is  $n + m$ . In simple reactions, the rate law, sometimes called the rate equation, can take one of the forms shown in Table 6.

**Table 6**

Rate law	Order of reaction
rate $\propto [A]^0$	0
rate $\propto [A]^1$	1
rate $\propto [A]^2$	2
rate $\propto [A]^1[B]^1$	2
rate $\propto [A]^1[B]^2$	3

These small integral values for the order of reaction are readily understandable if we realise that they refer to the actual number of particles involved in the single step of the reaction that controls the overall reaction rate, i.e. the rate-determining step. This is not necessarily the number of particles involved in the stoichiometric equation. For example, consider the reaction of hydrogen peroxide with hydrogen iodide:



The experimentally observed rate law is:

$$\text{rate} \propto [\text{H}_2\text{O}_2][\text{HI}]$$

and consequently the order of reaction is two, whereas the balanced equation

## KINETICS

has three reactant molecules. The order of reaction is entirely an experimental quantity that is determined solely by finding the rate equation that best fits the experimental data. It cannot be deduced from an examination of the chemical equation for the reaction.

### Determining rate constants and orders of reaction

The rate constant of a reaction can be determined from a series of experiments in which the initial concentrations of the reactants are changed. The initial rate of each reaction is calculated and comparisons made. The following two examples illustrate this experimental rate method.

#### *Example 13*

Consider the following data for an imaginary reaction:



and calculate the rate constant for this reaction.

Experiment	[A] (mol l <sup>-1</sup> )	[B] (mol l <sup>-1</sup> )	[C] (mol l <sup>-1</sup> )	Initial rate of D formed (mol l <sup>-1</sup> s <sup>-1</sup> )
1	1.0	1.0	1.0	20
2	2.0	1.0	1.0	40
3	1.0	2.0	1.0	20
4	1.0	1.0	2.0	80

From these results we can see that:

- (a) doubling [A] doubles the rate (compare 1 and 2)
- (b) doubling [B] has no effect on rate (compare 1 and 3)
- (c) doubling [C] increases the rate fourfold (compare 1 and 4).

Relating the effect of change in concentration of reactants to the rate of reaction, the experimental rate law becomes:

$$\text{rate} \propto [A][B]^0[C]^2$$

or, more simply:

$$\text{rate} \propto [A][C]^2$$

The reaction is first order with respect to A, second order with respect to C and zero order with respect to B. The overall order is  $(1 + 2 + 0) = 3$ .

The rate constant,  $k$ , for this reaction is obtained by substituting values from experiment 1 in the rate equation:

$$\begin{aligned} \text{rate} &= k[\text{A}][\text{C}]^2 \\ 20 &= k[1.0][1.0] \\ k &= 20 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-2} \end{aligned}$$

Identical values are obtained using any of the other three sets of results.

#### Example 14

Calculate the rate constant for the reaction between nitrogen monoxide and oxygen:



Experiment	Initial concentrations (mol l <sup>-1</sup> )		Initial rate of NO <sub>2</sub> formed (mol l <sup>-1</sup> s <sup>-1</sup> )
	[NO]	[O <sub>2</sub> ]	
1	2.0 × 10 <sup>-5</sup>	4.0 × 10 <sup>-5</sup>	1.4 × 10 <sup>-10</sup>
2	2.0 × 10 <sup>-5</sup>	8.0 × 10 <sup>-5</sup>	2.8 × 10 <sup>-10</sup>
3	4.0 × 10 <sup>-5</sup>	4.0 × 10 <sup>-5</sup>	5.6 × 10 <sup>-10</sup>

Inspection of the data shows that:

- (a) doubling [O<sub>2</sub>] doubles the rate (compare 1 and 2)
- (b) doubling [NO] increases the rate fourfold (compare 1 and 3).

This is consistent with the rate equation:

$$\text{rate} = k[\text{NO}]^2[\text{O}_2] \quad (\text{overall order} = 3)$$

Substitution of the values from experiment 1 in this rate equation allows us to calculate  $k$  as follows:

$$1.4 \times 10^{-10} \text{ mol l}^{-1} \text{ s}^{-1} = k \times (2.0 \times 10^{-5} \text{ mol l}^{-1})^2 \times (4.0 \times 10^{-5} \text{ mol l}^{-1})$$

$$\text{hence } k = 8.75 \times 10^3 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}.$$

Experiments 2 and 3 give the same value for  $k$ , confirming that the reaction is third order.

**Kinetics and reaction mechanism**

Chemical kinetics may be thought of as an example of the ‘bottle-neck principle’, which is frequently observed in everyday life. For instance, a large crowd of people leaving a football ground can only do so at a rate equal to the number who can squeeze through the exit in unit time. It makes no difference whether they run or walk to or from the exit.

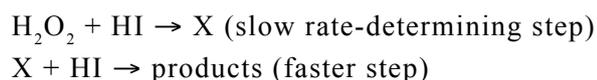
Similarly, if a chemical reaction proceeds in a series of sequential stages, the overall rate of reaction will be determined by the slowest step, which we call the rate-determining step. The kinetic parameters, which are determined experimentally, refer to this rate-determining step. By reversing the argument, experimentally determined rate equations and orders of reaction can give information about the way in which the reaction occurs. The following three reactions illustrate this.



Experimentally the rate equation is of the form:

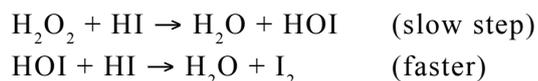
$$\text{rate} = k[\text{H}_2\text{O}_2][\text{HI}]$$

This tells us that the rate must be controlled by a step in which one molecule of hydrogen peroxide reacts with one molecule of hydrogen iodide. We can suggest that:



where X is an intermediate formed in the reaction.

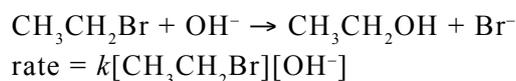
However, the kinetics themselves give us no direct information about either the nature of X or about the total number of steps involved. These must be deduced by other means, such as spectroscopy. The generally accepted mechanism for this reaction is:



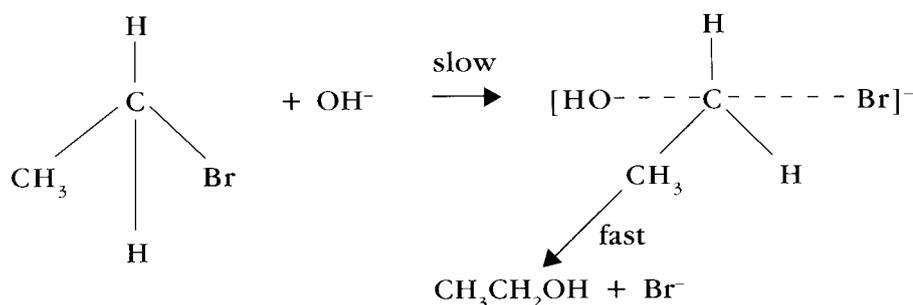
where HOI is an intermediate formed with a transient lifetime.

## 2. Hydrolysis of halogenoalkanes (see Unit 3)

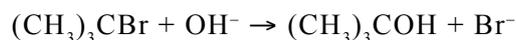
## (a) A primary halogenoalkane



From the rate equation we can deduce that both of the reactants are involved in the rate-determining step. How this takes place is shown in Figure 26. It can be seen that in the slow rate-determining step (in fact the only step in the reaction) the hydroxide ion displaces the bromide ion by attack at the 'back' of the molecule in an  $\text{S}_{\text{N}}2$  process (see Unit 3).

**Figure 26**

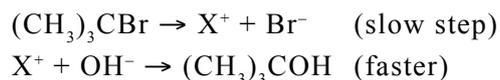
## (b) A tertiary halogenoalkane



The observed rate law depends only on the concentration of the halogenoalkane:

$$\text{rate} = k[(\text{CH}_3)_3\text{CBr}]$$

The rate-determining step does not, in this case, involve the hydroxide ion. The mechanism can be written as follows:



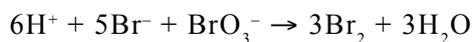
The reaction is a two-step (or, more accurately, more than one-step) process, involving some intermediate ( $\text{X}^+$ ), which by other means we can determine to be the carbocation  $(\text{CH}_3)_3\text{C}^+$ .

It has to be emphasised that, on the basis of kinetics alone, we cannot establish the exact mechanism of a reaction. We can only propose a possible mechanism that is consistent with the kinetics.

## KINETICS

### Questions

1. Bromide ions and bromate ions react in acid solution to give bromine according to the equation:



Rate measurements on four different reaction mixtures gave the following data.

Mixture	[H <sup>+</sup> ] (mol l <sup>-1</sup> )	[Br <sup>-</sup> ] (mol l <sup>-1</sup> )	[BrO <sub>3</sub> <sup>-</sup> ] (mol l <sup>-1</sup> )	Relative rate
1	0.45	0.375	0.075	1
2	0.45	0.75	0.075	2
3	0.9	0.375	0.075	4
4	0.45	0.375	0.15	4

- (a) What is the rate expression for the reaction?  
 (b) What is the order of the reaction with respect to each of the reactants?  
 (c) What is the overall order of the reaction?  
 (d) Explain why the rate equation and the overall equation are different.
2.  $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$

The reaction rates for the above reaction at various starting concentrations are given in the table.

[N <sub>2</sub> O <sub>5</sub> ](mol l <sup>-1</sup> )	Rate (mol l <sup>-1</sup> s <sup>-1</sup> )
2.20	$2.25 \times 10^{-5}$
2.00	$2.10 \times 10^{-5}$
1.52	$1.58 \times 10^{-5}$
0.93	$0.96 \times 10^{-5}$

- (a) Draw a graph of the rate against [N<sub>2</sub>O<sub>5</sub>].  
 (b) Calculate the value of the rate constant.

### 3. KINETICS

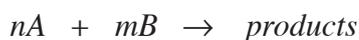
- 3.1 The **rate** of a chemical reaction normally depends on the **concentrations** of the reactants.
- 3.2 For a **first order reaction** the rate of reaction is proportional to the concentration of one reactant and the rate can be expressed as

$$\text{rate} = k [A]$$

where  $k$  is the **rate constant** and  $[A]$  is the concentration of reactant A in mol l<sup>-1</sup>.

- 3.3 The order of a reaction with respect to any one reactant is the power to which the concentration of that reactant is raised in the **rate equation**.
- 3.4 The **overall order of a reaction** is the sum of the powers to which the concentrations of the reactants are raised in the rate equation.

In general for a reaction of type



where the rate expression is of the form:

$$\text{rate} = k [A]^n [B]^m$$

the order of reaction is  **$n$  with respect to A**  
and  **$m$  with respect to B**  
and the **overall order is  $n + m$** .

- 3.5 The **rate constant** can be determined from initial rate data for a series of reactions in which the initial concentrations of reactants are varied.
- 3.6 **Reaction mechanisms** usually occur by a series of steps.
- 3.7 The rate of reaction is dependent on the **slowest step** which is called the '**rate determining step**'.
- 3.8 **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.

**Q1** The following exothermic reaction takes place in the upper atmosphere where the temperature is much lower than on the Earth's surface.



In a laboratory- simulated study carried out at room temperature, the following results were recorded.

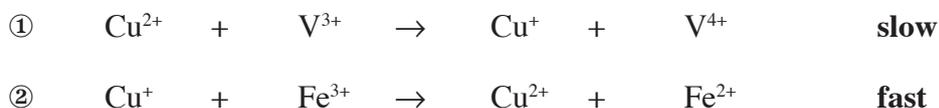
<i>Relative concentration</i> NO	<i>Relative concentration</i> O <sub>3</sub>	<i>Reaction Rate</i>
1	1	1
2	1	2
1	2	2

- Write out the rate expression for the reaction.
- What is the overall order of the reaction ?
- The reaction in the upper atmosphere is slower than the laboratory reaction for the same relative concentrations of NO and O<sub>3</sub>. Account for this observation.
- From the above equation, comment on the statement “NO catalyses the decomposition of ozone”.
- In the above reaction, NO removes ozone from the upper atmosphere. Suggest one possible man-made source of oxides of nitrogen which could contribute to this effect

**Q2** The reaction between iron (III) ions and vanadium (III) ions is first order with respect to both species.

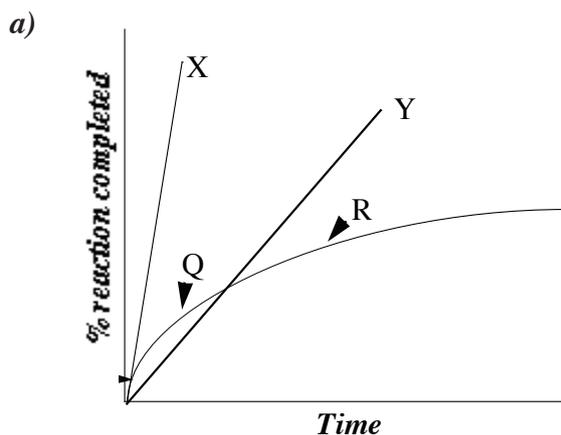


In the presence of copper (II) ions the reaction proceeds much more rapidly and there is evidence to suggest the following mechanism:



- Write the rate expression for the reaction between iron (III) ions and vanadium (III) ions.
- What is the order of reaction with respect to iron (III) ions when copper (II) ions are present ? Explain your answer.
- In addition to the observation that copper (II) ions alter the rate, what indication is there that the copper(II) ions are acting as a catalyst for the reaction

**Q3** The study of kinetics is the study of reaction rates, Since the rate of a reaction varies as the reaction proceeds, initial reaction rates are often used.



- At what stage, P, Q or R, is the reaction fastest ?
- What causes the rate of the reaction to change ?
- Which line, X or Y, represents the initial rate of the reaction ?

b) The table below gives information about the reaction of hydrogen and nitrogen oxides at 800°C.



Experiment number	Initial concentration of		Initial rate of production of $\text{N}_2$ mole $\text{l}^{-1} \text{s}^{-1}$
	NO mole $\text{l}^{-1}$	$\text{H}_2$ mole $\text{l}^{-1}$	
1	$6 \times 10^{-3}$	$1 \times 10^{-3}$	$3 \times 10^{-3}$
2	$6 \times 10^{-3}$	$2 \times 10^{-3}$	$6 \times 10^{-3}$
3	$1 \times 10^{-3}$	$6 \times 10^{-3}$	$0.5 \times 10^{-3}$
4	$2 \times 10^{-3}$	$6 \times 10^{-3}$	$2.0 \times 10^{-3}$

- Write the rate equation for the reaction. Explain how you derived it.
- Calculate the rate constant,  $k$ , for the reaction, giving the correct units.

**Q4** Dinitrogen pentoxide, dissolved in tetrachloromethane, decomposes to nitrogen dioxide and oxygen. The change in the rate with concentration of dinitrogen pentoxide is shown in the table. The rate is the decrease in dinitrogen pentoxide per second.

Concentration of dinitrogen pentoxide / mole $\text{l}^{-1}$	Rate of reaction mole $\text{l}^{-1} \text{s}^{-1}$
2.20	$2.25 \times 10^{-5}$
2.00	$2.10 \times 10^{-5}$
1.79	$1.93 \times 10^{-5}$
1.52	$1.58 \times 10^{-5}$
1.24	$1.21 \times 10^{-5}$
0.93	$0.96 \times 10^{-5}$

- Write the equation for the decomposition of dinitrogen pentoxide.

b) Draw the graph of the rate against the concentration of dinitrogen pentoxide. Use the graph produced in b) to answer the following questions.

- What is the rate expression for this reaction.
- What is the order of the reaction with respect to dinitrogen pentoxide.
- Find the value of the rate constant.

Q5 a) Hypochlorite ions can form chlorate and chloride ions according to:



In a reaction rate investigation the rate expression was determined as:

$$-\frac{d[\text{ClO}^-]}{dt} = k[\text{ClO}^-]^2$$

- Explain what is meant by  $-\frac{d[\text{ClO}^-]}{dt}$
- What is the overall order of this reaction ?
- State whether the chlorine has been oxidised or reduced in the conversion of  $\text{ClO}^-$  to  $\text{ClO}_3^-$ .

b) The stoichiometry for the reaction of bromide with bromate ions in acid solution is:



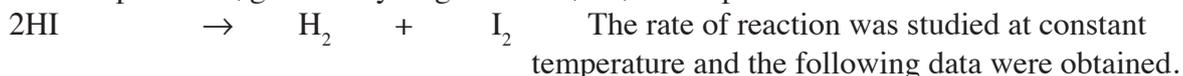
Rate measurements on several reaction mixtures provide relative rate data:

Reaction mixture	0.1 M H <sup>+</sup> cm <sup>3</sup>	0.1 M Br <sup>-</sup> cm <sup>3</sup>	0.1 M BrO <sub>3</sub> <sup>-</sup> cm <sup>3</sup>	H <sub>2</sub> O cm <sup>3</sup>	Relative rate
1	90	75	15	120	1
2	90	150	15	45	2
3	180	75	15	30	4
4	90	75	30	105	4

If the rate expression is given as :  $\text{rate} = k [\text{H}^+]^x [\text{Br}^-]^y [\text{BrO}_3^-]^z$

suggest values for x,y and z from the experimental data.

Q6 At elevated temperatures, gaseous hydrogen iodide, HI, decomposes as follows



initial rate of reaction / moles l <sup>-1</sup> s <sup>-1</sup>	initial concentration of HI / moles l <sup>-1</sup>
0.051	1.20 x 10 <sup>-2</sup>
0.034	0.98 x 10 <sup>-2</sup>
0.026	0.86 x 10 <sup>-2</sup>
0.019	0.73 x 10 <sup>-2</sup>

- Why was the reaction studied at constant temperature ?
- What is the order of the reaction ? Justify your answer.
- What is the rate constant for the above conditions ?

**Q7** When studying the kinetics of reactions various techniques are used for measuring the concentrations of the species involved. Colorimetric methods are often convenient.

In some cases titrimetric methods are used. To “stop” the reaction prior to titration, a sample is added to either

- i)* a large volume of cold solvent, or
- ii)* a known volume of “quenching agent” which reacts immediately with one of the reagents.

*a)* Outline the procedure for a colorimetric method.

*b)* For the reaction  $\text{CH}_3\text{COOCH}_3 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{CH}_3\text{OH}$  suggest a suitable quenching agent.

*c)* The reaction  $\text{CH}_3\text{COCH}_3 + \text{Br}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{Br} + \text{HBr}$  has the following rate law

$$\text{rate} = k [\text{CH}_3\text{COCH}_3]^1 [\text{Br}_2]^0$$

What is the order of this reaction ?

*d)* The kinetics of a reaction can be studied by measuring the concentration of a reactant at various times after the reaction has started. Kinetics data prove that a reaction is first order if a plot of  $\log_{10}[\text{reactant}]$  against time is a straight line.

The results below show data from an experiment. Find out, using a graph, if the data fits a first order reaction.

<i>time / s</i>	<i>[reactant] / moles l<sup>-1</sup></i>
0	2.0
100	1.7
200	1.5
300	1.3
400	1.1

**Q8** During the study of spontaneous decomposition of a radioactive nuclide the following data were obtained.

<i>Rate of decay / mole l<sup>-1</sup> s<sup>-1</sup></i>	<i>Concentration of nuclide / mole l<sup>-1</sup></i>
$1.18 \times 10^{-2}$	$2.81 \times 10^{-2}$
$0.86 \times 10^{-2}$	$2.04 \times 10^{-2}$
$0.79 \times 10^{-2}$	$1.88 \times 10^{-2}$
$0.55 \times 10^{-2}$	$1.32 \times 10^{-2}$

*a)* Using the above data, deduce the order of the process

*b)* What is the rate constant for the decomposition

*c)* How would an increase in temperature affect the rate of decay? Explain your answer.

# Answers

- Q1**
- a) Rate =  $k [\text{NO}][\text{O}_3]$
  - b) second order or 2
  - c) The reaction in the upper atmosphere will be at a lower temperature than the laboratory reaction.
  - d) This is a false statement as NO is consumed during the reaction/converted into  $\text{NO}_2$ .
  - e) Internal combustion engine / the spark in a petrol engine

- Q2**
- a) Rate =  $k [\text{Fe}^{3+}][\text{V}^{3+}]$
  - b) Zero order with respect to iron (III) ions as  $\text{Fe}^{3+}$  ions are not part of the (slow) rate determining step so have no effect on the overall rate of the reaction.
  - c) The  $\text{Cu}^{2+}$  ions are reformed in step ②

- Q3**
- a)
    - i) The reaction is fastest at stage P (initial rate).
    - ii) The concentration of reactant(s) decreases as reaction proceeds.
    - iii) X
  - b)
    - i) Rate =  $k [\text{NO}]^2 [\text{H}_2]$ .  
 In Experiment 1 & 2, the  $\text{H}_2$  concentration doubles and the rate doubles - a first order relationship.  
 In Experiment 3 & 4, the NO concentration doubles and the rate quadruples - a second order relationship.

ii)

$$\text{Rate} = k [\text{NO}]^2 [\text{H}_2] \quad \text{so} \quad k = \text{Rate} / ([\text{NO}]^2 [\text{H}_2])$$

Substitute results from Experiment 1:

$$k = (3 \times 10^{-3}) / (6 \times 10^{-3})^2 (1 \times 10^{-3})$$

$$k = 3/36 \times 10^6$$

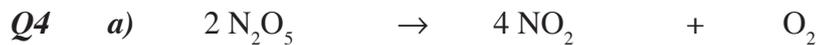
$$k = 8.3 \times 10^4$$

repeat using units:

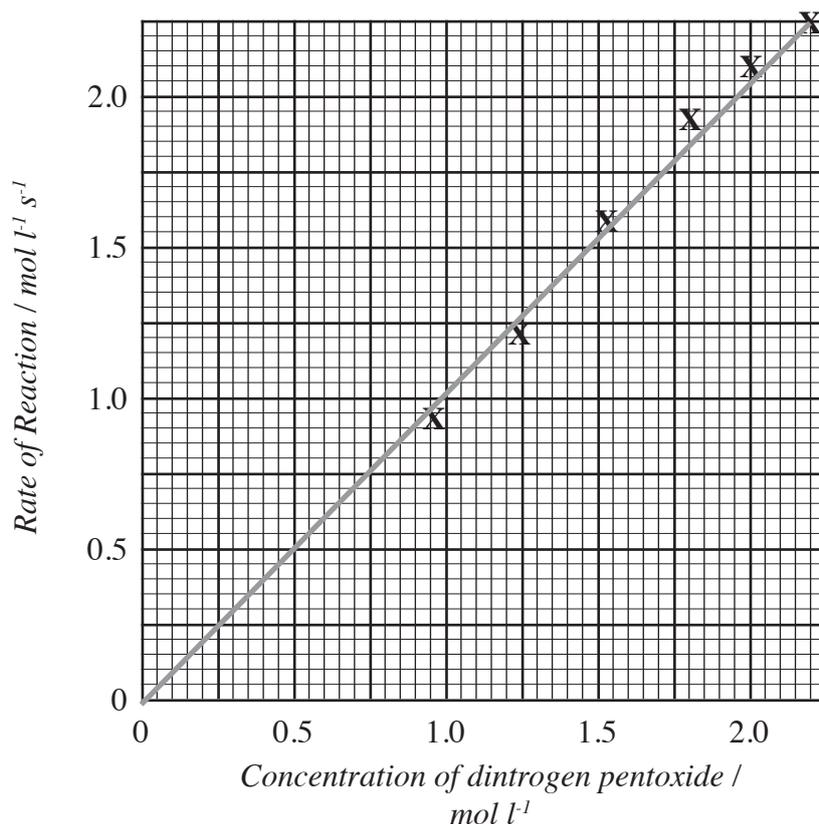
$$k = (\text{mol l}^{-1} \text{ s}^{-1}) / (\text{mol l}^{-1})^2 (\text{mol l}^{-1})$$

$$k = \text{mol}^{-2} \text{ l}^2 \text{ s}^{-1} \quad \text{or} \quad \text{l}^2 \text{ mol}^{-2} \text{ s}^{-1}$$

so  $k = 8.3 \times 10^4 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$



b)



i) As the graph is a straight line, rate is directly proportional to concentration - a first order relationship. so  $\text{Rate} = k [\text{N}_2\text{O}_5]$

ii) First order

iii)  $\text{Rate} = k [\text{N}_2\text{O}_5]$  so  $k = \text{Rate} / [\text{N}_2\text{O}_5]$

Substitute results from Experiment 1:  $k = (2.25 \times 10^{-5}) / (2.20)$

$$k = 1.02 \times 10^{-5}$$

**Q5** a) i) This represents Rate (of reaction).

ii) Second order

iii)  $\text{ClO}^-$  (O is 2- so Cl is 1+)

$\text{ClO}_3^-$  (3 x O is 6- so Cl is 5+) this is oxidation

b)  $\text{Rate} = k [\text{H}^+]^2 [\text{Br}^-]$

or  $x = 2 \quad y = 1 \quad z = 0$

- Q6** a) Rate constants (k) are temperature dependent so temperature must be kept constant to enable the effect of concentration to be studied.
- b) Harder than 'normal' as no obvious 'doubling' of concentration:

$$\text{compare two concentrations:} \quad 1.20 \times 10^{-2} / 0.73 \times 10^{-2} = 1.64$$

$$\text{compare relevant rates:} \quad 0.051 / 0.019 = 2.68$$

If first order, the two numbers should be very similar. If second order, there should be a square relationship.

$$(1.64)^2 = 2.69$$

Not perfect, but close enough. The rate order is 2 with respect to [HI].

c) Rate = k [HI]<sup>2</sup> so k = Rate / [HI]<sup>2</sup>

Substitute results from Experiment 1:  $k = (1.20 \times 10^{-2}) / (0.051)^2$   
 $k = 4.61$

- Q7** a) Prior to the kinetics study, calibration solutions of known concentration of the coloured substance would have been made up, absorptions measured and a calibration curve drawn to establish the numerical relationship between absorbance and concentration.

Assuming a data logging colorimeter/spectrophotometer:- as soon as last chemical is added and mixed, a portion would be transferred to a cuvette and absorbance readings taken at regular time intervals. (Where possible the final chemical would be added directly to the cuvette).

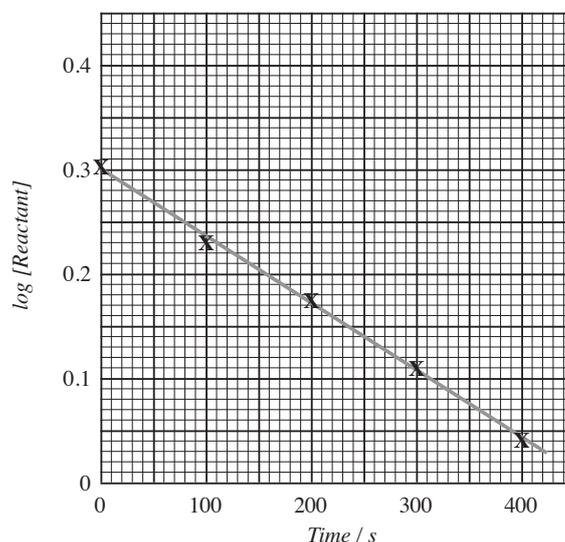
Alternatively, at regular intervals samples of the reaction mixture would be withdrawn (pipette), quenched and then some would be transferred to a cuvette to have absorbance measured.

- b) Given presence of OH<sup>-</sup> as a reactant, a suitable quenching agent would be an acid.

- c) First order.

- d) Graph confirms first order.

time / s	[reactant] / moles l <sup>-1</sup>	log [R]
0	2.0	<b>0.301</b>
100	1.7	<b>0.230</b>
200	1.5	<b>0.176</b>
300	1.3	<b>0.111</b>
400	1.1	<b>0.041</b>



**Q8** *b)* Again, harder than 'normal' as no obvious 'doubling' of concentration:

$$\text{compare two concentrations:} \quad 2.81 \times 10^{-2} / 1.32 \times 10^{-2} = 2.13$$

$$\text{compare relevant rates:} \quad 1.18 \times 10^{-2} / 0.55 \times 10^{-2} = 2.15$$

If first order, the two numbers should be very similar. If second order, there should be a square relationship.

Not perfect, but close enough.      The rate order is 1.

*b)* Rate =  $k$  [nuclide]      so       $k = \text{Rate} / [\text{nuclide}]$

Substitute results:       $k = (1.18 \times 10^{-2}) / (2.81 \times 10^{-2})$

$$k = 0.42$$

*c)* Nuclear decay is not affected by 'normal' factors such as temperature so there would be no change in the rate of decay.