Abstract
               This laboratory manual, part of a series
of instruction books on basic experimental chemistry, is
designed to provide the secondary school students of
developing countries in Asia with laboratory experiences
that bring out the fundamental concepts and ideas of
chemical kinetics. Taking into consideration the
possibility of limited facilities of the school
laboratories, the authors have (1) designed the experiments
on semi-micro-scale, (2) suggested the use of inexpensive
equipment and chemicals, and (3) selected experiments which
enable students to follow the course and rate of reaction
by visual indication, instead of using more sophisticated
instrumental techniques. Each experiment is introduced by a
statement of objective(s), followed by a detailed
description of the procedure. Important points of the
principles on which the experiment is based, are given in
the "Discussion" section. Sample questions on each
experiment are provided and the answers to these are
summarized at the end of the book. The appendix contains a
discussion of (1) the mole and molarity, and (2) the use of
the slide rule. (LC)

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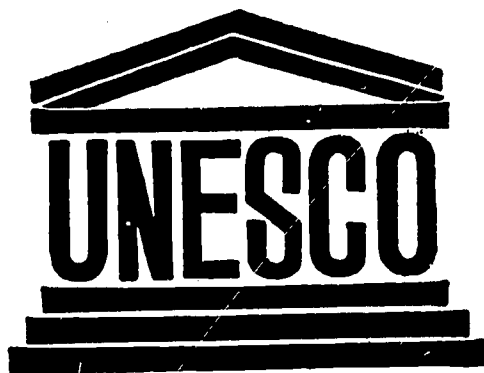
CHEMISTRY TEACHING PROJECT

IN ASIA

EXPERIMENTS ON
RATE OF CHEMICAL REACTIONS

1969

BANGKOK, THAILAND

The Unesco Project for Chemistry Teaching in Asia

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ABOUT THIS BOOK

This instruction book is the third one in the series of experiments on basic topics of chemistry, which can be used as an additional programme or as a part of an existing programme of chemistry teaching at secondary school level.

"The necessity of an experimental teaching media for chemistry is too obvious to need any justification. The success of any modern chemistry teaching programme, therefore, rests upon the presentation of the concepts and ideas of the subject through experiments. A greater challenge to chemistry teaching improvement, particularly in developing countries, however, is to devise experiments, which bring out the fundamental ideas of the subject, using chemicals and equipment within the easy reach of school laboratories. The experimental kit and this instruction book developed at the Project are a step in a direction of meeting this challenge and difficulty. The equipment and chemicals needed for the experiments are such that similar kits can be easily produced in every school laboratory. The price of the kit including both chemicals and equipment may vary from country to country, but in general, the average cost would not exceed $25."

The sentences in the above paragraph are taken from the preface to the first and the second instruction book in this series (Experiments on Chemical Equilibria, Bangkok, 1968 and Experiments on Compound Formation, Bangkok 1969) and hold for this volume on Rate of Chemical Reactions as well. As far as possible, the experiments were performed in semi micro-scale, using small amounts of chemicals and small volumes of solutions of reagents, in order to lower the cost of the experiments when repeated with larger groups of students.

The character of most of the experiments is a qualitative one. Droppers are used for measuring the volumes of the solutions, for diluting them and drops are used as volume "units". This is mainly in order to make the experiments feasible at schools, which are not equipped by a sufficient number of pipettes and burettes for a large group of students. The "dropping dilution technique" is also used in the experiments for preparing the solutions of the reagents in the proper concentration, starting from more concentrated commercially available solutions (e.g. H_2O_2, H_2SO_4).

The main aim of this kit and instruction book, is to show the reader that "Rate of Chemical Reactions" is one of the important topics in chemistry teaching. It is not easy to start at secondary school level with Chemical Kinetics and therefore we prefer to approach that topic by starting with the Rate of Chemical Reactions and with a selection of experiments, which can show the students the differences in chemical reaction rates and how the rate can be affected by temperature, concentration or by catalysts. The introductory chapter to the experiments was added as a general information about the topic of the kit and its level was adjusted to the average level of the students. In order to take into the consideration the limited facilities of the school laboratories, we selected experiments which enable the student to follow the course and rate of the reaction by visual indication and avoided the use of more sophisti-

cated techniques like spectrophotometry, electrochemical measurements, performing the experiments at higher or lower pressure, etc. This point of view, on the other hand, did not enable us to show a wider variety of examples of all effects, which can influence the rate of chemical reactions. Nevertheless, we do hope that even in this simplified form, the set of experiments can help the teachers to teach and the students to learn the subject or topic.

Each experiment is introduced by a short outline at the beginning and followed by a description of the procedure in detail. Important points of the principles on which the experiment is based, including explanation of relevant general backgrounds, are given in the "Discussion" of each experiment. In this volume, each experiment is followed by examples of questions which could help the teacher in the class-room; answers with the explanation in details are summarized at the end of this book. An instruction about the use of the slide rule (included in the kit) is added as the supplement to the experiments. This can give the students the chance to get familiar with its use for practical calculations.

This instruction book and kit should serve as an example for teachers and should not be considered as a standard or standardised aid. Success in teaching will always depend not on the facilities of the school laboratories, but on the teacher's interest in teaching. This holds also for this volume which should encourage the teacher to continue in developing similar experiments and support his creative ability.

The experiments were developed, tested, and the instruction book was written in the mutual cooperation of the Project's co-workers and staff members as follows:

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C O N T E N T S

EQUIPMENT FOR THE KIT

A. CHEMICALS

1. Ammonium molybdate

2. Arsenic trioxide

3. Bromothymol blue solution 0.1% in 96% ethanol

4. Glucose

5. Hydrochloric acid solution, 3M

6. Hydrogen peroxide solution, 10M

7. Iodine

8. Iodine solution, 0.1M in 0.3M KI

9. Magnesium ribbon

10. Manganese sulphate

11. Mercury(II) chloride

12. Methylene blue

13. Oxalic acid

14. Potassium iodate

15. Potassium iodide

16. Potassium permanganate

17. Sodium hydrogen sulphite, $NaHSO_3$

18. Sodium hydroxide

19. Sodium thiosulphate

20. Starch

21. Sulphuric acid solution, 1M

B. APPARATUS

1. Beakers, 2 x 50 ml, 100 ml, 150 ml

2. Conical flask, 100 ml

3. Droppers

4. Graph paper

5. Match box

6. Measuring cylinders, 2 x 10 ml, 100 ml

7. Reagent plastic bottles for solid chemicals (5 x 3 cm)

8. Reagent bottles for solutions, 25 ml capacity

9. Slide rule

10. Spatula

11. Spirit lamp with stand

12. Steel wool

13. Stirring rod

14. Stop watch

15. Test tubes, 8 x 1 cm

16. Test tube holder (wooden)

17. Test tube rack (styrofoam piece with holes)

18. Thermometer (graduated to $0.2^{\circ}C$, $0-50^{\circ}C$)

19. Wash bottle

20. Wire gauze, 7 cm x 7 cm.

21. Universal pH paper

B. APPARATUS
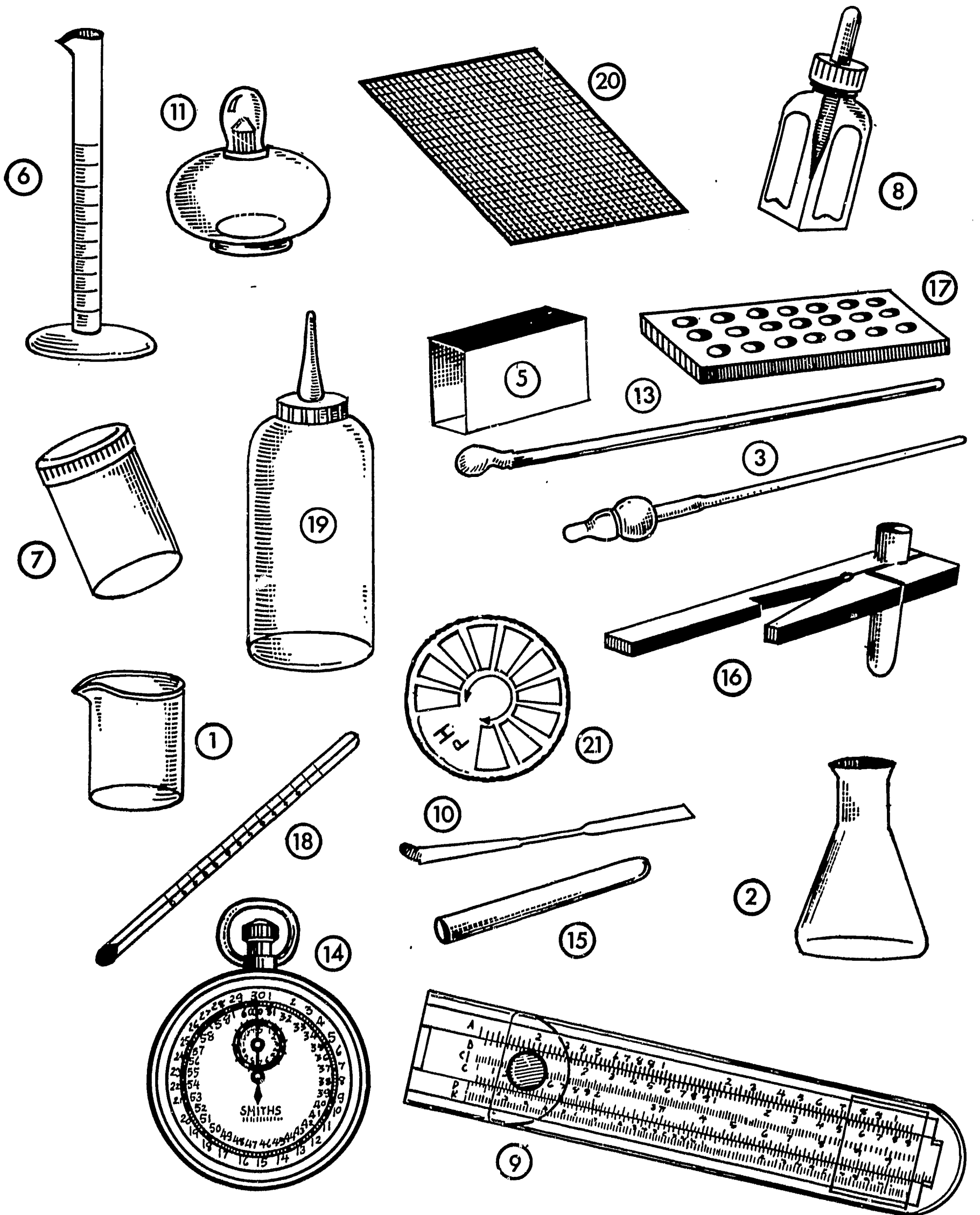
RATE OF CHEMICAL REACTION

Introduction

Many chemical reactions proceed from reactants to products rapidly or instantaneously, and some reactions require an appreciable time to reach their final state. The neutralization reaction between a dilute solution of hydrochloric acid and a dilute solution of sodium hydroxide takes place as rapidly as the solution containing the base is added to the solution containing the acid. On the other hand, the rusting of iron may take a month or even a year to complete the reaction. Other reactions may proceed between these two extremes.

Some chemical reactions do not take place at room temperature but do take place when the temperature is raised. For example, gaseous hydrogen and oxygen can be mixed together without any reaction taking place, but the mixture explodes if ignited.

To consider how fast or slow the reaction is, we speak in terms of the rate at which chemical changes take place. The rate of a reaction is the amount of reactants converted to products in a unit of time. The amount of reactants is usually expressed in moles per litre; the unit of time may be a second, a minute, an hour, or a day depending on whether the reaction is fast or slow.

What factors influence the rate of chemical reaction? Experiments show that five important factors are involved 1) nature of reactants, 2) concentration of reactants, 3) temperature, 4) catalyst, and 5) pressure.

1) Nature of reactants

The influence of the nature of reactants on the rate of reaction is apparent. Iron and silver standing in moist air show their reactions differently, though the same conditions prevail for both. The final appearance of iron will be rusty since it reacts with oxygen at an appreciable rate, whereas the silver changes relatively slowly. The reduction of permanganate ion in acid solution by iron(II) ion is obvious. The violet colour of permanganate disappears instantaneously when the solution of iron(II) sulphate is added. If in the same experiment iron(II) sulphate is replaced by oxalic acid, the colour of permanganate will fade slowly after mixing. That is, the rate of reaction depends on the nature of the reactants.

Chemical reactions which occur in the same physical state, either gaseous or in solution, are called homogeneous reactions. If the reaction takes place in different physical forms it is called a heterogeneous reaction. An example is the reaction of magnesium in hydrochloric acid solution.

It is found that the rates of heterogeneous reactions are complicated since the reactions take place at the surface of the

reacting phases.

2) Concentration of reactants

Most chemical processes are very complicated and the analyses of their rates are difficult. As the reaction proceeds, the reactants are used up and new products are formed. As long as the temperature remains constant, the rate of a chemical reaction must depend on the concentration of the reacting molecules. Let us look at the reaction of gaseous H_2 and I_2 to produce HI.

Into a container of fixed volume at constant temperature, we introduce a definite and equal number of molecules of H_2 and I_2. Then after a short time we analyse a sample of the mixture to determine the extent to which the gases have combined.

Now we repeat the experiment, this time introducing twice as many molecules of H_2 but using the same number of I_2 molecules, and again we analyse a sample of the mixture after the same time interval has elapsed. We find that the extent of the reaction of H_2 and I_2 is twice as great as in the first experiment. Thus at constant temperature, by doubling the concentration of H_2 and keeping the concentration of I_2 constant, the rate of the reaction of H_2 and I_2 is doubled.

Further experiments show that if the concentration of H_2 is kept constant and the concentration of I_2 doubled, the rate of reaction of H_2 and I_2 is doubled. Consequently if the concentration of both H_2 and I_2 is doubled, the reaction rate is increased four-fold.

The above observations illustrate that the rate of reaction of H_2 and I_2 is proportional to the concentration of H_2 multiplied by the concentration of I_2. Let $[H_2]$ represent the concentration of H_2, and $[I_2]$ the concentration of I_2, then

$$\text{Rate of combination of } H_2 \text{ with } I_2 \propto [H_2] \times [I_2]$$

or $\quad$ Rate of combination of H_2 with $I_2 = k [H_2] \times [I_2]$ where

k is a proportionality constant.

An equation relating reaction rate and concentration is called a rate law. The rate law for a reaction must be established by experimental measurement. It is largely dependent on the particular mechanism involved and cannot be predicted from consideration of the balanced equation for the nett reaction.

Since the rate of a chemical reaction is proportional to the concentration of the reacting substances, then the rate of the process must fall off as the reaction proceeds, for the reactants are being continuously used up. The change of reaction rate with time must be represented by a curve similar to that shown in Fig. 1.
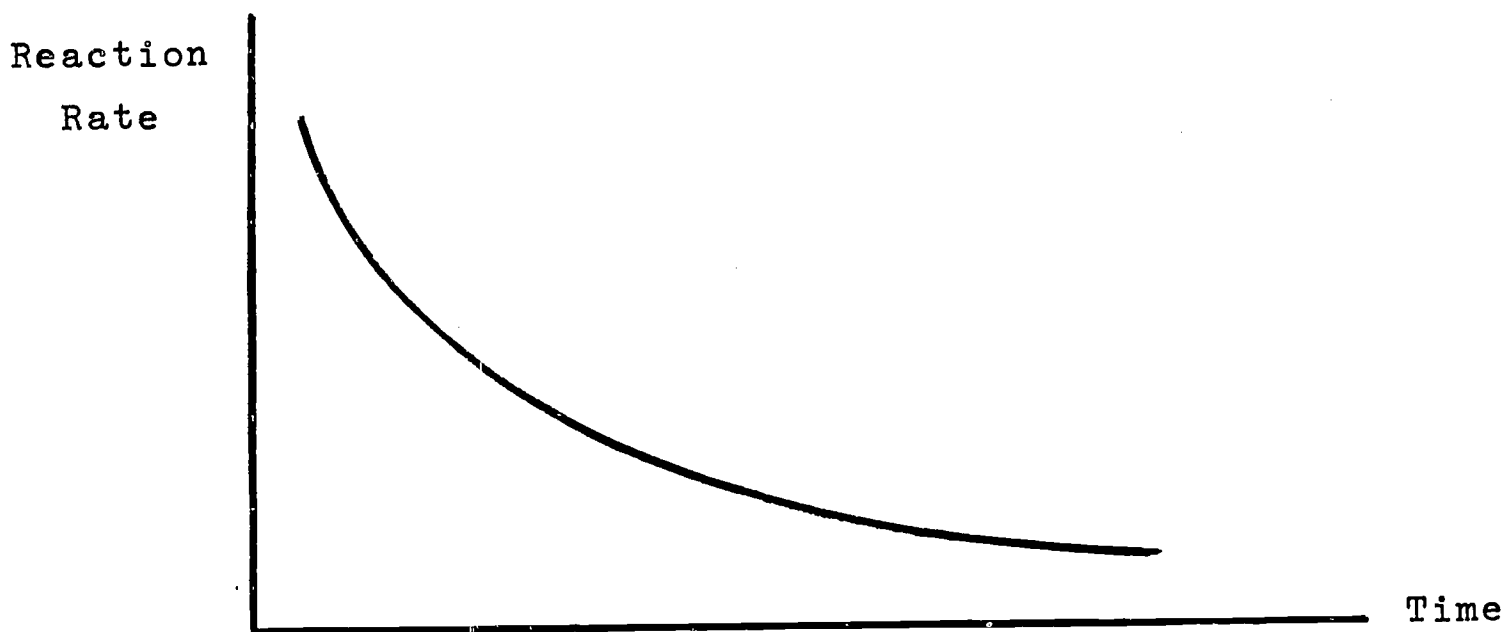
Fig. 1   Change of rate of reaction with time

The order of the reaction is the number of atoms or molecules whose concentration determines the velocity of the process. Stated in another way, the order of a reaction is related to the stoichiometry of the rate determining step(s).

In a first-order reaction the rate is directly proportional to the concentration of the reacting substance and is expressed mathematically as

$$-dc/dt = kc \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where c is the concentration of the reacting substance, k is the rate constant, and $-dc/dt$ is the reaction rate. This equation states that the rate of disappearance of the reactant at any instant is proportional to its concentration at that instant.

Rearranging eq. (1) gives

$$-1/c \quad \cdot \quad dc/dt = k$$

which can be expressed in the form

$$\log c \quad - \quad \log c_o \quad = \quad -kt/2.303 \ldots\ldots\ldots(2)$$

where c_o is the concentration of reactant at zero time. A plot of $\log c$ vs time is represented by Fig. 2. The linearity of the plot proves the reaction is first-order. The value of k can be obtained from the slope of the straight line: $-k = 2.303 \times$ slope. Examples of first-order reactions are the decomposition in carbon tetrachloride of dinitrogen pentoxide into nitrogen dioxide and oxygen, the

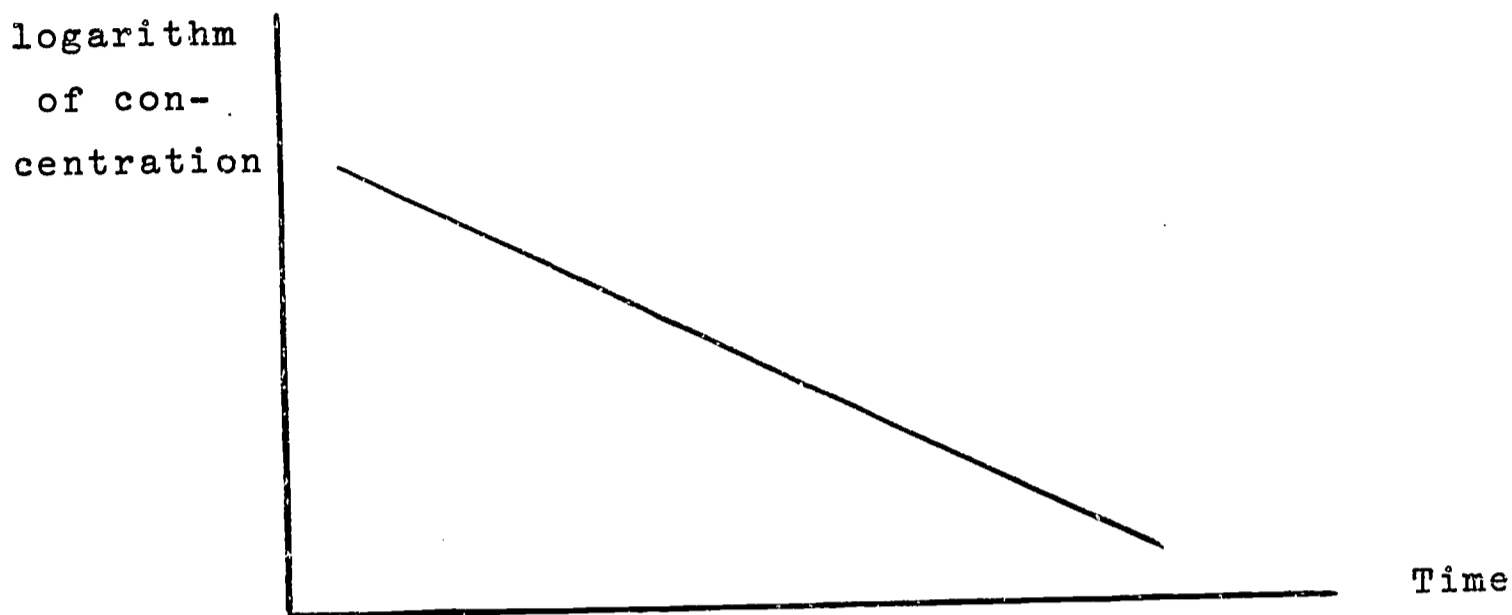Fig.2   A plot of log c vs t time

decomposition of ozone in carbon tetrachloride and of dibromosuc-
cinic acid into bromomaleic and hydrobromic acids in aqueous solu-
tion.   The decay of a radioactive isotope also conforms to a first-
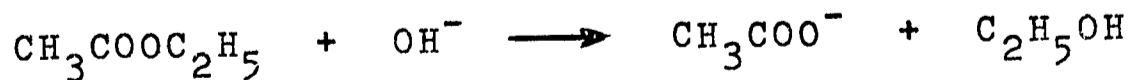order rate law.

When the rate of a reaction depends on two concentration terms
the process is said to be of the <u>second-order</u>.   This can be ex-
pressed mathematically as

$$-d[A]/dt = k[A]^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

and can be converted to

$$1/[A] = 1/[A]_o + kt \quad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

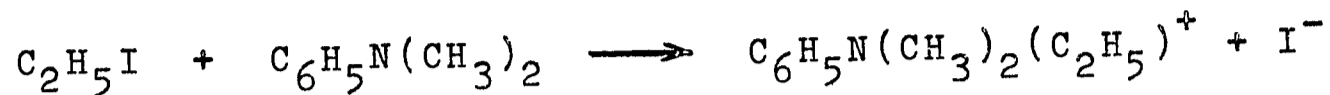where $[A]_o$ is the concentration of reactant at zero time. A plot of
$1/[A]$ vs time should be linear, the slope being k.* The combination
of hydrogen and iodine and reverse reaction, the decomposition of
hydrogen iodide are examples of second-order reaction. A second-
order reaction occuring in solution is that between ethyl acetate
and alkali metal hydroxide,

$$CH_3COOC_2H_5 + OH^- \longrightarrow CH_3COO^- + C_2H_5OH$$

* For a more rigorous approach to rate law see S. Glasstone 'Text-
book of Physical Chemistry' (D. Van Nostrand, Princeton) 2nd Edi-
tion. 1946, p. 1046-60, or any other Physical Chemistry textbooks.

Other second-order reactions taking place in solution are the inter-actions of alkyl halides with tertiary amines or pyridine, e.g. ethyl iodide and dimethylaniline

$$C_2H_5I \ + \ C_6H_5N(CH_3)_2 \longrightarrow C_6H_5N(CH_3)_2(C_2H_5)^+ + I^-$$

A reaction is said to be zero-order if the rate is independent of the concentration of the reactant. The graph of concentration against time is a straight line.

The following table gives a summary of graphical representation of order of reaction.

Order	Plot	Remarks
0	c vs t	Straight line
1	c vs t	curve
	1/c vs t	curve
	log c vs t	straight line
2	c vs t	curve
	log c vs t	curve
	1/c vs t	straight line

Thus to distinguish between first order and second order, plot log c vs t ; a first order reaction yields a straight line, second order a curve. Confirm by plotting 1/c vs t ; a first order reaction yields a curve, second order a straight line.

3) Temperature

Heat changes can produce complicated effects in chemical reactions. Increase of temperature increases the rate of a chemi-cal reaction to a marked extent, and for homogeneous processes the rate constant is in some cases doubled or trebled for each $10^{\circ}C$ rise of temperature. The marked influence of temperature is some-what surprising on first consideration, since the number of colli-sions between molecules will increase only by about 2 per cent for a rise of 10° at ordinary temperature. The most important effect of a temperature rise on the rate of reaction, is an increased fraction of activated molecules, rather than just an increased number of collisions.

4) Catalyst

A catalyst is a substance that increases the rate at which a chemical reaction takes place without itself undergoing permanent change. For example, the addition of MnO_2 increases the rate at which the thermal decomposition of $KClO_3$ takes place. Another

example is the decomposition of hydrogen peroxide into water and oxygen. The reaction occurs very slowly, but in the presence of finely divided platinum the reaction proceeds more rapidly.

When the reactants, the catalyst, and the products are all present in the same state, the catalysis is homogeneous. An example is the decomposition of H_2O_2 in an aqueous solution,

$$2H_2O_2 \rightleftharpoons 2H_2O + O_2 \quad ....(5)$$

The rate of decomposition of H_2O_2 can be increased by adding I^- ions to the solution. The mechanism of the decomposition is as follows:

$$H_2O_2 + I^- \rightleftharpoons H_2O + IO^- \quad ....(6)$$

$$H_2O_2 + IO^- \rightleftharpoons H_2O + O_2 + I^- \quad ....(7)$$

Adding eqs. (6) and (7) gives the overall eq. (5). Notice none of the I^- ions has been used up, and the I^- ions act as a catalyst.

5) Pressure

The equilibrium position of certain gaseous reactions may be shifted appreciably by changes in pressure, (Le Chatelier's Principle*) and this in turn affects the reaction rates. For example, consider the effect of a change in pressure on the equilibrium reaction of gaseous NO_2 to produce gaseous N_2O_4. The equilibrium reaction is as follows:

$$2NO_2 \rightleftharpoons N_2O_4$$
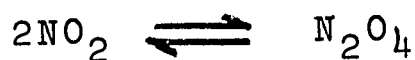
In a closed system is a mixture of NO_2 and N_2O_4 under a pressure of 1 atmosphere and at a constant temperature. If the pressure is increased by decreasing the volume of the system, formation of N_2O_4 is favoured. This is because for every two molecules of NO_2 only one molecule of N_2O_4 is produced.

The areas which seem to be important in the understanding of rates and mechanisms may be classified as
i) The variables which ordinarily affect the rate of chemical reaction (e.g. concentration, temperature, pressure)

ii) The mechanism by which chemical reaction actually occurs

iii) The relationship of this mechanism to the equilibrium.

No variables other than certain concentrations and the absolute temperature are ordinarily found to affect the rate of a given reaction. In consideration of reactions occuring at solid surfaces, a

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* Le Chatelier's Principle : If a system initially at equilibrium is subjected to a change, processes occur that tend to counteract partially the imposed change.

difficulty is introduced in defining the concentrations involved, but no new variable is introduced.

In many cases, observed rates are determined by a single slow step in what might be a whole series of complicated mechanisms. When there is a single slow step, the experimentally determined rate equation and the experimental dependence of the rate constant on absolute temperature turn out to be especially simple. Intermediate products are highly reactive, can exist at only small concentrations and generally build up to a constant level.

Once the general mechanism of a reaction is understood, it is easy to show that the equilibrium state involves a set of simultaneous reactions in which every step is proceeding in both directions at equal rates. The sum of all mechanistic steps must give the equation for the nett reaction.

I. THE USE OF STARCH AS AN INDICATOR
FOR DETECTING THE PRESENCE OF IODINE

This experiment illustrates the method how the sensitivity of the reaction can be determined and expressed.

Requirements

    Potassium iodide solution, 0.06M
    Potassium iodate solution, 0.07M
    Starch solution, 1%
    Hydrochloric acid solution, 0.1M

    Beaker, 150 ml
    Dropper, calibrated
    Measuring cylinder, 10 ml, 100 ml
    Test tubes
    Test tube rack
    Test tube brush

Procedure

Wash a dropper thoroughly with water and rinse with the solution for which it is to be used. Fill with solution and transfer dropwise to a measuring cylinder, counting the number of drops required to make 1 ml of solution. From this, the volume of solution corresponding to one drop is calculated.

Test the potassium iodide with starch solution to ensure that significant traces of iodine are not present.

Into a dry beaker add 1 drop of 0.06M potassium iodide solution and dilute it with 100 ml of water. This diluted solution is to be used in the starch sensitivity reaction only. Arrange 6 dry test tubes in the test tube rack and add the reagents as shown in Table I to each tube with shaking. Record the initial observations and enter them into Table I.

TABLE I: Detection of Iodine by Starch as Indicator

Tube	Drops of KI Solution	Drops of KIO$_3$ Solution	Drops of Starch Solution	Drops of HCl Solution	Initial Observation
1	1	1	2	2	colourless
2	2	1	2	2	colourless
3	3	1	2	2	colourless
4	4	1	2	2	pale blue
5	5	1	2	2	blue
6	6	1	2	2	blue

Discussion

When a dilute aqueous solution containing iodide ions is added to an acidified dilute aqueous solution containing iodate ions, the following reaction occurs.

$$2I^- \rightleftharpoons I_2 + 2e \quad (\times 3)$$

$$IO_3^- + 6H^+ + 6e \rightleftharpoons I^- + 3H_2O$$

$$\overline{IO_3^- + 5I^- + 6H^+ \rightleftharpoons 3I_2 + 3H_2O}$$
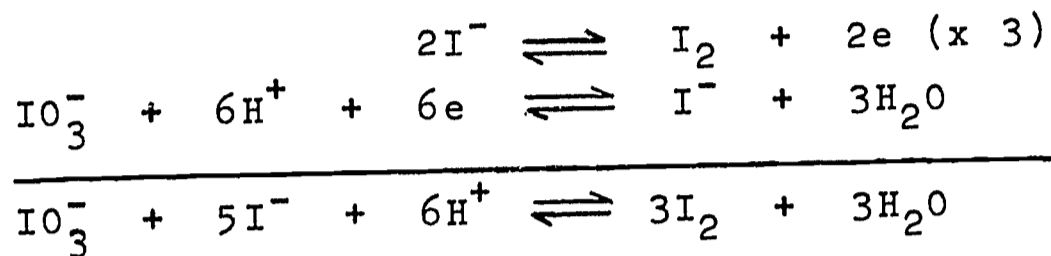
If a little starch solution is also added to the reaction mixture a blue colouration will develop. This is a sensitive method for detecting the iodine formed in this reaction, and a blue colouration will be visible with iodine concentration as low as 10^{-5} M.

In the first three observations, the fact that no colouration is visible does not mean that reaction has not taken place. It simply means that the concentration of iodine is too low to cause a colouration to develop with starch. In Tube 4 (with 4 drops of iodide solution), the concentration of iodine is high enough for a blue colour to appear.

Question

What is the approximate concentration of iodine in Tube 4?

II. REACTION OF SODIUM THIOSULPHATE WITH HYDROCHLORIC ACID

The object of the experiment is to demonstrate how the order of a reaction may be determined.

Requirements

Hydrochloric acid solution, 3M
Sodium thiosulphate solution, 0.15M

Beakers, 2 x 50 ml
Measuring cylinders, 10 ml, 100 ml
Stop-watch

Procedure

To a beaker add the volumes of reagents shown in Table 1. In all cases, mix the solution of thiosulphate and water before adding the acid solution. Agitate the beaker to ensure mixing of the contents. Time the reaction from the moment the acid is added until a turbidity is produced by the precipitation of sulphur. (Each experimenter may judge this point differently, but it must then be adopted consistently throughout the experiment.). Take at least two measurements for each reading. Enter the results into Table I.

Repeat the same procedures keeping the volume of thiosulphate solution constant and vary the volume of the acid solution according to Table II.

TABLE I: Reaction between Hydrochloric Acid with Varying Concentration of Sodium Thiosulphate

ml of 0.15M $Na_2S_2O_3$ Solution	ml of H_2O	Concn. of $Na_2S_2O_3$ (M) C	ml of 3M HCl Solution	Reaction Time in Seconds (t)	1/ t
25	-	0.15	4		
20	5	0.12	4		
15	10	0.09	4		
10	15	0.06	4		
5	20	0.03	4		

Discussion

The experiment involves the deposition of sulphur from sodium thiosulphate in the presence of acid. The free thiosulphuric acid formed is unstable and decomposes into sulphur and sulphur dioxide.
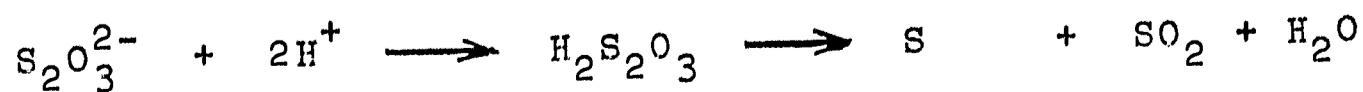
$$S_2O_3^{2-} + 2H^+ \longrightarrow H_2S_2O_3 \longrightarrow S + SO_2 + H_2O$$

TABLE II: Reaction between Sodium Thiosulphate and Varying
Concentration of Hydrochloric Acid

ml of 0.15M $Na_2S_2O_3$ Solution	ml of 3M HCl Solution	ml of H_2O	Concn. of HCl (M) Solution	Reaction Time in Seconds
25	5	-	3.0	
25	.3	2	1.8	
25	1	4	0.6	

The plot of concentration of thiosulphate versus time is a
curve, but the plot of concentration against the reciprocal of
time is a straight line (See fig. 1 and 2). 1/t may be taken as
a measure of the rate of reaction in this experiment. Fig. 2
shows that the rate of reaction is proportional to the concentra-
tion of thiosulphate i.e. the reaction is first order with respect
to thiosulphate.

It is also possible to calculate the rate constant from the
slope of the graph.
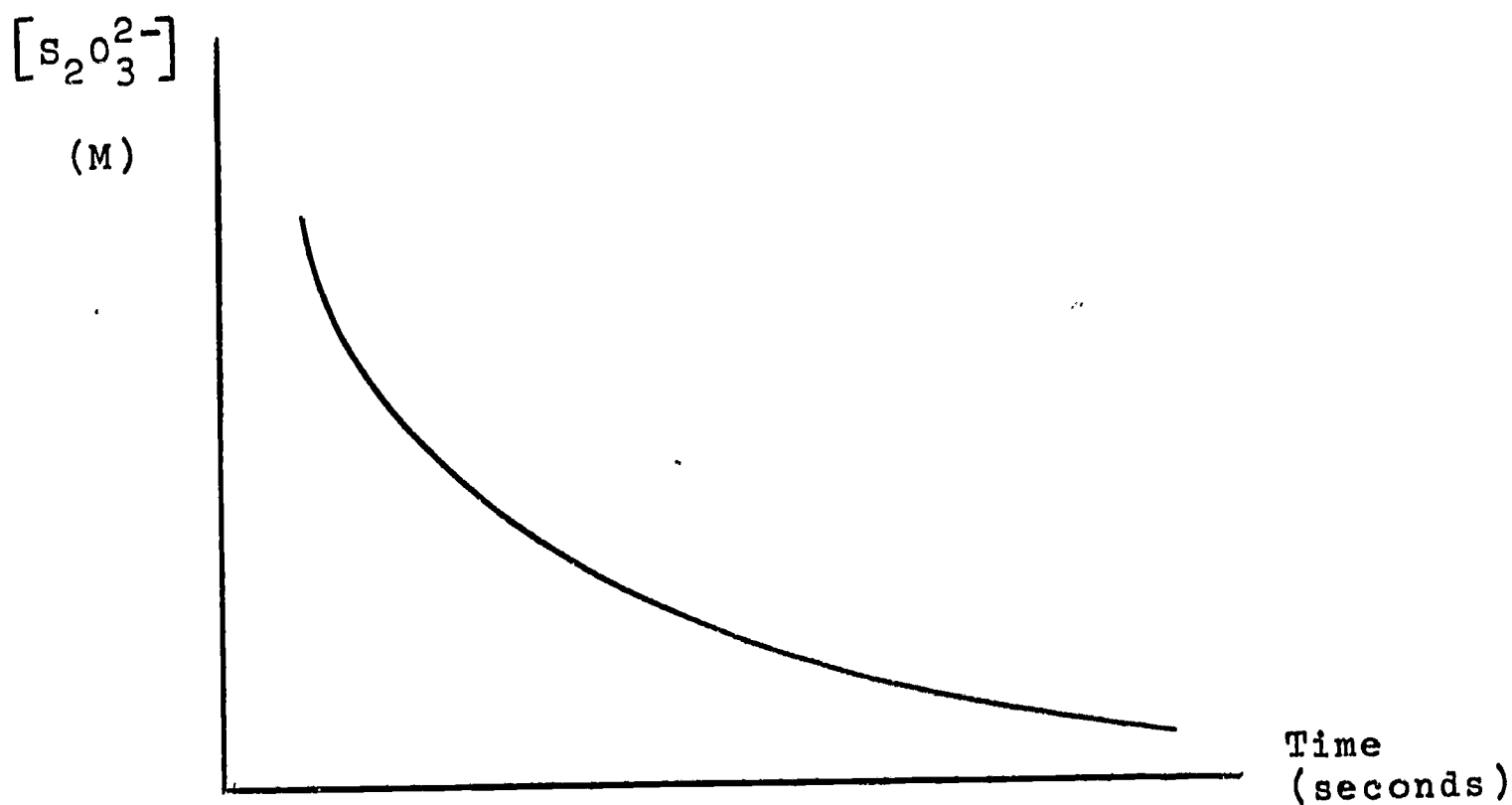
Fig. 1 Graph of thiosulphate concentration against reaction time.

$$[S_2O_3^{2-}]$$
$$(M)$$

Reciprocal
of time
(1/sec.)
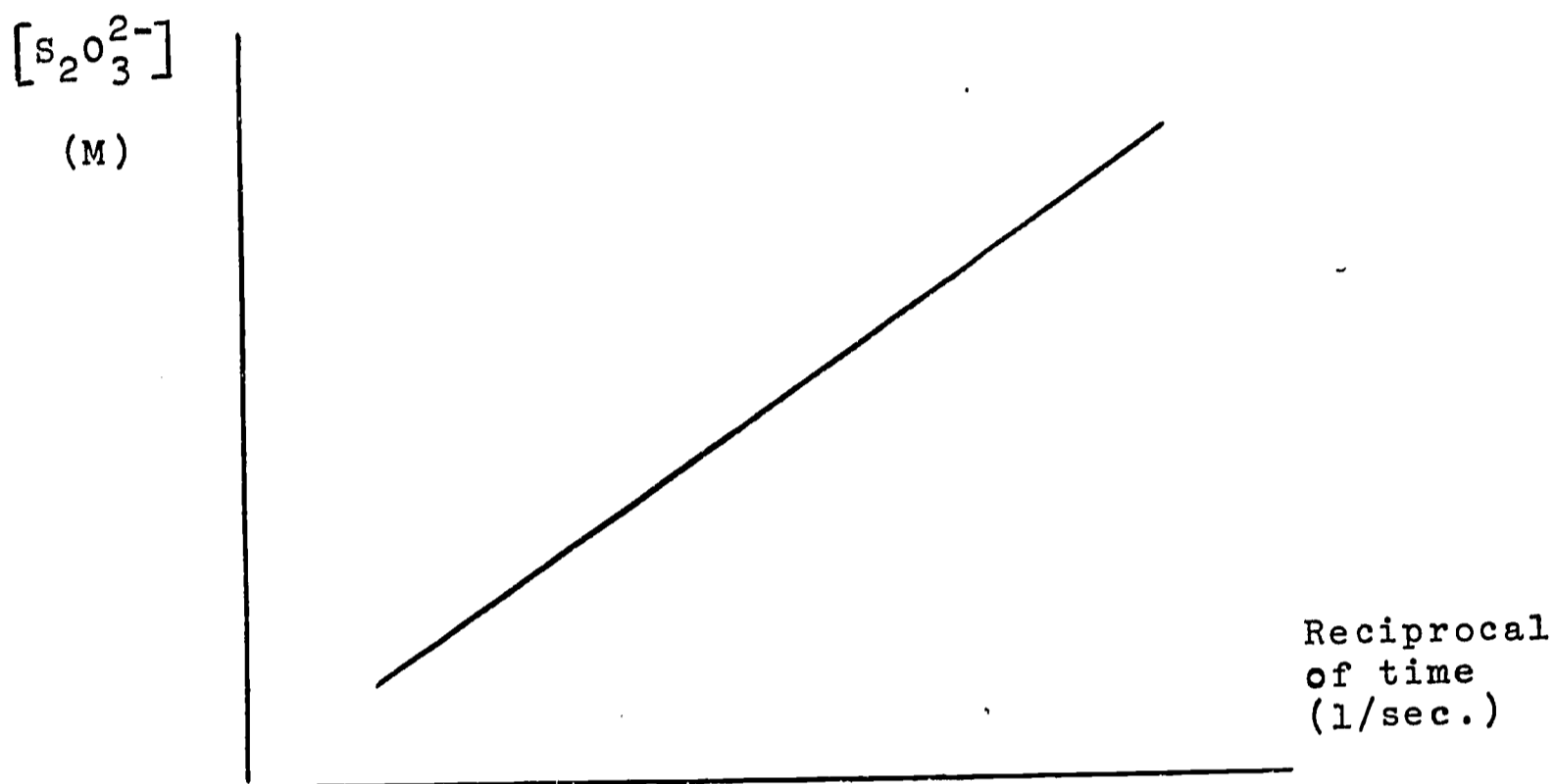
Fig. 2   First order rate graph for the reaction of sodium
thiosulphate with hydrochloric acid.

Table II indicates that the rate of reaction between thiosulphate and acid is independent on the concentration of acid. This means that as long as there is sufficient acid present, the rate of reaction is the same no matter how much acid is added. This indicates that the reaction is zero order with respect to the acid concentration.

This experiment shows that the rate law for a reaction can only be established by experimental measurement and cannot be predicted from the balanced equation for the nett reaction. The rate of this experiment is proportional to $[S_2O_3^{2-}]$ and not to $[S_2O_3^{2-}][H^+]^2$ as indicated by the equation.

Question:

Why does a solution of sodium thiosulphate become turbid when exposed to the atmosphere?

III. HOW REACTION SPEED DEPENDS ON INITIAL CONCENTRATION

The object of the experiment is to study the effect of initial concentration of reactants on the rate of reaction.

Requirements

Sulphuric acid solution, 0.5M
Starch solution, 1%
Hydrogen peroxide solution, 10M
Potassium iodide solution, 0.6M

Droppers, calibrated
Measuring cylinder, 10 ml
Stop-watch
Test tubes
Test tube rack
Beakers

Procedure

a. Dilution:

The 0.6M KI solution (Solution A) is diluted as shown in Table I.

TABLE I: Dilution of 0.6M KI solution (Solution A). Use Sample tubes and clearly label each solution.

Solution	Drops of Solution A	ml of water
B	1	1
C	1	2
D	1	3
E	1	4
F	1	5

The 10M H_2O_2 solution is diluted by 5 drops H_2O_2 made up to 25 ml with water (Solution L). This is further diluted as indicated in Table II.

TABLE II: Dilution of H_2O_2 solution (Solution L)

Solution	Drops of Solution L	ml of water
M	1	1
N	1	2
O	1	3
P	1	4
Q	1	5

b. Reaction:

Set up 6 dry test tubes in the rack and to each tube add with shaking the reagents in the order shown in Table III. From the moment the drop of KI solution is added, record with the stop-watch the time taken for the first definite blue colour to develop. Enter the results into Table III.

Repeat the same procedure using the quantities of reagents as shown in Table IV.

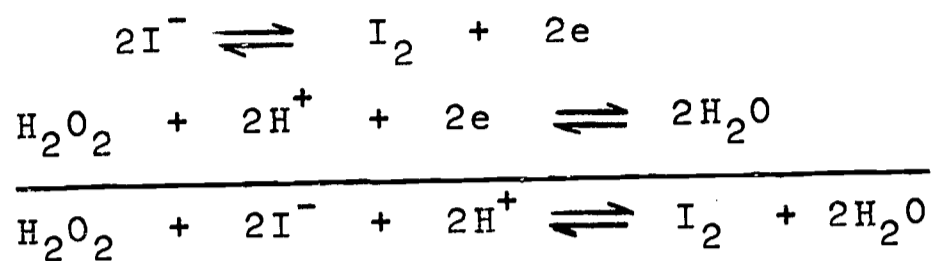TABLE III: Rate of Reaction of Hydrogen Peroxide with Varying Concentration of Potassium Iodide.

Solution	Drops of 0.5M H_2SO_4	Drops of Starch Solution	Drops of H_2O_2 Solution (Solution L)	Drops of KI Solution	Time in seconds
A	2	2	2	1	
B	"	"	"	"	
C	"	"	"	"	
D	"	"	"	"	
E	"	"	"	"	
F	"	"	"	"	

TABLE IV: Rate of Reaction of Potassium Iodide with Varying Concentration of Hydrogen Peroxide.

Solution	Drops of 0.5M H_2SO_4	Drops of Starch Solution	Drops of H_2O_2 Solution	Drops of KI Solution (Solution A)	Time in seconds
L	2	2	2	1	
M	"	"	"	"	
N	"	"	"	"	
O	"	"	"	"	
P	"	"	"	"	
Q	"	"	"	"	

Discussion

The experiment is based on the oxidation of iodide ions to iodine by hydrogen peroxide.

$$2I^- \rightleftharpoons I_2 + 2e$$

$$H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O$$

$$\overline{H_2O_2 + 2I^- + 2H^+ \rightleftharpoons I_2 + 2H_2O}$$

In the presence of iodine, starch turns blue and the appearance of this colour is used to follow the rate of appearance of iodine with time.

It can be seen from Table III that as the potassium iodide solution is diluted, the time taken for the appearance of the blue colour gets progressively longer. That is, the reaction rate is slower.

A similar result is observed when the concentration of potassium iodide is kept constant and the concentration of hydrogen peroxide is varied (see Table IV).

From these two series of measurements, it can be seen that the rate of reaction between hydrogen peroxide and iodide ions depends upon the initial concentration of the reactants.

Question

Suggest a reason for the increase of reaction rate with increasing reactant concentration.

IV. HOW TO FOLLOW A REACTION

The object is to study how changes in reactant concentration affect the rate of reaction.

Requirements

Potassium iodide solution, 0.6M
Sulphuric acid solution, 0.5M
Starch solution, 1%
Hydrogen peroxide solution, 10M
Sodium thiosulphate solution, 0.45M

Droppers, calibrated
Measuring cylinder, 10 ml, 100 ml
Stop-watch
Test tubes
Test tube rack

Procedure

a. This experiment requires team work between two persons - one to perform the experiment and the other to act as time-keeper.

b. Dilution: 0.6M KI solution (10 drops) made up to 1 ml with water (Solution A); 10M H_2O_2 solution (5 drops) made up to 25 ml with water (Solution B); 0.45M $Na_2S_2O_3$ solution (2 drops) made up to 25 ml with water (Solution C).

c. Into a test tube add 2 drops of 0.5M H_2SO_4 solution, 2 drops of starch solution, 1 drop of Solution A and 1 drop of Solution C. (This clears any slight blue colouration due to atmospheric oxidation of iodide). Then add 1 drop of Solution B and start the stop-watch at the same time. At the appearance of a blue colouration, add another drop of Solution C and record the time. Note elapsed time between successive additions of Solution C. When the blue colouration reappears, add another drop of Solution C and again record the time. Repeat this procedure for another 8 additions of Solution C. Enter the results into Table I.

Discussion

In this experiment, we again follow the rate of reaction, i.e. the formation of iodine, by the time taken for the blue colour of the starch indicator to appear.

$$H_2O_2 + 2I^- + 2H^+ \rightleftharpoons I_2 + 2H_2O \qquad (1)$$
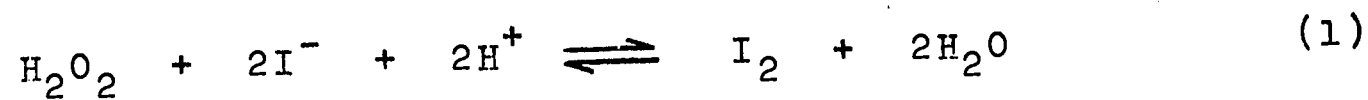
The liberated iodine reacts with the sodium thiosulphate according to eq. 2, and the blue colour is discharged.

$$I_2 + 2S_2O_3^{2-} \rightleftharpoons 2I^- + S_4O_6^{2-} \qquad (2)$$
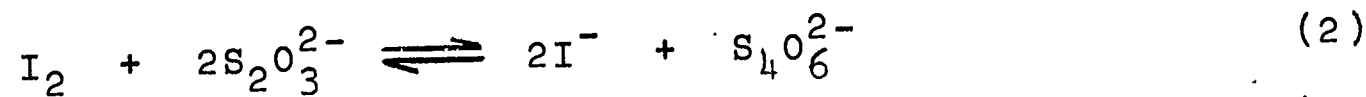
As the iodine is used up, more iodine will be produced (eq. 1) and after some time the blue colour will be regenerated (see Table 1)

TABLE I: Rate of Reaction of Potassium Iodide and Hydrogen
           Peroxide with Varying Concentration of Reactants.

Read-ings	Drops of H_2SO_4 Solution	Drops of Solution A. (KI)	Drops of Solution B. (H_2O_2)	Drops of Solution C. ($Na_2S_2O_3$)	Time in sec-onds	Reac-tion Time Inter-val
1	2	1	1	1		
2	"	"	"	2		
3	"	"	"	3		
4	"	"	"	4		
5	"	"	"	5		
6	"	"	"	6		
7	"	"	"	7		
8	"	"	"	8		
9	"	"	"	9		
10	"	"	"	10		

but not until all the sodium thiosulphate has been used up. At
this stage, another drop of sodium thiosulphate is added and the
whole process is repeated. Further drops of thiosulphate are added
till the blue colour is discharged permanently, i.e., when all the
iodine, formed by the oxidation of potassium iodide with hydrogen
peroxide, has been used up.

     The results listed in Table I show that the rate of reaction
decreases as reactants are consumed.

Questions

   1) Calculate the initial molarity of KI and H_2O_2 used in the
      experiment and determine which reagent is in excess.

   2) What are some of the differences between Experiments III
      and IV?

   3) Are the results of Experiment IV in agreement with the
      theory proposed in Experiment III?

V. REACTION OF SODIUM HYDROGEN SULPHITE AND POTASSIUM IODATE

The object of the experiment is to study the effects of concentration and temperature on the rate of reaction between sodium hydrogen sulphite and potassium iodate.

Requirements

Sodium hydrogen sulphite or sodium pyrosulphite
Starch, 1g
Sulphuric acid, 1M
Potassium iodate solution, 0.01M
Ice

Plastic sample bottles
Spirit lamp
Stop-watch
Thermometer

Procedure

In certain schools the reagent, sodium hydrogen sulphite, may not be available. It is possible to use sodium pyrosulphite (or sodium metabisulphite) as a substitute. Sodium pyrosulphite changes to sodium hydrogen sulphite in water

$$Na_2S_2O_5 \;+\; H_2O \longrightarrow 2NaHSO_3$$
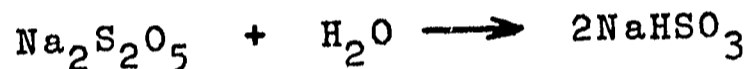
Label the 0.01M KIO_3 solution as Solution A. Solution B is made by the following manner:- Take 1g of starch and make into a paste with 1 ml of hot water, to this add 1 ml 1M H_2SO_4, 0.1g of sodium pyrosulphite and dilute it to 250 ml in a volumetric flask; or, use 0.11g of sodium hydrogen sulphite in place of sodium pyrosulphite. The concentration of sodium hydrogen sulphite in Solution B is 0.0042M.

Set up 10 plastic bottles and label them. To each bottle, add the volumes of Solution A and B as indicated in Table I. Always prepare Solution A first before adding Solution B. On the addition of Solution B, start the stop-watch and record the time taken for a blue colouration to appear. Record the room temperature and enter all results into Table I.

In the second part of the experiment, the rate of reaction (i.e. time taken for the appearance of the blue colour) is measured at different temperatures. This can be done by using a beaker of water and adding ice for temperatures below room temperature and hot water for those above room temperature. The temperature listed in Table II is only a guide and at least six readings below room temperature should be taken. It is not necessary to measure the rate of reaction above 50°C. In all measurements, 10 ml of solution A and 10 ml of Solution B are used, and in all instances, Solutions A and B must have attained the temperature at which the measurements are made (use the thermometer) before they are mixed together. Record the time for the blue colour to develop from the

moment of mixing the two solutions.

TABLE I: Reaction of $NaHSO_3$ and KIO_3 with Varying Concentration of KIO_3 at Room Temperature (29°C)

Tube	Solution A. (ml)	H_2O (ml)	Concentration of KIO_3 in Solution A.	Solution B. (ml)	Time in seconds
1	10	–	0.01	10	
2	9	1	0.009	10	
3	8	2	0.008	10	
4	7	3	0.007	10	
5	6	4	0.006	10	
6	5	5	0.005	10	
7	4	6	0.004	10	
8	3	7	0.003	10	
9	2	8	0.002	10	
10	1	9	0.001	10	

TABLE II: Reaction of 10 ml 0.01M KIO_3 and 10 ml 0.0042M $NaHSO_3$ Solutions at different Temperatures.

Temperature °C	Time in Seconds	Temperature °C	Time in seconds
2		25	
4		29 (RT)	
10		35	
15		40	
20		45	

Discussion

The rate of reaction depends on the concentration of the reactants and on the temperature at which the reaction is carried out. In most homogeneous reactions, the rate of reaction usually increases at higher temperatures.

This experiment is based on the reactions

$$IO_3^- + 3HSO_3^- \rightleftharpoons I^- + 3SO_4^{2-} + 3H^+$$

$$6H^+ + 5I^- + IO_3^- \rightleftharpoons 3I_2 + 3H_2O.$$
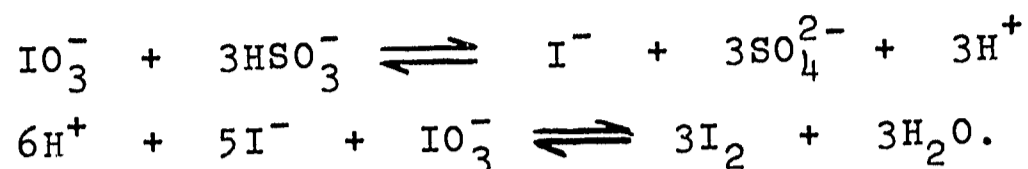
The second reaction takes place immediately the HSO_3^- ions have been all removed. A plot of concentration of iodate against reaction time gives a curve. No decision can be taken about the order because the effect of H^+ and other variables has not been studied.

Table II. will show that at higher temperatures, the reaction proceeds faster.

Question:

Why does an increase in temperature result in an increase in rate of reaction?

VI. EFFECT OF TEMPERATURE ON RATE OF REACTION

The object of the experiment is to study the effect increased temperature has on the reaction rate of i) potassium permanganate with oxalic acid and ii) sodium thiosulphate with hydrochloric acid.

Requirements

Oxalic acid solution 0.05M
Sulphuric acid solution 0.5M
Potassium permanganate solution 0.01M
Sodium thiosulphate solution 0.15M
Hydrochloric acid solution 3M

Beaker (150 ml)
Dropper, calibrated
Measuring cylinder, 10 ml
Spirit lamp
Stop-watch
Test tubes
Test tube holder
Test tube rack

Procedure

a. Dilution: Make 0.05M oxalic acid, 50 drops up to 25 ml with water (solution A) and make 0.01M potassium permanganate, 50 drops up to 25 ml with water (solution B).

b. To a clean test-tube add 2 drops of Solution A, 2 drops of 0.5M sulphuric acid, 1 drop of Solution B, and start the stop-watch at the last drop. Record the time taken for the solution to turn colourless and enter the result into Table I. Place another test-tube in the test-tube holder, then add 2 drops Solution A, 2 drops of 0.5M sulphuric acid. Boil a beaker of water and immerse the test-tube into the boiling water for 10 seconds, remove the test-tube from the water and add 1 drop of Solution B to the solution with shaking. Again record the time taken for the solution to turn colourless. Then add another drop of Solution B to the solution and record the time taken for the solution to turn colourless. Repeat the same procedure for another 6 drops of Solution B. Enter the results obtained into Table II.

TABLE I: Effect of Temperature on the Reaction Rate of Oxalic Acid and Potassium Permanganate.

Tube	Temperature °C	Drops of Solution A	Drops of H_2SO_4 Solution	Drops of Solution B	Time in seconds
1	25	2	2	1	
2	60	2	2	1	

TABLE II: Effect of Extra Permanganate on the Reaction Rate.

Tube	Drops of Solution A	Drops of H_2SO_4 Solution	Drops of Solution B	Time in seconds
2	2	2	1	
	2	2	2	
	2	2	3	
	2	2	4	
	2	2	5	
	2	2	6	
	2	2	7	
	2	2	8	

c. Place a black mark on a piece of white paper and place a test-tube on the mark. To the tube add 2 drops of sodium thiosulphate solution, 2 drops of hydrochloric acid and record the time taken for the precipitate to obscure the mark on the paper. Add 2 drops of sodium thiosulphate to another test tube and immerse the tube the boiling water for 10 seconds, then place the tube over the mark on the paper and add 2 drops of hydrochloric acid. Record the time taken for the precipitate to cover the mark. Enter the results into Table III.

TABLE III: Effect of Temperature on the Reaction Rate of Sodium Thiosulphate and Hydrochloric Acid.

Tube	Temp. $^\circ$C	Drops of $Na_2S_2O_3$ Solution	Drops of HCl Solution	Time in seconds
1	25	2	2	
2	60	2	2	

Discussion

At higher temperatures, homogeneous reactions usually proceed at higher rates. Thus when potassium permanganate and oxalic acid are mixed at 25°C, the time taken for the colour of permanganate to discharge is long. However, if the solution is heated, the permanganate colour discharges much faster. The reaction taking place is:

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O \qquad (x2)$$

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e \qquad (x5)$$

$$2MnO_4^- + 5\,C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 10\,CO_2$$

(pink)   (colourless)
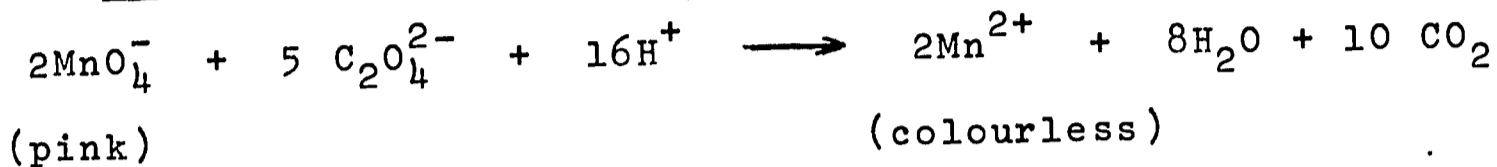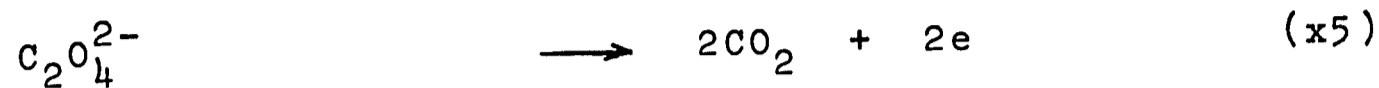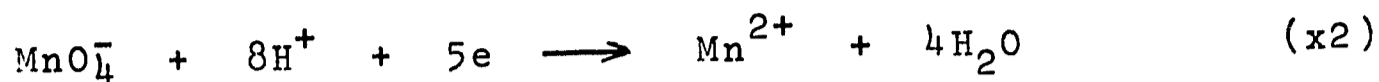
For the reaction between sodium thiosulphate and hydrochloric acid, the reaction proceeds slowly at room temperature. At $60^\circ C$, the reaction occurs rapidly and the time taken for the deposition of sulphur is less. The reaction is:

$$S_2O_3^{2-} + 2H^+ \longrightarrow S + SO_2 + H_2O$$
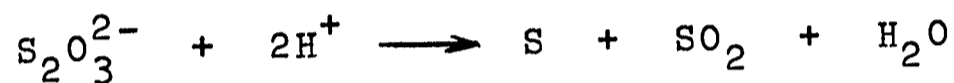
The rates of most reactions increase with temperature.

The results in Table II will show that if the temperature of the solution is kept constant the reaction proceeds faster when Mn^{2+} ions have already been formed.

Question:

The reaction between MnO_4^- and $C_2O_4^{2-}$ is important in analytical chemistry. Is it necessary to heat the solution during the reaction?

VII. EFFECT OF REACTION MEDIUM ON THE RATE OF REACTION

The object of the experiment is to study the effect of the reaction media on the reaction between sodium arsenite and iodine.

Requirements

      Sodium arsenite solution (neutralized), 0.05M
      Sulphuric acid solution, 0.5M
      Iodine solution, 0.1M in potassium iodide solution, 0.3M
            (henceforth referred to as KI_3 solution)
      Starch solution, 1%
      Sodium hydroxide solution, 0.1M

      Dropper, 1 calibrated
      Measuring cylinder, 10 ml
      Stop-watch
      Test tubes
      Test tube rack

Procedure

a. Dilution: iodine solution, 2 drops made up to 5 ml with water. Dilute the sulphuric acid and sodium hydroxide solutions as shown in Table I.

TABLE I: Dilution Chart for Sulphuric Acid and Sodium
              Hydroxide Solutions.

Solution	ml of 0.5M H_2SO_4	ml of H_2O	Concentration of H_2SO_4 Solution (M)	Solution	ml of 0.1M NaOH	ml of H_2O	Concentration of NaOH Solution (M)
A	10	–	0.5	G	–	10	0
B	8	2	0.4	H	2	8	0.02
C	6	4	0.3	I	4	6	0.04
D	4	6	0.2	J	6	4	0.06
E	2	8	0.1	K	8	2	0.08
F	–	10	0	L	10	–	0.1

b. Preparation of neutral sodium arsenite solution.

A solution of sodium arsenite is prepared by dissolving arsenic(III) oxide in sodium hydroxide solution and making the solution up to a known volume. (Dissolve 0.99 gm of arsenic(III) oxide in sodium hydroxide solution and make up to 100 ml). The alkaline solution of the arsenite is then neutralised by adding

sulphuric acid dropwise and testing the neutralization stage with the help of a universal pH test paper.

c. Mark 6 test tubes A to F and place them in the test tube rack. Add reagents in turn to each tube as indicated in Table II. In each instance, record the time required for the blue colour to discharge from the moment the drop of sodium arsenite is added. Agitate the solution after each addition. Enter the results obtained in Table II. Set up another 6 test tubes, marked G to L, add reagents in turn, to each tube as indicated in Table III. Again record the time required for the blue colour to discharge from the moment the drop of sodium arsenite is added. Enter the results obtained in Table III.

TABLE II: Effect of Acid Medium on Rate of Reaction between Sodium Arsenite and Iodine.

Solution	Drops of Acid Solution	Concentration of Acid Solution	Drops of Starch Solution	Drops of KI_3 Solution	Drops of Na_3AsO_3 Solution	Time in seconds
A	2	0.5	2	2	1	
B	2	0.4	2	2	1	
C	2	0.3	2	2	1	
D	2	0.2	2	2	1	
E	2	0.1	2	2.	1	
F	2	0	2	2	1	

TABLE III: Effect of Alkali Medium on Rate of Reaction between Sodium Arsenite and Iodine.

Solution	Drops of Alkali Solution	Concentration Alkali Solution	Drops of Starch Solution	Drops of KI_3 Solution	Drops of Na_3AsO_3 Solution	Time in seconds
G	2	0	2	2	1	
H	2	0.02	2	2	1	
I	2	0.04	2	2	1	
J	2	0.06	2	2	1	
K	2	0.08	2	2	1	
L	2	0.1	2	2	1	

Discussion

The above reaction between sodium arsenite and iodine takes place according to the following equation:

$$AsO_3^{3-} + I_2 + H_2O \rightleftharpoons AsO_4^{3-} + 2H^+ + 2I^-$$

The rate of reaction is dependent on the hydrogen ion concentration, i.e. upon the acidity and basity of the reaction medium.

A look at Tables II and III indicates how the concentration of the acid solution influences the rate of reaction of arsenite and iodine. When the acid concentration is high (i.e. low pH) it takes a long time for the blue colour to disappear. As the acid concentration decreases, the time taken for the disappearance of the blue colour decreases, and when reaction takes place in neutral water (pH 7) and basic solution, the reaction occurs instantaneously. The results show that the reaction between arsenite and iodine proceeds very quickly in alkali medium and slowly in acid medium.

Question

In the strongly alkaline solution (Solution L) why does the solution turn colourless before the addition of arsenite solution?

VIII. EFFECT OF CATALYST ON REACTION RATE

The object of the experiment is to show that reaction rates will be affected by the presence of catalysts in the reacting system.

__Part 1.__ Reaction of Potassium Permanganate and Oxalic Acid

__Requirements__

      Potassium permanganate solution, 0.01M
      Oxalic acid solution, 0.05M
      Sulphuric acid solution, 0.5M
      Manganese sulphate solution, 0.18M

      Dropper, 1 calibrated
      Measuring cylinder, 100 ml
      Stop-watch
      Test tubes
      Test tube rack

__Procedure__

a. Dilution: Make potassium permanganate, 50 drops made up to 25ml with water; make oxalic acid, 50 drops up to 25 ml with water.

b. To a test tube, add 2 drops of diluted oxalic acid solution, 2 drops of sulphuric acid solution and 2 drops of diluted potassium permanganate solution. Start the stop-watch on the addition of permanganate solution. Record the time taken for the permanganate to be decolourised. Add another drop of diluted permanganate solution and again record the time taken for the solution to be decolourised. Repeat the experiment adding drops of diluted permanganate solution till the decolourisation of the solution is instantaneous (approximately 12 drops of permanganate). To another test tube add 2 drops of diluted oxalic acid solution, 2 drops of sulphuric acid solution, 1 drop of manganese sulphate and 1 drop of diluted permanganate solution. Note the time required to decolourise the solution from the moment the drop of permanganate is added. Plot a graph of drops of permanganate added vs time in seconds.

TABLE I: Effect of Catalyst on the Rate of Reaction between Permanganate and Oxalic Acid

Tube	Drops of $H_2C_2O_4$ solution	Drops of H_2SO_4 Solution	Drops of 0.18M $MnSO_4$ Solution	Drops of $KMnO_4$ Solution	Time in seconds
1	2	2	-	1	
1	2	2	-	2	
1	2	2	-	3	
1	2	2	-	4	

Table I. (Continued)

Tube	Drops of $H_2C_2O_4$ Solution	Drops of H_2SO_4 Solution	Drops of 0.18M $MnSO_4$ Solution	Drops of $KMnO_4$ Solution	Time in seconds
1	2	2	-	5	
1	2	2	-	6	
1	2	2	-	7	
1	2	2	-	8	
1	2	2	-	9	
1	2	2	-	10	
1	2	2	-	11	
1	2	2	-	12	
2	2	2	1	1	

Part 2. Reaction of Potassium Iodide and Hydrogen Peroxide.

Requirements

Potassium iodide solution, 0.6M
Hydrogen peroxide solution, 10M
Sulphuric acid solution, 0.5M
Ammonium molybdate solution, 0.11M
Starch solution, 1%

Dropper, 1 calibrated
Measuring cylinder, 100 ml
Test tubes
Test tube rack

Procedure

a. Dilution: Make hydrogen peroxide, 10 drops up to 50 ml with water; potassium iodide, 2 drops up to 10 ml with water and ammonium molybdate, 2 drops up to 10 ml with water.

b. Into a test tube add 2 drops of sulphuric acid, 2 drops of starch solution, 2 drops of diluted hydrogen peroxide solution, 1 drop of diluted potassium iodide solution and record your observation. To another test tube add the same solution (same quantities) but add 2 drops of diluted ammonium molybdate solution before adding the diluted potassium iodide solution. Again record your observation in Table II.

TABLE II: Effect of Catalyst on the Rate of Reaction between
Potassium Iodide and Hydrogen Peroxide

Tube	Drops of H_2SO_4 Solution	Drops of Starch Solution	Drops of H_2O_2 Solution	Drops of $(NH_4)_2MoO_4$ Solution	Drops of KI Solution	Observation
1	2	2	2	-	1	
2	2	2	2	2	1	

Discussion

The rates of chemical reactions are influenced by a number of factors, one of which is the presence of catalysts in the reaction system. Catalysts may be described as substances that affect the rate of reactions, and always take part in the reaction they are catalysing.

From the plot of number of drops of permanganate against time for the first experiment, we see that the reaction time decreases as the number of drops of permanganate increases. The reaction involves the reduction of MnO_4^- to Mn^{2+} by oxalic acid. Thus as the concentration of Mn^{2+} increases, the reaction proceeds faster, and the Mn^{2+} ions act as a catalyst in this reaction. This was verified by the short time taken for the reaction with the presence of some Mn^{2+} (added in the form of $MnSO_4$) in the reaction mixture before the addition of permanganate.

When potassium iodide reacts with H_2O_2 hydrogen peroxide, iodine is formed and this is detected by a blue colouration with starch. When the concentration of the reactants is low, it is found that some seconds or even minutes must elapse before the blue colouration is visible. However, with the addition of traces of ammonium molybdate, the reaction is very fast and a blue colouration develops immediately. In this reaction, ammonium molybdate is acting as a catalyst.

Questions

1) Will a catalyst have any effect on the concentrations at equilibrium?

2) Why do catalysts affect the rate at which equilibrium is attained?

IX. REACTION OF MAGNESIUM WITH HYDROCHLORIC ACID

The object of the experiment is to study the rate of reaction between magnesium ribbon and dilute hydrochloric acid.

Requirements

Hydrochloric acid, 1M
Magnesium ribbon
Stop-watch
Strip of graph paper (2 inches)
Steel wool
Test tubes
Test tube rack

Procedure

The 1M hydrochloric acid is diluted as outlined in Table I. Magnesium ribbon 40 cm is cleaned with steel wool until the oxide coating is removed. Divide the length of magnesium into six approximately equal parts. 6 dry test tubes are placed in a test tube rack. To tube 1, place a piece of magnesium ribbon, ~~as shown in diagram~~. Place the strip of graph paper behind the test tube and estimate a length of 1 inch of the magnesium ribbon. Fasten the graph paper to the tube by means of cellulose tape. Remove the magnesium and add the hydrochloric acid (Solution A) up to the 1 inch mark. Replace the magnesium and record the time required for the 1 inch of magnesium to dissolve. Repeat the procedure using another piece of magnesium ribbon and a new solution of hydrochloric acid and in all measurements the length of magnesium immersed in the acid solution is constant (1 inch).
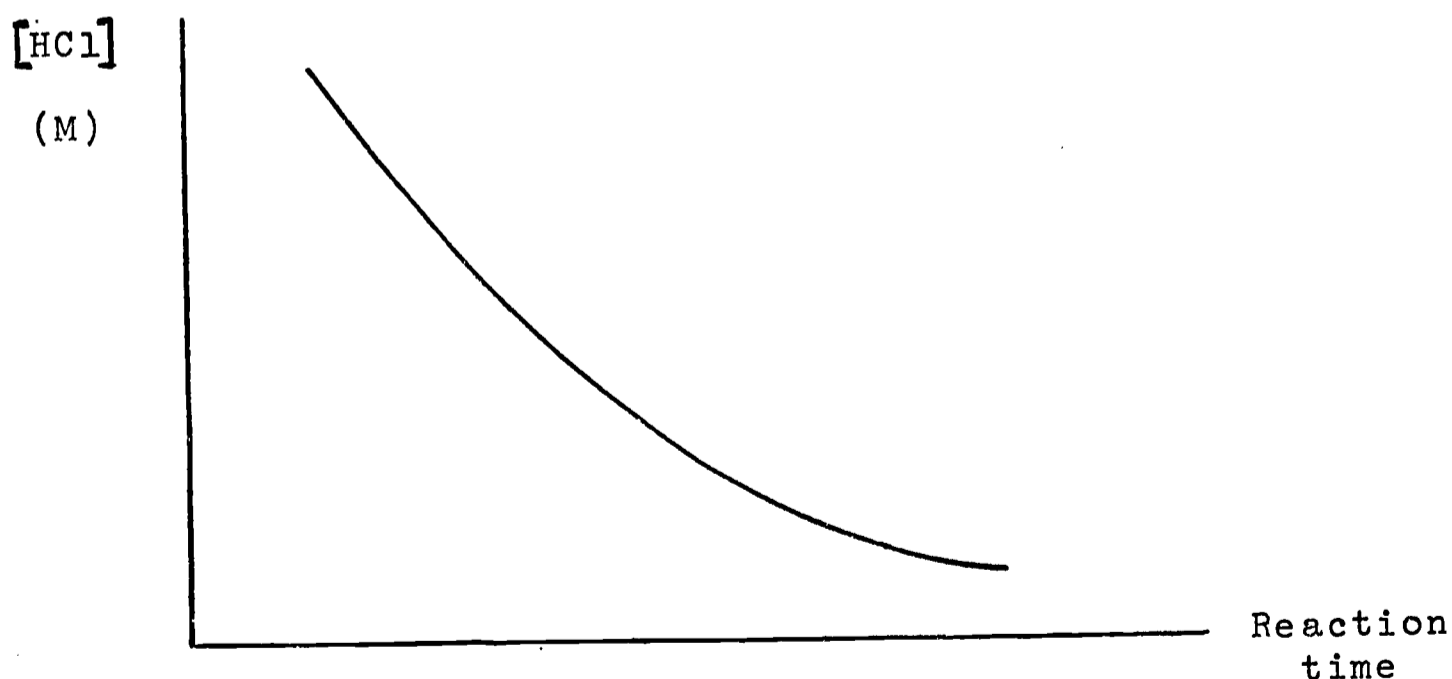
Fig. 1 Variation of reaction time with acid concentration.

TABLE I: Rate of Reaction of Magnesium (1 inch) with
Hydrochloric Acid of Varying Concentration.

Solution	ml of HCl Solution	ml of water	Molarity of HCl	Time of Reaction Seconds
A	50	–	1.0	
B	45	5	0.9	
C	40	10	0.8	
D	35	15	0.7	
E	30	20	0.6	
F	25	25	0.5	

Plot a graph of concentration of hydrochloric acid against
time of reaction.

Discussion

From the first few experiments, it has been shown that the
rate of a chemical reaction depends upon the concentrations of
some or all of the reactants. By measuring the time taken for
a constant amount of magnesium metal to react with varying concen-
tration of hydrochloric acid, the dependence of the rate of reaction
on the acid concentration can be measured. From the graph of con-
centration of acid against time, it can be seen that for more con-
centrated solutions of acid, the reaction is faster. If the square
of the acid concentration is plotted against the reciprocal of the
reaction time, a straight line plot is obtained. This means that
the reaction is Second Order and the rate of reaction of a con-
stant amount of magnesium ribbon is directly proportional to the
square of the acid concentration.

$$\text{rate} = k \times [\text{HCl}]^2$$

where k is the constant of proportionality.

A similar experiment is found in "Experiments on Compound
Formation" UNESCO Project for Chemistry Teaching in Asia, 1969.

Note the difference in mathematical treatment of data in
Experiments II and IX.

In experiment II, the amount of sulphur required to produce a turbidity, is small compared to the initial thiosulphate concentration. The reaction proceeds at a constant rate for a short period of time i.e. rate $\propto 1/t$.

This is not the case in Experiment IX, where a significant amount of the hydrochloric acid is used in the reaction. Remembering that the concentration of magnesium (at the reaction surface) remains constant for the purpose of this experiment, we have average rate of disappearance of hydrochloric acid is two times the rate of disappearance of magnesium which is expressed as the amount reacted divided by the time of reaction. Since the amount reacted is constant

$$\text{average rate} = \frac{\text{constant}}{\text{time}}$$
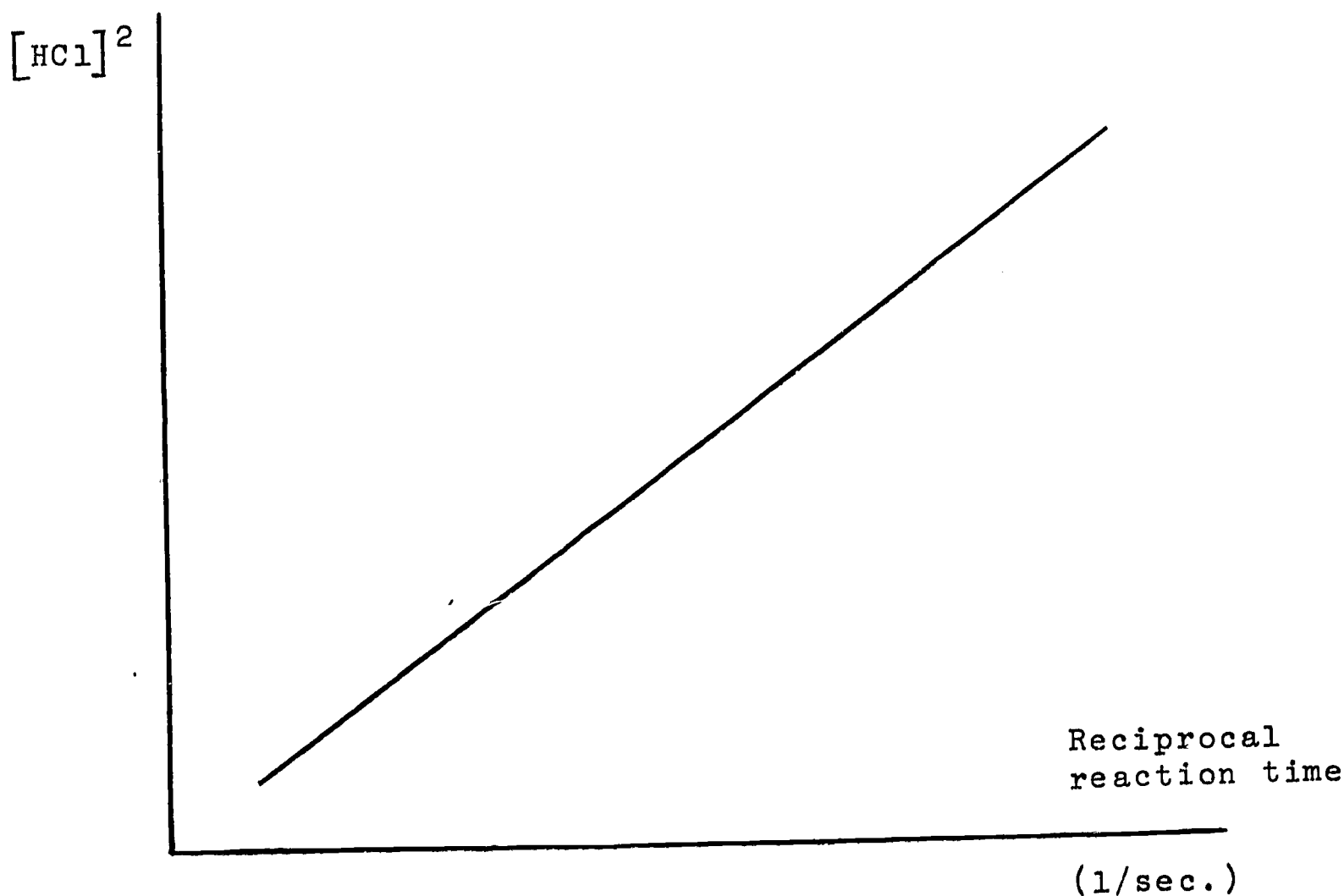
Fig. 2. Square of acid concentration against reciprocal reaction time ($\propto$ average rate of reaction).

Question

1) Why is it necessary to remove the oxide coating from the magnesium ribbon?

2) What are the units of k, the rate constant, in this experiment?

X. REACTION OF TIN AND IODINE IN BENZENE SOLUTION

The object of this experiment is to study the rate of reaction between tin and iodine in benzene solution. The reaction rate is followed by determining the rate of loss of weight of tin. The main apparatus for this experiment, viz. an accurate analytical balance, is not readily available in most schools. The purpose of including this experiment into the framework of the kit is to give another example of rate of reaction should the necessary apparatus be available. The experiment is reported in Journal of Chemical Education 43, 483, (1966).

Requirements

Tin squares of approximately 3g with a hole in the centre
Iodine solution, 10g I_2 dissolved in 100 ml of benzene.

Balance, Mettler Electrobalance Type H15
Beaker, 100 ml
Cotton thread, 30 cm
Platform to span balance pan
Stop-watch

Procedure

Tie the piece of tin with the thread and suspend it from the balance pan hook at approximately 4 cm above the balance pan. Weigh the tin and thread in air accurately. Place the platform over the balance pan and make sure that it does not touch the pan. Fill the beaker 3/4 full with the iodine solution and place it on the platform so that the tin is fully immersed in the iodine solution (see illustration). Weigh the piece of tin again (suspended in iodide solution) accurately and take this reading as being weight of tin at time 0. Weigh the piece of tin (suspended in solution) at 2 minute intervals till 30 minutes has elapsed. Plot a graph of weight of tin against time.

Repeat this experiment with iodine solutions containing 5g I_2 in 100 ml benzene and 2g I_2 in 100 ml benzene.
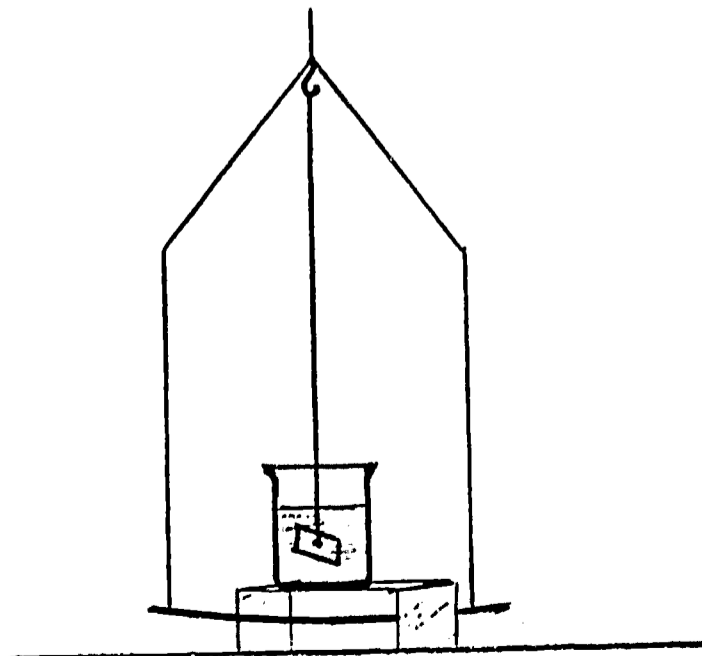
Weight of tin (and thread) in air = 2.9984
Weight of tin in Iodine solution = 2.6450

TABLE I: Determination of Weight Loss of Tin with Time in Iodine Solution.

Time (min.)	Weight of tin	Time (min)	Weight of tin
0		16	
2		18	
4		20	
6		22	
8		24	
10		26	
12		28	
14		30	

Discussion

The reaction between tin and iodine takes place slowly at room temperature according to the equation.

$$Sn + 2I_2 \longrightarrow SnI_4$$
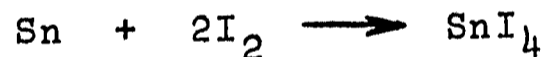
The rate of reaction may be followed by determining the weight of tin at regular intervals of time, and the plot of weight of tin against time shows qualitatively the rate of the reaction. (Fig. 1)

If the rate of reaction is plotted against the concentration of iodine then a straight line is given showing that the rate depends on the first power of the concentration of iodine (first order).

Fig. 1.

Reaction of tin and iodine in benzene.

(slope of line = rate of reaction)
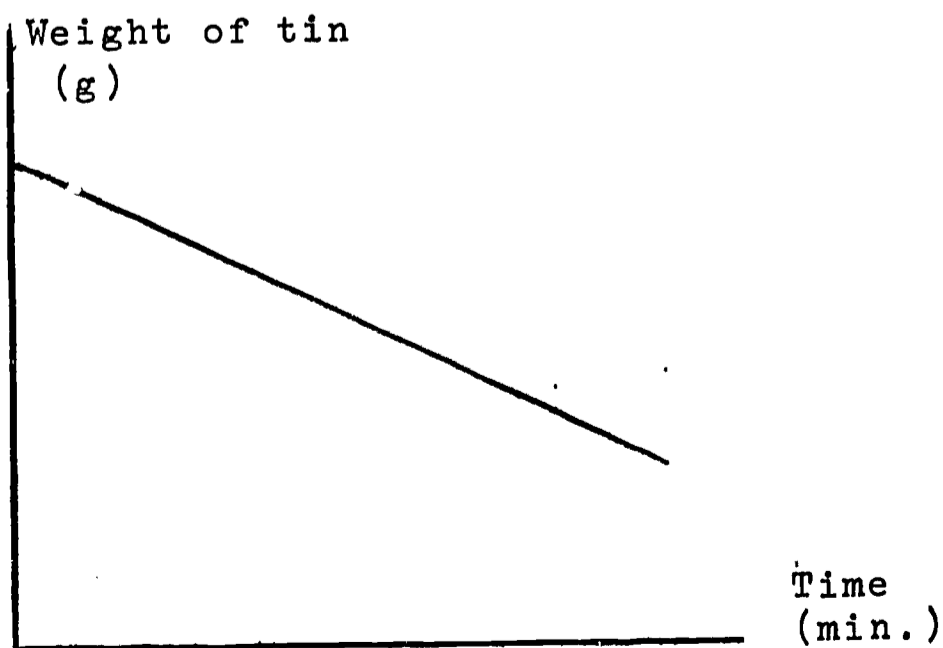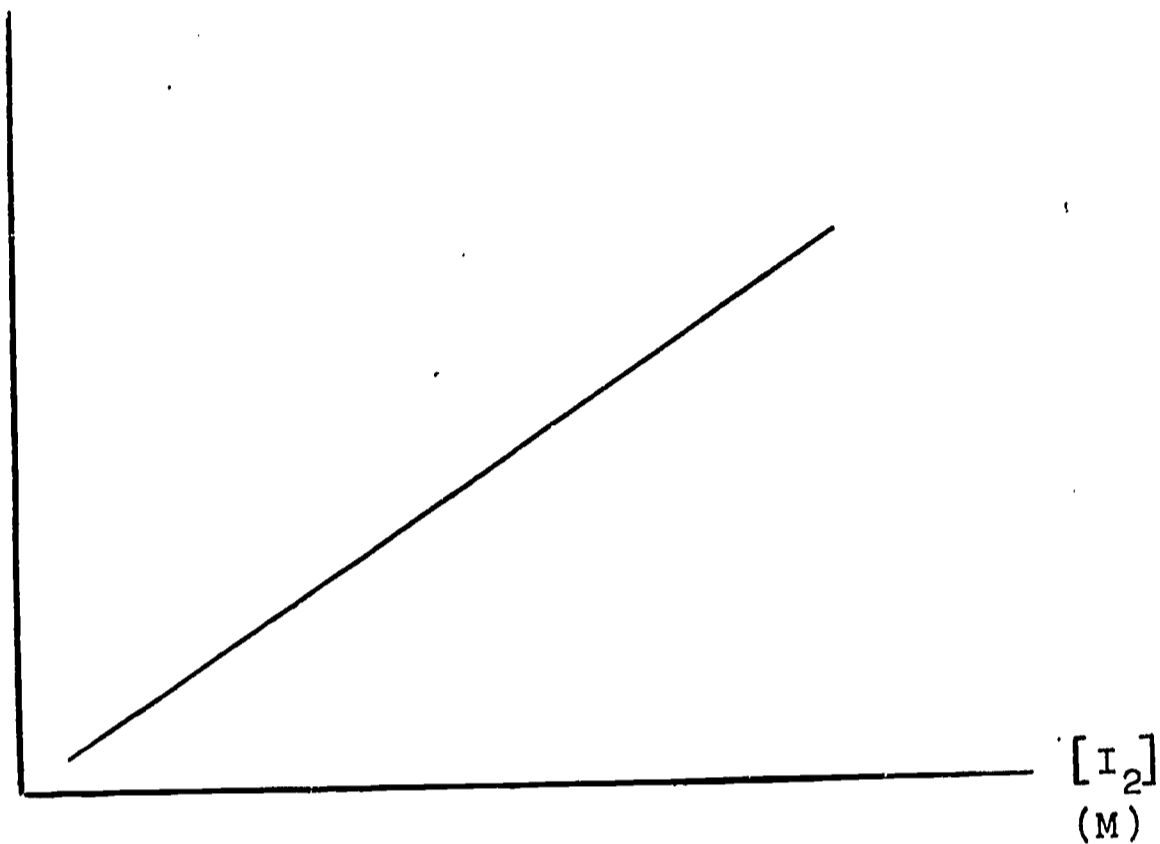
Fig. 2   Rate of reaction plotted against iodine concentration.

Question:

Could this experiment be successfully conducted in aqueous
solution?

XI. REACTION BETWEEN SOLIDS

The object of the experiment is to study the reaction of two solids, potassium iodide and mercury(II) chloride. In place of of mercury chloride, lead acetate may be used.

Requirements

Potassium iodide
Mercury(II) chloride

Beaker, 100 ml
Glass rod, fire polished

Procedure

Place approximately 2g each of potassium iodide and mercury chloride into a dry beaker and note any changes. Gently stir the mixture with the glass rod, then stir vigorously by grinding the solids together and finally, add 1 ml of water to the mixture and stir. Record all observations. Clean and dry the beaker, and this time grind the two solids to powders (separately) before placing them into the beaker. Stir the mixture with the glass rod and record your observations.

Discussion

Reactions between solids usually take place slowly. In this reaction, both the reactants and products are solids. The rate of the reaction is followed by the appearance of an orange-red colour due to the mercury iodide formed

$$2KI \quad + \quad HgCl_2 \longrightarrow \quad 2KCl \quad + \quad HgI_2$$
$$\text{(white)} \quad \text{(white)} \qquad\qquad \text{(white)} \qquad \text{(orange-red)}$$
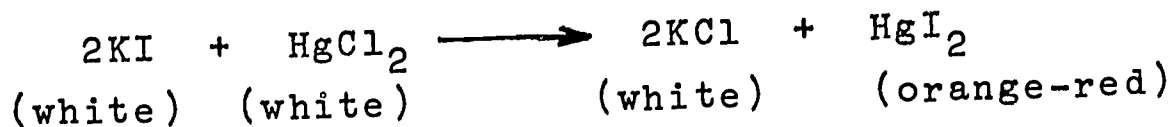
When crystals of KI and $HgCl_2$ are placed into the beaker, the surface area of contact turns orange-red. This is more so when the surface area of contact is increased by gentle stirring of the crystals. When the crystals are ground together, the rate of appearance of the orange-red colouration is more pronounced. If KI and $HgCl_2$ are placed together in a powdered form, the rate of formation of HgI_2 is quite rapid even with gentle mixing of the powders. This experiment shows that the rate of reaction between solids depends upon the surface area of contact. The larger the surface area of contact, the faster is the rate of reaction.

Question:

Explain what happens when water is added to the mixture.

XII. HYDROLYSIS OF TERT-BUTYL CHLORIDE

The object of the experiment is to study the reaction of an alkyl halide (t-butyl chloride) with water. It is realised that in some schools t-butyl chloride is not readily available and this experiment is included   as   another example of rate of reaction.

Requirements

Tert-butyl chloride, 0.1M in acetone solution
Sodium hydroxide solution, 0.1M
Bromothymol blue in ethanolic solution (indicator), 1%

Beakers, 2 x 50 ml
Measuring cylinder, 10 ml and 100 ml
Stop-watch

Procedure

To 20 ml of 0.1M t-butyl chloride add 0.1M NaOH and water as indicated in Table I. Add a few drops of bromothymol blue. This gives the solution a blue colour. The time (in seconds) is taken from the moment when the t-butyl chloride and the aqueous solution of NaOH containing a few drops of indicator is mixed until the colour changes from blue to yellow. Enter the result into Table I.

TABLE I: Rate of Hydrolysis of 20 ml of 0.1M t-butyl chloride (RH) with 0.1M NaOH (Resultant Concentration of RH (C^o_{RH}) is 0.05M)

ml of NaOH	ml of H_2O	Reaction time t (seconds)	C_{RH} Molarity	C^o_{RH} /C_{RH}
1.0	19.0		0.0475	1.052
1.5	18.5		0.0463	1.081
2.0	18.0		0.0450	1.111
2.5	17.5		0.0438	1.142
3.0	17.0		0.0425	1.176
3.5	16.5		0.0413	1.212
4.0	16.0		0.0400	1.250
4.5	15.5		0.0388	1.290

Discussion

When an alkyl halide is undergoing hydrolysis an excess of acid is produced in the reaction.

$$R-Cl \; + \; H_2O \; \rightleftharpoons \; R-OH \; + \; HCl$$
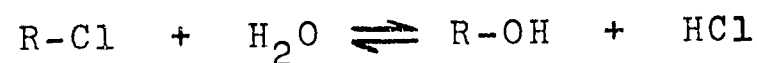
One way of following the course of the reaction is to measure how much HCl is produced. A method of following the reaction is to include a base and an acid-base indicator in the original reaction mixture. Thus when the hydrolysis reaction is proceeding the base is gradually being neutralised by the acid produced and the indicator changes colour when the pH has reached a certain value. The acid-base indicator should be one which is suitable for neutralization of NaOH with HCl, i.e. a strong base with a strong acid, and bromothymol blue in ethanolic solution is chosen.

The calculations involved in this experiment is as follows:-
Remaining concentration of RH at time t is calculated from

$$C_{RH} = C_{RH}^{O} \left(1- \frac{\text{vol. of NaOH}}{20}\right) .$$

Assuming this hydrolysis reaction is of first order with respect to t-butyl chloride,(and independent of alkali concentration) i.e.

$$-\frac{dC_{RH}}{dt} = k.C_{RH}$$

which on integration gives $\ln \dfrac{C_{RH}^{O}}{C_{RH}} = k.t$

where C_{RH}^{O} is the initial halide concentration, C_{RH} is the concentration at time t, and k is the rate constant. The plot of log (C_{RH}^{O}/C_{RH}) against time gives a straight line, which proves the hydrolysis reaction of t-butyl chloride is of first order with respect to alkyl halide concentration. (See diagram).
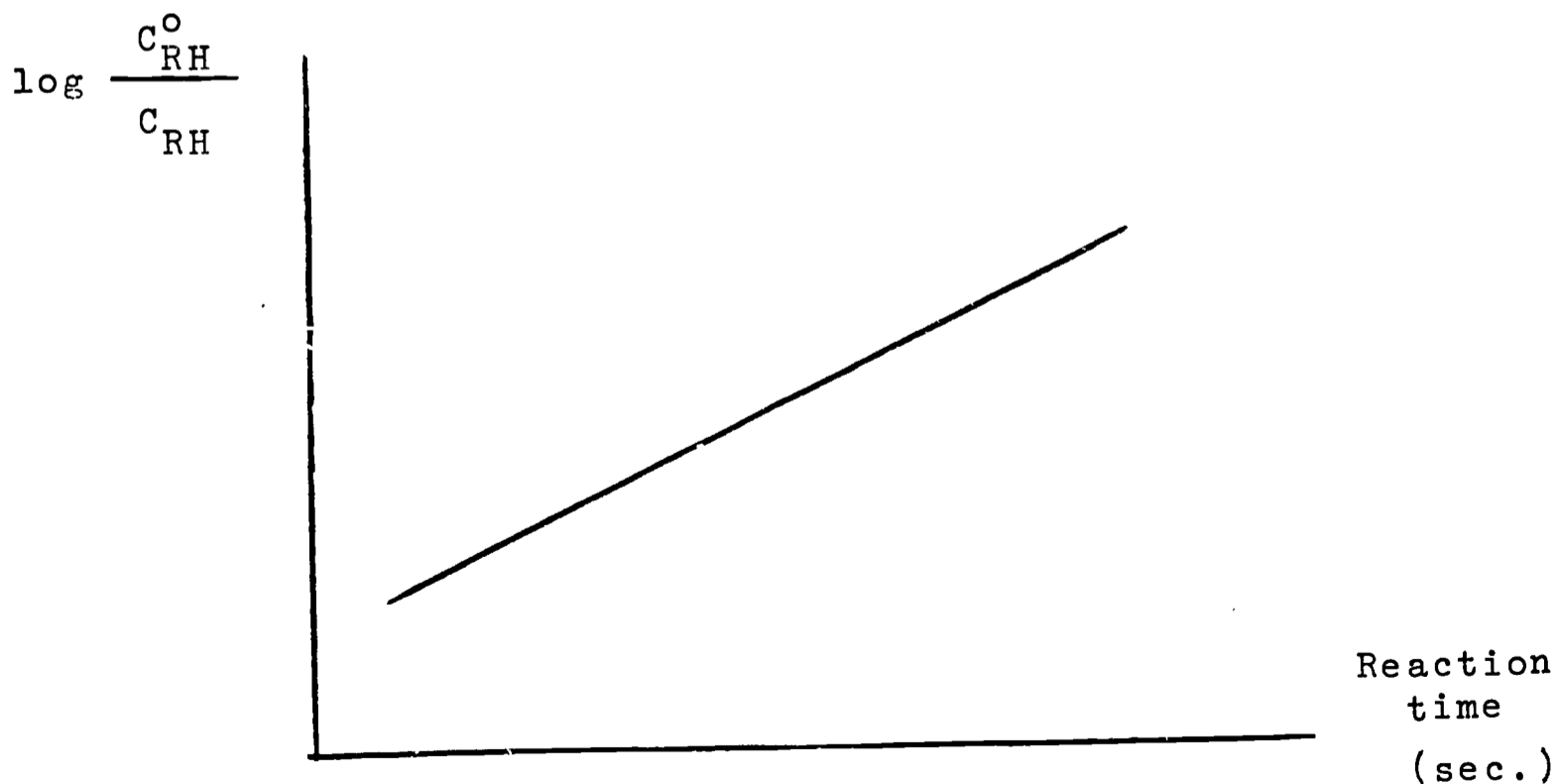
Fig.1. First order plot for hydrolysis of t-butyl chloride.

Question

Why is it necessary to use sodium hydroxide in this experiment?

XIII. THE BLUE BOTTLE EXPERIMENT*

This experiment has been included to demonstrate in a simple
way a number of the basic principles of rates of reaction. The
nature of chemicals and their interactions with one another are
illustrated in an elegant and informative way. The experiment is
essentially qualitative (although quantitative modifications sug-
gest themselves at various stages) and no detailed experimental
procedure has been given.

Requirements

Sodium hydroxide
Glucose solution
Methylene blue, 1% solution in ethanol 96%

Conical flask, 100 ml

Procedure

The system should contain the reagents in the approximate
proportion glucose (20 gm), sodium hydroxide (20 gm), 1% alcoholic
methylene blue solution (0.5 ml) per litre of water. A glass flask
is about half-filled with this solution and then sealed with a
rubber stopper. Shaking the flask causes the liquid to turn blue.
Upon standing, the blue liquid reverts to its original colourless
condition. Students then suggest explanations which may be checked
by experiment and a mechanism for the reaction may be developed.

Development

Students may suggest the following as explanations

(i)   coloured material on stopper
(ii)   increased contact with glass
       (Inversion of flask or gentle swirling to cover the
       glass does not produce a blue colour).
(iii) shaking increases the kinetic energy of the flasks con-
       tents.
       (This suggest that increased temperature would have the
       same effect. When warmed in the hand, blue colour does
       not appear.)
(iv)   two layers which mix on shaking and then settle out.
       (Upon inversion and shaking of the flask, the blue ~~colour~~
       colour is seen to disappear uniformly in the solution).

(v)   gas in the top of the flask.
       (Pressure has decreased in the flask and gentle removal
       of the stopper should show bubbles on the "liquid seal".
       Observation of the gas/liquid interface should show a

thin blue layer where mixing is occurring continually.
Replacement of the air in flask by natural gas leads
to a decrease or perhaps disappearance of the blue
colour).

Observations: Some ingredient of air reacts with the liquid to
form the blue solution. Initial "bluing reaction"
is quite rapid. Disappearance of the blue colour
takes longer (depending on conditions.

Conclusion: There must be at least three reactions occurring
a) solution of gas in the liquid phase
b) reaction with something in the liquid to give
a blue colour
c) reaction of the blue material to give colourless
products.

$$A \text{ (gas)} \longrightarrow A \text{ (soln.)}$$
$$A \text{ (soln.)} + X \longrightarrow B$$
$$B + Y \longrightarrow \text{products}$$
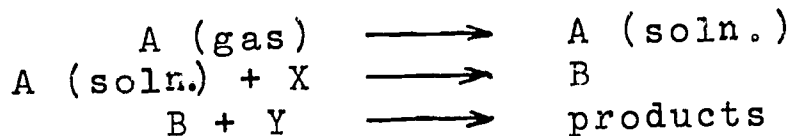
Further observations: Length of time of colour duration depends
on how long are shakes.
Intensity of colour is independent of how
long the flask is shaken.

Deduction: The concentration of the blue intermediate quickly
reaches a steady state which is maintained throughout the reaction,
quickly dropping to zero as the de-bluing reaction is completed.

One explanation of these results is that X is a limiting
reagent and a catalyst for the reaction whose overall mechanism
may be represented as

$$A \text{ (gas)} \xrightarrow{\text{fast}} A \text{ (soln.)} \qquad (1)$$

$$A \text{ (gas)} + X \xrightarrow{\text{fast}} B \qquad (2)$$

$$\underline{B + Y \xrightarrow{\text{slow}} X + \text{products}} \qquad (3)$$

$$A \text{ (gas)} + Y \longrightarrow \text{products}$$
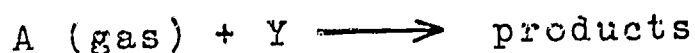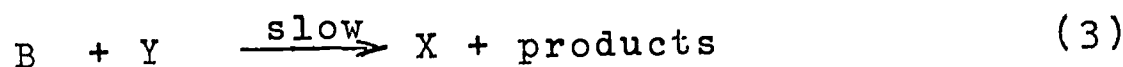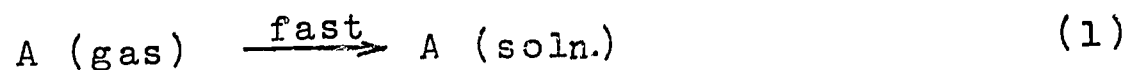
Concentration effects may now be investigated. Addition of water
(whose dissolved oxygen produces a blue colour) leads to decreased
rate of de-bluing and of intensity of colour, consistent with
mechanism. The concentrations of B and Y have been decreased,
resulting in a decrease in step 3).

It is possible to study the effect of temperature on the
rate of reaction by plotting the logarithm of de-bluing time as a
function of the reciprocal of absolute temperature. A straight
line results.

Hydroxide ion is used to convert the glucose to glucoside
(called Y previously) which takes part in the equation

$$G + OH^- \rightleftharpoons G^- + H_2O$$
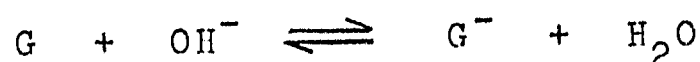
Question

Show that for reaction (3)   the rate law is

$$- \frac{d\,[B]}{dt} = k[glucose]\,[OH^-][methylene\ blue]$$

ANSWERS TO EXPERIMENT QUESTIONS

Experiment I

Concentration of potassium iodide solution = 0.06 M ;
Assuming each drop is 0.05 ml
Then, when 1 drop is diluted to 100 ml
Concentration of diluted solution $= \dfrac{0.05}{100} \times 0.06$ M

$$\text{i.e } 3 \times 10^{-5} \text{ M}$$

4 drops of diluted solution are in test tube with a total of 9 drops.

Concentration of potassium iodide in tube $= \dfrac{4}{9} \times 3 \times 10^{-5}$ M

$$\text{i.e } 4/3 \times 10^{-5} \text{ M}$$

From the overall reaction, 5 moles of iodide, when reacted with excess iodate, produce 3 moles of iodine.

Concentration of iodine $= \dfrac{3}{5} \times \dfrac{4}{3} \times 10^{-5}$ M

$$\text{i.e. approximately } 10^{-5} \text{ M}$$

Experiment II

Air contains carbon dioxide which dissolves in water to produce carbonic acid

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
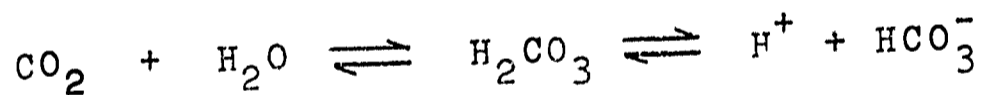
Even though a very weak acid, carbonic acid will precipitate sulphur from thiosulphate solution because of the instability of the free thiosulphuric acid, $H_2S_2O_3$, which is initially formed.

$$S_2O_3^{2-} + 2H^+ \longrightarrow H_2S_2O_3 \longrightarrow S + SO_2 + H_2O$$
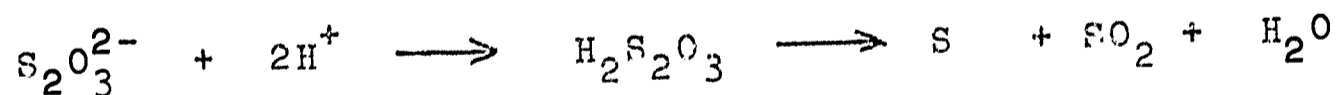
Experiment III

We may envisage chemical reactions as taking place by means of a collision process; atoms or molecules collide and either rebound or cohere to form new compounds. The chance of favourable collisions is increased with higher concentrations of reactants.

Experiment IV

1) Dilution : 10 drops of 0.6 M potassium iodide made up to 1 ml
Assuming 1 drop is 0.05 ml, then
Molarity of potassium iodide solution $= 0.6 \times \dfrac{0.05}{1.0} \times 10$

$$= 0.3 \text{ M}$$

5 drops of 10 M hydrogen peroxide made up to 25 ml

Molarity of hydrogen peroxide solution $= \dfrac{5 \times 0.05 \times 10}{25}$

$$= 0.1M$$

According to eq. (1), 1 mole of hydrogen peroxide will react with 2 moles of iodide, therefore in this experiment potassium iodide is in excess. This is rather important as an excess of hydrogen peroxide will react with the iodide liberated in eq.(2).

2)   Apart from the obvious differences suggested by the titles, the role of thiosulphate is an important modification in Experiment IV.

The blue colour of starch/iodine in Experiment III appears after the lower limit of sensitivity of the starch reagent is exceeded. It is possible to observe only one point of the reaction. In Experiment IV. any number of points may be observed, depending on the number of drops of thiosulphate added.

3) Yes. On the collision theory, rate of reaction is proportional to concentration of reactants. The same quantity of reactants in larger volumes means a decrease in concentration and hence a decrease in the rate.

Experiment V

An increase in temperature raises the kinetic energy of the reacting particles, increasing the rate at which collisions occur, thus leading to an increase in the rate of chemical reaction. It must be remembered that an increase in temperature increases the rate of forward and reverse reactions. For reversible reactions, the equilibrium concentrations are affected if the temperature is altered. For industrial applications of chemical reactions, the temperature must be optimised i.e. a balance must be reached between increased rate of reaction, and decreased concentration of product in the equilibrium system.

Experiment VI

It is necessary to heat the solution during the reaction. The reaction proceeds so slowly at room temperature that sharp end-points are not obtained by titration. The normal practice is to warm the solution to about $60^{\circ}C$ before the total stoichiometric amount of titrant has been added; the reaction then occurs rapidly and titration to the end point is possible.

Experiment VII

In strongly alkaline solutions, iodine is oxidised to hypoiodites and iodates. This removes iodine from solution and the blue colour fades

$$I_2 + 2OH^- \longrightarrow IO^- + I^- + H_2O$$

$$3IO^- \longrightarrow IO_3^- + 2I^-$$
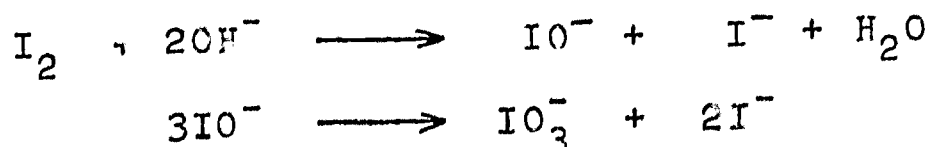
Experiment VIII

1) No. Catalysts only affect the rate at which equilibrium is attained.

2) By taking part in the reaction, they provide alternative pathways for the reaction to follow. These different pathways (mechanisms) have different energy requirements and the lower the energy requirement, the more easily will the reaction proceed and equilibrium be attained.

Experiment IX

1) The reaction involved is heterogeneous and takes place at the solid/liquid interface. Hydrochloric acid will behave differently towards a magnesium surface if the surface characteristics are modified by a coating of oxide. This may result in an "induction time" prior to reaction, while the acid removes the oxide coating.

2) The units of k are derived from the equation

$$-\frac{dc}{dt} = k\,c^2$$

$$\text{units of } k = \frac{\text{units of rate}}{\text{units of concentration squared}}$$

$$= \frac{\text{mole litre}^{-1}\text{ sec}^{-1}}{(\text{mole litre}^{-1})^2}$$

$$= \text{mole}^{-1}\text{ litre sec}^{-1}$$

or litres/mole/sec.

Experiment X

No. Tin (IV) iodide (SnI_4) is a covalent compound and is not soluble in an aqueous medium. Any initial reaction would produce an unreactive coating at the tin/water interface. This coating is soluble in benzene, however.

Experiment XI

Potassium iodide and mercuric chloride dissolve in water and are therefore most efficiently mixed, when water is added. An intense orange - red precipitate is formed immediately. Note that if too much iodide is present, the precipitate will dissolve to form a yellowish solution of the tetraiodomercurate (II) ion.

$$Hg\,I_2 + 2I^- \longrightarrow Hg\,I_4^{2-}$$
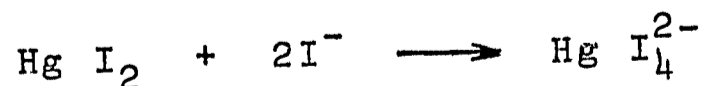
Experiment XII

Generally, alkyl halides react with aqueous alkali to undergo displacement of the halogen by -OH, with the formation of alcohols:

$$R\ Cl\ +\ OH^- \longrightarrow ROH\ +\ Cl^-$$

Tertiary alkyl halides do not require the presence of a strong alkali for hydrolysis. A weak base such as sodium bicarbonate may be used to neutralise the acid formed and prevent re-attack of the acid upon the alcohol.

$$\underline{t}-R\ Cl\ +\ H_2O \longrightarrow \underline{t}-ROH\ +\ H^+ + Cl^-$$

The use of sodium hydroxide to neutralize this acid formed, results in a sharp and easily discernable end-point because a strong acid-base neutralization is involved.

Experiment XIII

For the slow step 3) and thus for the whole reaction,

$$-\frac{d[B]}{dt}\ =\ k_3[B][G^-]$$

where B is the oxidised (blue) form of methylene blue.

For the equilibrium of the reversible glucoside reaction,

$$K\ =\ \frac{[G^-]}{[G][OH^-]}$$

$$[G^-]\ =\ K[G][OH^-]$$

$$-\frac{d[B]}{dt}\ =\ k_3\ K[G][OH^-][B]$$

$$=\ k\ [G][OH^-][B]$$

$$=\ k\ [glucose][OH^-][methylene\ blue]$$

APPENDIX I

MOLE AND MOLARITY

Atoms and molecules are far too small to be weighed on the most sensitive balance. However, we can take a definitely known number of atoms or molecules, a number big enough to weigh on an ordinary balance and use this number in calculations concerning weights of atoms and molecules. The number chosen is 6.02×10^{23}, and is called the Avogadro Number. This fantastically large number of atoms of a particular element has a weight equal to the atomic weight of the element expressed in grams. Also the number of molecules of any compound weigh the same number of grams as the molecular weight of that compound. In chemical calculations, the number 6.02×10^{23}, known as Avogadro Number, is called a mole.

It may be of help to think of a mole of molecules in the same way as we think of a dozen of anything - a dozen eggs, a dozen oranges, etc. Since an orange is bigger in size than an egg, it weighs more than an egg. Accordingly, a dozen oranges will weigh more than a dozen eggs. In the same way, a mole of sugar (large molecules) weighs more than a mole of water (light molecules, though each mole contains the same number of molecules.

Most of our work is concerned with solutions and it is, therefore, necessary to know how we generally express concentrations of solutions. From amongst the various methods of expressing concentration, the most convenient unit of concentration for use in equilibrium calculations is molarity. Molarity is defined as the number of moles of a substance dissolved per litre of the solution.

A 1M solution of NaCl or CH_3COOH or any other substance is one which contains one mole of a substance in one litre of its solution. Similarly a 0.1 M solution of a substance is one which contains one tenth of a mole of the substance in one litre of its solution.

Knowing that 1 mole of a compound has a weight equal to the molecular weight expressed in grams, the weight corresponding to a given number of moles can be calculated as follows:

1 mole of sodium chloride = 58.5 g

0.1 mole of sodium chloride = 5.85 g

The number of moles of a substance in a litre of the solution is called the molar concentration and is represented by the formula of the substance enclosed in square brackets. For example, [NaCl] signifies the molar concentration of sodium chloride in one litre of the solution.

The difference between mole and molarity must be clearly understood. Moles represents an amount whereas molarity represents an amount per unit volume. For example, the molarity of either 1 ml or 10 litres of 0.1M HCl is the same but the amount of HCl in 1 ml of 0.1M HCl is 0.0001 mole and in 10 litres of 0.1M HCl is 1 mole.

APPENDIX II
SLIDE RULE - HOW TO USE IT?*

The arithmetical operations of multiplication and division occur
frequently in practical calculations. Very often the work involved
would be tedious if effected by the ordinary rules of arithmetic,
and a great saving in time would result from the use of some
mechanical means of computing.

The slide rule has been designed with this end in view, and
with its aid, results sufficiently accurate for most practical pur-
poses may be readily obtained. Compared with ordinary or contracted
methods of multiplication and division, or with the use of loga-
rithms, computation by slide rule is less laborious, less liable
to error, and very much more expeditious.

The scales are in most cases divided in decimals, and prac-
tice in reading them may be necessary. It is obviously quite im-
possible to number every line, and in reading a value in any scale,
the nearest number to the left, or to the right, must be carefully
observed, and the divisions of the scale followed until the exact
position is reached. A transparent cursor with a fine line drawn
across it is supplied to assist in certain operations. (The Cursor
index is referred to as X in the instructions which follow.)

MULTIPLICATION is effected by using scale C in conjunction
with scale D. Supposing multiplication of 15 and 45 is desired,
the procedure is: Move the slide so that the 1 on C is brought
opposite 15 on D, and read the answer 675 in Scale D, opposite 45
in scale C. In some cases when the 1 of scale C is used, the
answer is off the scale, and the 10 of scale C must be used instead
of the 1. For example, if 25 x 45 is to be computed, the procedure
is: Set the 10 of C opposite 25 in D and, coincident with 45 in
C, the result, 1125, will be found in D. Scales A and B may be
used for multiplication if desired. The result will always be on
the scale, and the slight delay occasioned by the double setting
avoided. It is for this reason that the upper pair of scales is
sometimes employed in multiplication, but greater accuracy will
always be obtained when scales C and D are used, and their use in
multiplication and division generally is strongly recommended.

In the example above the answer is 1125, but the manipulation
of the slide rule would be exactly the same in the multiplication
of any two numbers in which two five, and four five are the only
significant figures, for example, 25 x 45 = 1125; 2.5 x 45 = 112.5;
.25 x 4.5 = 1.125; .025 x .45 = .01125. The position of the
decimal point in the answer is easily determined by inspection.
When three or more numbers are to be multiplied together, the
computation is effected by a series of operations, X being used to
mark the intermediate answers until the final result is reached.

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* Taken from "Kutsuwa" instruction booklet.

APPENDIX II
SLIDE RULE - HOW TO USE IT?[*]

The arithmetical operations of multiplication and division occur frequently in practical calculations. Very often the work involved would be tedious if effected by the ordinary rules of arithmetic, and a great saving in time would result from the use of some mechanical means of computing.

The slide rule has been designed with this end in view, and with its aid, results sufficiently accurate for most practical purposes may be readily obtained. Compared with ordinary or contracted methods of multiplication and division, or with the use of logarithms, computation by slide rule is less laborious, less liable to error, and very much more expeditious.

The scales are in most cases divided in decimals, and practice in reading them may be necessary. It is obviously quite impossible to number every line, and in reading a value in any scale, the nearest number to the left, or to the right, must be carefully observed, and the divisions of the scale followed until the exact position is reached. A transparent cursor with a fine line drawn across it is supplied to assist in certain operations. (The Cursor index is referred to as X in the instructions which follow.)

MULTIPLICATION is effected by using scale C in conjunction with scale D. Supposing multiplication of 15 and 45 is desired, the procedure is: Move the slide so that the 1 on C is brought opposite 15 on D, and read the answer 675 in Scale D, opposite 45 in scale C. In some cases when the 1 of scale C is used, the answer is off the scale, and the 10 of scale C must be used instead of the 1. For example, if 25 x 45 is to be computed, the procedure is: Set the 10 of C opposite 25 in D and, coincident with 45 in C, the result, 1125, will be found in D. Scales A and B may be used for multiplication if desired. The result will always be on the scale, and the slight delay occasioned by the double setting avoided. It is for this reason that the upper pair of scales is sometimes employed in multiplication, but greater accuracy will always be obtained when scales C and D are used, and their use in multiplication and division generally is strongly recommended.

In the example above the answer is 1125, but the manipulation of the slide rule would be exactly the same in the multiplication of any two numbers in which two five, and four five are the only significant figures, for example, 25 x 45 = 1125; 2.5 x 45 = 112.5; .25 x 4.5 = 1.125; .025 x .45 = .01125. The position of the decimal point in the answer is easily determined by inspection. When three or more numbers are to be multiplied together, the computation is effected by a series of operations, X being used to mark the intermediate answers until the final result is reached.

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[*] Taken from "Kutsuwa" instruction booklet.

DIVISION. Set the slide so that the divisor on scale C is coincident with the dividend on scale D. The result will be found in D opposite 1 or 10 in C.

For example, suppose it is desired to divide 13.9 by 5.65. Adjust the slide so that 565 in scale C is coincident with 139 in scale D. Opposite 10 in C will be found the result in D, viz., 246. Inserting the decimal point, the result 2.46 is obtained.

In computing the value of an expression such as the following: $\dfrac{86.2 \text{ x } .049 \text{ x } 18 \text{ x } 1.7}{22.5 \text{ x } 11.45 \text{ x } .8}$ it is evident that repeated multiplication of the four numbers of the numerator, followed by division separately, by the three numbers of the denominator will give the result, but time is saved by dividing and multiplying alternately. Using scales C and D, find 862 in D, and bring 225 on C into coincidence: adjust X to 18 in C, then move slide to bring 8 on C under X; move X into position above 49 in C and adjust slide so that 1145 in C lies under X; read the answer, 627, in D opposite 17 in C. Approximate cancellation of the numbers will fix the position of decimal point in the answer. 22.5 divides 86.2 approximately 4, and the 4 thus obtained divides 11.45 nearly 3, which leaves 6 in the numerator when divided into 18; .8 into 1.7 give roughly 2, and the result is approximately 6 x 2 x.05 = 12 x .05 = .6. The answer therefore, is .627.

Frequently the position of decimal point may be determined without resorting to the approximation indicated above, e.g., suppose the fraction $\dfrac{51.9}{69.7}$ is desired as a percentage. Using the Slide Rule to divide 519 by 697, the result, 745, obtained, is obviously 74.5 per cent.

Those using the Slide Rule for the first time are advised to master the operations of multiplication and division, as explained above, before reading any further. Practice with simple numbers giving results easily checked is recommended, e.g., using scales C and D evaluate $\dfrac{2 \text{ x } 12 \text{ x } 6}{4 \text{ x } 9}$ and see if the answer is 4. Now repeat, taking the numbers in a different order, and see if the result is the same. Take note of the time saved by dividing and multiplying alternately, as described in the example given earlier. Half-an-hour spent on similar simple examples will suffice to teach the use of the rule for the fundamental operations of multiplication and division.

The following rules, based upon the manipulation of the Slide Rule, are sometimes used to fix the decimal point, but their use is not recommended. In multiplication, when the 1 of scale C is used in the setting of the slide, the number of digits occuring before the decimal point of the answer is one less than the sum of the numbers of digits appearing, before the decimal points of the original numbers. When the 10 of scale C is used in setting, the

number of digits before the decimal point of the answer is the
same as the sum of the number of digits preceding the decimal
points of the original numbers. When dividing, if the answer ap-
pears opposite 1 in C the number of digits preceding the decimal
point of the answer is one greater than the difference obtained
by subtracting the number of digits lying before the decimal point
of the divisor from the number of digits appearing before the deci-
mal point of the dividend, but if the answer is found opposite 10
in C the number of digits preceding its decimal point is the same
as the difference between the numbers of digits appearing before
the decimal points of dividend and divisor respectively. When
the numbers to be multiplied together or divided are of values
less than unity, the number of ciphers immediately following the
decimal points must be taken into account and reckoned as negative
in the application of the rules for fixing the position of decimal
point in the answer.

SQUARES. Numbers may be squared by multiplication direct,
but results are more readily obtained by reading in scale A the
squares of numbers directly opposite in scale D, the cursor or,
preferably the slide, being used to project from one scale to the
other.

The calculation of the area of a circle from the diameter is
a computation often desired. Find the number representing diameter
on D and bring the 1 or 10 of scale C into coincidence with it.

The answer appears in A opposite the value of 785 in B.

SQUARE ROOTS. The square roots of all numbers in scale A
appear directly below in scale D. Since, however, any number ap-
pears twice in scale A, care is necessary in selecting the one to
be used. The rule is: if the original number has an odd number
of digits preceding its decimal point, or,when less than unity, has
an odd number of ciphers immediately following its decimal point,
the left-hand half of scale A must be used. When the number of di-
gits preceding, or the ciphers immediately following the decimal
point in the original number is even, the right-hand half of
scale A must be used.

RECIPROCAL SCALE.

This slide rule is equipped with a reversed C scale (sub-
sequently referred to as the Cl scale) placed along the middle of
the Slide. The uses of this scale are indicated in the following
examples:

Reciprocals are obtained by projecting, from C to Cl or vice
versa, e.g., 4 in C projects into .25, i.e., $\frac{1}{4}$ in Cl.

Multiplication and Division. To compute the value of an
expression such as 2.8 x 3.2 x 6.5, find 2.8 scale D, then with
the aid of the Cursor, bring 3.2 in Cl into coincidence and read
the result, 58.2 in D, opposite 6.5 in C, with one setting of the
Slide. The factors may be selected in any order and the operations

repeated, if necessary, to cover any number of factors.

To find the value of $\dfrac{82}{3.6 \text{ x} .78}$ find 82 in D and bring 36 in C into coincidence. Then opposite 78 in C1 find the result 29.2 in D, the decimal point being inserted by inspection.

CUBES of numbers in scale D can be obtained by projecting directly (by means of X) into scale K (Cube).

CUBE ROOTS are obtained by means of the reverse of this process.

Aims and Objectives of this Project

The General Conference of Unesco, at its thirteenth session, adopted Resolution 2.122 to organize a Pilot Project for Chemistry Teaching in Asia for the purpose of initiating a fundamental re-orientation in the way of teaching chemistry through the use of modern technical devices and methodology. An agreement was signed between the Government of Thailand and Unesco on 13 July 1965 to locate the Project at Chulalongkorn University, Bangkok. The Project started as a regional project. In addition to its regional activities, the Project centre has increasingly served as a national centre for Thai science education.

The primary aim of the Project is to assist science educators in Asia in their task of carrying out reform of chemistry teaching. The Project is operating along two major lines which are distinct but co-ordinated:

1. Modernization of the chemistry courses and development of new teaching materials.

2. Assistance in carrying out in-service and pre-service teacher training, improvement of examinations and use of the latest methods of teaching.

Science educators in Asia may wish to request some or all of the following resource materials (at no cost) in sample quantities to help them carry out curriculum reform:

1. Programmed Instruction Sequence, 1966.
2. Teachers' Guide to the above programmed sequence, 1966.
3. 8 mm. Film Loops in Cassettes.*
4. Film Loop Production Notes, 1967.
5. Teachers' Guide to Film Loops, 1967
6. Compound Formation (Vols, I and II), Teachers' Digest, 1967, 1968.
7. Chemical Equilibria, A Teachers' Digest, 1968.
8. Experiments on Chemical Equilibria, 1968.
9. Experiments on Compound Formation, 1969.
10. Compound Formation Vol. 1 (Thai translation), 1969.
11. Experiments on Chemical Equilibria (Thai translation), 1969.
12. Newsletter, a bi-monthly periodical.
13. Prototypes of low cost kits:** "Teaching Experiments on Chemical Equilibria", "Teaching Experiments on Compound Formation" and "Teaching Experiments on Rate of Chemical Reactions."
14. Experiments on Rate of Chemical Reactions, 1969.

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* Available at a cost of U.S. $ 6.00 per film loop.
** Cannot be supplied outside Thailand.