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ABSTRACT

This UNESCO newsletter is divided into these three sections: (1) a student chapter on the rates of chemical reactions; (2) the student laboratory guide; and (3) the teacher laboratory guide. The laboratory guides describe 14 experiments showing students the differences in chemical reactions and how the rate can be affected by temperature, concentration or catalysts. In the student's guide each experiment is introduced by a short outline followed by a description of the procedure in detail. Important points concerning the principles on which the experiment is based, including explanation of relevant general background, are given in the "discussion" of each experiment. Each experiment is followed by examples of questions which could help the teacher in the classroom; answers, with the explanation in detail, are summarized in the teachers' guide. (Author/PR)

UNESCO

SCIENCE TEACHING PROJECT IN ASIA

NEWSLETTER

VOLUME 3, NUMBER 4/5

MAY 1970

P.O. BOX 1425
BANGKOK, THAILAND

The Unesco Project for Science Teaching in Asia

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REPORT ON THE THAI-UNESCO CHEMISTRY SUMMER INSTITUTE

30 March to 24 April 1970

I. Aims of the 1970 Summer Institute in Chemistry.

In staff discussions, the following aims of the Summer Institute were agreed upon explicitly:

A. To teach, in simple terms, the concepts involved in Rates of Reaction -- the content of rates of reaction.

B. To teach how these can be taught at school level -- the methodology of rates of reaction.

C. To teach the participants to evaluate and adapt classroom and laboratory materials to their own situations.

D. To help them learn how to introduce these materials and other similar materials for improving their own syllabi and curricula -- the techniques of curriculum reform.

II. Implementation of the Aims.

Lectures, discussions, and lecture experiments covered the content of rates of chemical reactions. Discussions and laboratory work made clear to the participants how these can be covered in high school work.

A special set of laboratory experiments, together with further discussions, explored the participants, ability to evaluate and adapt some materials to a developing country's situation.

Discussions on examinations, how to set and how to evaluate them, together with discussions on syllabus content helped to show many participants directions which could be taken towards curriculum reforms. A special group of Thai staff members and participants was formed into a working group to draft a set of recommendations which shall be transmitted to the Ministry of Education through the Summer Institutes' Organizing Committee.

III. Evaluation

All in all the conduct of the Chemistry Summer Institute was satisfactory. As in all of this type of endeavor, some lines of action which should have been taken became clear only at the end of the session.

The aim of teaching content and methodology of rates of reaction was fulfilled quite adequately. There was certainly need to educate the participants in this area. The theme Rates of Reaction this year completes the programme of covering the most important topics in chemistry teaching at pre-university level. Previous Summer Institutes have dealt with Energy, Compound Formation, Stoichiometry and Equilibria.

RATE OF REACTION

STUDENT CHAPTER

Unesco Science Teaching Project
Bangkok Thailand
1970

RATES OF REACTION

The world is full of changes. Some are rapid as are fires. Some are slow as is rusting. Most, including fires and rusting, are fast or slow depending on the conditions. For example, the time needed to cook food varies with the cooking temperature, and the time needed to remove a crowd of people by bus varies with the number of people and number of buses available. The amount of change per unit of time is called the rate of change, and, in chemistry, the rate of reaction.

Fast and Slow Reactions.

Most of the chemical reactions you have studied have been rather fast, for example, the precipitation of solids, the generation of gases, and the changes in color observed in your study of chemistry. Such reactions stop after a few seconds or minutes. But, of course, they were chosen as examples because their rates are rapid enough for you to observe the change in the available time.

Very rapid reactions (such as explosions) may be over in one thousandth of a second whereas slow reactions may take years (iron rusting, wood rotting), centuries (decomposition of concrete), or even millions of years (mountains growing and wearing down).

Of course, explosives, such as gun powder, need not explode. They can burn at a slower rate or they can decompose even more slowly just sitting at room temperature. These changes in rate are primarily due to changes in temperature. There is an increase in rate for the great majority of reactions when the temperature of the system increases and one of the simplest methods of varying a rate of reaction is to vary the temperature. If accurate measurements of rates are to be made it is essential that the temperature be constant during the reaction.

Half-Lives

Radioactive (nuclear) reactions have the longest range of rates, and the most accurately measured rates, known. Some nuclear reactions are so slow that most of the starting material still remains after a million or more years. In order to describe such a long range of rates of reaction scientists have used the term half-life. The half-life for any reaction is the time which would be required (under a given set of conditions) for half the initial material to react. See Figure 1. Can you see that the concept of half-life suggests reactions never "go to completion?" Can you also see that 0.1 lives, 0.01 lives, and so forth are also useful in discussing rate of reaction?

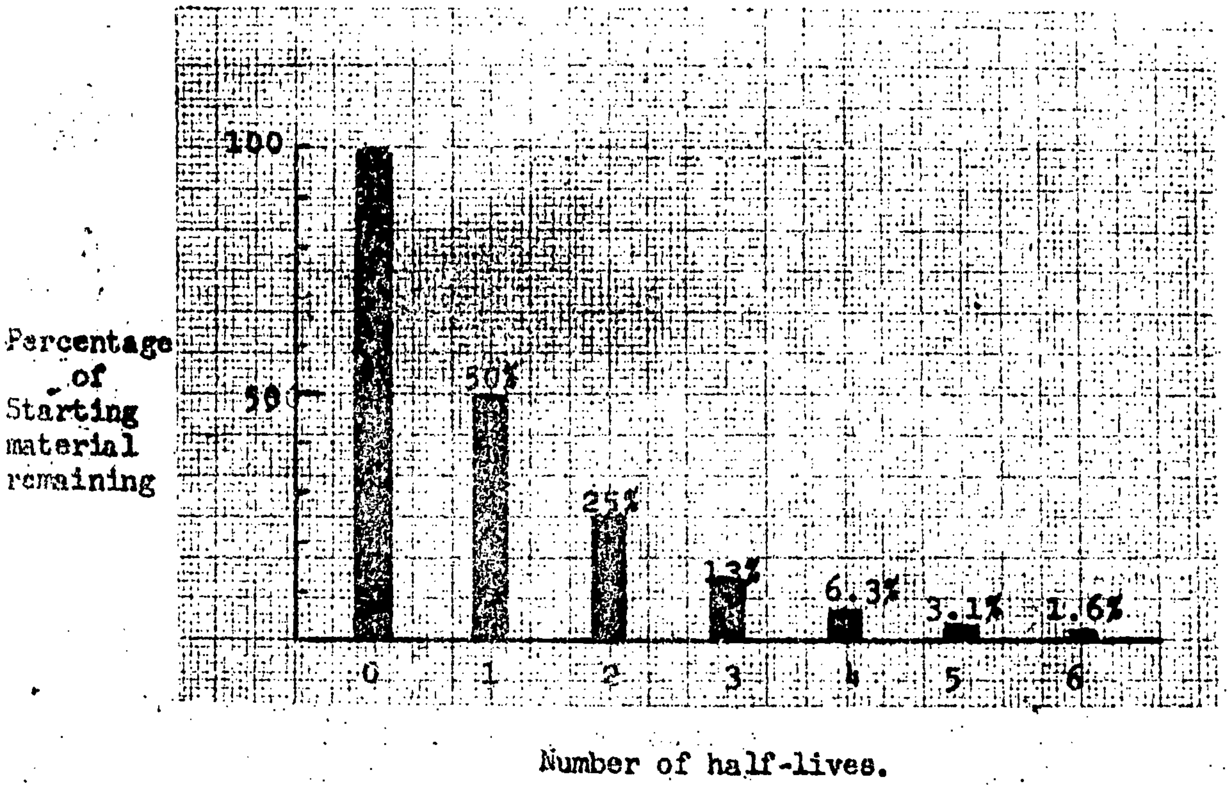


Fig. 1. Percentage of starting material remaining after zero to six half-lives have elapsed. After 10 half-lives only 0.1% of the starting materials remain. This is often a negligible amount and the reaction is often said to "go to completion". Actually, of course, reaction continues.

Radioactive reactions are especially easy to describe in terms of half-lives since the half-life of each reaction is constant regardless of the concentration or amount of the starting material and is almost unchanged by changes in external conditions. Known radioactive half-lives range from about 10^{-10} seconds to 10^{10} years. Shorter and longer half-lives cannot be measured with present techniques. For shorter half-lives the materials disappear too rapidly to be detected. For longer half-lives the rate is too small to measure.

The half-life for a reaction can be measured more accurately than the time for the reaction to finish or go to completion, especially for reactions lasting an hour or longer. Furthermore, reactions generally do not "go to completion" (See Figure 1) nor is it easy to decide when a change is "finished". We shall, therefore, usually use half-lives to discuss rates. For fast reactions of the type you will deal with in the laboratory both the half-lives and the time until observable change stops are of the order of a few seconds or minutes. On the other hand, for a slow radioactive reaction, with a half-life of 1 year, there will still be about 6% of the material left at the end of four years (See Figure 1). Clearly there is a readily observable difference between half-life and time to "finish" the reaction in such cases. But if the half-life is 1 second, only one thousandth of the original material would be left in 10 secs. (See Figure 1). In effect, fast reactions are over by the time ordinary observations can be made. Do you think that all reactions then cease?

We shall discuss rates in terms of half-lives in order to emphasize that reactions do not "go to completion" in any readily definable time. The half-life is the time which would be required for half the original materials to react. For most reactions you will study, the half-life and "time to completion" do not differ greatly. Quite often it is convenient to measure the time for a smaller fraction of reaction than one half-life. The ideas are the same.

How Do Reactions Occur?

Iron and water react, in the presence of air, to give rust. If any one of the three reactants is absent, rusting will not occur. Only when substances are mixed can they react. At the molecular level, we rephrase this to say that molecules must collide before they can react.

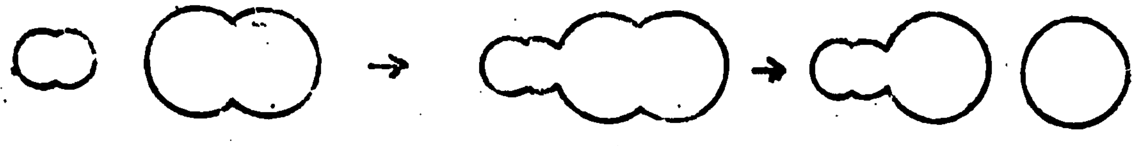
Yet collisions alone are clearly not enough to give reaction. Gun powder is a mixture of charcoal, sulfur, and potassium nitrate. The molecules are in continual motion and jostling against one another. Yet they explode only when ignited by a spark or a sharp blow, both of which raise the temperature of the gun powder. For reaction to occur molecules must collide, but the likelihood of reaction increases as the temperature rises. At higher temperatures these molecules collide more vigorously. They are more apt to react rather than merely rebound.

Molecules also have shapes and their different sides may be different. Each side will have its own tendency to react and this tendency may well vary from side to side. The reaction gaseous H_2O with gaseous CO to produce H_2 and CO_2, for example, requires not only that H_2O collides with CO with enough energy to react, but that the collision be of a configuration like $^{H}_{H}{>}O\text{ ---}C{=}O$, not $^{H}_{H}{>}O\text{ ---}O{=}C$. Only in the first collision is there a reasonable possibility of $O{=}C{=}O$ forming. The molecule which forms during a collision leading to reaction is called an intermediate molecule or an activated molecule. It is like other molecules in that it has a most probable shape. It differs in that its half life is usually only about 10^{-12} seconds before it files apart.

We shall find that these three ideas are sufficient to interpret the observations about rates of chemical reactions:

1) a collision must occur,
2) the energy of the collision must be great enough to allow reaction,
3) the orientation of the collision must be appropriate to allow reaction. See Figure 2.

Reaction occurs



No reaction

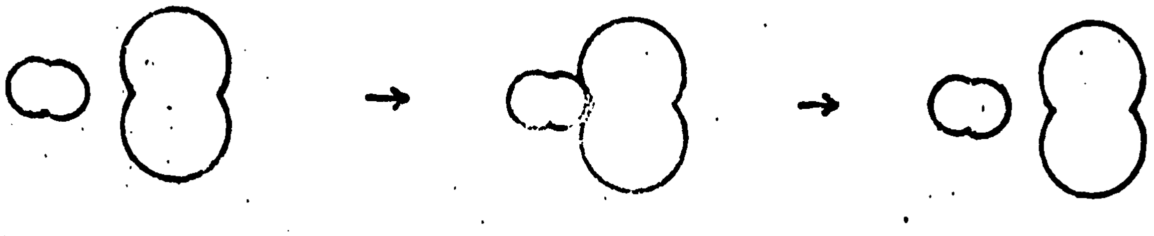


Fig.2. Formation and decomposition of an activated, intermediate molecule.

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The rate is determined by the interplay of these three factors. We now need to determine what experimental factors determine the number o collisions, the energy of the collision, and the orientation during collision.

We have developed these factors in terms of chemical reactions, but they apply to other changes as well. The chance of damaging an automobile fender is determined by the likelihood of collision, the energy of the collision, and the orientation of the automobile. The same ideas apply to other changes. As we develop ideas on rates by studying rather simple chemical reactions, you should continually try to extend these ideas to interpreting the many changes you see around you.

Collision Probability.

If you are in a grove of trees and throw a ball at random, the likelihood of it hitting a tree is proportional to the number of trees within range of the ball, that is, to the concentration of the trees. If there are three times as many trees, there is three times the chance of a collision. Or if you throw three balls at random, the collision probability again increases by three. If both the concentration of trees and the concentration of balls increases three times, then the collision probability increases by a factor of 3 x 3 or 9 times.

Similarly in chemical systems the collision probability is related to the concentrations of the colliding molecules. For a simple bimolecular collision ($A+B = AB$) in a large collection of two kinds of molecules, A and B, the relationship is:

$$\text{rate of collision} \propto \{A\}\{B\}$$

$$\text{or} \quad \text{rate of collision} = k_2\{A\}\{B\}$$

where k_2 is called the rate constant for the bimolecular collision.

The chance of three molecules of kinds A,B, and C colliding in a mixture is

$$\text{rate of collision} = k_3\{A\}\{B\}\{C\}$$

and similarly for more complicated collisions.

But consider for a moment the relative probability of two and of three molecules colliding, for example in a gas at customary pressures and temperatures. Average molecular velocities are about 10^5 cm/sec and average molecular sizes about 10^{-7} cm in radius. If we assume a collision occurs whenever two molecules are within 10^{-7}cm of each other, the collision lasts about 10^{-7}(cm)/10^5 (cm/sec) or 10^{-12} sec. This is consistent with a great deal of other direct experimental evidence. For a third molecule to participate in the collision it has to arrive at the spot during this 10^{-12} second interval. This is a small time and it turns out that the likelihood of a collision between three molecules in a gas is about 1/1000 that of a collision between two molecules. A similar statement can be made about collision probabilities in liquids and solids.

Thus, without performing any actual rate experiments at all, we arrive at the conclusion that collisions between two molecules are far more likely than those involving larger numbers. From this we may infer that the great majority of actual chemical reactions involve only two molecules colliding at a time (not counting solvent molecules). All experimental evidence supports this idea. For example, how many cars collide at once in a "multiple collision"?

Net Equations and Mechanistic Steps

When we look at a net equation such as

$$5Fe^{++}(aq) + MnO_4^-(aq) + 8H^+(aq) = Mn^{++}(aq) + 4H_2O(l) + 5Fe^{+++}(aq)$$

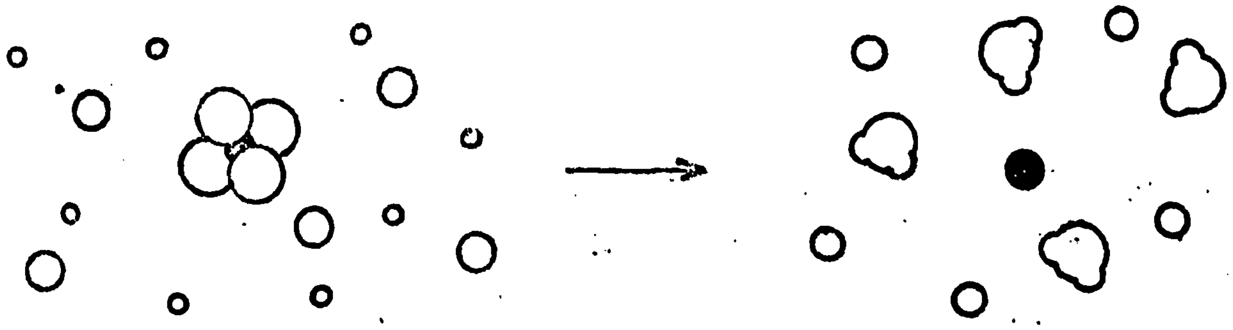

Fig. 3. Net equations generally do not represent mechanistic steps.

it is only reasonable to assume that this equation does not represent a single reaction. The likelihood of a single collision involving $5Fe^{++}(aq)$ + $MnO_4^-(aq)$, and $8H^+(aq)$ is negligibly small. Furthermore, the chance that such a collision, even if it were possible in terms of collision probability, would occur in the correct orientation to produce the observed products is too small even to consider. See Figure 3. Trace the changes in any one atom.

Again, without doing any experiments on rates of reaction, we arrive at the conclusion that net equations usually do not represent actual mechanisms. They only give the net change in species, not the steps by which the changes occur. We anticipate that each actual step will probably involve a collision between two molecules only, with a simple orientation, and with as low an energy requirement as possible. For fast reactions all steps must be fast and meet these three criterion. Slow reactions are those in which at least one step has difficulty meeting the collisional, energetic, and orientation requirement. No matter how fast the rest of the steps may be this slow step will determine the overall rate.

Having developed a general framework for interpreting rates in terms of collision, energy, and orientation probabilities, let us now study some experimental data. The test of the validity of the collision, energy, and orientation ideas will be their usefulness in interpreting experimental observations. We shall sometimes deliberately select systems you are not familiar with so that you will concentrate on the experimental observations on an unfamiliar system. But we shall also study familiar systems so you may see the ideas are generally useful. You should keep trying to apply these ideas yourself to changes you observe.

Concentration and Rate

Gaseous hydrogen and sulfur dioxide react with a measurable half-life according to the net equation:

$$2H_2(g) + SO_2(g) = 2H_2O(g) + \frac{1}{8} S_8(c) \qquad \text{(Eqn. 1)}$$

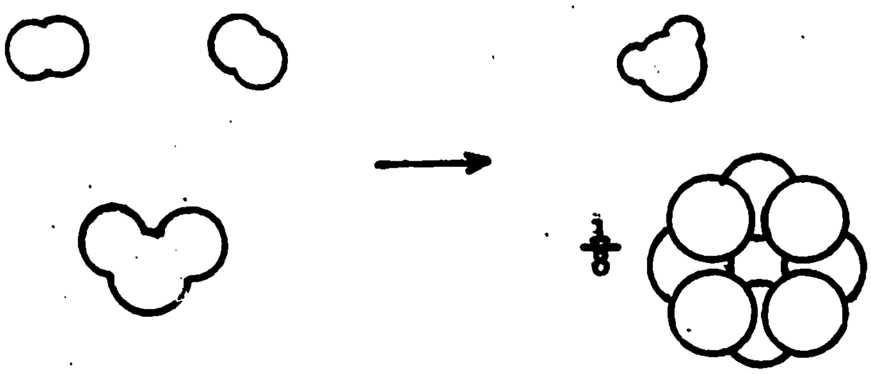

Fig. 4. Molecular changes required for net reaction

Note that three molecules must disappear and that a single collision is unlikely to accomplish this. See Figure 4. Trace some single atoms.

Table 1 gives some experimental data on the time, t, required for a constant small amount of reaction to occur under varying relative concentrations of H_2 and SO_2 all at constant temperature.

Table 1

	Relative	Conc.	
Expt.	$\{H_2\}$	$\{SO_2\}$	t (sec)
a	25	100	36
b	50	100	18
c	100	100	9
d	100	50	18
e	100	25	36

We see in experiments a, b and c (run at constant $\{SO_2\}$) that increasing $\{H_2\}$ decreases t proportionately. Doubling $\{H_2\}$ decreases t to half its former value. Thus

$$\text{rate of reaction (at constant } \{SO_2\}) = k'\{H_2\} \qquad \text{(Eqn. 2)}$$

Similarly from experiments c,d and e (run at constant (H_2)) we observe that

rate of reaction (at constant (H_2)) $= k''(SO_2)$ (Eqn. 3)

Combining these two equations to express the effect of both (H_2) and (SO_2) gives

rate of reaction $= k_1(H_2)(SO_2)$ (Eqn. 4)

The overall rate is proportional to the hydrogen concentration times the sulfur dioxide concentration. How could this relate to molecular collisions?

Moews and Petrucci studied another reaction with moderate half-lives in 1964 and obtained the data in Table 2 where t is the time for a constant, small fraction of reaction to occur, that is a constant fractional life.

Table 2

Net equation: $S_2O_8^{2-}(aq) + 3I^-(aq) = 2SO_4^{2-}(aq) + I_3^-(aq)$ (Eqn. 5)

Experiment	$(S_2O_8^{2-})$	(I^-)	t(sec)
a	0.077	0.077	21
b	0.038	0.077	44
c	0.019	0.077	91
d	0.077	0.038	42
e	0.077	0.019	89

Note that four molecules (ions) disappear and a simple collision is unlikely to give the net reaction. See Figure 5. The data are not as neatly organized as in Table 1 so let's reorganize them first as in Table 3.

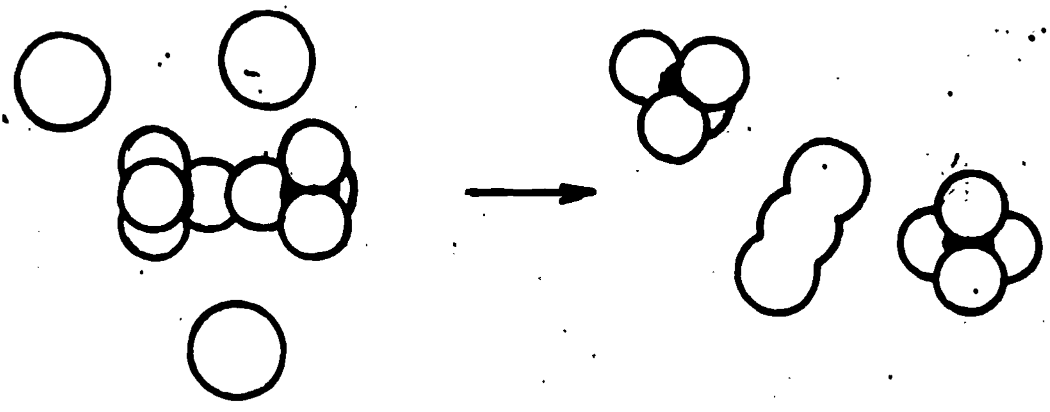

Fig. 5. Molecular changes required for net reaction

$S_2O_8^{=}(aq) + 3I^-(aq) = 2SO_4^{2-}(aq) + I_3^-(aq)$

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Table 3

Experiment	$\{S_2O_8^{2-}\}$	$\{I^-\}$	t
c	0.019	0.077	91
b	0.038	0.077	44
a	0.077	0.077	21
d	0.077	0.038	42
e	0.077	0.019	89

Do you see why we reorganized the table so that the $\{S_2O_8^{2-}\}$ increased (or remained constant) in its column, while the $\{I^-\}$ decreased (or remained constant) in its column? Examination of the t values shows that, while there is some experimental uncertainty in the data, (about ± 1 second in t) the overall rate equation is

$$\text{rate of reaction} = k_2\{S_2O_8^{2-}\}\{I^-\} \qquad \text{(Eqn. 6)}$$

Both equation 4 and equation 6 state that the rate of reaction at constant temperature in the corresponding system is proportional to the product of two concentrations. This is by far the most common kind of simple rate law.

Gaseous hydrogen iodide reacts with convenient half-lives according to the net reaction

$$2HI_{(g)} = H_{2(g)} + I_{2(g)}$$

The rate is given by the equation

$$\text{rate of reaction} = k_3\{HI\}^2 = k_3\{HI\}\{HI\} \qquad \text{(Eqn. 7)}$$

Again we get the most commonly found form of rate law; one which involves the product of two concentrations. In this case the mechanistic step might reasonably be the same as the net equation. Do you see why? But actually it is not. The actual mechanism involves formation of iodine atoms.

Order of A Reaction

Reactions which give rate laws like these of equations 4,6, and 7 are said to be second order. This means they consist of the simple product of two concentration terms. Second order reactions always have rate equations like

$$\text{rate of reaction} = k\,\{A\}\{B\} \qquad \text{(Eqn. 8)}$$

If A and B are identical as in the HI case, the rate equation becomes

$$\text{rate of reaction} = k\{A\}\{A\} = k\{A\}^2 \qquad \text{(Eqn. 9)}$$

Hinshelwood and Green studied the gaseous reaction for which the net equation is

$$2H_{2(g)} + 2NO_{(g)} = 2H_2O_{(g)} + N_2 \qquad \text{(Eqn. 10)}$$

and obtained the data in Table 4. Again we do not anticipate a mechanistic step yielding the net equation since four molecules disappear.

Table 4

Experiment	$\{H_2\}$	$\{NO\}$	relative rate
a	400	152	25
b	400	300	103
c	400	359	150
d	300	232	45
e	300	310	92
f	300	400	174
g	289	400	160
h	205	400	110
i	147	400	79

From experiments a and b we see that keeping $\{H_2\}$ constant and doubling the $\{NO\}$ increased the rate by a factor of four. Similarly in d and e increasing $\{NO\}$ by about 50% doubled the rate. The rate appears to be related to $\{NO\}^2$, second order in $\{NO\}$. Similarly, in experiments f and i where the $\{NO\}$ is kept constant, the $\{H_2\}$ decreased to half and the rate drops to half suggesting first order in $\{H_2\}$. All the data fit these two conclusions (allowing for some experimental uncertainties) so the rate equation is

$$\text{rate of reaction} = k_4\{H_2\}\{NO\}^2 \qquad \text{(Eqn. 11)}$$

This rate law is third order overall, first order in $\{H_2\}$ and second order in $\{NO\}$.

The order of a reaction with respect to any one reactant is given by the exponent of that reactant's concentration in the simple rate law. The overall order is the sum of these exponents.

Some reactions have complicated rate equations even when the net equation may be simple. Some may even involve fractional exponents For example:

Net equation; $H_2(g) + Br_2(g) = 2HBr(g)$

Rate equation: $\text{rate of reaction} = \dfrac{k_a\{H_2\}\{Br_2\}^{1/2}}{k_b + \{HBr\}\{Br_2\}^{-1}}$ (Eqn. 12)

Discovering and interpreting such rate laws is a principal problem of scientists studying rates. The concept of the order of the reaction is not very useful here. We shall study only systems which have simple rate laws containing products of concentration to the first or second power. All will be first, second, or third order reactions. They constitute the largest group of reactions and allow us to study almost all factors affecting rates.

Rate Determining Steps.

A large number of reactions have rate equations with one of the following four forms, where $\{A\}\{B\}$ are generalized sysbols for the concentrations of substances A and B.

I First order: rate of reaction $= k\{A\}$ (Eqn. 13)
II Second order: a) rate of reaction $= k\{A\}\{B\}$ (Eqn. 14)
b) rate of reaction $= k\{A\}^2$ (Eqn. 15)
III Third order: rate of reaction $= k\{A\}\{B\}^2$ (Eqn. 16)

(other third order forms are possible, of course, but only this one is common).

It is quite remarkable that, considering the great variety found in net equations, the rate equations are so simple and relatively few in type. Any scientist is bound to ask why this is so. The simplest suggestion which has been made to date (and a very useful idea it is) is that many reactions proceed by a mechanism in which there is a single step, or bottle-neck, which determines the overall rate. The rate equation represents the rate of this slow step.

Equation 14 is the most common rate equation. It is usually assumed to mean that there is a slow, or rate-determining, step in the mechanism involving a collision between a molecule of A and a molecule of B. Similarly equation 15 suggests a slow step involving. A colliding with A. Very often the slow step is the first step in the mechanism and is followed by a series of fast steps (which therefore do not limit the rate) to give the final products. The sum of the mechanistic steps equals the net equation. Let's try this idea on the systems mentioned so far.

Gaseous Hydrogen and Sulfur Dioxide: For this system we have

Net equation: $2H_2(g) + SO_2(g) = 2H_2O(g) + S(c)$ (Eqn. 1)

Rate equation: rate of reaction $= k_1(H_2)(SO_2)$ (Eqn. 4)

Mechanism

Presumed slow step: $H_2(g) + SO_2(g) \longrightarrow SO_2H_2(g)$ (Eqn. 17)

Possible fast steps: $SO_2H_2(g) \longrightarrow H_2O(g) + SO(g)$ (Eqn. 18)

$SO(g) + H_2(g) \longrightarrow SOH_2(g)$ (Eqn. 19)

$SOH_2(g) \longrightarrow H_2O(g) + S(g)$ (Eqn. 20)

$[nS(g) \longrightarrow S_n(c)]$ (condensation of gaseous S to solid) (Eqn. 21)

Net equation: $2H_2(g) + SO_2(g) = 2H_2O(g) + S(c)$ (Eqn. 4)

Note that:
1) The sum of the mechanistic steps must equal the rate equation.
2) Each mechanistic step (equation 17-21) involves reaction of only one or two molecules.
3) Each mechanistic step involves only one bond forming and/or one bond breaking.
4) Each fast mechanistic step involves one highly unstable reactive molecule, but never more than one.
5) The slow step involves two stable molecules requiring a special type of collision where the H_2 hits one of the SO_2 in a position such that the SO_2 H_2 forms (possibly $O\text{-}S\text{-}O\text{-}H_2$).

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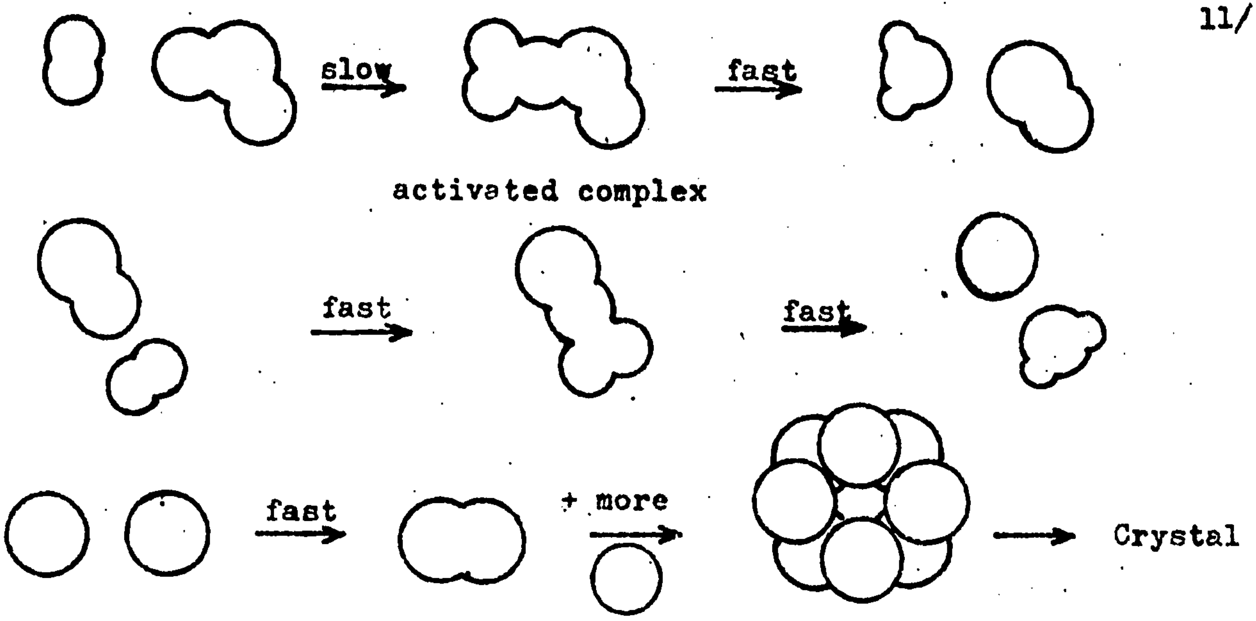

Fig. 6. Possible mechanism for the net reaction:

$$2H_2(g) + SO_2(g) = 2H_2O(g) + \frac{1}{8} S_8(c)$$

Aqueous Peroxydisulfate and Iodide Ions

For this system we have leaving the (aq) symbol out of the mechanistic steps for simplicity.

Net equation: $S_2O_8^{2-}(aq) + 3I^-(aq) = 2SO_4^{2-}(aq) + I_3^-(aq)$ (Eqn. 5)

Rate equation: rate of reaction $= k_2\{S_2O_8^{2-}\}\{I^-\}$ (Eqn. 6)

Mechanism

Presumed slow step: $S_2O_8^{2-} + I^- \xrightarrow{slow} S_2O_8I^{3-}$ (Eqn. 22)

Possible fast steps: $S_2O_8I^{3-} \xrightarrow{fast} SO_4^{2-} + SO_4I^-$ (Eqn. 23)

$SO_4I^- \xrightarrow{fast} SO_4^{2-} + I^+$ (Eqn. 24)

$I^+ + I^- \xrightarrow{fast} I_2$ (Eqn. 25)

$I_2 + I^- \xrightarrow{fast} I_3^-$ (Eqn. 26)

Net equation: $S_2O_8^{2-} + 3I^- = 2SO_4^{2-} + I_3^-$ (Eqn. 6)

Note in this aqueous reaction, of very different net equation and different mechanistic steps, the same generalizations (1-4) can be made as in the gaseous H_2-SO_2 system. See Figure 7. The slow step here, as there, involves stable molecules. But its slowness here may well be primarily due to the fact that each of the two colliding molecules is electrically negative. This is never true in any of the fast steps suggested. In general, ions of similar charge would be expected to collide infrequently and so to react slowly.

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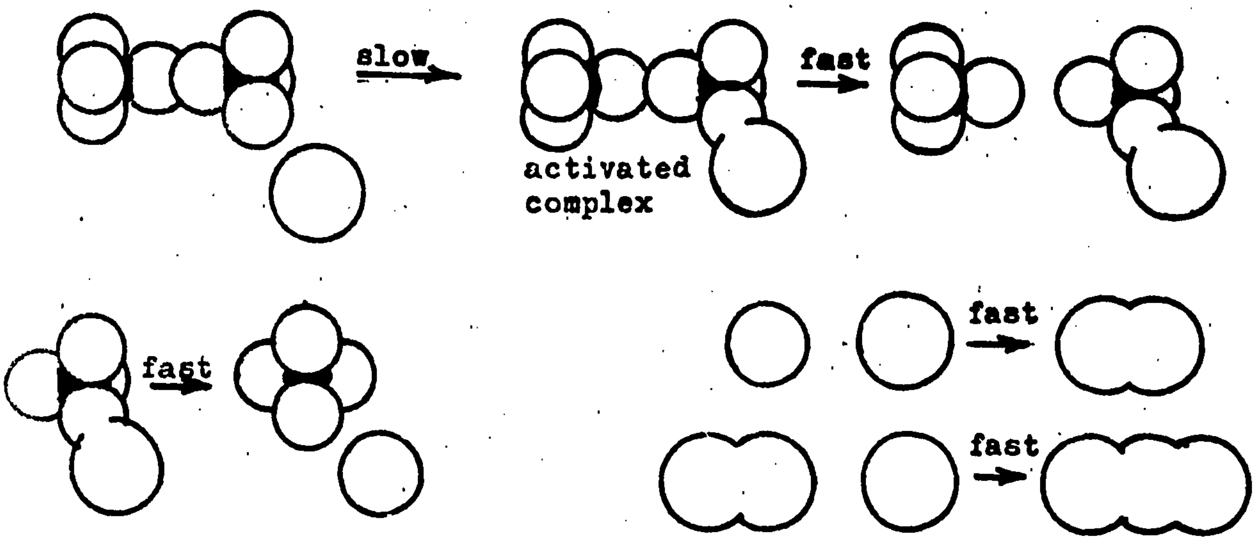


Fig. 7. Possible mechanism for the net reaction:

$$S_2O_8^{2-}(aq) + 3I^-(aq) = 2SO_4^{2-}(aq) + I_3^-(aq)$$

Gaseous Hydrogen and Nitric Oxide

For this system we have

Net equation: $2H_2(g) + 2NO(g) = 2H_2O(g) + N_2(g)$ (Eqn. 10)

Rate equation: rate of reaction $= k_4\{H_2\}\{NO\}^2$ (Eqn. 11)

This rate equation could be interpreted as suggesting $H_2+NO+NO \longrightarrow H_2N_2O_2$ as a slow step in the mechanism. But you should doubt this at once. One reason is because it involves a simultaneous collision of three molecules (which is always unlikely). A second reason is because the collision would have to produce the special orientation which would give $H_2N_2O_2$ a structure from which the N_2 and H_2O products could come. It would, for example, have to have an N-N bond. Both the triple collision and the required orientation are unlikely. $H_2 + 2NO \longrightarrow H_2N_2O_2$ is an unlikely mechanistic step for both reasons.

We shall not prove it, but there are at least two possible mechanisms which fit the rate equation and the net equation requirements. They are:

$$\begin{array}{lll} \text{I.} & NO(g) + H_2(g) \overset{\text{fast}}{\rightleftharpoons} NOH_2(g) \\ & NOH_2(g) + NO(g) \xrightarrow{\text{slow}} N_2(g) + H_2O_2(g) \\ & H_2O_2(g) + H_2(g) \xrightarrow{\text{fast}} 2H_2O(g) \end{array}$$

$$\begin{array}{lll} \text{II.} & NO(g) + NO(g) \overset{\text{fast}}{\rightleftharpoons} N_2O_2(g) \\ & N_2O_2(g) + H_2(g) \xrightarrow{\text{slow}} N_2O(g) + H_2O(g) \\ & N_2O(g) + H_2(g) \xrightarrow{\text{fast}} N_2(g) + H_2O(g) \end{array}$$

In both cases the second step is slow and is preceded by a rapid, ually-reversible equilibrium between two of the reacting substances. se I they are NO and H_2, in case II they are two NO molecules.

Can you examine the two possibilities and decide which mechanism is more reasonable? Note that they both meet generalizations 1,2, and 4 deduced in the preceding two cases.

Most kineticists would tend to reject I in favor of II because of the complex orientation required in the slow step of I compared to II. See Figure 8.

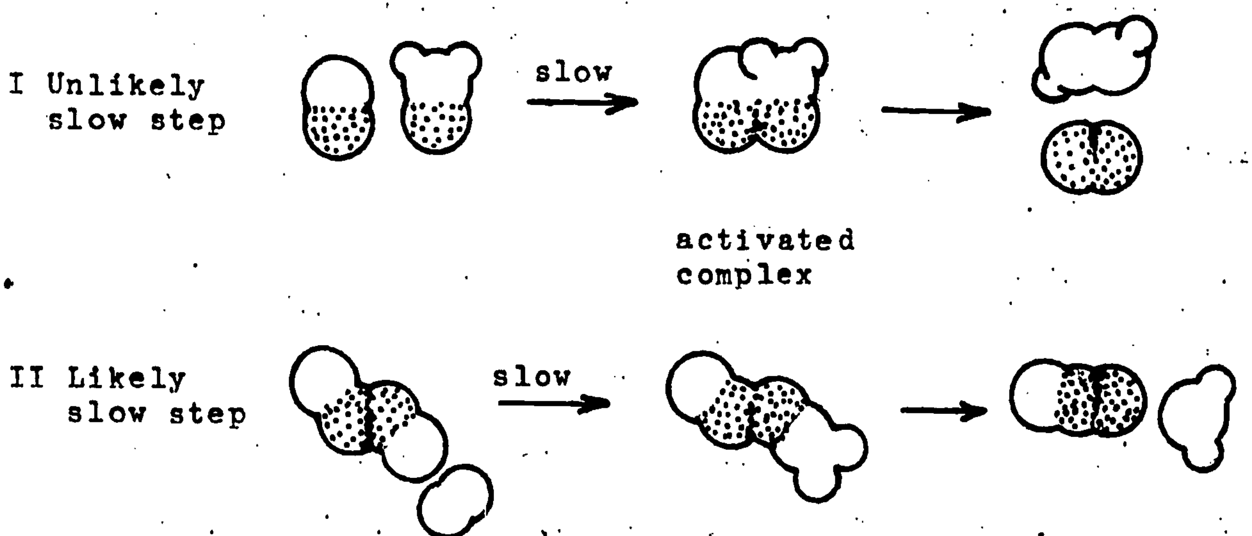


Fig. 8. Unlikely (restrictive configuration) and likely (less restrictive configuration) slow steps. Note that the likely step can occur at either "end" of the O-N-N-O molecule.

This complexity in I violates generalization (3) which suggests that usually no more than one bond breaks and/or one bond forms in a mechanistic step. In I a N-N bond must form (possibly $O\text{-}N\text{-}N\text{-}O{<}^{H}_{H}$), but then so must an O-O bond form to give H_2O_2 and how can two bonds form readily? There is no way to join NOH_2 and NO such that only one bond forms and one breaks in giving N_2 and H_2O_2. So mechanism I. is rejected.

Such rejection neither disproves I nor proves II. In fact, regardless of the amount of data on hand there is no way to prove any mechanism. There is always the possibility that some undiscovered path exists. In spite of this, knowledge of rates and mechanisms is increasing rapidly and there are now thousands of mechanisms concerning whose details the arguments seem overwhelming.

In general, third order equations having rate equations of the type

$$\text{rate of reaction} = k\{A\}\{B\}^2 \qquad \text{(Eqn. 12)}$$

have a mechanism involving an initial rapid, readily-reversible equilibrium between two of the reactants, followed by a slow step, as in I and II above.

First Order Reactions.

Radioactive reactions are first order

$$\text{rate of reaction} = k\{A\} \qquad \text{(Eqn. 13)}$$

Each nucleus is essentially independent of all the rest with its own unchanging energy content distributed among the particles present there. Random fluctuations of the energy over the particles in some nuclei may suddenly give a particle enough energy to escape and radioactivity is observed. Only at very high temperatures (usually greater than one million degrees) is the external energy high enough to change a nuclear half-life.

One of the most useful experimental properties of first order reactions is the constancy of the half-life regardless of concentration of the reacting species. Consider the data in Table 5. System (a) is for gaseous nitrogen pentoxide. System (b) is common hydrogen peroxide and represents the reaction going on in every bottle of hydrogen peroxide in the lab, drugstore, or your home.

Table 5.

a) $2N_2O_5(g) = 4NO_2(g) + O_2(g)$

$\{N_2O_5\}$	5.00	2.48	1.25	0.65	0.32	(all x 10^{-3})
t (min)	0	4	8	12	16	

b) $2H_2O_2(aq) = 2H_2O(aq) + O_2(g)$

$\{H_2O_2\}$	0.0461	0.0371	0.0298	0.0196	0.0123	0.0050
t (min)	0	5	10	20	30	50

c) $I^-(aq) + OCl^-(aq) = OI^-(aq) + Cl^-(aq)$

$\{I^-\}$	0.00200	0.00147	0.00101	0.00067
t (sec)	0	2	4	8

The initial half-life in system (a) is about 4 min (concentration drops from 5.00 to 2.50 x 10^{-3}) and each succeeding half-life is also 4 min so this is a first order reaction

(a) rate of reaction $= k_5\{N_2O_5\}$

In system (b) the first half-life (to go from a concentration of 0.0461 to 0.023 M is about 15 minutes), the second half-life (to 0.012 M) is also 15 min, as is the third. So system (b) is also first order.

(b) rate of reaction $= k_6\{H_2O_2\}$

The first half-life in system (c) (from concentration of 0.00200 to 0.00100 is 4 sec, the second is greater than 4 sec. Clearly this is not a first order reaction. The half life increases with decrease in concentration. Closer examination, which you need not be able to undertake, shows this reaction is second order

(c) rate of reaction $= k\{I^-\}\{OCl^-\}$

Why are some mechanisms first order and some second order?

First order reactions usually involve molecules at least as complicated as H_2O_2 which can absorb collisional energy and store it in the many ways such complicated molecules can vibrate. Thus, as with radioactive nuclei, from time to time the energy will concentrate in one bond which will break, initiating the whole mechanism. The rate determining step is that of concentrating sufficient energy from the rest of the molecule in one bond which then breaks.

The two first order systems above appear to react through the following mechanism.

a) $N_2O_5(g) \xrightarrow{slow} NO_2(g) + NO_3(g)$

$NO_3(g) + NO_3(g) \xrightarrow{fast} 2NO_2(g) + O_2(g)$

where the second equation may actually represent several fast steps.

b) $H_2O_2(aq) \xrightarrow{slow} 2OH(aq)$

$OH(aq) + H_2O_2(aq) \xrightarrow{fast} H_2O\ (aq) + HO_2(aq)$

$HO_2(aq) + OH(aq) \xrightarrow{fast} O_2(aq) + H_2O\ (l)$

The final reaction in each of the above mechanisms violates the principle that two reactive species seldom become concentrated enough to have a high collision probability. But in both cases the molecules are free radicals and react with one another even at low concentrations.

Zero Order Reactants

A discovery which suprises many students when they learn about rates of reaction is that in many systems there are reactants whose concentrations have no effect on the rate. For example aqueous iodine reacts with acetone as follows:

Net reaction: $I_2 + CH_3COCH_3 = CH_3COCH_2I + I^- + H^+$

Rate equation: rate of reaction = $k_7\{CH_3COCH_3\}\ \{H^+\}$

Changing the iodine concentration has no effect on the rate of reaction. The order with respect to $\{I_2\}$ is zero. The same thing is true for the reaction of bromine with acetone. Zero order reactants are common in chemistry. As one more example:

At low concentrations of hydrogen ion, the following reaction is zero order in $\{H^+\}$.

Net equation: $H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) = 2H_2O(l) + I_2(aq)$

Rate equation: rate of reaction = $k_8\{H_2O_2\}\{I^-\}$

Clearly if one is to control a system, he needs to know which reactants have an effect on the rate. These zero order reactants must be present, of course, but they do not participate in the rate determining step. Consider the problems posed if every food you ate increased your rate of reaction.

16/.

Concentration Effects

We may summarize our discussion of concentration effects as follows:

1. There is no way of deducing from the net equation what rate effects will result if concentrations are changed.

2. It is common to find reactants of zero order. Changes in their concentrations have no effect on the rate of reactions.

3. The rate equation which summarizes how concentration changes do affect rates can only be found by experimentation on the system.

4. Many rate equations are simple second order. In such cases there is usually a rate determining step in which two reactant molecules collide to form an activated complex and initiate the reaction mechanism. The colliding molecules are those whose concentrations appear in the rate equation. The formula of the activated complex is the sum of their formulas and its shape is near the sum of their shapes.

5. The interpretation of rate equations never produces an unambiguous answer to the question of the reaction mechanism. But see the discussion on pages 13 and 15 for common interpretations of third and first order rate equations respectively.

6. The mechanisms deduced usually follow simple, reasonable generalizations as pointed out on page 10.

We have discussed only a small fraction of the techniques available for studying concentration dependence of rates. Isotopes, equipment for very rapid measurements, and many other special techniques are used. The main generalizations are still those made in 1-6 above. They are not changed by the information from these more advanced studies.

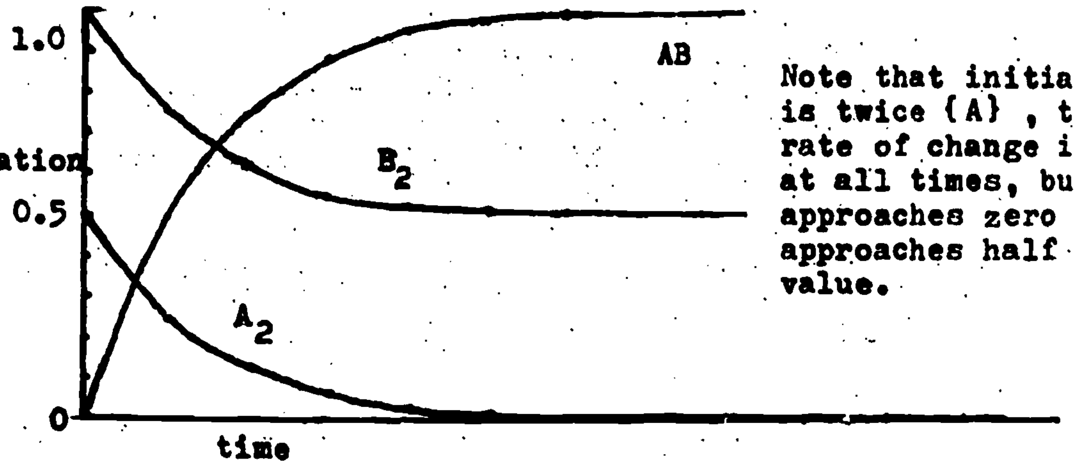
Any net reaction consists of a more or less extended set of mechanistic steps (usually involving one or two molecules per step) which constitute the actual reactions. The overall rate is often determined by that of the slowest step, which often involves a collision of two of the reactant molecules whose concentrations appear in a second order rate equation.

Concentration is usually expressed in molarity (moles per litre) but (especially for gas phase reactions) the pressure of a component may also be used. Changing either the molarity or pressure of a substance whose concentration appears in the rate equation affects the rate correspondingly. Changing concentrations or pressures of zero order reactants has no such effect.

In heterogueous reactions one must remember that stirring and the amount of reacting surface area can also affect rates. These are directly related to concentration effects and need no special treatment. Increasing surface area and/or stirring rate normally increases the speeds of heterogueous reactions. Can you suggest any biological advantages to a rise in heart rate when you are frightened? Any disadvantages?

Reaction Rate as a Function of Time

In most reactions, the reactants are consumed and their concentration decreases with time. See Figure 9. Thus the rates of reaction also decrease as the rate-determining concentrations decrease. Even first order reactions, which have constant half-lives, decrease in rate with time. Only half as much material disappears in the second half-life as in the first half-life. See Figure 1. The rate of a first order reaction decreases in proportion to the elapsed time. The rates of second order reactions, since they depend on two concentrations, decrease even more rapidly since both concentrations are diminishing. Only zero order reactions have rates independent of amount reacted.



Note that initially {B} is twice {A}, that their rate of change is the same at all times, but that {A} approaches zero whereas {B} approaches half its initial value.

Fig. 9. Change of concentrations with time for a reaction of net equation

$A_2 + B_2 = 2AB$. For example $H_2(g) + Cl_2(g) = 2HCl(g)$

It is possible to derive mathematical expressions for the change in all such rates as time increases. Simple mathematical treatment gives rather simple equations in many cases. But here we need only note that this change of rate with time should be kept in mind, not calculated. For our purposes it is sufficient to compare initial rates of reaction during the early stages of the reaction. At the beginning, the concentrations change only slowly with time so the rates remain constant long enough to make measurements from which useful data on order can be obtained with no complications due to changing rates.

Catalysis

There is one class of reactants for which the problem of concentration changing with time does not arise even though they react and their concentrations appear in the rate equation. Such substances are called catalysts. These concentrations do not change with time because the mechanism regenerates the catalyst.

Your stomach uses hydrogen ions to catalyze the conversion of table sugar to simple sugars. In fact, a very large fraction of the chemical reactions in your body are catalyzed by large protein molecules called enzymes -- each enzyme being quite specific as to which physiological it controls. The conversion of fuel oil to automobile fuel is catalyzed at the oil refineries. Indeed most of the materials which you buy or use in your daily life (whether synthetic or natural) exist because some catalyst allowed them to be synthesized at an appreciable rate.

To treat only one example in detail, consider the hydrolysis of table sugar in your stomach. Table sugar consists of two ring-shaped sections connected by an oxygen bridge. $C_6H_{11}O_5\text{-}O\text{-}C_6H_{11}O_5$. The problem in the stomach is to separate the rings by breaking one of the bonds to the bridge oxygen. In pure water this is a slow process, which accelerates rapidly as acid is added. In fact we find:

Net Equation: $C_6H_{11}O_5\text{-}O\text{-}C_6H_{11}O_5(aq) + H_2O(aq) = C_6H_{12}O_6(aq) + C_6H_{12}O_6(aq)$

Rate equation: rate of reaction $= k\{C_{12}H_{22}O_{11}\}\{H^+\}$

Presumed slow step: $C_6H_{11}O_5\text{-}O\text{-}C_6H_{11}O_5(aq) + H^+(aq) \xrightarrow{slow} C_6H_{11}O_5\text{-}\overset{H^+}{\dot{O}}\text{-}C_6H_{11}O_5(aq)$
activated complex

Possible mechanism: $C_6H_{11}O_5\text{-}\overset{H^+}{\dot{O}}\text{-}C_6H_{11}O_5(aq) \xrightarrow{fast} C_6H_{11}O_5^+\ (aq) + C_6H_{12}O_6(aq)$

$C_6H_{11}O_5^+ + H_2O \xrightarrow{fast} C_6H_{12}O_6(aq) + H^+(aq)$

The catalyzing positive hydrogen ion collides with the bridge oxygen (which is slightly negative) weakening the oxygen bonds so one breaks, giving a simpler sugar molecule and a positive sugar ion. The positive sugar ion then reacts with a nearby water molecule leaving a second simple sugar molecule and regenerating the hydrogen ion. It is this reaction followed by some regeneration process which characterizes catalysts. The total reaction proceeds faster, of course, since a new or additional mechanism has been provided which adds to the rate of the still continuing original reaction, raising the net rate. Often the catalyzed rate is much faster than the original so the net rate increases markedly. This is a characteristic of a good catalyst.

We now have two main questions to answer before finishing our discussion of rates: 1) why are some catalysts so good? , and 2) why does increasing the temperature of any reacting system normally increase the net rate? It turns out that the answers to these questions are related.

Temperature and Rate of Reaction.

Raising the temperature of a system always increases molecular velocities. On first thought it might appear that rates increase at higher temperatures because of an increased number of collisions. But molecular velocities are related to the square root of the Kelvin temperature $[v = c\ (T)^{1/2}]$ so that a rise from $T = 300^\circ K$ to $T = 310^\circ K$ would increase the collision rate about 1%. Yet the rate often more than doubles. The average kinetic energy of the molecules $(KE = \frac{1}{2} mv^2 \propto T)$ increases at the same rate as does T, but again the $10^\circ K$ increase above only increases the average kinetic energy 3%, no where near the increases observed in reaction rates. What, then, does increase the rate?

The answer lies, not in the average kinetic energy or velocity, but in the percentage of high energy molecules. We have already surmised that molecules need enough energy to loosen or to break an existing bond if reaction is to proceed, and that only the more energetic molecules will have this required activation energy. Just as a match must be "struck" before it will burn, or water must be pumped to the top of a siphon before flow begins, or mountains must be crossed to get from one valley to another, so energy must often be supplied to get molecules to react from one set of structures to another set. We may picture the situation as in Figure 10 where we plot energy against reaction coordinate for a simple single-step reaction, AB+C = A+BC. The reaction coordinate is a generalized variable which represents the various intermediate molecular structures.

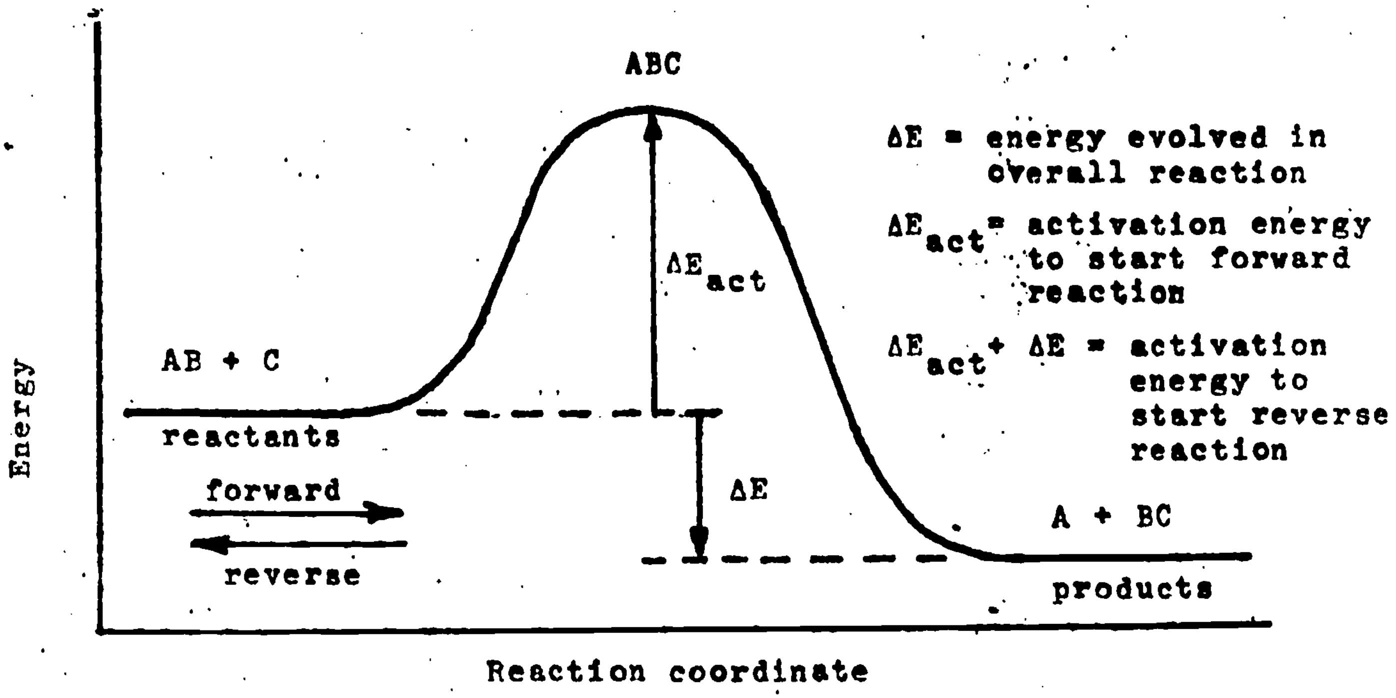


Fig. 10. Energy relations in a simple, single-step reaction. The reaction coordinate schematically represents the changing orientations of the reacting atoms.

The larger ΔE_{act} becomes, the slower is the reaction and vice versa. In Figure 10 the forward reaction would be faster than the reverse as far as ΔE_{act} is concerned. What effect does increasing T have on rate if ΔE is positive?

AVAILABILITY OF ACTIVATION ENERGY

The relative availability of ΔE_{act} as a function of T is apparent if one plots molecular kinetic energy versus probability as in the well-known Maxwell-Boltzmann curve of Figure 11.

A small increase in T shifts the Maxwell-Boltzmann curves only slightly but can make a large percentage difference in the number of molecules having kinetic energy equal to ΔE_{act} (or more). The higher the value of ΔE_{act} the greater the effect of increasing T.

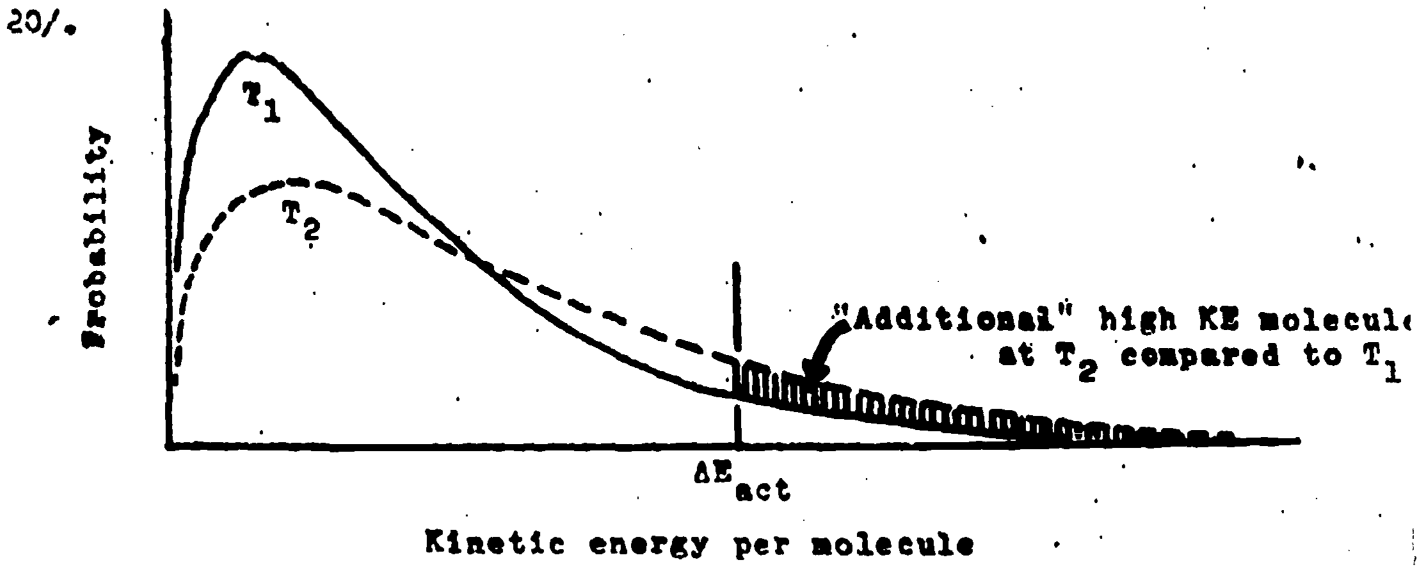


Fig. 11. Probability of a molecule having a given kinetic energy such as ΔE_{act} at two different temperatures, $T_1 < T_2$.

A mathematical analysis of Figure 11 shows that the number of molecules with energy ΔE_{act} or higher is related to $e^{-\Delta E_{act}/RT}$ where e is the natural base of logarithms (2.718), ΔE_{act} is the activation energy in cal/mol R is the gas constant (1.99 cal/mole°K) and T is the Kelvin temperature. This means that the rate of reaction, if all concentrations are kept constant should be related to this number as in

$$\text{rate of reaction} = c_1 e^{-\Delta E_{act}/RT} \qquad \text{(Eqn. 14)}$$

or $\log(\text{rate of reaction}) = -\Delta E_{act}/RT + \text{constant}$. Thus from data on rates of reaction (keeping concentrations constant) at different temperatures we can plot log(rate) as a function of 1/T to give a straight line, allowing the calculation of ΔE_{act} in a simple, straightforward way. Since quite good agreement is obtained between experiment and this simple theory (that molecules having more energy than ΔE_{act} can react and no others), we accept the theory as a satisfactory interpretation of the experimental observations. (If base 10 logarithms are plotted, $R = 2.30 \times 1.99 = 4.58$ cal/mole °K.)

But you will remember we suggested that there was a relationship between the temperature effect and that of a catalyst. It is that most good catalysts are good because they provide a path with a ΔE_{act} much lower than the non-catalysed path. See Figure 12. Thus the catalyst accomplishes at low temperatures what the non-catalyzed reaction could accomplish only at high temperatures. Since high temperatures often cause undesirable additional reactions, good catalysts are much sought after. Such search accounts for a large fraction of chemical research.

ORIENTATION EFFECTS

We have already used the idea that mechanisms and rates of reaction are affected by molecular shapes and orientation effects. In some cases these effects may be among the most important in limiting the rate and determining the fastest mechanism. Remember the discussion of the gaseous reaction between NO and H_2, of the slow reaction between negative $S_2O_8^{=}$ ions and negative I^- ions, and of the positively charged hydrogen ion and the negative bridge oxygen in the hydrolysis of table sugar. Every activated complex does have a "preferred" configuration for rapid reaction and only

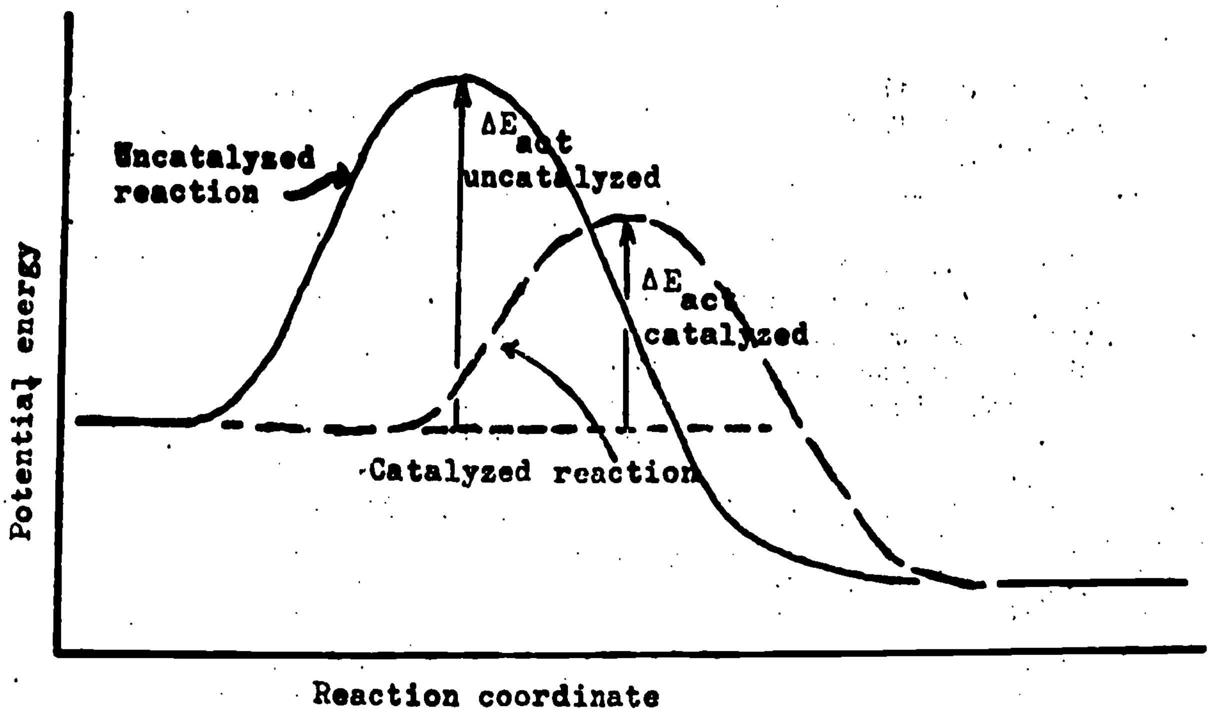


Fig. 12. Most catalysts not only generate a new reaction mechanism but also one of lower activation energy compared to the uncatalyzed reaction. The initial and final states are the same for both reactions, but the activated complex is different.

attainment of this shape (which must be very close to the sum of the reactants) leads to rapid reaction.

Enzymes, the catalysts for many biological reactions, are good examples of molecules whose shape is critical to their function. We know that the enzymes are very large molecules (contain hundreds and thousands of atoms), that usually only a single small site on their surface is catalytically active and that small changes in their shapes can greatly decrease or even destroy their catalyzing powers. Unfortunately, as yet, the exact shapes of only a few enzymes are known and in no case is detailed knowledge of actual orientations achieved during enzyme reactions known. This statement will almost certainly not remain true more than a few more years, since details of enzyme structures are rapidly being discovered.

LIFE PROCESSES AND RATES OF REACTION. One of the greatest discoveries in studying biological systems has been that their enormous variety and complex inter-relationships may be interpreted in terms of chemical reactions involving the same type of simple mechanistic steps and following the same generalizations as we have been discussing. For example, digestive processes produce energy through a series of simple bimolecular reactions in many of which one bond breaks and one bond forms, catalyzed by enzymes and/or hydrogen ions. Oxygen consumption in humans involves migration across a lung membrane, combination with hemoglobin, random migration in and out of cells until a cell is entered in which oxygen is being consumed. Typically there then occur the complex series of simple reactions mentioned above as digestive processes to give CO_2 and H_2O as common products. These then follow a complex series of simple chemical steps through the body until they are eliminated. Of great importance o biochemists is the fact that, while the total system is complex, the individual steps are simple and can be studied and understood in terms of well-established chemical principles.

A few minutes thought should indicate that this must be so if a biochemical system is to function reproducibly over a long period of time. For example you consist of about 10^{13} cells each of which contains a replica of the genes you received from your parents. Thus you have performed this synthesis of a set of very complicated molecules (molecular weights of hundreds of thousands) about a million million times. If the mechanistic steps were complicated it is extremely unlikely that this degree of reproducibility could be obtained. All that we know about gene replication confirms that the individual steps are simple. Were they otherwise, in fact, it would be most difficult to have made the great progress which has been made in discovering, following, and, indeed, beginning to control the synthesis of genes and other biochemical substances.

It should not surprise you to know that many large scale actions of biological systems are limited by the rates of rather simple chemical reactions. The rate at which cold-blooded snails can turn a corner is a simple function of their temperature. The ultimate speed a runner can achieve, or the reaction time of a race car driver, is limited by the rate of chemically transmitted nerve impulses into muscle action. The speed of a distance runner, on the other hand, is limited by slower reactions, like oxygen absorption. The times at which marked growth phenomena such as crawling, walking, talking, maturing, and aging occur are all affected by the rates of limiting chemical reactions. The ability to learn, we now believe, may be limited in an irretrievable fashion by the nature of the protein eaten by a child before the age of five or six years. Clearly all these discoveries can be intimately related to the nature of human life.

Rates in Large Systems

Just as a biological individual contains many simple chemical reactions interacting in a complex total pattern, so a society is a complex interaction of individuals. It is interesting, and some say profitable, to speculate on how many scientific ideas invented to describe and interpret microscopic molecular behavior are also applicable to societies. The correspondence of bottle necks in human relations and rate determining steps in molecular systems is at least intriguing. In both cases, it is quite foolish to try to alter the rate of change in the system unless some variable affecting the rate determining step (or bottle neck) can be found. In both cases there are many "zero order reactants." You may find it amusing and even instructive to consider how the changes you see about you are related to the ideas of collision probability, orientation, and activation energy, coupled with the idea that actual changes occur by a series of simple steps which go together to yield the complex net changes we usually observe.

Rate and Equilibrium

We have explicitly stated and implicitly used the idea that reactions do not "go to completion." Yet it is demonstrably true that many systems in a short time achieve a state of no net change. Such systems are said to be at equilibrium. It is simple to account for equilibrium states in terms of the ideas we have developed to deal with rates if we remember that while the concentrations of initial reactants are decreasing (as shown in Fig. 9) the concentrations of products are simultaneously increasing (as shown in the same Fig. 9). These products can, of course, react to reform the original reactants. The potential hills and activated complexes shown in Figures 10 and 12 may be approached from either the products or the reactants side. As the concentration of products does rise their rates of reaction also rises. At some set of concentrations the rising rate of back reaction will become equal to the falling rate of forward reaction. When the two rates become equal the system will be at equilibrium. No net change will be occuring. Yet all reactions will continue and their rates will be affected by the factors we have alread discussed. Adding ingredients will increase the rates of reactions using these ingredients and the concentrations will all shift to new equilibrium values. Changing the temperature will increase rates with high activation energies more than those with lower activation energies. Again the equilibrium concentrations will shift.

This concept of microreversibility applies to all known chemical systems and leads us to generalize that all such systems, if isolated from their surroundings, will come to a dynamic equilibrium in which the rate of each "forward" reaction is exactly equal to the rate of its own "backward" reaction and no net change results. Only in systems which are open, that is to which new materials and/or energy is being supplied, can continued change occur. Living systems must, of course, be open systems. Suffocation in a small space, for example, is usually due to CO_2 poisoning not oxygen deficiency. Why?

SUMMARY

Rates of change are determined by collision probabilities, orientation requirements, and the availability of activation energies. Chemical reactions proceed through a series of relatively simple mechanistic steps. Most such steps are bimolecular, involve simple orientational requirements, and usually have no more than one bond break and/or one bond form. The activated complex, thus, is the sum of the colliding molecules and its shape is very close to the sum of their shapes. Catalysts provide a new mechanism hence increase the rate of reaction. They usually also provide a mechanism of lower activation energy and/or simpler orientation requirements. The catalyst is regenerated and thus its concentration remains constant during the reaction.

Dynamic equilibrium is attained in an isolated system when each forward reaction is exactly balanced by a reverse reaction of equal rate. Under this condition no net change is observable even though all reactions are still proceeding.

RATE OF REACTION

LABORATORY GUIDE

Unesco Science Teaching Project
Bangkok Thailand
1970

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 medium 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 semiquantitative.. 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 with a sufficient number of pipettes and burettes for a large group of students. The "drop 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 allow a student to study rates of chemical reactions as 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 catalysts. The introductory chapter to the experiments was added as general information about the kit, and its level was adjusted to the average level of the students. In order to take into consideration the limited facilities of 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 sophisticated 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 wide 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 background, 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 detail are summarized in the teachers' guide.

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 and tested, and the instruction book was written with the cooperation of the Project's coworkers and staff members as follows:

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The revision was made by Drs. Hugo Herm, Amando Kapauan, and J. Arthur Campbell while they were at the Project in 1970.

CONTENTS

EQUIPMENT FOR THE KIT

A. CHEMICALS

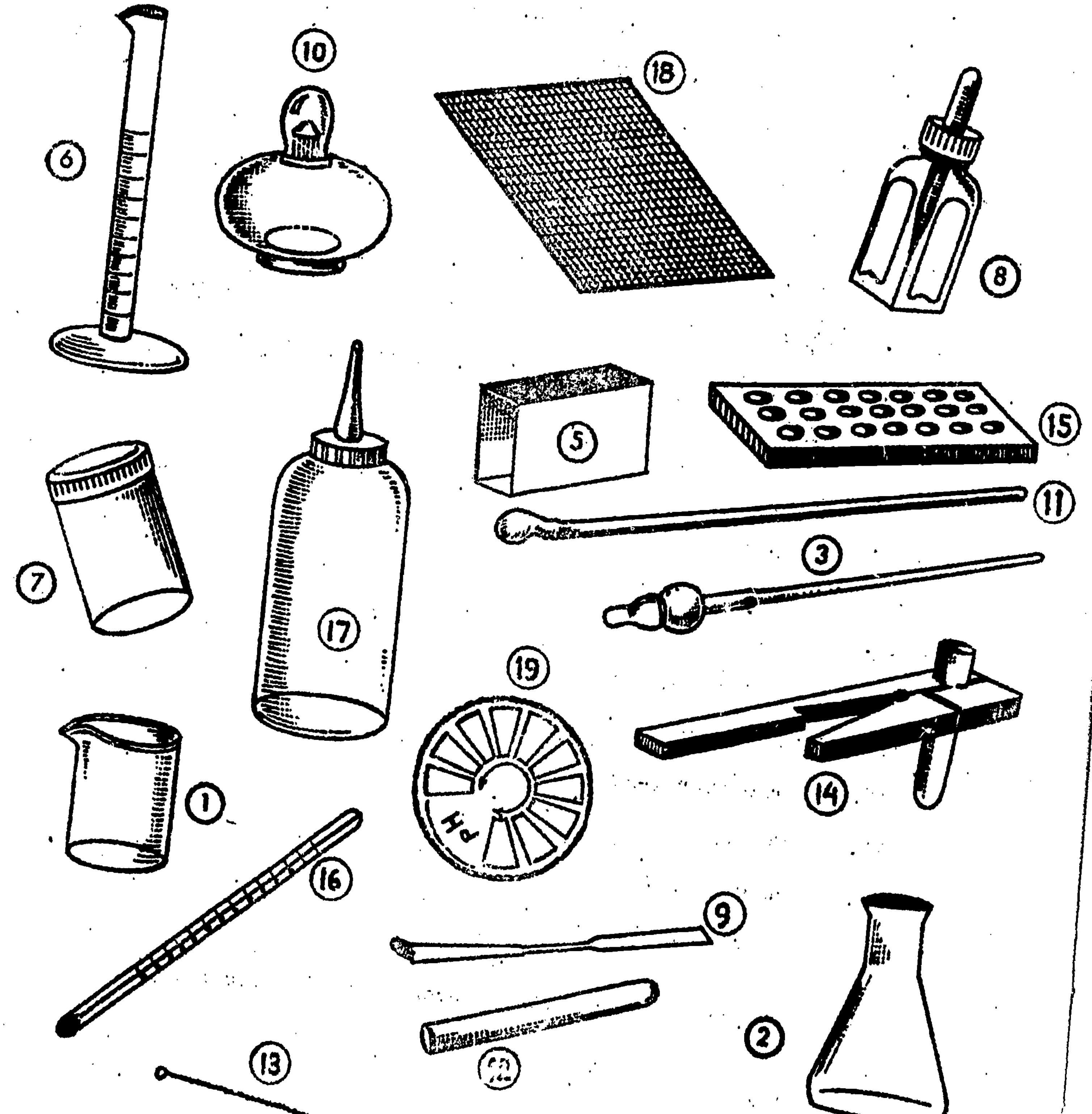
1. Ammonium molybdate, crystal and 0.1M
2. Arsenic trioxide, crystal
3. Benzene
4. Bromothymol blue solution, 0.1% in 95% ethanol
5. t-Butyl chloride, 0.1M in acetone
6. Calcium carbonate (marble or egg-shells)
7. Glucose, crystal
8. Hydrochloric acid solution, 3M
9. Hydrogen peroxide solution, 10M
10. Iodine, crystal
11. Iodine solution, 0.1M in 0.3M KI
12. Manganese sulphate·$4H_2O$, crystal and 0.2M
13. Mercury(II) chloride, crystal
14. Methylene blue, 1% solution in 95% ethanol
15. Oxalic acid, crystal and 0.05M
16. Potassium iodate, crystal and 0.07M
17. Potassium iodide, crystal and 0.6M
18. Potassium permanganate, crystal and 0.01M
19. Sodium hydrogen sulphite, $NaHSO_3$, crystal
20. Sodium hydroxide, crystal and 0.1M
21. Sodium thiosulphate·$5H_2O$, crystal and 0.5M
22. Starch
23. Sulphuric acid solution, 1M
24. Tin

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. Spatula
10. Spirit lamp with stand
11. Stirring rod
12. Test tubes, 8 x 1 cm
13. Test tube brush
14. Test tube holder
15. Test tube rack (styrofoam piece with holes)
16. Thermometer (-20 to 100°C)
17. Wash bottle
18. Wire gauze, 7 cm x 7 cm
19. Universal pH paper

Note: A watch or clock with a second hand is also needed.

B. APPARATUS



RATE OF CHEMICAL REACTION

Introduction

Many chemical reactions proceed from reactants to products rapidly, but others 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 repidly as the solution containing the base is added to the solution containing the acid. On the other hand, the rusting of iron may take months or even years to come to equilibrium. The reactions controlling aging in human beings take about 70 or 80 years, those in insects often less than one week to run their course.

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

To consider how fast or slow a reaction is, we speak in terms of the rate at which change takes place. The rate of a reaction may be measured by the amount of a reactant converted to product in a unit of time. The amount of reactant 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. Moles per litre per second is the most common unit.

What factors influence the rate of chemical reaction? Experiments show that four important factors are: 1) nature of reactants, 2) concentration of reactants, 3) temperature, and 4) catalyst. State of subdivision, pressure, and stirring are often listed, but they are merely different ways of controlling concentration.

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. Iron will become rusty rather rapidly, whereas silver changes relatively slowly. The reduction of permanganate ion in acid solution by iron(II) ion is fast. The violet colour of permanganate disappears instantaneously when added to a solution of iron(II) sulphate. 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 phase, either gaseous or in solution, are called homogeneous reactions. If the reaction involves different phases it is called a heterogeneous reaction. The reaction of solid calcium carbonate and aqueous hydrochloric acid solution to give gaseous carbon dioxide as one product is a heterogeneous reaction. The reaction of aqueous NaOH and HCl to give aqueous NaCl and H_2O is a homogeneous reaction.

It is found that the rates of heterogeneous reactions are often difficult to control since the reactions take place at the surface of the reacting phases and the surface conditions may vary with time. Homogeneous reactions are generally easier to study.

2) Concentration of reactants

Most chemical processes are complicated, and full analyses of their rates are difficult. As the reaction proceeds, the reactants are used up and new products are formed. The energy change may heat or cool the system. Only careful attention to temperatures and concentrations and their possible variation with time will lead to interpretable results.

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 number of moles 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, perhaps by noting the intensity of the color which is proportional to the iodine concentration.

Now we repeat the experiment, this time introducing twice as many moles of H_2 but using the same number of moles of I_2. 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 tripled, the rate of reaction of H_2 and I_2 is tripled. Furthermore, if the concentration of both H_2 and I_2 is tripled, the reaction rate is increased nine-fold. $(3 \times 3 = 9)$.

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

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

$$\text{or Rate of combination of } H_2 \text{ with } I_2 = k [H_2] \times [I_2] \text{ where}$$

k is a proportionality constant called the rate 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 depends on the particular mechanism, or series of steps, involved in the overall change and, as we shall see over and over, cannot be predicted from the equation for the net reaction.

If the rate of a chemical reaction is proportional to the concentration of a reacting substance, then the rate of the process must fall off as the reaction proceeds, for the reactant is being continuously used up. However, some rates are constant regardless of the concentrations of the reactants. They are also independent of time. Such reactions are said to be zero order. The decomposition of ammonia gas on a tungsten surface is zero order.

$$\text{ZERO ORDER RATE EQUATION: rate of reaction} = k [NH_3]^0 = k \qquad (0)$$

When the rate of reaction is directly proportional to the concentration of some reactant, the rate is said to be first order in that reactant. Thus the H_2 and I_2 reaction is first order with respect to $[H_2]$ and to $[I_2]$, or second order overall.

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

FIRST ORDER RATE EQUATION: rate of reaction = $-k[A]$ (1)

where $[A]$ is the molar concentration of the reacting substance A, and k is the rate constant. This equation states that the rate of <u>disappearance</u> of the reactant at any instant is proportional to its concentration at that instant.

Examples of first-order reactions are the decomposition in carbon tetrachloride of dinitrogen pentoxide into nitrogen dioxide and oxygen, and the decomposition of ozone in carbon tetrachloride. The decay of a radioactive isotope also conforms to a first order rate law.

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

SECOND ORDER RATE EQUATION: rate of reaction = $-k[A][B]$ (2 a)

If A and B are identical or if the initial concentration of A and B are identical and they react in a one to one ratio., then $[A]=[B]$ at all times and:

SECOND ORDER RATE EQUATION: rate of reaction = $-k[A]^2$ (2 b)

The combination of hydrogen and iodine as well as the reverse reaction (the decomposition of hydrogen iodide) are examples of second-order reactions. A second-order reaction occuring in solution is that between ethyl acetate and hydroxide ion:

$$CH_3COOC_2H_5 + OH^- = CH_3COO^- + C_2H_5OH$$

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

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

The reaction is said to be zero-order in any reactant whose concentration does not affect the rate. A large number of reactions involving more than two reactants turn out to be zero order with respect to several reactants and often first or second order with respect to the rest.

An increase in the pressure of any gas at constant T increases its concentration. Thus, reaction rates in gases are often changed by changes in pressure of the reactants. Grinding of solids provides more surface, so also speeds reactions involving solids. Similarly, stirring heterogeneous systems may increase rates by bringing the reactants into more frequent contact.

3) Temperature

Increase of temperature increases the rate of most chemical reactions to a marked extent. The rate constant is in some cases doubled or trebled for each $10^{\circ}C$ rise of temperature. The marked influence of temperature is somewhat surprising on first consideration, since the number of collisions 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 high energy molecules, rather than just an increased number of collisions. The fraction of molecules having enough energy to react (having the activation energy) increases much more rapidly than the average molecular velocity.

Some net reactions appear to proceed more slowly as T increases. This is always due either to thermal destruction of an intermediate molecule or to a competing reaction, for example the reverse reaction, increasing in rate faster than does the forward reaction. All actual mechanistic steps increase in rate as T increases, and decrease as T decreases.

4) Catalyst

A catalyst is a substance that increases the rate at which a chemical reaction takes place by entering into the reaction then being regenerated. This provides a new mechanism and always increases the rate. Since the catalyst unlike most molecules, is regenerated, it is not permanently changed. For example, the addition of MnO_2 increases the rate at which the thermal decomposition of $KClO_3$ takes place by forming intermediate manganese oxides. 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 since the platinum adsorbs the peroxide and provides a new mechanism for O_2 production.

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.

$$2H_2O_2 = 2H_2O + O_2 \tag{3}$$

The rate of decomposition of H_2O_2 can be increased by adding I^- ions to the solution. The rate equation is: rate $= k[H_2O_2][I^-]$ suggesting a slow step involving a collision of H_2O_2 and I^- molecules, followed by a series of much faster steps which give the H_2O and O_2 products and regenerate the I^-. The mechanism of the decomposition is thought to be:

$$H_2O_2 + I^- \xrightarrow{slow} OH^- + HOI \xrightarrow{fast} H_2O + OI^- \tag{4}$$

$$H_2O_2 + OI^- \xrightarrow{fast} HO_2^- + HOI \xrightarrow{fast} O_2 + H_2O + I^- \tag{5}$$

Adding Eqs. (4) and (5) gives the overall Eq. (3). Notice that none of the I^- ions has been used up. The I^- ions react and are then regenerated, as is true of all catalysts.

SUMMARY

Some ideas important in the understanding of rates and mechanisms are:

i) The variables which ordinarily affect the rate of chemical reaction (e.g. concentration, temperature, pressure).

ii) The mechanism by which a chemical reaction actually occurs.

iii) The relationship of this mechanism to the rate.

No variables other than concentrations and the absolute temperature are ordinarily found to affect the rate of a given reaction. Heterogeneous reactions occurring at phase surfaces, introduce a difficulty in defining the concentrations involved, but no new idea is introduced.

In many cases, the observed rate is determined by a single slow step out of a whole series of reactions in a complicated mechanism. When there is a single slow step, the experimentally determined rate equation and the experimental dependence of the rate constant on absolute temperature often turn out to be especially simple. The rate equation often takes a second order form, rate = $k[A][B]$, where A and B are the species which react in the slow step, $A + B \rightarrow$ products. Similarly, a plot of log (rate at constant concentrations) vs (1/T) often gives a straight line whose slope is $(\Delta E_{act}/4.575)$, where ΔE_{act} is the activation energy of the slow step. Mechanistic steps involving two intermediate products seldom occur since such intermediates usually exist at only small concentrations and are unlikely to collide with one another, as they must if they are to react with one another.

Regardless of whether the general mechanism of a reaction is understood or not, it is easy to show that the equilibrium state involves a set of simultaneous reactions in which every step of the mechanism is proceeding in both directions at equal rates. The sum of all mechanistic steps must give the equation for the net reaction.

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

This experiment explores extent of reaction and the sensitivity of your eyes to detecting change.

Requirements

Potassium iodide solution, 0.6M
Potassium iodate solution, 0.07M
Starch solution, 1%
Hydrochloric acid solution, 0.1M(stock diluted with 29 volumes H_2O)

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 solution with starch solution to ensure that significant traces of iodine are not present.

Into a dry beaker add 1 drop of 0.6M 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 diluted KI Solution	Drops of 0.07M KIO_3 Solution	Drops of Starch Solution	Drops of HCl Solution	Resulting color
a	1	1	2	2	
b	2	1	2	2	
c	3	1	2	2	
d	4	1	2	2	
e	5	1	2	2	
f	6	1	2	2	

Discussion

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

$$
\begin{array}{rcl}
 & 2I^- \rightarrow & I_2 + 2e \ (\times 3) \\
IO_3^- + 6H^+ + 6e & \rightarrow & I^- + 3H_2O \\
\hline
IO_3^- + 5I^- + 6H^+ & = & 3I_2 + 3H_2O
\end{array}
$$

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 may be visible with iodine concentration as low as 10^{-5}M.

In the first tubes, 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 visible colouration to develop with starch. In later tubes the concentration of iodine is high enough to give a blue colour.

Question

What is the approximate concentration of iodine in the first tube to show color?

II. REACTION OF THIOSULPHATE IONS WITH HYDROCHLORIC ACID

The object of the experiment is to explore how the order of a reaction may be determined, and to allow you to suggest a possible mechanism.

Requirements

Hydrochloric acid solution, 3M
Sodium thiosulphate solution, 0.15M (stock diluted with 2 volumes H_2O)

Beakers, 2 x 50 ml
Measuring cylinders, 10 ml, 100 ml
Watch with second hand.

Procedure

To one beaker add the volume of thiosulphate solution and of water shown in Table 1. To the other beaker add the HCl stir the solution of thiosulphate and water then pour it into the acid solution. Pouring the larger volume into the smaller insures good mixing. Time the reaction from the moment the solutions are mixed 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.). One method of timing is to measure until the first detectable precipitate forms. Another is to place the beaker on a piece of white paper bearing a pencilled x, and measure until the x is invisible. Take at least two measurements for each set of concentrations. 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 $S_2O_3^{2-}$ (M)	ml of 3M HCl Solution	Reaction Time in Seconds (t)	1/t
25	-	0.15	5		
20	5	0.12	5		
15	10	0.09	5		
10	15	0.06	5		
5	20	0.03	5		

Discussion

The experiment involves the deposition of sulphur from sodium thiosulphate in the presence of acid. Free thiosulphuric acid is formed then decomposes into sulphur and sulphur dioxide.

$$S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow H_2S_2O_3(aq) \longrightarrow S(c) + SO_2(aq) + H_2O(e)$$

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

ml of 0.15M $S_2O_3^{2-}$ Solution	ml of 3M HCl Solution	ml of H_2O	Concn. of H(aq)(M) in Final Solution	Reaction Time in Seconds t	1/
25	5	-	0.5		
25	3	2	0.3		
25	1	4	0.1		

1/t may be taken as a measure of the rate of reaction in this experiment. Plot rate (1/t) versus initial concentration (M) of $S_2O_3^{2-}$ ions. Is the reaction first or second order in $S_2O_3^{2-}$?

It is also possible to calculate the rate constant from the slope of the graph. Try this in units of moles/liter and seconds.

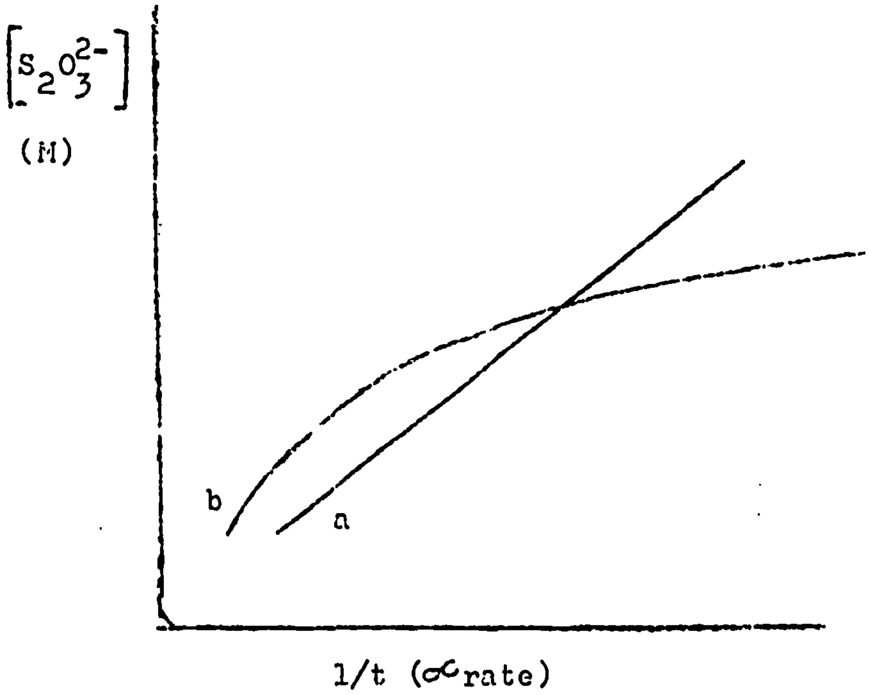


Fig. 1. Rate graph which will be obtained if the reaction of thiosulphate with hydrochloric acid is:
a) first orders b) second order

Deduce from Table II the order with respect to the acid concentration, $[H^+]$. Is mechanism I or II below more likely? Note that $H_2S_2O_3$ is a weak acid.

Mechanism I. $2H^+ + S_2O_3^{2-} \xrightarrow{slow} H_2O + SO_2 + S$

Mechanism II. $H^+ + S_2O_3^{2-} \rightleftharpoons HS_2O_3^-$ (fast equilibrium)

$H^+ + HS_2O_3^- \rightleftharpoons H_2S_2O_3$ (fast equilibrium)

$H_2S_2O_3 \xrightarrow{slow} H_2SO_3 + S$

$H_2SO_3 \xrightarrow{fast} H_2O + SO_2$

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 net reaction. The rate in this experiment is not proportional to $[S_2O_3^{2-}][H^+]^2$ as might be guessed from the net equation.

Question:

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

III. 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 (stock diluted with 1 volume H_2O)
Starch solution, 1% (see Experiment I)
Hydrogen peroxide solution, 10M
Sodium thiosulphate solution, 0.5M

Droppers, calibrated
Measuring cylinder, 10 ml, 100 ml
Test tubes
Test tube rack
Watch with second hand

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); 0.5M $Na_2S_2O_3$ 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 (with shaking) add 1 drop of Solution B and start timing. At the appearance of a blue colouration, immediately add another drop of Solution C, shake and record the time. When the blue colouration reappears, immediately add another drop of Solution C, shake 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 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.

$$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightleftharpoons I_2(aq) + 2H_2O(l) \qquad (1)$$

The liberated iodine reacts with the added thiosulphate ions according to eq. 2, and the blue colour is discharged.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons 2I^-(aq) + S_4O_6^{2-}(aq) \qquad (2)$$

But iodine will continue to be produced (eq. 1) but not until all the thiosulphate is used up, 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

Readings	Drops of H_2SO_4 Solution	Drops of Solution A (I^-)	Drops of Solution B (H_2O_2)	Drops of Solution C ($S_2O_3^{2-}$)	Time in seconds	Reaction Time Interval
a	2	1	1	1		
b	"	"	"	2		
c	"	"	"	3		
d	"	"	"	4		
e	"	"	"	5		
f	"	"	"	6		
g	"	"	"	7		
h	"	"	"	8		
i	"	"	"	9		
j	"	"	"	10		

At this stage, another drop of thiosulphate solution is added. The whole process is repeated until a total of 10 drops of thiosulphate solution has been added.

The results listed in Table I show whether the rate of reaction changes as concentrations are changed. Interpret your results.

Question

Calculate the initial molarity of I^- and H_2O_2 used in the experiment.

IV. 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 (stock diluted with 1 volume H_2O)
Starch solution, 1%
Hydrogen peroxide solution, 10M
Potassium iodide solution, 0.6M, solution A

Droppers, calibrated
Measuring cylinder, 10 ml
Test tubes
Test tube rack
Beakers
Watch with second hand.

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 lable 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

Dilute 5 drops of the 10M H_2O_2 solution with 25 ml water to give Solution L. Then dilute further as indicated in Table II.

TABLE II: Dilution of Solution L (H_2O_2 solution)

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 (to the closest second) the time taken for the first definite blue colour to develop. Enter the results into Tuble III.

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

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

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 until colour appears	1/t	Relative Concentration of I^-
2	2	2	1 of B			1
"	"	"	" C			1/2
"	"	"	" D			1/3
"	"	"	" E			1/4
"	"	"	" F			1/5

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

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 until colour appears	1/t	Relative Concentration of H_2O_2
2	2	2 of M	1			1
"	"	" N	"			1/2
"	"	" O	"			1/3
"	"	" P	"			1/4
"	"	" Q	"			1/5

Discussion

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

$$2I^-(aq) \longrightarrow I_2(aq) + 2e^-$$

$$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O(l)$$

$$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) = I_2(aq) + 2H_2O(l)$$

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. Here, again, rate is proportional to 1/t.

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. Estimate the order of the reaction with respect to $[I^-]$. With respect to $[H_2O_2]$. See the introduction to this volume for a possible mechanism. Are your data consistent with the mechanism?

Questions:

1. Suggest a reason for the increase of reaction rate with increasing reactant concentration.
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 HYDROGEN SULPHITE AND IODATE IONS

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

Requirements

Sodium hydrogen sulphite or sodium pyrosulphite, 0.1g.
Starch, 1g
Sulphuric acid, 1M
Potassium iodate solution, 0.01M (stock diluted with 6 volumes H_2O)
Ice

Plastic sample bottles
Spirit lamp
Thermometer
Watch with second hand

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

$$Na_2S_2O_5(c) + H_2O(l) \longrightarrow 2NaHSO_3(c) \longrightarrow 2Na^+(aq) + 2HSO_3^-(aq)$$

Label the 0.01M KIO_3 solution as Solution A. Solution B is made as follows. 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 whichever sodium sulphite is used and dilute to 250 ml. The concentration of hydrogen sulphite ion in Solution B is 0.004M.

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 add H_2O as required to Solution A before adding Solution B. On the addition of Solution B, start timing 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 ($\propto 1/t$) (that is reciprocal of the 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 are only a guide but several readings below and above room temperature should be taken. It is not necessary to measure the rate of reaction above 50°C. In all measurements, 10 ml of diluted 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 HSO_3^- and IO_3^- with Varying Concentration of IO_3^- at Room Temperature (___ °C)

Tube	Solution A. (ml)	H_2O (ml)	Concentration of IO_3^- (M) in diluted Solution A.	Solution B. (ml)	Time in seconds	1/t
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 IO_3^- and 10 ml 0.004M HSO_3^- Solutions at Different Temperatures.

Temperature °C		Time in seconds	1/t	Temperature °C		Time in seconds	1/t
Suggested	Actual			Suggested	Actual		
2				25 (room)			
10				35			
20				45			

Discussion

You have seen that 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 increases at higher temperatures. In all mechanistic steps the rate increases as temperature increases.

This experiment is based on the net reactions

$$IO_3^-(aq) + 3HSO_3^-(aq) = I^-(aq) + 3SO_4^{2-}(aq) + 3H^+(aq)$$

$$6H^+(aq) + 5I^-(aq) + IO_3^-(aq) = 3I_2(aq) + 3H_2O(l)$$

The second reaction takes place immediately the HSO_3^- ions have been all removed. Do your data indicate that the rate is influenced by $[IO_3^-]$? No definite decision can be made about the order because the concentration of H^+, for example, was not kept constant.

Table II. will show that at higher temperatures, the reaction proceeds faster. Plot log(1/t) vs 1/T(°K). If you get a straight line, its slope should equal the energy of activation (in cal/mol) divided by -4.575. Note that the rate is proportional to 1/t and, at constant concentrations, rate is proportional to **k**, so log k is **proportional** to log (1/t). See the introduction to this booklet.

Question:

Why does an increase in temperature generally result in an increase in rate of reaction? When is this not so?

VI. EFFECT OF TEMPERATURE ON RATE OF REACTION

The object of the experiment is to study the effect of changing temperature on the reaction rate of i) permanganate ions with oxalic acid and ii) thiosulphate ions with hydrogen ions.

Requirements

Oxalic acid solution 0.05M
Sulphuric acid solution 0.5M (stock plus 1 volume H_2O)
Potassium permanganate solution 0.01M
Sodium thiosulphate solution 0.15M (stock plus 2 volumes H_2O)
Hydrochloric acid solution 3M

Beaker (150 ml)
Dropper, calibrated
Measuring cylinder, 10 ml
Spirit lamp
Test tubes
Test tube holder
Test tube rack
Watch with second hand

Procedure

a. Dilution: Dilute 50 drops of 0.05M oxalic acid up to 25 ml with water (solution A). Also dilute 0.01M potassium permanganate 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 timing at the last drop. Record the time taken for the solution to turn colourless and enter the result in 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 in 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. Enter the results obtained into Table I.

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

Tube	Temperature °C		Drops of Solution A	Drops of H_2SO_4 Solution	Drops of Solution B	Time in seconds
	Approx.	Actual				
1	~25		2	2	1	
2	~40		2	2	1	
3	~60		2	2	1	

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 as you look down the tube. Add 2 drops of sodium thiosulphate to another test tube and immerse the tube in 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 II.

TABLE II: Effect of Temperature on the Reaction Rate of Thiosulphate and Hydrogen Ions.

Tube	Temp. °C		Drops of $S_2O_3^{2-}$ Solution	Drops of H^+ Solution	Time in seconds
	Approx.	Actual			
1	~25		2	2	
2	~40		2	2	
3	~60		2	2	

Discussion

At higher temperatures, homogeneous reactions usually proceed at higher rates. Thus when permanganate ions 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 net reaction taking place is:

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

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

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

(pink) (colourless)

The net reaction between thiosulphate ions and hydrogen ions also proceeds slowly at room temperature. At 60°C, the reaction occurs rapidly and the time taken for the deposition of sulphur is less. The net reaction is (see Expt. II):

$$S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow S(c) + SO_2(aq) + H_2O(l)$$

The rates of most reactions increase with temperature.

Question:

1. 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 ACID CONCENTRATION ON A RATE OF REACTION

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

Requirements

Sodium arsenite solution (neutralized), 0.05M
Sulphuric acid solution, 0.5M (stock plus 1 volume H_2O)
Iodine solution, 0.1M in potassium iodide solution, 0.3M
(henceforth referred to as KI_3 solution)
Starch solution, 1% (See Experiment I)
Sodium hydroxide solution, 0.1M

Dropper, 1 calibrated
Measuring cylinder, 10 ml
Test tubes
Test tube rack
Watch with second hand

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. Mark 6 more 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 arsenite is added. Enter the results obtained in Table III.

TABLE II: Effect of Hydrogen Ion Concentration on Rate of Reaction between Arsenite Ions and Iodine.

Solution	Drops of H_2SO_4 Solution from stock A,B,C, etc.	Concentration of H^+(M)	Drops of Starch Solution	Drops of I_3^- Solution	Drops of AsO_3^{3-} Solution	Time in seconds
A	2	1.0	2	2	1	
B	2	0.8	2	2	1	
C	2	0.6	2	2	1	
D	2	0.4	2	2	1	
E	2	0.2	2	2	1	
F	2	10^{-7}	2	2	1	

TABLE III: Effect of Hydroxide Ion Concentration on Rate of Reaction between Arsenite Ions and Iodine.

Solution	Drops of OH^- Solution from stock G,H,I,etc	Concentration of OH^-(M)	Drops of Starch Solution	Drops of I_3^- Solution	Drops of AsO_3^{3-} Solution	Time in seconds
G	2	10^{-7}	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 may be represented by the following net equation:

$$AsO_3^{3-}(aq) + I_3^-(aq) + H_2O(l) = AsO_4^{3-}(aq) + 2H^+(aq) + 3I^-(aq)$$

A look at Tables II and III indicates how the concentration of acid influences the rate of reaction of arsenite and iodine. Can you suggest any interpretation? Remember H_3AsO_3 is a weak acid as are $H_2AsO_3^-$ and $HAsO_3^{2-}$.

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 explore how reaction rates are affected by the presence of catalysts.

Part 1. Reaction of Permanganate Ions and Oxalic Acid

Requirements

Potassium permanganate solution, 0.01M
Oxalic acid solution, 0.05M
Sulphuric acid solution, 0.5M (stock plus 1 volume H_2O)
Manganese sulphate solution, 0.2M

Dropper, 1 calibrated
Measuring cylinder, 100 ml
Test tubes
Test tube rack
Watch with second hand

Procedure

a. Dilution: Dilute 50 drops of 0.01M $KMnO_4$ up to 25 ml with water.

b. To a test tube, add 2 drops of oxalic acid solution, 2 drops of sulphuric acid solution and 1 drop of diluted potassium permanganate solution. Start timing upon 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 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 Account for the <u>shape</u> of the curve.

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 0.2M $MnSO_4$ Solution	Drops of $KMnO_4$ Solution	Time in seconds
a	2	2	-	1	
"	2	2	-	2	
"	2	2	-	3	
"	2	2	-	4	
				.	

Table I. (Continued)

Tube	Drops of $H_2C_2O_4$ Solution	Drops of H_2SO_4 Solution	Drops of 0.2 M $MnSO_4$ Solution	Drops of $KMnO_4$ Solution	Time in seconds
a	2	2	-	5	
"	2	2	-	6	
"	2	2	-	7	
"	2	2	-	8	
"	2	2	-	9	
"	2	2	-	10	
"	2	2	-	11	
"	2	2	-	12	
b	2	2	1	1	

Part 2. Reaction of Iodide Ions and Hydrogen Peroxide.

Requirements

Potassium iodide solution, 0.6M
Hydrogen peroxide solution, 10M
Sulphuric acid solution, 0.5M (stock plus 1 volume H_2O)
Ammonium molybdate solution, 0.1 M
Starch solution, 1% (See Experiment I)

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

Procedure

a. In separate tubes dilute 10 drops of hydrogen peroxide up to 50 ml with water, 2 drops of potassium iodide up to 10 ml with water; and 2 drops of ammonium molybdate 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 1 drop 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
c	2	2	2	-	1	
d	2	2	2	1	1	

c. Try some other species for catalytic activity. Possibly Fe^{+++} instead of Mn^{++}, Br^- instead of I^-, others of your own choice. Note that the pairs suggested are isoelectronic; they have the same electronic structures.

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, but are regenerated so that they are not used up. In these experiments neither the manganous ions nor the molybdate ions were used up. Can you estimate their relative effectiveness as catalysts?

Questions:

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

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

IX. REACTION OF CALCIUM CARBONATE WITH HYDROCHLORIC ACID

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

Requirements

Hydrochloric acid, 3M
Calcium carbonate (marble chips, or clean eggshells)

Test tubes and corks to fit
Test tube rack

Experiment

Procedure: Select 5 pieces of calcium carbonate of equal surface area which are about the size of a pea or grain of corn. Prepare 5 test tubes with cork stoppers, and file a shallow notch in the side of each stopper so gas can escape from the tube. Fill the first tube with 3 M HCl, fill the second half-full, the third one-third full, the fourth one-fourth full, the fifth one-fifth full of 3 M HCl. Then fill tubes 2-5 nearly to the top with water. Shake each tube to insure uniform dilution of the acid. Add a lump of $CaCO_3$ to tube 5, invert the tube, and place it in a beaker half full of water. Repeat for each of the other tubes. Measure the time required for each tube to fill with gas. Repeat the experiment to check your data. You may use the same lumps of $CaCO_3$, but it is better to put each lump in a different tube. Use the second run to get an estimate of how the lumps differ in area. How is it possible to make this estimate?

TABLE I: Rate of Reaction of Calcium Carbonate with Hydrochloric Acid of Varying Concentration.

Solution	Relative Amount of HCl Solution	Molarity of HCl	Time of Reaction in Seconds
A	1	3.0	
B	1/2	1.5	
C	1/3	1.0	
D	1/4	.75	
E	1/5	.60	

Plot a graph of concentration of hydrochloric acid against rate of reaction (inverse of time). Try plotting $[H^+]^2$ versus rate of reaction. Any conclusion?

Discussion

From the first few experiments in this booklet you have found that the rate of chemical reaction usually depends upon the concentrations of some or all of the reactants. By measuring the time taken for a constant amount of calcium carbonate to react with varying concentrations of hydrochloric acid you have measured the dependence of the rate of reaction on the acid concentration.

Estimate the order of reaction with respect to $[H^+]$. Suggest a possible mechanism.

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

Questions

1) Why is it necessary that the pieces of calcium carbonate be of equal area?

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. It is also possible to build a simple relative balance from a spring or a thin steel rod, and to use it to measure relative weight losses. 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 capable of detecting changes to at least 0.001 g
Beaker, 100 ml
Cotton thread, 30 cm
Platform to span balance pan
Watch with second hand

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.

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 (suspended in iodine 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.

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

Time (min.)	wWeight of tin in I_2 soln. of			Time (min)	Weight of tin in I_2 soln of		
	100g/1	50g/1	20g/1		100g/1	50g/1	20g/1
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.

$$Sn(c) + 2I_2(C_6H_6) = SnI_4(C_6H_6)$$

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 since $[I_2]$ remains almost unchanged.

If the rate of reaction plotted against the concentration of iodine gives a straight line then the rate depends on the first power of the concentration of iodine (first order). If the rate plotted against $[I_2]^2$ is linear, the reaction is second order. What is the order suggested by your data?

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 mercury chloride, lead acetate may be used. Mercury compounds are expensive and highly corrosive to lead joints in most plumbing. Do not place them in the sink. Mercury and lead compounds are also poisonous if taken internally.

Requirements

Potassium iodide
Mercury(II) chloride, or lead acetate

Beaker, 100 ml
Glass rod, fire polished

Procedure

Place approximately 0.2g each of potassium iodide and a lead or mercury salt into a dry beaker and note any changes. Gently stir the mixture with a 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 in 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.

$$\begin{array}{ccccccc} 2KI(c) & + & HgCl_2(c) & = & 2KCl(c) & + & HgI_2(c) \\ \text{(white)} & & \text{(white)} & & \text{(white)} & & \text{(orange-red)} \end{array}$$

When crystals of KI and $HgCl_2$ are placed into the beaker, the surface area of contact turns orange-red. Discuss your observations.

The reactions with lead are analogous.

Question:

Explain what happens when water is added to the mixture.

XII. HYDROLYSIS OF TERTIARY-BUTYL CHLORIDE (t-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 but 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), 0.1%

Beakers, 2 x 50 ml
Measuring cylinder, 10 ml and 100 ml
Watch with second hand

Procedure

To separate 20 ml samples 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 are mixed until the colour changes from blue to yellow. Enter the results in Table I.

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

Tube	ml of NaOH	ml of H_2O	Reaction time t (seconds)	C_{RCl} Molarity	C^o_{RCl}/C_{RCl}	log C^o_{RCl}/C_{RCl}
a	1.0	19.0		0.0475	1.05	
b	1.5	18.5		0.0463	1.08	
c	2.0	18.0		0.0450	1.11	
d	2.5	17.5		0.0438	1.14	
e	3.0	17.0		0.0425	1.18	
f	3.5	16.5		0.0413	1.21	
g	4.0	16.0		0.0400	1.25	
h	4.5	15.5		0.0388	1.29	

Discussion

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

$$R\text{-}Cl(l) + H_2O(l) \longrightarrow R\text{-}OH(l) + H^+(aq) + Cl^-(aq)$$

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 proceeds, the base is gradually neutralised by the acid produced and the indicator changes colour when the pH reaches 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 are as follows: Remaining concentration of RCl at time t is calculated from

$$C_{RCl} = C^{o}_{RCl}\left(1 - \frac{\text{vol. of NaOH}}{20}\right) .$$

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

$$-\frac{dC_{RCl}}{dt} = k\, C_{RCl}$$

on integration this gives $\ln \frac{C^{o}_{RCl}}{C_{RCl}} = k\, t$

where C^{o}_{RCl} is the initial halide concentration, C_{RCl} is the concentration at time t, and k is the rate constant. Then a plot of log (C^{o}_{RCl}/C_{RCl}) against time should give a straight line, if the hydrolysis reaction of t-butyl chloride is of first order with respect to alkyl halide concentration.

Both acetone and t-butyl chloride are highly volatile and in order to reduce the evaporation covered beakers can be used. Even better is to perform the experiment in a stoppered test tube.

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 suggest themselves at various stages) and no detailed experimental procedure has been given.

Requirements

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

Conical flask, 100 ml

Procedure

A glass flask is about half-filled with a 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 conditon. You should suggest explanations which you can check by experiment and so develop a mechanism for the reaction.

Development

You may wish to try the following as explanations

(i) coloured material on stopper
(ii) increased contact with glass

Further possible observations:	Does length of time of colour duration depends on the number of equal shakes?
	Does the intensity of colour depend on the number of equal shakes?

Concentration effects may also be investigated by diluting slightly with water. 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. How do you interpret the resulting graph?

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*A detailed account of this experiment is given by J.A. Campbell: Journal of Chemical Education, Vol. 40, No. 11, 1963 pp. 578-583 and is also reprinted in the UNESCO publication: New Trends in Chemistry Teaching, Vol.1, 1964-1965 pp. 162-167.

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. The number 6.02×10^{23} of identical particles (atoms, ions, molecules), known as Avogadro Number, is called a mole of that substance.

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 duck eggs, a dozen oranges, etc. An orange weighs more than an egg. Accordingly, a dozen oranges will weigh more than a dozen eggs. In the same way, a mole of sugar (heavy molecules) weighs more than a mole of water (light molecules), though each mole contains the same number, 6.02×10^{23}, 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 chemical calculations is molarity, M. Molarity is defined as the number of moles of a substance dissolved per litre of the solution.

A 1 M solution of NaCl or CH_3COOH or any other substance is one which contains one mole of that 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 that 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 (formula NaCl) = 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.

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

DEVELOPMENT OF RATE EXPERIMENTS

I.a. The Peroxydisulfate Clock Reaction (all aqueous)

$$S_2O_8^= + 2I^- \longrightarrow 2SO_4^= + I_2$$

Use stock solution: A $0.02M\ S_2O_8^=$

B $0.3M\ I^-$ with starch

C $0.001M\ S_2O_3^=$

Vary amounts of A and B but keep amount of C and final volume constant. Mix B and C first and then add A to start reaction at zero time. Rate is proportional to 1/t where t is time between adding A to mixture of B and C and the appearance of blue starch-iodine color.

Problems to study. 1. Devise an experiment using these solutions in drop quantities. 2. Determine the rate law.

I b. Using constant amounts of A,B and C above, vary the temperature. Determine the activation energy..

I c. Try various substances (metallic salts or mixtures) as possible catalysts to this system.

I d. Instead of A, use a peroxydisulfate solution which is made quite concentrated in some non-reacting ions like Na^+, NO_3^-, and ClO_4^-. Try making the solution 1M and 2M in $NaNO_3$. How is the rate affected by the presence of other ions?

I e. Try changing the solvent to a 50% alcohol or acetone solution. What is the effect on the rate?

II. Oxygen Evolution from Hydrogen Peroxide (all aqueous)

$$2H_2O_2 \xrightarrow{I^-} 2H_2O + O_2(gas)$$

Ordinary drugstore hydrogen peroxide (3%) can be catalyzed into decomposition by I^- in solution. Try varying amounts of a 0.1M KI solution in varying volumes of 3% peroxide, keeping the final volume constant.

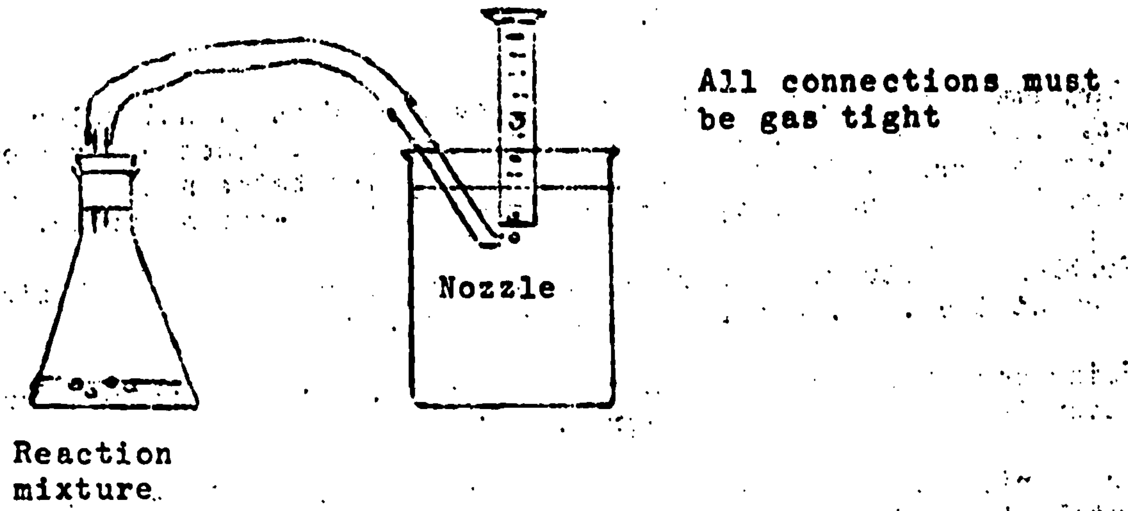
Follow the reaction by leading a glass nozzle from the reaction vessel (a flask or a test tube) to a water container.

a) Count rate of formation of bubbles b) Collect the gas in a 10 ml graduated cylinder and measure the time needed to collect a certain volume.

Problems to study. 1. Does the shape and volume of the reaction vessel play an important part in the success of the experiment? Try a test tube. 2. Is it important to shake the reaction vessel during the experiment? 3. Determine the rate law. 4. Can you replace the iodide by another catalyst, say Mn^{++} or $Cu(NH_3)_4^{++}$? Try varying amounts of 1M solutions of the above.

Figure 1 suggests a possible set-up you can try. Think of others.

Fig.1

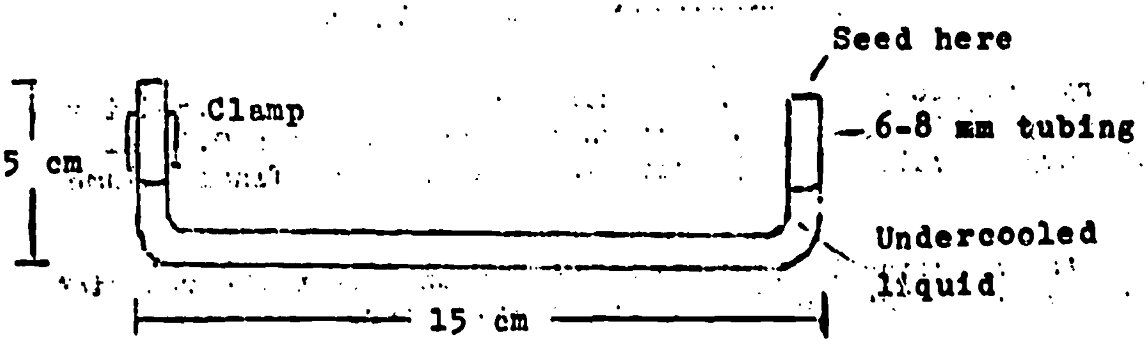


III. Rate of Crystallization

Rate of crystal growth can be followed in a glass tube by measuring the growth of the solid. Salol and hypo ($Na_2S_2O_3 \cdot 5H_2O$) can be easily undercooled after heating to around $70^\circ C$.

Make a tube shown in Figure 2 and undercool salol or hypo in it.

Fig.2



Seed with a small crystal at one end. Follow rate of crystallization down the tube. Repeat several times.

Problem to study. Vary the degree of undercooling by warming or cooling the tube and its contents slightly. Does this affect the rate of crystallization?

3/.

IV. The Ferric Clock Reaction

$$2Fe^{+++} + 2I^{-} \longrightarrow 2Fe^{++} + I_2$$

Use these stock solutions: A. 0.003M $FeCl_3$ in 0.06M HNO_3

B. 0.02M I^{-} with/starch

C. 0.001M $S_2O_3^{=}$

Try varying amount of A, keeping amounts of B and C and the total volume constant. Vary B keeping A and C and total volume constant. Always mix B and C first before adding A to start the reaction.

Problems to study. 1. Determine the rate law. 2. Can you determine temperature effect and activation energy in this system?

V. Rate of Inversion of Sucrose

$$\text{Sucrose} + H_2O \xrightarrow{H^+} \text{glucose} + \text{fructose}$$

All three sugars in the above equation are optically active. The rate at which sucrose 'inverts' into glucose and fructose can be followed using a polarimeter.

Build a polarimeter using polaroid sheets.

Problem to study. Determine the rate law for the inversion of sucrose. Try starting with 5-20% sucrose solutions and 0.5 to 4M H^+ solutions.

VI. Decomposition of Formic Acid

$$HCOOH \xrightarrow{\text{conc } H_2SO_4} H_2O + CO(\text{gas})$$

Study rate of CO evolution as function of temperature. Drop formic acid into 5-10 ml concentrated sulfuric acid.

VII. Iodination of Acetone
(A spectrophotometer experiment)

$$CH_3COCH_3 + I_2 \xrightarrow{H^+} CH_3COCH_2I + HI$$

Follow rate of consumption of iodine (in KI soln.) using optical density at 347.5 nm wavelength. Reacting solution must be around 0.005M in I_2 (0.05M in KI), 0.02 to 0.5M in H^+ and 0.01 to 0.2M in acetone.

Determine the rate law and value for rate constant.

RATE OF REACTION

TEACHERS' GUIDE

Unesco Science Teaching Project
Bangkok Thailand
1970

RATE OF REACTION

(Teachers' Guide)

Most introductory syllabi include, "Rate of reaction: effect of temperature, pressure, concentration, catalyst." It is common to emphasize that an increase in temperature or in concentration or pressure of reactant, or addition of a catalyst leads to an increase in rate of reaction. Occasionally the phrase "negative catalyst" is introduced to cover those substances which lower apparent rates but are not themselves consumed. Seldom are rates referred to outside the small section of the course in which they are first discussed, and few, if any, experiments are studied to investigate the generalizations and their validity.

If a range of experiments were discussed it would soon be discovered that none of the usual generalizations is completely correct. There are many changes which occur more slowly at higher temperatures. Enzyme reactions are a good example. There are many reactants for whom a change in pressure or a change in concentration in solution has no effect on the rate of reaction. Many catalyzed gas phase reactions and many aqueous solution reactions have rates quite independent of the concentrations of several of the reactants under ordinary conditions. Furthermore, negative catalysts actually work by speeding up a competing reaction and removing reactive intermediates necessary for the reaction being discussed. They do not themselves slow down any reaction.

In our discussion we shall present a model of molecular behavior which is simple, yet which interprets most of the effects actually observed in studying rates of reaction. We shall also apply these ideas more widely than is customary and use them to interpret a wide range of chemical observations not usually correlated with rate effects.

This treatment of rate of reaction should not be viewed as an addition to an already overcrowded curriculum in chemistry but as a simple molecular model which 1) makes the learning and correlation of chemical observations more simple and 2) allows the student to retain and use the ideas longer and in a wider context than is common.

A. Important concepts.

1. Molecules collide at rates proportional to their concentrations.
2. Rate of reaction is determined by collision rate, probable orientations upon collision, and availability of activation energy.
3. Reactions proceed through a series of simple mechanistic steps of which one is usually slower than the others and so determines the overall rate. Usually only two molecules collide in each step.
4. Experimental determination of the effects of changing concentrations and temperatures often lead to rate laws from which a probable mechanism can be deduced.
5. A catalyst increases a reaction rate by providing a new mechanism, one in which the catalyst first reacts then is regenerated.
6. The factors found to control reaction rates in simple systems appear to be identical to those controlling rates in complex systems.

B. Outline

1. Fast and slow reactions. Rates of different reactions obviously vary, but the rate of any given reaction can also vary.
2. Half-lives. Reactions, in general, do not "go to completion" nor do they stop. It is, therefore, common to discuss rate of reaction in terms of half-lives. (The half-life of a reaction is time required for the concentration of a reactant to decrease to half its original value.)
3. How do reactions occur? Reactions can occur only if the reactants collide in a configuration favorable for forming the products, and with enough energy to begin to break any old bonds which must disappear as new bonds form.
4. Collision probability. The frequency of collision between reactant molecules helps determine their rate of reaction and is itself proportional to the product of the concentrations of the colliding molecules.
5. Net equations and mechanistic steps. A net equation summarizes the state of the system before reaction (the reactants) and after (the products). It does not describe the process of change. Each mechanistic step describes a change which actually occurs as the original reactants convert to the products.
6. Concentration and rate. Often the experimental data show that the observed rate is related to the concentrations of one or more reactants. The relation is called the rate law for the reaction and is often of the form:

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

where A and B are reactant molecules.

7. Order of a reaction. The power (exponent) of each concentration term in a rate law (consisting only of products of concentration terms) is called the order of reaction with respect to that concentration. The rate laws for many reactions contain a simple product of concentration terms each of first or second order. In such cases, the sum of the exponents is called the order of the reaction.

8. Rate determining steps. Many reactions have simple rate equations and are of first or second order. This is usually interpreted to mean that the overall rate is determined by a single slow mechanistic step involving a collision between the species whose concentrations appear in the rate equation.

9. Gaseous hydrogen and sulfur dioxide provide data to check the above ideas. All the data are consistent with a slow step involving a collision of H_2 and SO_2 molecules, followed by a set of faster steps.

10. Aqueous peroxydisulfate and iodide ions give rate data consistent with a slow step involving a collision between these two ions followed by slower steps.

11. Gaseous hydrogen and nitric oxide give rate data subject to at least two different mechanistic interpretations. Arguments based on probable orientations during collision favor, but do not prove, one mechanism.

12. First order reactions most commonly involve complex structures like radioactive nuclei or polyatomic molecules in which the rate determining step is the accumulation of energy from within the complex system itself into a bond which then breaks.

13. Zero order reactants are those for which a change in concentration has no effect on the rate since they are not involved in the collision of the slow rate determining step, but only in the fast mechanistic steps.

14. Concentration effects can be discovered only by experimentation, never from the net equation, but they may be interpreted in terms of mechanisms made up of simple steps. Each step involves a molecular collision (usually of only two molecules) and one step is usually slower than any others.

15. Reaction rate as a function of time decreases as reactions are consumed.

16. Catalysis is the phenomenon in which a rate increases upon addition of a substance which is not used up, or consumed, in the reaction. The added substance reacts and provides a new mechanism for the reaction but is regenerated continually, hence is not used up.

17. Temperature and rate of reaction. A rise in temperature increases the rate of every mechanistic step, mainly by increasing the fraction of molecular collisions which are energetic enough (have the activation energy) to begin to break old bonds as new ones form.

18. Availability of activation energy is correlated with the Maxwell Boltzmann curve of energy distribution among gaseous molecules. Molecules of all energies are available at all ordinary temperatures but the fraction of those with high energy (well above average) is very sensitive to changes in temperature. (The actual relationship is an exponential one.)

19. Orientation effects are important in determining whether a given collision, even if between energetic molecules, can lead to formation of product or will merely result in rebounding of the molecules.

20. Life processes and rates of reaction are intimately related, since every living system must undergo continual changes (food into energy and structure, for example) in order to maintain itself. The same methods of measurement and ideas apply to these systems as to those studied in test tubes.

21. Rates in large systems such as machines, factories, living organs, individuals, and populations can be described and correlated in the same framework of favorable collisions with ample energy to lead to change.

22. Rate and equilibrium. The rate of every "forward" reaction decreases with time as the concentration of reactants (and likelihood of their collision) drops. Simultaneously the rate of the reverse reaction increases as the concentrations of the products rise. At some set of concentrations the two rates become identical and net change ceases. In this equilibrium state every possible reaction is still occurring, but each is balanced by its reverse so that the net change is zero.

C. EXPERIMENTS

Many teachers find that groups of 2-4 students are the most effective for experimental work. The teacher must help make sure that each member of each group is actively involved in performing the experiment. Otherwise one student is apt only to read the clock, another only to write down numbers, another only to clean glassware, or do some other job involving minimum contact with the chemistry of the experiment.

The ideal laboratory period for most 12 year-olds is 40-60 minutes, for 17 year-olds from 90-120 minutes, with a general increase between these two ages. Longer periods tend to exceed the interest span, shorter periods to encourage superficial work. Many teachers feel that a desirable division of the available time is: 5-10 minutes of prelab discussion, the experiment, 5 minutes for clean-up and review of notes and calculations, 10-20 minutes of immediate postlab discussion. Further prelab and postlab discussions are desirable in many cases to insure adequate understanding of the problems being investigated and of the experimental results obtained. Since some teachers will use these experiments for lecture experiments we shall outline time requirements for each experiment both for lab and class.

Prelab discussions should not discuss expected results or interpretations of them. These points should be part of the postlab discussions. Prelab should make sure the students understand: 1) the problem behind the experiment, 2) any safety precautions, (none of the procedures or stock or working solutions used here is dangerous though the acids and base will attack skin and clothes on any contact), 3) the location of any special equipment (though this is much better done in writing on the board or on a special instruction sheet).

The experimental period, especially if it is short, will be much more effective if all necessary equipment and chemicals are at the student's place of work. Use of semi-micro equipment, dropper bottles for reagents, and wash bottles for a water supply all simplify this problem. All observations and measurements should be recorded at once by the student, in the appropriate table. There is ample space in the lab book for calculations and answering questions. If the teacher wishes to use one set of lab manuals for more than one class he may wish to issue separate report sheets to each student for each experiment. Examples are given in this guide.

The postlab discussion should concentrate on student results for the experiment. It will often be desirable to tabulate the results for the whole class. Eliminating the 10-20% which are most variant above and below the mean value will get rid of gross blunders. This gives sets of data covering about one standard deviation plus and minus. Since most students do each experiment only once, this postlab discussion will allow them to become familiar with the experimental uncertainties, with the necessity (and problem) of generalizing from such dats, and to evaluate their own work with respect to that of their peers.

1. Stock Solutions

While it is true that rates of reaction are often affected by changing concentrations, it is also true that these concentrations need not be accurately known in order to perform the experiments here. One significant figure accuracy (that is, about ± 10%) in making up solutions is quite adequate. Since all students will work from the same stock solutions, their results will be directly comparable even though the absolute values of the concentrations are unknown. Thus one liter milk bottles, or other similar containers, are quite adequate "volumetric flasks" for liquids, and crude postal scales are sufficiently good to weigh out the solids to the closest gram. Dilution, of HCl for example, can be done merely by estimating the relative volumes by eye. Table 1. gives directions for making up one liter of each stock solution. It is recommended that this volume be made up and kept in stock for all solutions except for 3M HCl, 0.1M NaOH 0.5M $Na_2S_2O_3$, and 1M H_2SO_4 for each of which five liters is recommended, and 1% bromthymol blue and 1% methylene blue for which one tenth of a liter should be adequate.

2. Obtaining Chemicals

All the chemicals listed in Table 1 may, of course, be obtained from chemical supply houses. Many of them may also be obtained, often more quickly and more cheaply, from other sources. The best alternate sources are pharmacies and hospitals plus local research labs. They may have any or all of the chemicals and are usually quite happy to help stock schools with small quantities. In addition, the following special sources may be available. The purity of their material is quite satisfactory for these experiments.

hydrochloric acid--plumbers, water treatment plans (called muriatic acid)

hydrogen peroxide--beauty parlors and dye shops (for bleaching)

oxalic acid--dry cleaners and laundries (rust spot remover)

sodium hydroxide--taxidermists, leather tanneries, water treatment plants (called caustic soda; potassium hydroxide is just as good)

sodium thiosulfate--photographer (called hypo)

starch--general store, laundry

sulfuric acid--battery shop, petrol station (called battery acid)

Practically all the experiments require water. Distilled water is fine if available but ordinary tap water is quite adequate. Even stream water is satisfactory if it is clear enough to see through. The student can satisfy himself that impurities in the water are not influencing his observations by performing the experiment omitting one of the reactants (for example iodide in Expt.1), and seeing the water alone does not give a reaction.

Table 1. Stock Solutions

Name	Usual Formula	Formula wt.	Stock M	g/1	Special notes
Ammonium molybdate	$(NH_4)_2MoO_4$	196	0.1	20	20 g/1 of water
Bromothymol blue	-	-	(1%)	10	1 g in 100 ml 95% alcohol is adequate
Hydrochloric acid	HCl	36.5	3	10	Add 250 ml commercial (12M) acid to 750 ml water. 5 1 of stock recommended (1.2 1 12 M HCl + 3.6 1 H_2O)
Hydrogen peroxide	H_2O_2	34	10	340	Use commercial 30% solution
Iodine	$I_2(I_3^-)$	254	0.1	25	Dissolve 50g KI (0.3 moles) in 1 liter of water; add 25g I_2.
Manganese sulfate	$MnSO_4 \cdot 4H_2O$	223	0.2	45	45g/1 of water
Methylene blue	-	-	(1%)	10	1 g in 100 ml 95% alcohol is adequate
Oxalic acid	$H_2(COO)_2 \cdot 2H_2O$	126	0.05	6	6 g/1 of water
Potassium iodate	KIO_3	214	0.07	15	15 g/1 of water
Potassium iodide	KI	166	0.6	100	100 g/1 of water
Potassium permanganate	$KMnO_4$	158	0.01	1.6	1.6 g/1 of water
Sodium hydroxide	NaOH	40	0.1	4	4 g/1 of water, 5 1 recommended
Sodium thiosulfate	$Na_2S_2O_3 \cdot 5H_2O$	248	0.5	120	120 g/1 of water, 5 1 recommended
Starch	-	-	(1%)	10	10 g/1 of water; grind starch with 20 ml H_2O first, add to rest of water
Sulfuric acid	H_2SO_4	98	1	98	Slowly pour 55 ml commercial (18 M) acid into 945 ml H_2O. 5 1 of stock recommended (270 ml 18 M H_2SO_4 into 4.7 1 H_2O or add 500 g 18 M H_2SO_4 to 4.7 1 H_2O.)

3. Experimental Uncertainty

One of the potentially most useful ideas a student can explore in a science course is the nature of experimental uncertainties. Normally these are lumped with experimental errors. The term error should more usefully be reserved for mistakes which can be rectified with the equipment at hand and should be applied to blunders in mixing reagents, mistakes in reading measurements, and mathematical errors in the calculations. All of these can be removed by careful students who understand what they are doing. But there remain sources of uncertainty which cannot be removed no matter how careful one is with the available equipment.

All measurements are subject to at least two sources of experimental uncertainty: 1) the measuring devices may be incorrectly calibrated, and 2) there is always an uncertainty in reading any scale. The first type of uncertainty is systematic in that it will always be in the same direction (plus or minus depending on the sign of the error in the calibration.) This uncertainty for the student is, of course, due to an error on the part of someone else. Such calibration errors can be detected by careful recalibration of the equipment, but this is seldom possible or worthwhile at the school level.

Uncertainty in reading measurements is inherent in all experimental work. It is non-systematic and leads to both positive and negative deviations from the average. This uncertainty can be minimized by careful work but is impossible to remove. These uncertainties are partly due to variations from individual to individual as for example in the ability of their eyes to detect faint colors. They are also due to the impossibility of reading any scale to an infinite number of significant figures. At some point it becomes impossible to say what the next figure would be with any certainty. This range can be determined by experimental observation. Once the students learn to do this they become much more aware of the nature and limitations of experimental observations. They begin to understand the always limited validity of evidence. And they become more confident in evaluating and interpreting their own experimental data. Time spent discussing experimental uncertainties can be among the most effective periods in a science course.

4. Guides to Experiments

Experiment I. The Use of Starch as an Indicator for Detecting the Presence of Iodine.

Preparation

Check supply of stock solutions. Check starch solution for mold. Atmospheric oxygen oxidizes aqueous iodide ions to iodine. A visible brown color indicates a fresh KI solution should be prepared.

Prelab

Starch consists of coiled spiral molecules whose core is just large enough for an I_2 molecule to fit in lengthwise. The resulting binding to the starch helix changes the electron structure of the I_2 enough that its color changes from the red-brown found in aqueous solution to an intense deep blue. The question to be explored is "what concentration of iodine must be present to give a visible color?"

Experiment

Should require no more than 30 minutes if students have had lab experience. 60 minutes if not. As a lecture experiment 5-10 minutes is plenty. See Section D for a possible data sheet.

Answer to question

Concentration of potassium iodide solution = 0.6M;
Assuming each drop is 0.05 ml
Then, when 1 drop is diluted to 100 ml
Concentration of diluted solution $= \frac{0.05}{100} \times 0.6M$

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

If 5 drops of diluted KI solution are in test tube with a total of 10 drops.

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

$$\text{i.e. } 3/2 \times 10^{-4}\ M$$

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

Concentration of iodine $= \frac{3}{5} \times \frac{3}{2} \times 10^{-4}M$

$$\text{i.e. approximately } 10^{-4}M$$

Post lab

Tabulate class results of tube numbers first showing color, and concentrations of the tube. Discuss experimental uncertainties, dilution technics, size of drops, eye sensitivity, cleanliness. Discuss calculation of concentrations. Compare concentration of iodine giving visible color to an aqueous solution and to a starch suspension.

Experiment II. Reaction of Thiosulfate Ions with Hydrochloric Acid.

Preparation

Check stock solutions. A little sulfur (usually white grains) in the bottom of the bottle will cause no problems. A great deal of precipitate indicates that much of the thiosulfate has been oxidized so a new stock solution should be made up.

Prelab

Discuss first order (rate = $k[A]$) and second order (rate = $k[A]^2$) reactions. Emphasize order cannot be obtained from examining net equation, but only from experimental data. Do not try to prove that the two shapes of the $[S_2O_3^{2-}]$ versus (1/t) curves are consistent with first and second order. Leave this for post lab.

Experiment

Time required: lab, about 30-40 minutes; class, about 5-10 minutes. Urge at least the best and fastest students to repeat some of their experiments in order to determine their reproducibility and the nature and size of the experimental uncertainties. A principal one is the time at which a fixed amount of sulfur has formed.

Answer to question If the solution is free of dissolved gases and not in contact with air, thiosulphate does not undergo any changes. But when CO_2 or other acid gases from the air is in contact with the solution the decomposition starts. CO_2 makes the solution slightly acidic and the reaction above takes place. Oxygen in air will slowly convert aqueous thiosulphate ions to sulphate ions and sulphur.

Post lab

Collect class data on order with respect to $[S_2O_3^{2-}]$, with respect to $[H^+]$, and values of k. Select best values. Discuss possible mechanisms, drawing structural formulas to show orientation required in each step.

As long as $[H^+] > [S_2O_3^{2-}]$ the reaction appears to be zero order in $[H^+]$ and first order in $[S_2O_3^{2-}]$. Note this is actually the total thiosulfate concentration. Thus

$$\text{rate} = k[S_2O_3^{2-}]_{tot}, \quad \text{when } [H^+] > [S_2O_3^{2-}] \qquad \text{(Eqn. II. 1)}$$

As $[H^+] \simeq [S_2O_3^{2-}]_{tot}$ the reaction becomes approximately first order in $[H^+]$ as well

$$\text{rate} = k[H^+]\,[S_2O_3^{2-}]_{tot} \quad \text{when } [H^+] \approx [S_2O_3^{2-}]_{tot} \qquad \text{(Eqn. II. 2)}$$

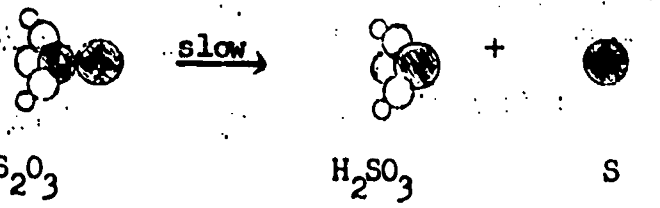
This change is presumably due to the fact that at high $[H^+]$ all the thiosulfate is in the form of $H_2S_2O_3$ whose concentration is independent of $[H^+]$, but equal to the total thiosulfate present. The rate determining step is the decomposition of $H_2S_2O_3$.

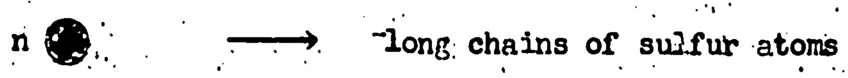
$$\left.\begin{array}{lll} S_2O_3^{2-}(aq) + H^+(aq) & \longrightarrow & HS_2O_3^-(aq) \\ HS_2O_3^-(aq) + H^+ & \longrightarrow & H_2S_2O_3(aq) \end{array}\right\} \text{Practically all thiosulfate is in form of } H_2S_2O_3(aq)$$

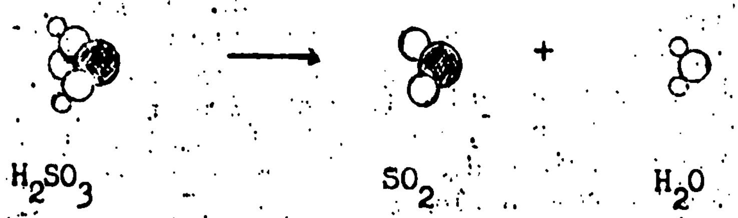
$$H_2S_2O_3(aq) \xrightarrow{slow} H_2SO_3(aq) + S(aq) \qquad \text{Rate determining step}$$

$$n\,S(aq) \xrightarrow{fast} S_n(c)$$

$$H_2SO_3(aq) \xrightarrow{fast} SO_2(aq) + H_2O(l)$$







The same mechanism holds if $[H^+] = [S_2O_3^{2-}]_{tot}$ but now $[H_2S_2O_3]$ depends on $[H^+]$ so the rate law of equation II. 2 applies.

Note that the plot of $[S_2O_3^{2-}]$ against (1/t) must go through the origin, if first order.

Experiment III. How to Follow a Reaction

Preparation

Check stock solutions. Aqueous iodide solutions are oxidized to iodine by dissolved oxygen especially in the presence of light. So aqueous iodide solutions should be made up only a week or so before use. See preparation section of Expt. II for a similar discussion about thiosulfate. Hydrogen peroxide also slowly decomposes. Bottles more than one year old should be checked as to usefulness.

Prelab

Discuss division of labor when two people work together. Insist that roles be reversed ~~sometime~~ during experiment so each person must have a chance to do everything. Suggest students try to estimate experimental uncertainties.

Experiment

Time required: lab about 30-40 minutes; class, about 10 minutes.

Answer to question

Dilution: 10 drops of 0.6M potassium iodide made up to 1 ml
Assuming 1 drop is 0.05 ml, then
Initial Molarity of iodide in solution $= 0.6 \times \frac{0.05}{1.0} \times 10 \times \frac{1}{7} \simeq 0.04M$

5 drops of 10M hydrogen peroxide made up to 25 ml
Initial molarity of hydrogen peroxide in solution $= \frac{5 \times 0.05 \times 10}{25} \times \frac{1}{7} \simeq 0.01M$

Note that 1 out of 7 drops is iodide and H_2O_2 respectively.

Post lab

Collect student results. Defer discussion of mechanism until Expt. IV supplies more data. Discuss trends in concentration of each reactant during the experiment. The concentrations of H_2O_2 and I^- change by a factor of 7/16 as far as dilution is concerned. Original volume = 7 drops, final volume = 16 drops. But they are also used up in each stage of the reaction. However, the few moles of $S_2O_3^{2-}$ added each time shows that the changing concentration of I^- and H_2O_2 due to reaction is small compared to the change caused by dilution. You will be able to estimate the total order of reaction (second) from the data, but will not know the order with respect to either I^-, H_2O_2 or H^+ (actually first, first, zero). Some students may note another possible $H_2O_2 - I^-$ reaction in the Introduction to this lab manual: the catalytic decomposition of H_2O_2 by I^-. This catalyzed rate is not appreciable at the acidity used in this experiment. But, of course, both reactions occur.

Experiment IV. How Reaction Speed Depends on Initial Concentration.

Preparation

Check stock solutions. See discussion in Expt. III, Preparation of aqueous H_2O_2 and KI.

Prelab

Review the starch test for iodine (Expt. I). In this experiment it is used to measure the time required for a constant amount of reaction to occur. Note that in these experiments all concentrations but one are kept constant. In one set of experiments the initial concentration of iodide ions is varied. In the second set the initial concentration of hydrogen peroxide is varied. The question is: what effects, both qualitative and quantitative, do such variations have on the rate, that is on the time required to produce a constant amount of iodine.

Experiment

Time required: lab, about 20-30 minutes; class, about 5-10 minutes. Students must shake tubes to mix reactants uniformly. The reaction is first order in I^- and first order in H_2O_2.

Answers to questions

1. 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.

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

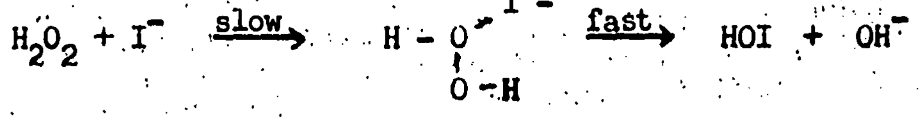
The blue colour of starch/iodine in Experiment IV appears after the lower limit of sensitivity of the starch reagent is exceeded. It is possible to observe only one point of the reaction. In Experiment III, any number of points may be observed, depending on the number of drops of thiosulphate added.

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.

Post lab

This reaction is mentioned in the student chapter p. 15 as being zero order in H^+. Tabulate class data to check agreement on reaction order, rate equation, and probable rate determining step (collision of I^- with H_2O_2). Discuss orientation and energy requirements, presence of unshared electrons on oxygen and empty orbitals on iodide, and the effects of each of these on the formation of the $H_2O_2I^-$ intermediate molecule.

A probable mechanism is



$$H_2O_2 + I^- \xrightarrow{slow} \begin{array}{c} \quad I^- \\ H - O \\ | \\ O - H \end{array} \xrightarrow{fast} HOI + OH^-$$

$$HOI + I^- \xrightarrow{fast} HOII^- \xrightarrow{fast} OH^- + I_2$$

$$2(OH^- + H^+ \xrightarrow{fast} H_2O).$$

Net reaction: $H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) = 2H_2O(l) + I_2(aq)$

Note that each step involves a collision between only two molecules, at least one of which is common in the solution, and that the presumed slow reaction does have the most demanding orientation and electrical barrier to overcome. (Both I^- and the oxygen in peroxide are negatively charged. In HOI colliding with I^- the I in HOI is slightly positive.)

Experiment V. Reaction of Hydrogen Sulfite and Iodate Ions.

Preparation

Check stock chemicals. Aqueous sulfite solutions should not be made up ahead of time as they are readily oxidized by atmospheric oxygen to sulfate. Ice is not mandatory for this experiment, but is desirable so some runs can be made below room temperature. Plastic bottles are recommended since they make it easier to keep the temperature constant, but glass containers, paper cups, or any water proof vessels are quite satisfactory. Plastic bottles are often available at the hospital. Baby bottles are excellent. They also make good wash bottles.

Prelab

Emphasize the need for uniform mixing and for accurate measurements of time (± 2 sec.) and temperature (± 0.2°C).

Discuss interpolation of readings on a 1°C thermometer.

Experiment

Time required: lab, about 30-40 minutes; class, about 10 minutes. Pouring solutions rapidly from one container to another twice gives uniform mixing.

Answer to question:

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 the equilibrium concentration of desired product in the equilibrium system.

If raising T destroys a necessary intermediate molecule or increases the rate of the reverse reaction much more than that of the forward reaction, the rate may appear to decrease even though T increases.

Post lab

Collect class data and plot $[IO_3^-]$ versus time, and temperature versus time. Discuss sources and sizes of experimental uncertainties. Collect class data and plot log (1/time) versus 1/T (°K). Calculate: $\Delta E_{act} = 4.6 \times$ change in log (1/time) / change in (1/T).
That is: $\Delta E_{act} = -4.6$ slope of the log (1/time) versus (1/T) plot.
Use the straight line plot to predict the reaction time for a temperature not measured. Discuss advantages of straight line (compared to curved line) plots for interpolating and extrapolating data. Discuss relative validity of interpolations and extrapolations.

Students should see from inspection of the net equation that this mechanism must be complicated and would require much experimentation to discover.

Experiment VI. Effect of Temperature on Rate of Reaction.

Preparation

Check stock solutions. Crystalline oxalic acid is a fairly poisonous material but the dilute solutions used here, while they should not be drunk, are not dangerous. See Expt. II. for comments on thiosulfate solution.

Prelab

Mention desirability of highly colored permanganate ion as an indicator of its own presence. It can be seen at a concentration of less than one ion per million molecules of water. Do not anticipate the experimental observation that Mn^{++} catalyzes the reaction.

Experiment

Time required: lab, about 20-30 minutes; class, about 5-10 minutes. Encourage the better (or faster) students to make rate measurements at three or more temperatures so they can plot log (1/t) vs (1/T) and estimate ΔE_{act}.

Answer to question:

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°C before the total stoichiometric amount of titrant has been added; the reaction then occurs rapidly and titration to the end point is possible.

Post lab

Collect class data on time vs temperature and plot t vs T. Plot log (1/t) vs (1/T) if time is available. Slope $= -\Delta E_{act}/4.6$ if base 10 logs are used ($4.6 = 2.30 \times 1.99$). As in Expt. V the net equation shows this will be a complicated mechanism in (b). See Expt. II for a discussion of (c).

Experiment VII. Effect of Acid Concentration on a Rate of Reaction.

Preparation

Check stock solutions. Aqueous arsenite solutions must be made up fresh since they may be oxidized by atmospheric oxygen to arsenate in a week or so. (Remember the similar problem with aqueous sulfite.) Arsenic compounds are poisonous. You should make up the fresh stock solution by dissolving 1 g of As_2O_3 in about 10 ml of 1M NaOH, diluting to 100 ml with water and adding 1 M H_2SO_4 until the solution is neutral to litmus or pH test paper.

Prelab

All concentrations will be kept constant except $[H^+]$ (and, of course, $[OH^-]$). Suggest that the students consider what effects H^+ might have on the reactants directly as well as in the rate but do not explicitly discuss the conversion of AsO_3^{3-} to less negatively charged species by H^+.

Experiment

Time required: lab about 30-40 minutes; class, about 10-15 minutes.

Answer to question

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

$$I_2(aq) + 2OH^-(aq) \longrightarrow IO^-(aq) + I^-(aq) + H_2O(l)$$

$$3IO^-(aq) \longrightarrow IO_3^-(aq) + 2I^-(aq)$$

Post lab

Collect class data, and suggestions as to their interpretation. Emphasize the effect of H^+ in reacting with the unshared pairs of electrons on the AsO_3^{3-} thus hindering an effective collision with I_3^-. H_3AsO_3 is the most common arsenite species below pH2, $H_2AsO_3^-$ from pH 2-7, $HAsO_3^{2-}$ from pH 7-12, and AsO_3^{3-} above pH 12. The availability of unshared pairs apparently predominates over the net ionic charge effect. Using ionic charge arguments, one would guess I_3^- would react more slowly with AsO_3^{3-} than with $HAsO_3^{2-}$ and the other even less negative arsenite species. It is also possible in basic solution that OI^- ions from the reaction

$$I_3^- (aq) + 2OH^-(aq) \rightleftharpoons 2I^-(aq) + OI^-(aq) + H_2O(l)$$

are the species which react most rapidly with arsenite. Only careful experiments will reveal the most probable mechanism.

A probable mechanism is:

$$I_3^- \rightleftharpoons I_2 + I^-$$

$$\begin{array}{ll} I_2 + As(OH)_3 \text{ (or another form of arsenite)} \xrightarrow{\text{slow}} & IAs(OH)_3^+ + I^- \\ & \downarrow H_2O \\ & IAs(OH)_4 + H^+ \\ & \downarrow \\ & As(OH)_4^+ + I^- \\ & \downarrow \\ & AsO(OH)_3 + H^+ \end{array}$$

Net: $I_2(aq) + As(OH)_3(aq) + H_2O(l) = AsO(OH)_3(aq) + 2H^+(aq) + 2I^-(aq)$

Experiment VIII. Effect of Catalyst on Reaction Rate.

Preparation

See preparation comments on Expt. III and VI.

Prelab

Review the advantage of highly colored aqueous MnO_4^- as an indicator of its own presence (Expt. VI). Discuss the technique of measuring the time to decolorize successive drops of aqueous MnO_4^- by a solution becoming less and less concentrated in both $H_2C_2O_4$ and MnO_4^-. Do not reveal the experimental observation that the time to decolorize will first decrease even though all the concentrations of reactants are decreasing. Do not discuss the catalysis by Mn^{++}. Leave both these items to the post lab.

Experiment

Time required: lab, about 30-40 minutes; class, about 10-15 minutes.

Answer to question:

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.

Post lab

Collect class data. Discuss minimum in time in Part 1. Note that the mechanism must have many steps (it is not known in detail) since both MnO_4^- and $H_2C_2O_4$ have many bonds which must be broken. Discuss unlikely nature of collisions between "oxygen surrounded" MnO_4^- and $H_2C_2O_4$ leading to reaction and likelihood that Mn^{++} could provide "bridges" between such molecules and so catalyze their reaction. Molybdenum does form peroxy compleses. These presumably form then react rapidly with I^-, probably due to a low activation energy.

Experiment IX. Reaction of Calcium Carbonate with Hydrochloric Acid.

Preparation

Check stock chemicals.

Prelab

This is the first heterogeneous system studied. Raise some questions about the nature and area of surfaces and the problem of a reactant from solution getting to the surface while a gas is forming on it. Discuss design of reaction tube and use of constant volume of gas generated to measure rate.

Experiment

Time required: lab about 30-40 minutes; class, about 10-15 minutes. It may be wise to dip the pieces of calcium carbonate in 1 M HCl until vigorous bubbling occurs (5-10 secs.) to clean off the surfaces.

Answers to questions:

1) The reaction involved is heterogeneous and takes place at the solid/liquid interface: Only if the surface areas are the same can we attribute differences in rate solely to differences in $[H^+]$.

2) The units of k are derived from the equation

$$\text{rate} = k\,c^n \quad (n = 1 \text{ or } 2 \text{ depending on } [H^+])$$

$$\text{units of } k = \frac{\text{units of rate}}{\text{units of concentration to the } n^{th} \text{ power}}$$

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

$$\left.\begin{array}{l} = \text{mole}^{-1}\ \text{litre sec}^{-1} \\ \text{or litres/ (mole sec)}^{-1} \end{array}\right\} \text{if } n = 2$$

$$\text{units of } k = \frac{\text{mole litre}^{-1}\ \text{sec}^{-1}}{\text{mole litre}^{-1}} = \text{sec}^{-1}\text{, if } n = 1$$

Post lab

Collect student results. Note that M x t = constant at high M, M^2 x t = constant at low M.

At high hydrogen ion concentrations the rate appears to be first order in $[H^+]$; at lower concentrations it appears to change to second order in $[H^+]$. This is consistent with the idea that, at high $[H^+]$, the reactive sites in the surface are always covered with one H^+ per reactive CO_3^{2-} site. The rate determining step is the diffusion of another H^+ to this site. Thus:

1) fast at high $[H^+]$: $CO_3^{2-}(c) + H^+(aq) \longrightarrow HCO_3^-(c)$

2) slow: $HCO_3^-(c) + H^+(aq) \longrightarrow H_2CO_3$(on surface)

3) fast: H_2CO_3(on surface) $\longrightarrow H_2O(l) + CO_2(aq)$

4) fast: $CO_2(aq) \longrightarrow CO_2(g)$

At low $[H^+]$ steps 1-4 above still occur, but now 1 is also slow so rate becomes second order in $[H^+]$ because two successive slow collisions of H^+ with a reactive CO_3^{2-} site are required to produce products.

Changing orders as concentrations change are common in rate processes since the rates of each step also change. Thus one step is slowest (and rate determining) at one set of concentrations. But a different step can become slowest and rate determining at another set of concentrations. Remember, for example, that at equilibrium the rate of each forward reaction becomes identical to that of its own reverse reaction, though during the net reaction they differ.

A typical set of data is given in Table 1. Remember that the actual times will vary with the surface area of the pieces of calcium carbonate.

M HCl	3.0	1.5	1.0	0.75	0.6	0.3
t	85	185	260	430	600	2000
M x t	255	280	260	300	360	600
M^2 x t	760	410	260	170	220	180

Experiment X. Reaction of Tin and Iodine in Benzene Solution.

Preparation

We produce here the article "The Dissolution of Tin in Iodine — A Kinetic Experiment," J.F. Davies and A.F. Trotman-Dickenson, Edward Davies Chemical Laboratory, Aberystwyth, U.K.

Reactions that can be followed by physical methods offer considerable didactic advantages when used as an introduction to chemical kinetics. Chief among these is that the student can see the progress of the reaction with time. Unfortunately, most physical methods require expensive apparatus, and hence are unsuitable for large classes. Moreover, they usually take an hour or so to set up and adjust before measurements can begin. The dissolution of tin in solutions of iodine in benzene, however, can be set up rapidly, and the apparatus required is widely available. The progress of the reaction can be followed by the loss of weight of a tin disc.

Prepare tin discs about 1.5 cm in diameter and 2 mm thick by casting a bar of tin metal in a clean glass tube. The tin bar can be put into discs with a small hacksaw or on a lathe. Then drill fine holes through the discs. Each disc should be cleaned with fine emery paper and then handled carefully by the edges. Hang on a thread from the hook of a single pan balance. Monofilament nylon thread is suitable for this purpose. Adjust the length of the thread so that the disc hangs about 1 cm below the surface of 10 ml of iodine solution contained in an open 25 ml weighing bottle placed on an Archimedian bridge. The disc must hang horizontally, but thermostating is not necessary because the temperature coefficients of diffusion controlled reactions are very low. Benzene is the most suitable, readily available solvent because of its low viscosity and the high solubility for iodine and tin (IV) iodide in benzene. It is convenient to prepare solutions of 10 g of iodine in 100 ml benzene and to obtain weaker solution by dilution.

Rate of Loss of Weight of Tin Disc
with Time

Solution: 0.6 g iodine in 10 ml benzene

Time (min)	Weight (g)
0	2.0091
1	2.0075
2	2.0052
4	1.9985
6	1.9930
8	1.9878
10	1.9830
12	1.9782
14	1.9738
15	1.9716

Readings can be taken at 2 min intervals as soon as the balance is steady. Seven or eight readings are usually taken as is shown in the table, but reasonably accurate rate constants could be obtained in a shorter time. The loss of weight occurs fast enough for the student to see a continuous movement of the scale of the balance. Runs with a succession of iodine solutions of differe concentrations yield the plots shown in Figure 1. These can be combined to give the plot in Figure 2. From the latter the students can clearly see that:

$$\text{Rate of loss of tin} = k\,[I_2]\ .$$

Thus the nature of first-order behavior can be established. This interpretation of the results can be recognized by students who have not yet learned to integrate.

It may be of interest to note that this experiment originated in his last year at school, and his chemistry master E.J.F. James[1] (now Lord James of Rusholme, Vice-Chancellor of the University of York).

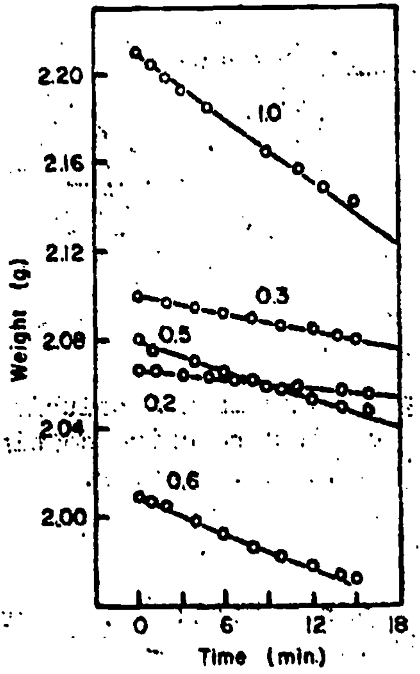


Figure 1. Variation of weight of discs with time when immersed in solutions of different concentrations. Concentrations (g I_2 in 10 ml) marked on lines.

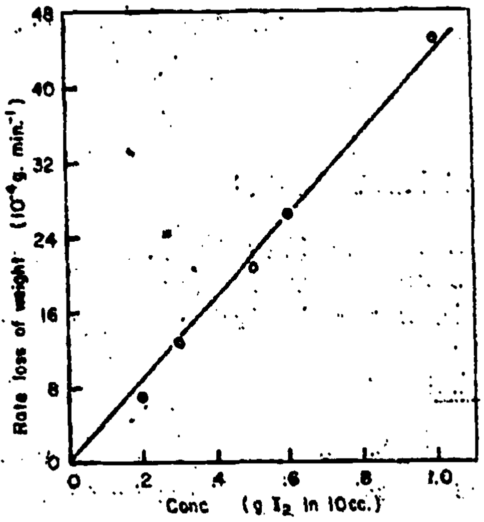


Figure 2. Dependence of rate of weight of tin discs on concentration of iodine solutions.

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1) Trotman-Dickenson, A.F. and James E.J.F., J. Chem. Soc., 736 (1947)

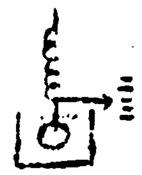
Prelab

Discuss the difference between heterogeneous and homogeneous reactions and between the diffusion of H^+ by a Grotthus chain chain mechanism (passing H^+ from H_3O^+ to H_2O with a different H^+ passing on to the next H_2O) and the movement of I_2 through benzene, C_6H_6. Ask the class to guess which process probably leads to a faster rate.

Experiment

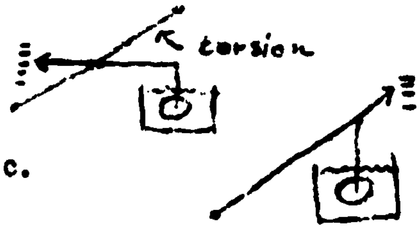
Time required: lab, about 40-50 minutes; class, about 30 minutes. Only the rate of weight change needs to be measured in this experiments not actual weights. Thus a cheap, sensitive spring can be used instead of an expensive balance. Three types are possible:

1) a very weak coil spring with indicator attached



2) a torsion wire with indicator attached

3) a weak linear spring, metal, bamboo, etc.



Answer to question:

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.

Post lab

Collect class results. Discuss possible rate determining steps. Assume diffusion rates are proportional to the concentration.

Possible mechanism:

$$I_2 \text{ (in } C_6H_6) \longrightarrow I_2 \text{ (at surface)} \qquad (1)$$

$$I_2 \text{ (at surface)} \longrightarrow I_2 \text{ (adsorbed)} \qquad (2)$$

$$I_2 \text{ (ads)} + Sn \text{ (c)} \longrightarrow SnI_2 \text{ (ads)} \qquad (3)$$

$$SnI_2 \text{ (ads)} \longrightarrow SnI_2 \text{ (in } C_6H_6) \qquad (4)$$

$$SnI_2 \text{ (in } C_6H_6) + I_2 \text{ (in } C_6H_6) \longrightarrow SnI_4 \qquad (5)$$

Note that steps (3) and (5) probably consist of at least two steps each because of orientation problems. However steps 1,2,3, and 5 all appear to be first order in iodine. Only a more detailed study could tell what the actual mechanism and actual rate determining step is.

Experiment XI. Reaction between Solids.

Preparation

Check reagents. Remember mercury and lead salts are poisonous and mercury salts corrode lead plumbing rapidly. All waste mercury compounds should be dumped rather than washed down a sink.

Prelab

Discuss whether these reactions will be heterogeneous or homogeneous. What is the likely rate determining step?

Experiment

Time required: lab, about 10-25 minutes; class, about 5 minutes.

Answer to question:

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.

$$\mathrm{Hg\,I_2(c) + 2I^-(aq) \longrightarrow Hg\,I_4^{2-}(aq)}$$

Post lab

Collect class observations. Discuss crystal structures and their change upon reaction. Surface contact and/or growth of new crystals are the usual rate determining steps.

Experiment XII. Hydrolysis of Tertiary-Butyl Chloride (t-butyl chloride).

Preparation

Check reactants.

Prelab

None

Experiment

Time required: lab, about 30-40 minitues; class, about 15-20 minutes. The experiment could be modified by measuring the times required to neutralize successive 1 drop additions of 1 M NaOH. This requires much less time.

Answer to question:

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 neutralize the acid formed and prevent re-attack of the acid upon the alcohol.

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

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.

Post lab

Collect class results on linearity of graph (it should extrapulate through the origin since $C_{RCl} = C^o_{RCl}$ at $t = 0$), and k. Discuss possible first order mechanisms. Note that the concentration of H_2O remains essentially unchanged, so reaction could actually be second order, if

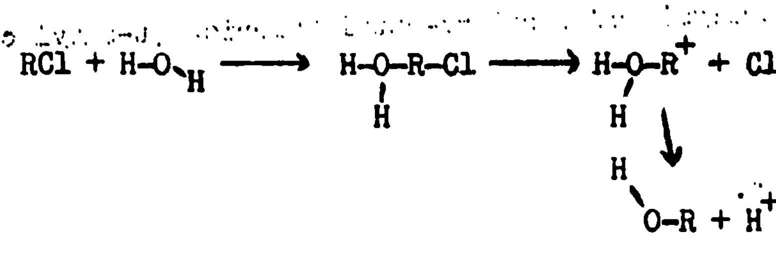
$$\text{rate} = k\,[RCl]\,[H_2O] \qquad \text{(Eqn. XII. 1)}$$

If H_2O is not involved, a possible mechanism is

$$RCl \xrightarrow{\text{slow}} R^+ + Cl^- \qquad \text{(Eqn. XII. 2)}$$

$$R^+ + H_2O \xrightarrow{\text{fast}} ROH + H^+ \qquad \text{(Eqn. XII. 3)}$$

If H_2O is involved, a possible mechanism is



$$RCl + H{-}O_{\searrow H} \longrightarrow H{-}\underset{H}{\underset{|}{O}}{-}R{-}Cl \longrightarrow H{-}\underset{H}{\underset{/}{O}}{-}R^+ + Cl^- \;\downarrow\; \overset{H}{\underset{}{\searrow}}O{-}R + H^+ \qquad \text{(Eqn. XII. 4)}$$

In any case, the activation energy is certainly provided by H_2O molecules colliding with R-Cl which, in first order kinetics, then eventually concentrates enough of its internal energy into the R-Cl bond for ionization to occur as in Eqn. XII. 2.

Experiment XIII. The Blue Bottle Experiment.

Preparation

Check reactant supply. See one of the literature references:

Journal of Chemical Education, 40 578-583 (1963)
New Trends in Chemistry Teaching, 1 162-167 (1964-65)
Why Do Chemical Reactions Occur?, Prentice-Hall, Englewood Cliffs, N. Jersey, U.S.A. (1963)

Prelab

Shake a prepared flask once and pose the question, "How many ingredients must be in the flask?" Or if you prefer, list the ingredients as H_2O, NaOH, glucose, air, and methylene blue and ask for a possible mechanism. The first question is strongly advised since it forces the students to base interpretations on observations rather than on chemical symbolism and formulas.

Experiment

Time required: lab, about 30 minutes to 90 minutes depending on student interest; class, about 15-30 minutes.
Solution per liter should contain about 20 g NaOH, 20 g glucose, 0.5 ml 1% methylene blue.

Post lab

See literature articles for a full discussion of the possible uses of this experiment.

A possible mechanism is

$$O_2(g) \xrightarrow{\text{fast}} O_2(aq) \qquad \text{(Eqn. XIII. 1)}$$

$$O_2(aq) + MeB(\text{colorless}) \xrightarrow{\text{fast}} MeB\cdot O_2\ (\text{blue}) \qquad \text{(Eqn. XIII. 2)}$$

$$\text{glucose}\ (aq) + OH^-(aq) \xrightarrow{\text{fast}} \text{glucose}^-(aq) + H_2O(l) \qquad \text{(Eqn. XIII. 3)}$$

$$\text{glucose}^-(aq) + MeB\cdot O_2(\text{blue}) \xrightarrow{\text{slow}} \text{products} + MeB(\text{colorless}) + OH^-(aq) \qquad \text{(Eqn. XIII. 4)}$$

$$\text{Net:}\ O_2(g) + \text{glucose}(aq) \longrightarrow \text{products.} \qquad \text{(Eqn. XIII. 5)}$$

Note that both OH^- and methylene blue are catalysts. Methylene blue acts as an oxygen carrier to catalyze glucose oxidation. Point out that a standard treatment in carbon monoxide poisoning is injection of methylene blue. Apparently, like hemoglobin, methylene blue can carry either O_2 or CO and changes color in the process.

Experiment I. Use of Starch as Indicator for Detecting the Presence of Iodine.

Name ____________________ Date ________________ Partner(s) ____________________

Tube	a	b	c	d	e	f
Drops of KI	1	2	3	4	5	6
Resulting colour	colourless	colourless	colourless	colourless	light blue	blue

<u>Calculation of I_2 in first coloured tube</u>: 1 drop = $\boxed{0.05}$ ml

Molarity of KI used $= \frac{0.05 \text{ ml} \times 0.6M}{100 \text{ ml}} = 3 \times 10^{-4}$ M

$[I^-]$ in tube e $= \frac{5}{10} \times 3 \times 10^{-4} = 1.5 \times 10^{-4}$ M

(5 out of 10 drops is KI)

5 moles of I^- gives 3 moles of I_2 according to equation

$[I_2]$ in tube c $= \frac{3}{5} \times \boxed{1.5 \times 10^{-4} = 9 \times 10^{-5} \approx 10^{-4} \text{ M}}$

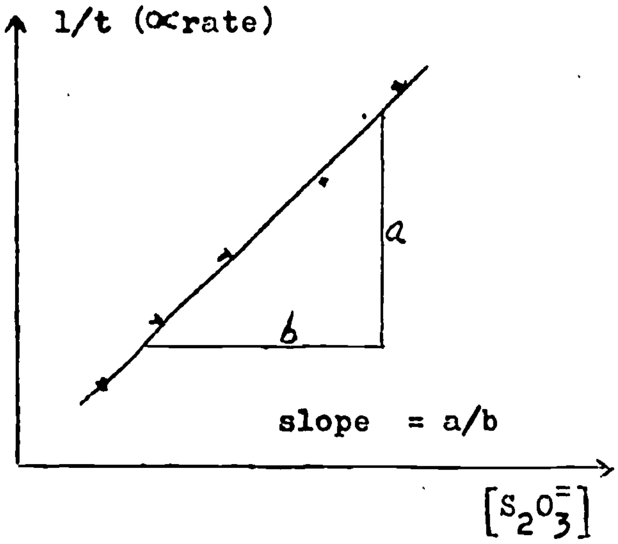
<u>Answer to question</u>: $\boxed{10^{-4}}$ M

$\boxed{}$ indicates typical results

Experiment II. Reaction of Thiosulphate Ions with Hydrochloric acid

Name__________ Date __________ Partner(s) __________

$[S_2O_3^=]$	$[H^+]$	t	1/t
0.15	0.5	13	.076
0.12	0.5	16	.062
0.09	0.5	19	.052
0.06	0.5	33	.030
0.03	0.5	65	.013
0.15	0.5	11	.091
0.15	0.3	11	.091
0.15	0.0	12	.083



Probable order in $[S_2O_3^=]$ is first.

Probable rate equation is (supply exponents)

$$\text{rate} = k\,[H^+]^0 \times [S_2O_3^=]^1$$

Calculate k:

$$k = \text{slope} = a/b \simeq 1.9$$

Possible mechanism for the net reaction

$$S_2O_3^= (aq) + 2H^+(aq) = S(c) + SO_2(aq) + H_2O\ (l)$$

is

$H^+(aq) + S_2O_3^=(aq) \rightleftharpoons HS_2O_3^-(aq)$	fast equilibrium
$H^+(aq) + HS_2O_3^-(aq) \rightleftharpoons H_2S_2O_3(aq)$	" "
$H_2S_2O_3(aq) \longrightarrow H_2SO_3(aq) + S(c)$	slow step
$H_2SO_3(aq) \longrightarrow H_2O(l) + SO_2(aq)$	fast step

☐ indicates typical results

Answer to question: If the solution is free of dissolved gases and not in contact with air thiosulphate does not undergo any changes. But when CO_2 from the air is in contact with the solution the decomposition starts. CO_2 makes the solution slightly acidic and the reaction above takes place.

Experiment III. How to Follow a Reaction

Name____________________Date_______________Partner(s) _______________

Reading	a	b	c	d	e	f	g	h	i	j
Time (sec)	7	15	26	40	58	83	111	144	187	240
Interval		9	11	14	18	25	28	33	43	53

Interpret the observations

As one of the reactants (H_2O_2) is used up its concentration will decrease and the rate of reaction will decrease.

Answer to question

$[I^-]$: 1 ml = 22 drops. Dilute 10 drops of 0.6M I^- to 1 ml

$$\text{Initial } [I^-] : 0.6\text{M} \times \frac{10 \text{ drops}}{22 \text{ drops}} \times \frac{1}{7} \simeq \underline{0.04\text{ M}}$$

$[H_2O_2]$: 1 ml = 25 drops. Dilute 5 drops of 10M H_2O_2 to 25 ml

$$\text{Initial } [H_2O_2] : 10\text{M} \; \frac{5 \text{ drops}}{25 \times 25 \text{ drops}} \times \frac{1}{7} \simeq \underline{0.01\text{ M}}$$

Note that only H_2O_2 is consumed in the reaction. I^--ions are regenerated by $S_2O_3^=$ and when no blue iodine-starch colour is seen I^--concentration is practically constant.

☐ indicates typical results.

Experiment IV. How Reaction Speed Depends on Initial Concentration

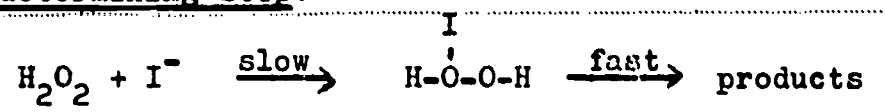
Name____________________Date________________Partner(s)____________________

Solution used	B	C	D	E	F	M	N	O	P	Q
Relative Concentration $[I^-]$	1	1/2	1/3	1/4	1/5	← constant →				
$[H_2O_2]$	← constant →					1	1/2	1/3	1/4	1/5
Time (sec)	4	7	10	15	22	8	16	20	30	42
1/t ($\propto$ rate)	.25	.14	.10	.07	.05	.13	.06	.05	.03	.02

Rate law: rate $= k\,[I^-]^1 \times [H_2O_2]^1$, (supply exponents)

first order in $[I^-]$ and first order in $[H_2O_2]$

Probable Rate determining step:



$$H_2O_2 + I^- \xrightarrow{slow} \overset{I}{\overset{|}{H\text{-}O\text{-}O\text{-}H}} \xrightarrow{fast} \text{products}$$

Answers to Questions:

1. Increasing the concentrations of the reactants results in more collisions between molecules and thus a higher rate of reaction.

2. The iodine-starch colour in Exp. IV appears when the lower limit of sensitivity is reached. Each experiment gives only one time reading. In Exp. III a third reagent $S_2O_3^=$ is added in small consecutive amounts. The $S_2O_3^=$ reacts with I_2 and thus removes the I_2-starch colour. First when the $S_2O_3^=$ is used up the characteristic blue colour reappears when enough I_2 has been formed. A series of data can be obtained from one test tube.

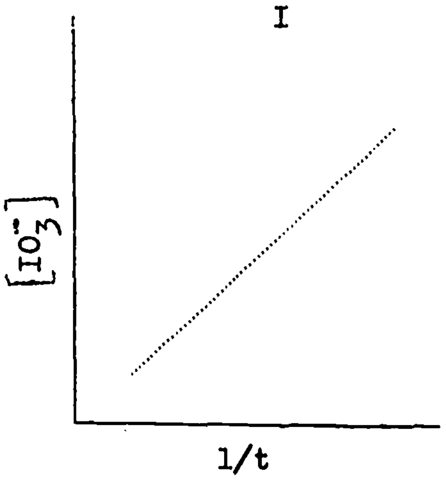
3. Yes

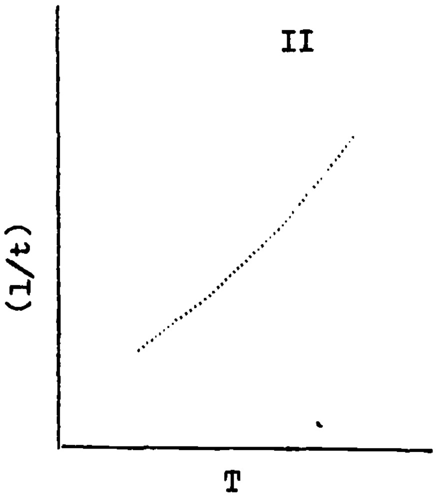
⬚ indicates typical results

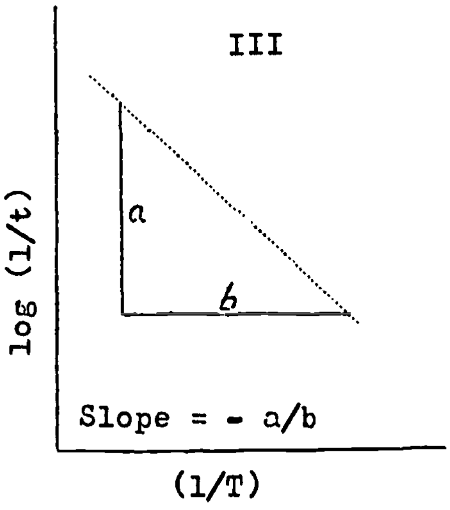
Experiment V. Reaction of Hydrogen Sulphite and Iodate Ions

Name____________________Date______________Partner(s)____________________

	Tube	1	2	3	4	5	6	7	8	9	10
	$[IO_3^-]$	0.01	0.009	0.008	0.007	0.006	0.005	0.004	0.003	0.002	0.001
I	t (sec)	63	71	83	96	103	117	154	205	360	840
	1/t ($\propto$rate)	.0159	.0141	.0120	.0104	.0097	.0086	.0065	.0049	.0028	.0012
	T (°C)	2		16		30(room)			35	43	
II	T (°K)	275		289		303			309	316	
	t	128		88		59			56	41	
	1/t	.0078		.0114		.0170			.0178		.0244
III	log (1/t)	-2.108		-1.944		-1.771			-1.748		-1.613
	(1/T)	.00367		.00345		.00330			.00324		.00316







Calculation of ΔE_{act} (optional)

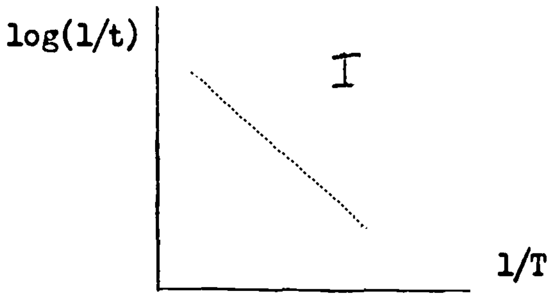
Slope of curve III $= -\frac{a}{b} = -\frac{\Delta E_{act}}{4.6}$; $\boxed{\Delta E_{act} = 4500 \text{ cal/mole}}$

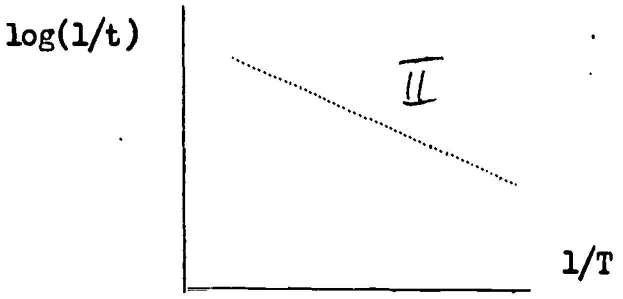
Answer to question An increase in temperature raises the kinetic energy of all reacting particles and increases the rate of collision, thus leading to increased rate of reaction. For reversible reactions both forward and reverse reaction rates increase with temperature but the reverse rate may increase more than the forward rate and thus it may appear that the overall rate decreases even though temperature increases.

Experiment VI. Effect of Temperature on Rate of Reaction

Name____________________ Date_______________ Partner(s)__________________

System	MnO_4^- / $H_2C_2O_4$			$S_2O_3^{2-}$ / H^+		
T °C	29	40	60	29	40	60
T °K	302	313	333	302	313	333
t (sec)	144	45	11	35	20	9
1/t (rate)	.007	.022	.091	.029	.050	.111
log (1/t)	-2.158	-1.653	-1.041	-1.544	-1.301	-0.954
1/T	.00333	.00320	.00300	.00333	.00320	.00300





Calculation of activation energy ΔE_{act}:

$$\Delta E_{act} = 4.6 \times (\text{slope of the straight line})$$

I. $\Delta E_{act} \simeq$ 15500 cal/mole
(15.5 kcal/mole)

II. $\Delta E_{act} \simeq$ 8500 cal/mole
(8.5 kcal/mole)

Answer to question: Yes, the reaction between MnO_4^- and $C_2O_4^=$ is too slow at room temperature to observe a sharp end point.

⬚ indicates typical results

Experiment VII. Effect of Acid Concentration on Rate of Reaction

Name ____________________ Date ______________ Partner(s) __________

Solution	A	B	C	D	E	F	G	H	I	J	K	L
$[H^+]$	1.0	0.8	0.6	0.4	0.2	10^{-7}						
$[OH^-]$							10^{-7}	0.02	0.04	0.06	0.08	0.1
t (sec)	39	30	22	15	8	2	2	1	1	1	1	1

Interpretation of effect of changing $[H^+]$

The results show that rate of reaction between AsO_3^{3-} and I_3^- increases as the solution becomes more and more alkaline and decreases as the solution becomes more and more acidic. The reaction is an equilibrium reaction and the rate of the backward reaction is very low in alkaline media since H^+ is one of the products and it will quickly be combined with OH^- to form H_2O.

Answer to question about solution L

Very strong alkaline solutions of iodine turn colourless even before adding AsO_3^{3-} because iodine is oxidized to hypoiodites and iodates. The iodine-starch colour then fades.

$$I_3^-(aq) + 2OH^-(aq) \longrightarrow IO^-(aq) + 2I^-(aq) + H_2O(l)$$

$$3IO^-(aq) \longrightarrow IO_3^-(aq) + 2I^-(aq)$$

⬚ indicates typical results

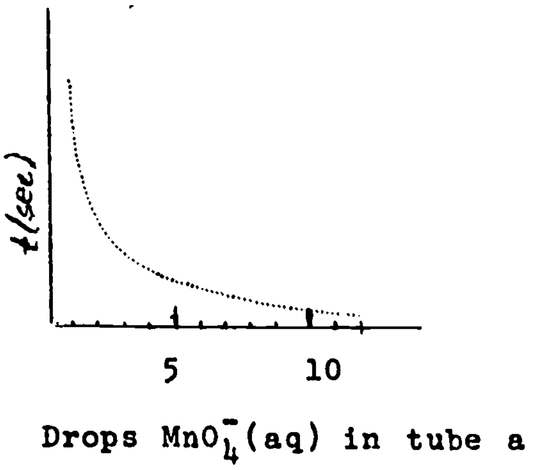
Experiment VIII. Effect of Catalyst on Reaction Rate

Name____________________Date______________Partner(s)____________________

Tube	a	a	a	a	a	a	a	a	a	a	a	a	b
Drops MnO_4^-(aq)	1	2	3	4	5	6	7	8	9	10	11	12	1
Time (sec)	140	57	43	34	30	25	20	17	15	15	14	13	instantaneous

Tube	c	d
Drops MoO_4^{2-}(aq)	0	1
Time (sec)	20	1

other trials	e	f
Drops of Fe^{3+}(aq)	0	1
Time (sec)	20	1



Interpretation of shape of curve:

First the reaction is slow but becomes faster despite reactant concentrations decreases. The product Mn^{2+} however catalyses the reaction and the more Mn^{2+} is produced the faster the reaction

Comment on relative effectiveness of catalysts:

Fe^{3+} seems to be as effective as Mn^{2+} in catalyzing this reaction.

Answers to questions

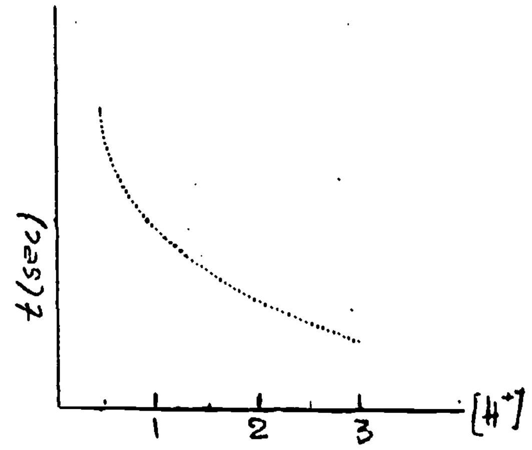
1. No, catalysts only effect the rate at which equilibrium is reached.
2. By providing alternative pathways (mechanisms) for the reaction. These other pathways have different energy requirements (activation energies) and the lower the activation energy the faster the reaction will proceed and equilibrium be attained.

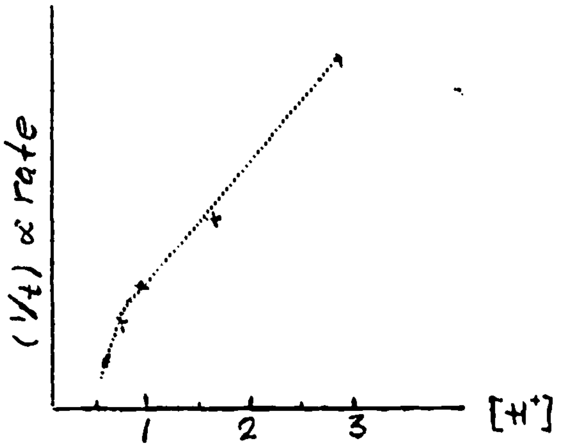
☐ indicates typical results

Experiment IX. Reaction of Calcium Carbonate with Hydrochloric Acid

Name______________ Date______________ Partner (s)______________

Solution	A	B	C	D	E
Molarity, m of H^+	3	1.5	1.0	0.75	0.60
Time, t (sec)	109	194	319	410	900
1/t ($\propto$ rate)	.009	.005	.003	.002	.001
m x t	327	291	319	308	540
m^2 x t	981	437	319	231	324





<u>Conclusions</u>: The reaction appears to be firse order in $[H^+]$ at higher H^+-concentrations, since m x t is roughly constant which means the same that the plot (1/t) vs $[H^+]$ is a straight line.

<u>Answers to questions</u>:

1. Reaction takes place on the liquid/solid interface. Only if the surface areas the same can differences in the rate of reaction be related to $[H^+]$.

2. Assume first order: $\text{unit } k = \dfrac{\text{unit rate}}{\text{unit } [H^+]} = \dfrac{\text{mole } l^{-1}\ \text{sec}^{-1}}{\text{mole } l^{-1}} = \text{sec}^{-1}$

" second order: $\text{unit } k = \dfrac{\text{unit rate}}{(\text{unit } [H^+]\ )^2} = \dfrac{\text{mole } l^{-1}\ \text{sec}^{-1}}{(\text{mole } l^{-1})^2} = l\ \text{mole}^{-1}\text{sec}^{-1}$

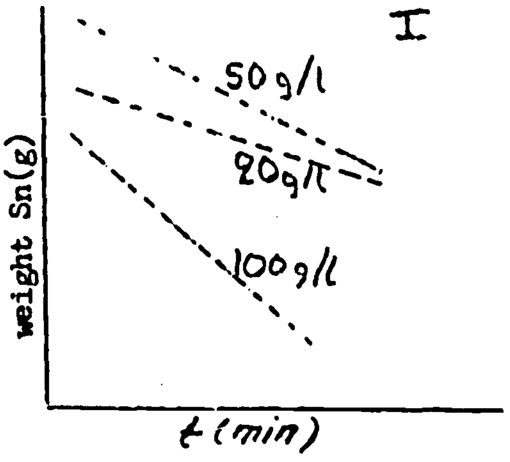
⬚ indicates typical results

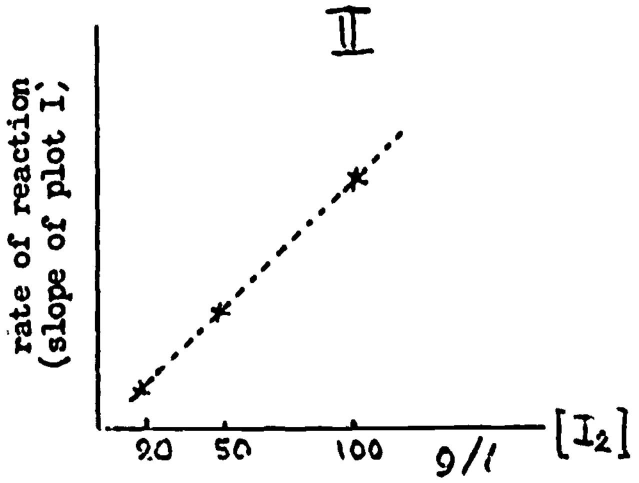
Experiment X. Reaction of Tin and Iodine in Benzene Solution

Name____________________Date__________________Partner(s)________________

Wt. of Sn in I_2 (g)

Time (min)	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
100 g/l	2.880	867	857	847	837	825	814	804	794	784	774	765	755	748	740	2.734
50 g/l	3.030	026	023	019	015	012	008	004	3.000	2.986	980	979	976	973	970	2.967
20 g/l	2.955	954	954	953	952	950	947	946	945	944	943	942	941	940	939	2.938





Probable rate equation rate = $k[I_2]$

Answer to question: No. SnI_4 which is formed in the reaction is not soluble in H_2O however it is soluble in benzene so that new tin surface is made available for further reaction.

☐ indicates typical results

Experiment XI. Reaction Between Solids

Name__________________Date_______________Partner(s)__________________

Observations:	Dry powders mixed:	Reaction very slow at the surfaces of the solids. Orange-red solid is formed.
	<u>Stirred vigorously</u>:	More and more orange-red solid product is formed.
	<u>Ground powders together</u>:	Even more reaction occurs colour more intense. No white solid reactants seen any more.
	<u>Water added</u>:	The previous orange-red precipitate dissolves not, but even more of it is formed.

<u>Conclusions</u>: Rate of reaction is faster the better the contact is between the reacting components. The orange-red compound is HgI_2.

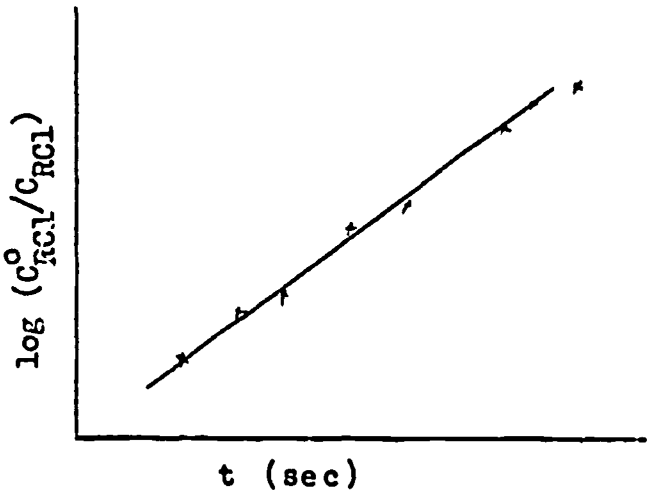
<u>Answer to question</u>: H_2O dissolves both reactants and in aqueous solution Hg^{2+} and I^- ions can meet much more frequently than in the solid.

[indicates typical results

Experiment XII. Hydrolysis of Tertiary-butyl Chloride (t-butyl chloride)

Name__________________Date____________Partner(s)________________________

Tube	a	b	c	d	e	f	g	h
C^o_{RCl}/C_{RCl}	1.05	1.08	1.11	1.14	1.18	1.21	1.25	1.29
log (C^o_{RCl}/C_{RCl})	.021	.033	.045	.057	.072	.083	.097	.111
t (sec)	75	140	225	265	335	425	510	595



Probable rate equation

rate = k x $[RCl]^1$

Possible mechanism $RCl \xrightarrow{slow} R^+ + Cl^-$

$$R^+ + H_2O \xrightarrow{fast} ROH + H^+$$

Answer to question OH^- ions neutralize the H^+ ions formed in the reaction. The sharp end point of the strong base/strong acid neutralization with a proper indicator (bromthymol blue) is used to time the hydrolysis reaction. When so much OH^- are used that the solution becomes acidic the indicator changes colour.

☐ indicates typical results

Experiment XIII. The Blue Bottle Experiment.

Name____________________Date______________Partner(s)________________________

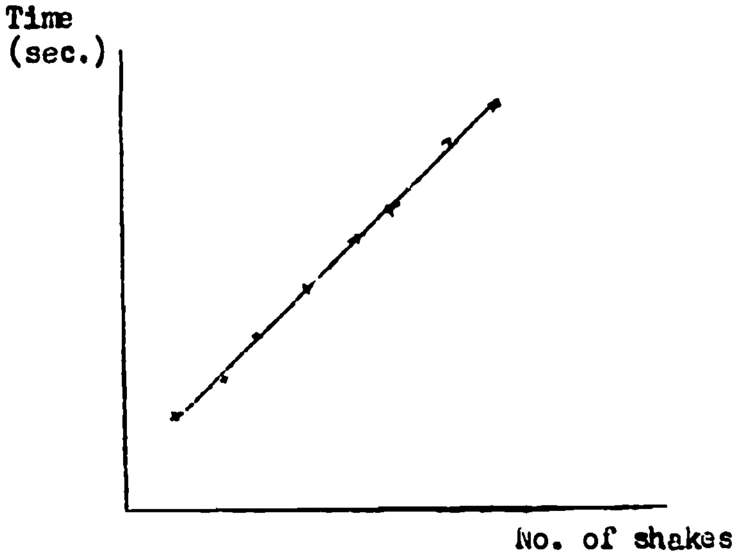
Record observations and conclusions. Construct your own tables and graphs as needed.

$$\text{Colourless solution} \underset{\text{stand}}{\overset{\text{shake}}{\rightleftharpoons}} \text{Blue solution}$$

Number of shakes	2	4	6	8	10	12	14
Time for (sec) decolourization	5	7	10	12	13	15	17

When the air in the flask was displaced by buten the solution turned very pale blue on shaking several times. This indicates that air (probably oxygen) causes the deep blue colour. Methylene blue without oxygen is colourless.

$$\underset{\text{colour less}}{\text{MeB}} + O_2 \longrightarrow \underset{\text{blue}}{\text{MeB-}O_2}$$



On standing MeB-O_2 loses it's oxygen, but no gas bubbles are seen, so apparently something else (probably glucose) is reacting with oxygen and MeB is regenerated.

The fact that the same solution can be used over and over again with no appearent fade of the blue colour indicates that MeB is not used up.

Probable mechanism:

$O_2(g) \longrightarrow O_2(aq)$ oxygen from air dissolves

$\text{MeB}(aq) + O_2(aq) \longrightarrow \text{MeB-}O_2(aq)$

$\text{MeB-}O_2(aq) + \text{glucose }(aq) \longrightarrow \text{products} + \text{MeB }(aq)$

Net equation: $O_2(g) + \text{glucose }(aq) \longrightarrow \text{products}$

Typical results

5. Laboratory Techniques

Most of these experiments on rates of reaction are designed to be done with a minimum amount of equipment. The scale of experiments usually involves only a few milliliters of solution with quantities often measured in drops. Some of the techniques which should be used are different from those used in larger scale experiments.

USE OF DROPPERS. Most droppers consist of a glass tube with one end drawn to a tip and the other inserted in a rubber bulb. Liquid should be drawn into the dropper by inserting its end beneath the level of the desired liquid, COMPRESSING THE RUBBER BULB SLIGHTLY so a few drops of air are expelled, then releasing the pressure so the liquid rises into the dropper. Only enough liquid to fill 2-4 cm of dropper length should be drawn in at a time. Otherwise liquid may enter the rubber bulb and become contaminated. Similarly the dropper should always be held with the RUBBER BULB UP so no liquid enters the bulb. The tip of the dropper is then placed over the desired tube and the required number of drops delivered to the tube.

Droppers should not be put into reagent bottles or into the tubes to be filled, since contamination will then occur. Rather, small quantities of the stock solution should be placed in a beaker or test tube and the liquid withdrawn from this container with the dropper. Just as the dropper should never be put into a stock solution (except for dropper cap bottles each having its own separate dropper) so stock solution once removed from a stock bottle should never be returned. Any excess should be thrown away. Clearly the best way to avoid excessive loss is to have each stock solution in its own small dropper bottle at the student's desk.

MEASURING VOLUMES. Most of the experiments in this set are quantitative, but only to one significant figure. Thus the expected experimental uncertainty is about ± 10%, primarily determined by the uncertainty in drop sizes. Calibration will show that most droppers deliver about 20-25 drops per cubic centimeter. Since most of the experiments involve measuring solutions in terms of drops, there is no need to use volumetric equipment such as special flasks, pipets, or burets at any time. Rough dilutions by eye are quite adequate and any containers may be used to measure reproducible volumes as mentioned under sources of equipment.

Thus all calculations of concentrations should involve only one significant figure and no values should be expressed to more than one significant figure.

MEASURING TIMES. Since volumes can be measured only to one significant figure there is no reason to measure times more accurately than this. Thus there is no need for stop watches. Ordinary cheap watches or wall clocks with second hands are more than adequate. They are available for $2 (US), or even less, in the markets. If such watches are not available, students can easily learn to count seconds. A common method in English is to say: one thousand and one, one thousand and two, and so on. In Thai a suitable substitute would be: Chulalongkorn nung, Chulalongkorn song, Chulalongkorn sarm, and so on.

MEASURING TEMPERATURES. Temperatures, unlike volumes and times, are not usually used in calculations in these experiments. They are used primarily in plotting data or merely as a variable which is to be determined for each experiment. Since rates are often much changed by small changes in temperature, it is essential that they be measured as accurately as possible. Ordinary thermometers (-20 to 110°C, for example) calibrated to one degree are quite satisfactory. They can be read, and should be, to ± 0.2° by simple interpolation between the degree marks. A simple hand lens, if available, makes such readings even easier. A great deal of time will be saved if a single source of hot water (a large tea kettle, for example) is available for the whole class. Each student can fill his thermostat from the kettle and return to his desk to make all further measurements. The same is true for ice water, rather than supplying each student with ice.

Not only must temperatures be determined as accurately as possible, they must remain as constant as possible during each experiment. Furthermore the temperatures of reagents to be mixed should be the same. The simplest way to meet these criteria is to place the reaction vessel, or reactant vessels, in a beaker of water which is at the desired temperature, (a thermostat). A Thermometer is used to read the temperature of the water in the beaker. Gentle stirring by moving the reactant containers by hand will insure they come to the water temperature within a minute. Since the thermometer is never put in the reactants they cannot be contaminated or diluted. After the reactants come to the desired temperature they are quickly mixed by pouring the contents of container A into B then all contents back into B and replacing B in the thermostat until measurements are finished. The two pourings give efficient mixing and no further stirring is needed unless drops are later added. If drops are added, stir the contents with a glass stirring rod, not with the thermometer which is easily broken.

STIRRING. Small volumes especially in small tubes are often more difficult to mix than larger volumes. It is essential to mix thoroughly if useful results are to be obtained. In small tubes this is most easily accomplished by tapping the bottom gently with one hand while holding the top of the tube in the other. When a few drops are to be mixed with a large volume (as in Experiment I) vigorous stirring is especially needed. The simplest method is to pour the liquid back and forth between two containers two or three times.

DATA SHEETS. A person is usually judged primarily by his ability to communicate with other people. We suggest the use of data sheets to teach each student some effective methods of communication. They are brief yet require the student to do more than fill in blanks, organized but allow for freedom of response, readily filled out, easily read, and easy to comment on. They can greatly simplify both the student's and teacher's role in communication. But there are good and bad techniques to their use.

Data sheets should be records of all the original observations (accurate and inaccurate, used and discarded). All records should be kept on the data sheets, and all calculations shown. The back of the sheet is excellent for calculations. If an observation, a record, or a calculation is not to be used, this is indicated by a single line drawn through it. Thus, no extra paper should be allowed in the lab and no copying of data or calculations on to the data sheet should be permitted. Each sheet should be an accurate record of what actually happened during the experiment, not a neat, edited summary of the "correct" conclusions.

This practice is insisted upon in all scientific research labs and should be begun in schools at the earliest contact with science. Such use of data sheets is a highly effective way of encouraging 1) thoughtful planning before an experiment is undertaken, 2) careful observation, 3) systematic recording of data, 4) directed calculations rather than random juggling of numbers, and 5) satisfaction in a job well done with minimum effort and time expended.

VISUAL OBSERVATIONS. Most chemical experiments involve visual observations by the experimenter. Only a few are limited to smell or taste (both dangerous to use on unknown chemicals), and hearing and touch are even less used. Most lectures, on the other hand rely primarily on hearing. Since it is well-established that, for most people, visual learning is more rapid and more long-lasting than aural (ear) learning, a well-designed set of experiments should be a better teaching device than lectures without experiments.

It is also well-established that, for most people, the ears can follow only a simple set of sounds in a "linear-code." One cannot listen to two people at once. Eyes, on the other hand, can receive many visual impressions simultaneously (the total code is "non-linear"), but these impressions are most effective if they are related to one another and also related to the sounds (words) heard at the same time. Thus, the best experiments concentrate the visual observations on a small number of changes, preferably dramatic changes, preferably colored changes, and preferably over the course of no more than a few minutes. Thus most of the experiments in this set may be completed in a few minutes, involve color changes, and attract attention to themselves.

If you know something of the nature of visual observations, your students will be able to observe your experiments, especially the color changes, more effectively. The human eye is not particularly good at identifying isolated colors but is excellent at color comparison. Providing a white background and looking down (rather than through) the tubes allows students to see color changes that would be invisible to most against a colored print dress, or the usual classroom desk, wall, black board, or sky. Furthermore, the changes become even more visible if a tube of the initial non-reacting material is displayed next to the reacting system. Thus the best condition for performing experiments involving changes in color is to hold two systems, a non-reacting one and a reacting one, against a white background. For color formation, a container of water is the most effective non-reacting system. For color disappearance, a container of all the initial materials except the one causing color is good. But if the disappearance is to be followed up to some previously established color (say colorless) then a container of this desired end-point color is the preferred comparison. In all cases the eye should be asked to compare some fixed system with a changing one if maximum sensitivity is to be obtained.

PERFORMING CLASS EXPERIMENTS. All the experiments in this set on rate of reaction are presented so they can be done by the students themselves with minimum equipment, supplies, and special facilities. However, some schools will not have even these minimum facilities and no school will have sufficient time for the students to do all the experiments. But all these experiments can also be readily done by the teacher in class, or even by a student in class. Use of experiments in class will considerably increase the effectiveness of the learning there.

The most common objections to class experiments are: 1) no materials are available, 2) no time is available, 3) the experiment may not work. Consider these one at a time.

A kit for all the experiments in this set can be assembled for less than $20(US) with sufficient materials in it to perform class size experiments at least 100 times. This is enough for 5 classes per year for 20 years at a cost of about $1(US) per year.

The phrase "I have no time" really means "I think other things are more important." But if it is true that visual learning plus aural learning is more effective than aural learning alone how can one say that visual experiments are less important than "chalk talk." The principal time requirement is actually that for setting up and cleaning up the experiments. These times are held to very small values by use of a portable kit which can be opened and available in one or two minutes at most. The small equipment can also be cleaned up in a minute or two by rinsing out immediately at the end of the experiment.

As to point (3). Experiments always work, molecules and equipment never make mistakes. The problem lies in the experimenter either 1) not performing the experiment he intended to perform (using incorrectly identified materials, for example), 2) being insufficiently familiar with the experiment to make observations and interpret them. The kit minimizes both difficulties by containing all the necessary materials and being based on simple observations.

NEWS FROM OTHER AREAS

Activities of Singapore Chemistry Group, 1969 - 1970:

1. Talk-cum-Demonstration on "The Equilibrium Kit" by Prof. J. Zyka and Dr. H. Herm (Director and Associate Expert from Unesco Chemistry Project) at Teachers' Training College.

2. "Development of a Chromatography kit for Schools" a joint project between some STAS (Singapore Science Teachers' Association) members and the Unesco Chemistry Project.

3. Workshop on Reaction Rates by Dr. J.A. Campbell, Chem Study Director.

4. Workshop on Selected Experiments from Chem Study Programme by Scholarship Returnee Mr. Swaran Singh.

5. A course in Modern Chemistry Teaching designed to assist Pre-University teachers to tackle the Alternative T Syllabus at HSC Level. This is a joint effort between Chemistry and Extra Mural Studies Depts of Singapore University and the Chemistry Group of STAS. It was held during April vacation 1970. The Course held at the University of Singapore dealt with the following topics via lecture/discussion/form/demonstration/practical:

    1. Glass Blowing Techniques
    2. Spectroscopy
    3. Chromatography, Electrophoresis, Ion exchange
    4. Radiochemistry
    5. Orbitals and Chemical Bonding
    6. Energetics and Equilibria
    7. Mechanisms of Reactions
    8. Industrial Chemistry
    9. Modern Methods of Teaching Chemistry.

    The lecturers for the Course were members of Chemistry Dept. University of Singapore. For the Forum on Industrial Chemistry some panel members were drawn from the Industries. For the discussion on Teaching Methods two members from the teaching profession were incorporated in the panel.

    All in all the course proved useful to teachers teaching the Alternative T Chemistry Syllabus at the HSC level.

6. A total of 5 Newsletters containing extracts from Chemistry education materials was circularised to interested members. Mimeographed copies of "Reaction Rates" a Unesco Chemistry Project Publication were reproduced for the benefit of chemistry teachers in the Pre-University classes.

Indonesia:

The Chemistry Group in Bandung, Indonesia organized with Unesco assistance their first in-service training course for chemistry teachers 26 January - 21 February 1970.

The Group has been working under Dr. S.A. Achmad's leadership since 1967. The group members are from Institute Teknologi Bandung (ITB), the Teachers Training College (IKIP) and the Science Teaching Centre and they all work as volunteers. They have for long time had in mind to organize in-service courses to teachers but couldn't realize it because of financial difficulties. At this stage Unesco provided TA-funds for 6 man-months expert assistance to realize the first in-service training course for chemistry teachers. The Unesco consultants (G.H. Aylward and E.C. Watton) drew up the plans for the course and they also assisted in the preparations and running of it.

The Unesco Chemistry Project in Bangkok sent two consultants, J.A. Campbell (2 weeks) and H. Herm (1 week).

The topics dealt with were solution chemistry (mainly acid-base and redox) energy in chemical reactions and chemistry of natural products.

NEWS NOTES

Prof. J. Zyka the previous director of the Chemistry Project has returned to his home university in Prague after serving at Unesco Headquarters for six months. We hope he will join the Division of Science Teaching soon again.

Dr. R.H. Maybury who was replaced temporarily by Zyka during his year of study leave will return to Unesco around August/September 1970. He will then among other duties be project officer to the Thai National Institute for Improvement of Teaching Science and Technology.

The first phase of the Thai National Institute (2 years) has been sanctioned by UNDP, and we expect the arrival of the experts as soon as Unesco Headquarters finished the recruitment.

Mr. Jay Ratnaike an old coworker and friend of the Project has been attached to Unesco Regional Office in Bangkok as Education Officer. His presence in Bangkok will certainly stimulate the improvement of science teaching in Thailand.

Dr. A.F. Kapauan from Ateneo de Manila University who worked on the preparation and running of the Chemistry Summer Institute has returned to the Philippines.

A sad news note for our readers is that this issue of the Newsletter may be the last but one. How Unesco will continue the regional activities after the Chemistry and Physics projects merge into the Thai National Institute and when Dr. J.A. Campbell's contract expires in July 1970 is for the moment not clear.

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 (Vols. I and II) (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.
15. Experiments on Nuclear Science, 1969.
16. Experiments on Compound Formation (Thai translation), 1969

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* Available at a cost of U.S. $ 6.00 per film loop.

** Cannot be supplied outside Thailand.