Chemical Kinetics
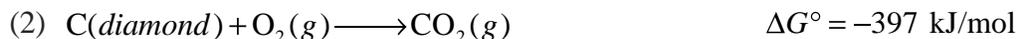
CONCEPT NOTES

Chemical Kinetics

Section - 1	RATE OF REACTION AND RATE LAW

MOTIVATION

Consider the following two reactions and their corresponding $\Delta G°$ values:

(1) $2HCl(aq) + Mg(OH)_2(s) \longrightarrow MgCl_2(aq) + 2H_2O(l)$ $\Delta G° = -97$ kJ/mol

and

(2) $C(diamond) + O_2(g) \longrightarrow CO_2(g)$ $\Delta G° = -397$ kJ/mol

In the first reaction, a strong acid reacts with a strong base to form a salt and water (neutralisation reaction.) Its $\Delta G°$ is -97 kJ/mol i.e., the products are more stable than the reactants. In the second reaction, Carbon in the state of diamond reacts with oxygen to produce carbon dioxide and the measured value of $\Delta G°$ is -397 kJ/mol. So, in the second reaction, according to thermodynamics, the products acquire a much more stable state as compared to the first reaction. If that is so, then, would it be correct to expect that the second reaction would occur much more rapidly as compared to the first reaction because in the second reaction, the products are becoming much more stabler than their corresponding reactants? Let us investigate.

The neutralisation reaction between any strong acid and strong base (an example of which is the first reaction) is found to take place almost instantly as the reactants are brought together to give the products. So, we can say that this reaction is "fast"

However, in our day to day life, there are many occasions of diamonds being put on display at museums or jewellery stores where they are exposed to atmosphere which contains oxygen. Since the $\Delta G°$ for the reaction is negative we would expect the diamond to react with oxygen to give carbon dioxide spontaneously! But we know that this is not the case at least from our day to day observation. So, is thermodynamics wrong in predicting the negative $\Delta G°$ for this reaction? The answer is No.

Thermodynamics is correct here but the limitation of thermodynamics lies in the fact that although it can predict if a reaction is favourable or not, it cannot predict the rate at which a reaction would occur if it is favourable. So, although the second reaction does take place, it takes place very slowly.

The branch of chemistry that deals with how fast a reaction takes place and so as to why is called *Chemical Kinetics.*
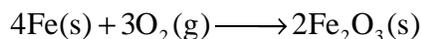
INTRODUCTION

We are all familiar with processes in which some quantity changes with time–an automobile travels at 40 km/hour, or a factory produces 32,000 tires/day. Each of these ratios is called a rate. The **rate of a reaction** describes how fast reactants are used up and products are formed. **Chemical Kinetics** is the study of *rates* of chemical reactions and the *mechanisms* (the series of steps) by which they occur.

Our experience tells us that different chemical reactions occur at very different rates. For instance, combustion reactions—such as the burning of methane, CH_4, in natural gas and the combustion of isooctane, C_8H_{18}, in gasoline—proceed very rapidly, sometimes even explosively.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

$$2C_8H_{18}(g) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g)$$
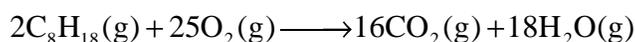
On the other hand, the rusting of iron occurs only very slowly:

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$$

In our study of thermodynamics we learned to assess whether a particular reaction was favourable. The question of whether substantial reaction would occur in a certain time period is addressed by kinetics. If a reaction is not thermodynamically favoured, it will not occur appreciably under the given conditions. However, even though a reaction is thermodynamically favoured, it can occur, but not necessarily at a measurable rate.

One of our major goals in this chapter, is to learn about the factors that control how rapidly chemical changes occur. These can be divided into four main categories (We will discuss these in detail later in this chapter):

1.   *The nature of the reactants and products.* All other factors being equal, some reactions are just naturally fast and others are naturally slow, depending on the chemical makeup of the molecules or ions involved.

2.   *The concentrations of the reacting species.* For two molecules to react with each other, they must meet, and the probability that this will happen in a homogeneous mixture increases as their concentrations increase. For heterogeneous reactions–those in which the reactants are in separate phases–the rate also depends on the area of contact between the phases. Since many small particles have a much larger area than one large particle of the same total mass, decreasing the particle size increases the reaction rate. For example, cropping a log of wood into small pieces increases the total surface area of the wood and hence, it is easier to start a fire with it (as much more surface area is available for combustion).

3.   *The effect of temperature.* Nearly all chemical reactions take place faster when their temperatures are increased.

4.   *The influence of outside agents called catalysts.* The rates of many reactions, including virtually all biochemical reactions, are affected by substances called catalysts that undergo no net chemical change during the course of the reaction.

Studying how these factors affect the rate of a reaction serves several purposes. For example, it allows us to adjust the conditions of a reaction system to obtain the products as quickly as possible. The importance of this in the commercial manufacture of chemicals is obvious. It also allows us to adjust conditions to make a reaction occur as slowly as possible. This is helpful, for instance, in controlling the growth of fungi and other microorganisms that spoil foods.

For chemists, one of the most significant benefits that comes from studying reaction rates is knowledge about the details of how chemical changes take place. We will see later in this chapter that a chemical reaction usually does not occur in one single step that involves the simultaneous collision of all the reactant molecules described in the balanced overall equation. Instead, the net change is the result of a sequence of simple reactions. This sequence is called the **mechanism** of the reaction, and studying reaction rates gives clues to what the mechanism is. In this way we gain insight into the fundamental reasons of why substances react the way they do.

Please don't worry if you have not understood very clearly so as to what is discussed above. It is just an introduction to all the topics we are going to study in this chapter, wherein all the above topics will be discussed in detail.

THE RATE OF A REACTION

Rates of reactions are usually expressed as moles per liter per unit time. If we know the chemical equation for a reaction, its rate can be determined by following the change in concentration of any product or reactant that can be detected quantitatively.

To describe the rate of a reaction, we must determine the concentration of a reactant or product at various times as the reaction proceeds.

If the progress of a reaction causes a change in the total number of moles of gas present, the change in pressure of the reaction mixture (held at constant temperature and constant volume) lets us measure how far the reaction has gone. For instance, the decomposition of dinitrogen pentoxide, $N_2O_5(g)$, has been studied by this method.

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$
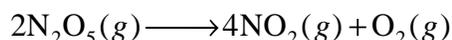
For every 2 moles of N_2O_5 gas that react, a total of 5 moles of gas is formed (4 moles of N_2 and 1 mole of O_2). The resulting increase in pressure can be related by the ideal gas equation to the total number of moles of gas present. This indicates the extent to which the reaction has occurred.

(Please note that, in reactions involving gases, rates of reactions may be related to rates of change of partial pressures. Pressures of gases and concentration of gases are directly proportional.)

Once we have measured the changes in concentrations of reactants or products with time, how do we describe the rate of a reaction? Consider a hypothetical reaction.

$$aA + bB \longrightarrow cC + dD$$

The amount of each substance present can be given by its concentration, usually expressed as molarity (mol/L) and designated by brackets. The rate at which the reaction proceeds can be described in terms of the rate at which one of the reactants disappeared, $-\Delta[A]/\Delta t$ or $-\Delta[B]/\Delta t$, or the rate at which one of the products appears, $\Delta[C]/\Delta t$ or $\Delta[D]/\Delta t$. The reaction rate must be positive because it describes the forward (left-to-right) reaction, which consumes A and B. The concentrations of reactants A and B decrease in the time interval Δt. Thus, $\Delta[A]/\Delta t$ and $\Delta[B]/\Delta t$ would be *negative* quantities. The purpose of a negative sign in the definition of a rate of reaction is to make the rate a positive quantity.

The changes in concentration are related to each other. For every a mol/L that [A] decreases, [B] must decrease by b mol/L, [C] must increase by c mol/L, and so on. We wish to describe the rate of reaction on a basis that is the same regardless of which reactant or product we choose to measure. Therefore, we divide each change by its coefficient in the balanced equation.

Lets take up the study of an analogy to understand clearly so as to what we have discussed above.

Suppose we make sandwiches by the following procedure:

$$2 \text{ bread slices} + 3 \text{ cucumber slices} + 1 \text{ pickle} \longrightarrow 1 \text{ sandwich}$$

The number of sandwiches increases, so Δ(sandwiches) is positive; the rate of the process is given by $\dfrac{\Delta(\text{sandwiches})}{\Delta(\text{time})}$. Alternatively, we could count the decreasing number of pickles at various times. Because Δ(pickles) is negative, we must multiply by (–1) to make the rate positive; rate $= -\Delta$(pickles)/Δ(time). If we choose to measure the rate by counting slices of bread, we must also take into account that bread slices are consumed *twice as fast* as sandwiches are produced, so rate $= -\frac{1}{2}(\Delta\text{bread})/\Delta(\text{time}))$. Four different ways of describing the rate all have the same numerical value.

$$\text{rate} = \left(\frac{\Delta(\text{sandwiches})}{\Delta t}\right) = -\frac{1}{2}\left(\frac{\Delta(\text{bread})}{\Delta t}\right) = -\left(\frac{\Delta(\text{pickles})}{\Delta t}\right) = -\frac{1}{3}\left(\frac{\Delta(\text{cucumber slices})}{\Delta t}\right)$$

This allows us to write the rate of reaction based on the rate of change of concentration of each species.

$$\text{rate or reaction} = \overbrace{\frac{1}{a}\left(\begin{array}{c}\text{rate of}\\ \text{decrease}\\ \text{in [A]}\end{array}\right) = \frac{1}{b}\left(\begin{array}{c}\text{rate of}\\ \text{decrease}\\ \text{in [B]}\end{array}\right)}^{\text{in terms of reactants}} = \overbrace{\frac{1}{c}\left(\begin{array}{c}\text{rate of}\\ \text{increase}\\ \text{in [C]}\end{array}\right) = \frac{1}{d}\left(\begin{array}{c}\text{rate of}\\ \text{increase}\\ \text{in [D]}\end{array}\right)}^{\text{in terms of products}}$$

$$\text{rate or reaction} = -\frac{1}{a}\left(\frac{\Delta[A]}{\Delta t}\right) = -\frac{1}{b}\left(\frac{\Delta[B]}{\Delta t}\right) = +\frac{1}{c}\left(\frac{\Delta[C]}{\Delta t}\right) = +\frac{1}{d}\left(\frac{\Delta[D]}{\Delta t}\right)$$

This representation gives several equalities, any one of which can be used to relate changes in observed concentrations to the rate of reaction.

Consider as a specific chemical example the gas phase reaction that occurs when we mix 1.000 mole of hydrogen and 2.000 moles of iodine chloride at 230°C in a closed 1.00 liter container.

$$H_2(g) + 2ICl(g) \longrightarrow I_2(g) + 2HCl(g)$$

The coefficients tell us that 1 mole of H_2 disappears for every 2 moles of ICl that disappear and for every 1 mole of I_2 and 2 moles of HCl that are formed. In other terms, the rate of disappearance of moles of H_2 is one-half the rate of disappearance of moles of ICl, and so on. So we write the rate of reaction as

$$\text{rate or reaction} = \left(\begin{array}{c}\text{rate of}\\ \text{decrease}\\ \text{in [H}_2\text{]}\end{array}\right) = \frac{1}{2}\left(\begin{array}{c}\text{rate of}\\ \text{decrease}\\ \text{in [IC}l\text{]}\end{array}\right) = \left(\begin{array}{c}\text{rate of}\\ \text{increase}\\ \text{in [I}_2\text{]}\end{array}\right) = \frac{1}{2}\left(\begin{array}{c}\text{rate of}\\ \text{increase}\\ \text{in [HCl]}\end{array}\right)$$

$$\text{rate or reaction} = -\left(\frac{\Delta[H_2]}{\Delta t}\right) = -\frac{1}{2}\left(\frac{\Delta[ICl]}{\Delta t}\right) = \left(\frac{\Delta[I_2]}{\Delta t}\right) = \frac{1}{2}\left(\frac{\Delta[HCl]}{\Delta t}\right)$$

The following figure shows graphically the rates of change of concentrations of all reactants and products. Please study it for a while.
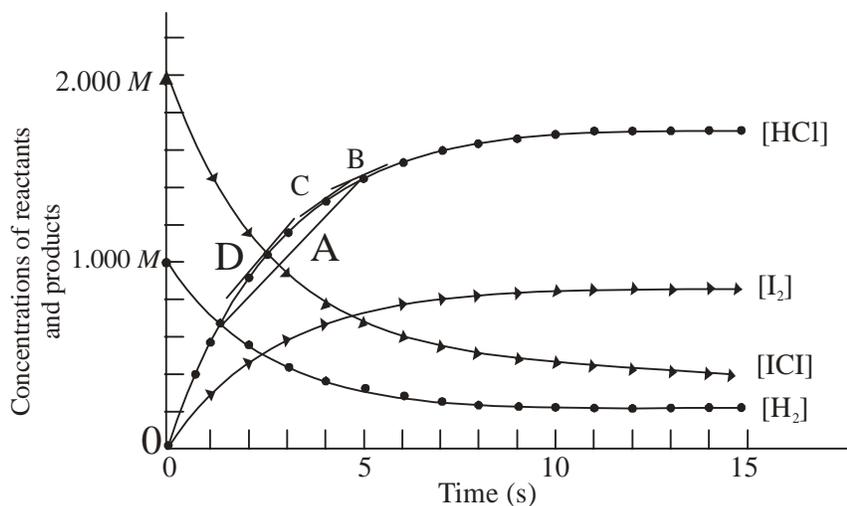
Figure - 1: *Plot of concentration of all reactants and products versus time in the reaction of* 2.000 *M ICl with* 1.000 *M H$_2$(at* 230°C*).*

Note that the expressions just given describe the **average** rate over a period of time Δt.

Let us take some examples to understand this clearly. In the figure above, if we want to know the rate of the reaction between the instants $t=1$ sec and $t=5$ sec, then, using [HCl], we will have to find the difference between the concentration of HCl at $t=1$ sec and $t=5$ sec. Dividing this by the time interval $(\Delta t = 4)$ would give us the required rate of reaction over the given time interval. But what about the rate of reaction at $t=1$ sec. and not over any time interval. It will be the slope of the tangent drawn to the [HCl] curve at $t=1$ sec. We can see from the figure that the value of this slope is not same as the slope of the secant A which gave us the rate of reaction over the entire period of $t=1$ sec to $t=5$ sec. Similarly, we see that the slopes of curve as we proceed further becomes lesser and lesser at points D, C and B. These slopes actually give the instantaneous rate of the reaction at particular instants whereas the slope of secant A gives the average rate of reaction over a period of time, $\Delta t = 4$ seconds (between $t=1$ sec. and $t=5$ sec).

The rigorous expressions for the rate at any instant involve the derivatives of concentrations with respect to time.

$$-\frac{1}{a}\left(\frac{d[A]}{dt}\right), \frac{1}{c}\left(\frac{d[C]}{dt}\right), \text{ and so on.}$$

The shorter the time period, the closer $\dfrac{\Delta(\text{concentration})}{\Delta t}$ is to the corresponding derivative.

We give an analogy to help you understand the above discussion on instantaneous and average rate of reactions:

Suppose a driver goes 40 kms in an hour; we describe his average speed (rate) as 40 km/h. This does not necessarily mean that he traveled at a steady speed. He might have stopped at a few traffic signals, made a fuel stop, driven sometimes faster, sometimes slower – his instantaneous rate (the rate at which has was traveling at any instant) was quite changeable. (Can you relate this analogy with the "rate of reactions" discussed above?)

Chemistry / Chemical Kinetics

To conclude our discussion on this topic, lets try to observe the rate of reaction of the example described above more closely with respect to one of the products, say, $[H_2]$. Consider the following figure:
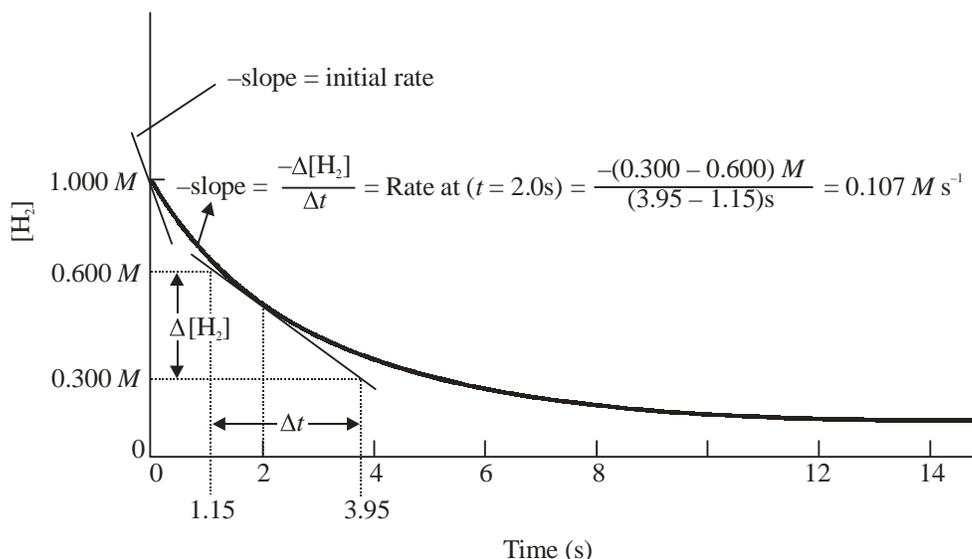
Figure - 2. *Plot of H_2 concentration versus time for the reaction of 2.000 M ICl with 1.000 M H_2. The instantaneous rate of reaction at any time, t, equals the negative of the slope of the tangent to this curve at time t. The initial rate of the reaction is equal to the negative of the initial slope (t = 0). The determination of the instantaneous rate at t = 2 seconds is illustrated.*

Figure 2 is a plot of the hydrogen concentration versus time. The initial rate, or the rate at the instant of mixing the reactants, is the negative of the slope at $t = 0$. The *instantaneous* rate of reaction at time t(2.0 seconds, for example) is the negative of the slope of the tangent to the curve at time t. We see that the rate decreases with time; lower concentrations of H_2 and ICl result in slower reaction. Had we plotted concentration of a product versus time, the rate would have been related to the *positive* slope of the tangent at time t.

Important Point

As we have seen in this discussion, the units of the rate of a reaction are $\dfrac{mol}{L.\ time}$. We often abbreviate this as mol/ L. time or M. time^{-1}.

Please attempt the following problems before seeing their solution:

• Shown here is a plot of the concentration of a reactant D versus time.
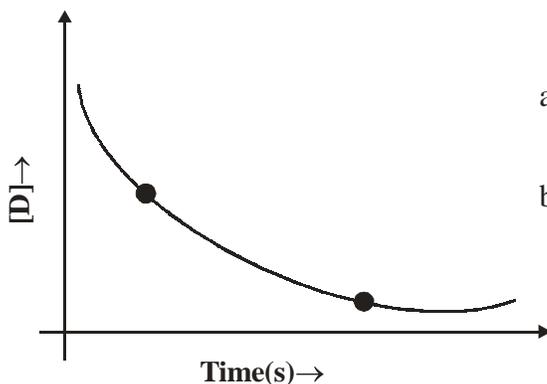
a. How do the instantaneous rates at points A and B compare?

b. Is the rate for this reaction constant at all points in time?

Solution: a. Since the slope is steeper at point A, point A must be a faster instantaneous rate.

b. Since the curve is not a flat line, the rate of the reaction must be constantly changing over time. Therefore, the rate for the reaction cannot be constant at all points in time.

- Consider the reaction : $3A \rightarrow 2B + C$.

a. One rate expression for the reaction is : Rate of formation of $C = +\dfrac{\Delta[C]}{\Delta t}$. Write two other rate expressions for this reaction in this form.

b. Using your two rate expressions, if you calculated the average rate of the reaction over the same time interval, would the rates be equal?

c. If your answer to part b. was no, write two rate expressions that would give an equal rate when calculated over the same time interval.

Solution: a. You can write the rate expression in terms of the depletion of A:

$$\text{Rate of depletion of } A = -\frac{\Delta[A]}{\Delta t.}.$$

Or, you can write the rate expression in terms of the formation of B:

$$\text{Rate of formation of } B = +\frac{\Delta[B]}{\Delta t}.$$

b. No. Consider the stoichiometry of the reaction which indicates that the rate of depletion of A would be faster than the rate of formation of B: for every three moles of A that are consumed, two moles of B would be formed.

c. Taking into account the stoichiometry of the reaction, the two rate expressions that would give an equal rate when calculated over the same time interval are

$$\text{Rate} = -\frac{\Delta[A]}{3\Delta t} = \frac{\Delta[B]}{2\Delta t}.$$

RATE LAWS

In this section we begin to examine the factors that control the rate of reaction. Not all reactions take place at the same rate. Ionic reactions are virtually instantaneous: the speed is determined by how rapidly we can mix the chemicals. Other reactions, such as the digestion of food, take place more slowly. These different rates exist primarily because of chemical differences among the reacting substances.

For any given reaction, one of the most important controlling influences is the concentrations of the reactants. Generally, if we follow a chemical reaction over a period of time, we find that its rate gradually decreases as the reactants are consumed. From this we conclude that the rate is related, in some way, to the concentrations of the reacting species. In fact, the rate is nearly always proportional to the concentrations of the reactants, each raised to some power. This means that for the general reaction

$$A \longrightarrow B$$
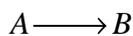
the rate can be written as

$$\text{rate} \propto [A]^x \qquad\qquad ...(1)$$

where the exponent, x, is called the **order of the reaction.** When $x = 1$, we have a first-order reaction. An example is the decomposition of cyclopropane:

$$\text{rate} = \propto [\text{cyclopropane}]^1$$

Second-order ($x = 2$), third-order ($x = 3$), and higher-order reactions are also possible, as are reactions in which x is a fraction or a negative integer. There are also examples of zero-order reactions, for which $x = 0$. For a zero-order reaction the rate is constant and does not depend on the concentrations of the reactants. An example is the decomposition of ammonia on a platinum or tungsten metal surface. The rate at which the ammonia decomposes is always the same, regardless of its concentration.

In some cases an exponent can even be negative, which means that increasing the concentration of that reactant *decreases* the reaction rate.

A very important fact is that there is not necessarily any direct obvious relationship between the coefficients in the balanced chemical equation for a reaction and the order of the reaction. *The value of x can only be determined from experiment.*

If we consider a slightly more complex reaction, for example,

$$A + B \longrightarrow products$$
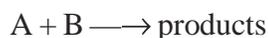
the rate usually depends on the concentrations of both A and B. Normally, increasing the concentration of either A or B will increase the reaction rate, and the rate is proportional to the product of the concentrations of A and B, each raised to some power.

$$rate \propto [A]^x[B]^y \qquad\qquad ...(2)$$

In this case, we say that the order of the reaction with respect to A is x and the order with respect to B is y. We can also describe the **overall order** of the reaction, which is the sum of the exponents on the concentration terms. In this example, the overall order is the sum $x + y$. Once again, x and y can have whole-number, fractional, negative or even zero values. When one of the exponents is zero, this simply means that the rate of the reaction does not depend on the concentration of that substance. For example, if the exponent y in Equation (2) were zero, the equation would become

$$rate \propto [A]^x[B]^0$$

Any quantity raised to the zero power is equal to 1, so the equation reduces to

$$rate \propto [A]^x(1)$$

or $\qquad rate \propto [A]^x$

A real chemical example is the reaction

$$NO_2(g) + CO(g) \longrightarrow CO_2(g) + NO(g)$$

at temperatures below 225°C, the relationship between concentration and rate is

$$rate \propto [NO_2]^2$$

The rate is independent of the CO concentration but depends on the *square* of the NO_2 concentration. We say that the reaction is second-order with respect to NO_2 and zero-order with respect to CO. Notice that there is no relationship between the coefficients and the exponent. As mentioned previously, the order of a reaction can only be determined experimentally.

The proportionality represented by Equation (2) can be converted to an equality by introducing a proportionality constant, k, which we call the **rate constant.** The resulting equation, termed the **rate law** for the reaction, is

$$\text{rate} = \propto [A]^x[B]^y$$

For example, the rate law for the reaction between ICl and H_2,

$$2ICl(g) + H_2(g) \longrightarrow I_2(g) + 2HCl(g)$$

at 230°C has been found experimentally to be

$$\text{rate} = 0.163 \text{ L mol}^{-1}\text{s}^{-1}[ICl][H_2]$$

This reaction therefore is first-order with respect to both ICl and H_2 (hence, *second-order*, overall) and has as its rate constant $k = 0.163$ L mol^{-1}s^{-1}. It should be noted that this value of k applies only at 230°C for this particular reaction. Other reactions have other values of k, and as we will see later, k varies with the temperature.

Note that, the rate law lets us calculate the rate for any particular set of concentrations.

Before we move further, it would be prudent to study the rate constant in a little more detail.

The rate constant, k is often called the *specific rate constant* also. It is constant for a reaction at a particular temperature. It is important to remember the following points about the specific rate constant, k.

1.   Its value is for a *specific reaction*, represented by a balanced equation.

2.   Its units depend on the *overall order* of the reaction. (can you see how?)

3.   Its value does not change with concentrations of either reactants or products.

4.   Its value does not change with time (to be discussed)

5.   Its value refers to the reaction *at a particular temperature* and changes if we change the temperature (to be discussed)

6.   Its value depends on whether a *catalyst* is present (to be discussed)

7.   Its value must be determined experimentally for the reaction at appropriate conditions.

Determining the rate law

How can a rate law such as the one above be determined? One way is to perform a series of experiments in which the initial concentration of each reactant is systematically varied. Once again we can use as our example the simple reaction

$$A \longrightarrow B$$

The rate law for this reaction would take the form

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

If the reaction were first-order were first-order, the value of x would be 1, and the rate expression would then be

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

This means that the rate of the reaction varies directly with the concentration of A raised to the first power. As a result, if we were to double the concentration of A from one experiment to another, we would also find that the rate increases by a factor of 2. We conclude, therefore, that *when the reaction rate is doubled by doubling the concentration of a reactant, the order with respect to that reactant is* 1.

Suppose, now, that the rate law were, instead,

$$rate = k[A]^2$$

In this instance, a twofold increase in the concentration would cause a fourfold increase in rate. To see this, lets imagine that the initial rate was measured with the concentration of A equal to, say, a mol/L. This rate would be given by

$$rate = k(a)^2$$

Now, if the reaction were repeated with $[A] = 2a$, the rate would be

$$rate = k(2a)^2$$

or $$rate = 4ka^2$$

which is four times the previous rate. Thus, *if the rate is increased by a factor of 4 when the concentration of a reactant is doubled, the reaction is second-order with respect to that reactant. Similarly, we predict that the rate of a third-order reaction would undergo an eightfold increase when the concentration is doubled* ($2^3 = 8$). From analyses like these, we can formulate a general rule.

> When the concentration of a reactant changes by some factor (i.e., the concentration is multiplied or divided by some number), the rate changes by this same factor raised to a power that is equal to the exponent in the rate law for that reactant.

The following examples illustrate how we can use these ideas to obtain the rate law for a reaction by varying the concentrations of reactants.

Example – 1

Below are some data collected in a series of experiments on the reaction of nitric oxide with bromine at 273°C:

$$2NO(g) + Br_2(g) \longrightarrow 2NOBr(g)$$
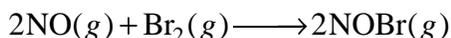
Experiment	Initial Concentrations (mol/L)		Initial Rate of Formation of NOBr $(mol\,L^{-1}s^{-1})$
	NO	Br_2	
1	0.10	0.10	12
2	0.10	0.20	24
3	0.10	0.30	36
4	0.20	0.10	48
5	0.30	0.10	108

Determine the rate law for the reaction and compute the value of the rate constant.

Critical thinking

The rate law for the reaction will have the form

$$\text{rate} = k[NO]^x[Br_2]^y$$

To determine each exponent, we will study how the rate changes when the concentration of one reactant varies while that of the other reactant stays the same. For instance, when the NO concentration is held constant, we can see how changes in the Br_2 concentration affect the rate and thereby determine what y must be. The value of x is determined in a similar way. With this strategy in mind, let's study the data.

Solution: In experiments 1 to 3, the concentration of NO is constant and the concentration of Br_2 is varied.

When the concentration of Br_2 is doubled (experiments 1 and 2), the rate is increased by a factor of 2; when it is tripled (experiments 1 and 3), the rate is increased by a factor of 3. The only way this could happen is if the concentration of Br_2 appears to the first power in the rate law. Therefore, $y = 1$.

Comparing experiments 1 and 4, we see that when the Br_2 concentration is held constant, the rate increases by a factor of 4 when the NO concentration is multiplied by 2. Similarly, raising the concentration of NO by a factor of 3 causes a ninefold increase in rate (experiments 1 and 5). This means that the exponent on the NO concentration in the rate law must be 2. Therefore, $x = 2$ and the rate law is

$$\text{rate} = k[NO]^2[Br_2]$$

The rate constant can be evaluated using the data from any of these experiments. Working with experiment 1, we have

$$12 \text{ mol L}^{-1}\text{s}^{-1} = k(0.10 \text{ mol L}^{-1})^2(0.10 \text{ mol L}^{-1})$$

$$12 \text{ mol L}^{-1}\text{s}^{-1} = k(0.0010 \text{ mol}^3 \text{ L}^{-3})$$

Solving for k, we get

$$k = \frac{12 \text{ mol L}^{-1}\text{s}^{-1}}{1.0\times10^{-3} \text{ mol}^3\text{L}^{-3}} = 1.2\times10^4 \text{ L}^2 \text{ mol}^{-2}\text{s}^{-1}$$

You might wish to verify for yourself that the same rate constant is obtained from the other data. (That's why it's called the rate *constant*.)

Example – 2

The following data were collected for the reaction of t-butyl bromide, $(CH_3)_3CBr$, with hydroxide ion at 55°C.

$$(CH_3)_3CBr + OH^- \longrightarrow (CH_3)_3COH + Br^-$$

Experiment	Initial Concentrations (M)		Initial Rate of Formation of $(CH_3)_3COH$ $(mol\,L^{-1}s^{-1})$
	$(CH_3)_3\,CBr$	OH^-	
1	0.10	0.10	0.0010
2	0.20	0.10	0.0020
3	0.30	0.10	0.0030
4	0.10	0.20	0.0010
5	0.10	0.30	0.0010

What is the rate law and rate constant for this reaction?

Critical thinking

Apply the same approach as the previous problem

Solution: Based on the equation, we expect a rate law of the form

$$rate = k[(CH_3)_3CBr]^x[OH^-]^y$$

To obtain x and y, we follow the same approach as in the previous example.

Let's examine experiments 1, 2 and 3 first. In each of these the OH^- concentration is the same. Doubling the $(CH_3)_3CBr$ concentration doubles the rate; tripling it triples the rate. The order with respect to $(CH_3)_3CBr$ must therefore be 1.

In Experiments 1, 4, and 5, the $(CH_3)_3CBr$ concentration is held constant while the OH^- concentration is varied. Notice, however, that no matter what the OH^- concentration is, the rate is the same. In effect, we find that when the $[OH^-]$ is increased by a factor of 2 in experiments 1 and 4, the rate changes by a factor of $2^0 = 1$ (i.e., the rate in experiment 4 equals the rate in experiment 1 multiplied by a factor of 1). This means that the reaction is zero-order with respect to OH^-. Therefore,

$$rate = k[(CH_3)_3CBr]^1[OH^-]^0$$

Since anything raised to the zero power is 1,

$$\text{rate} = k[(CH_3)_3CBr]^1 \cdot 1$$

$$= k[(CH_3)_3CBr]$$

The final rate law contains only the concentration of $(CH_3)_3CBr$, because this is the only concentration that affects the rate. To solve for the rate constant we can use the results of any of the experiments. Using experiment 1 and substituting the rate and concentration into the rate law give

$$0.0010 \text{ mol L}^{-1}\text{s}^{-1} = k(0.10 \text{ mol L}^{-1})$$

$$k = \frac{0.0010 \text{ mol L}^{-1}\text{s}^{-1}}{0.10 \text{ mol L}^{-1}}$$

$$= 0.010 \text{ s}^{-1}.$$

In Example 1, the exponents in the rate law just happen to be the same as the coefficients in the balanced equation. This is not true in Example 2. Please keep in mind that the *only* way we can find the exponents in the rate law for a chemical reaction is by experimentally measuring the way that the concentrations of the reactants affect the rate. It is also important to remember that since temperature is another factor that influences the rate, a given value of k applies only at *one* temperature (the temperature at which it was measured).

The method used in the above two examples is called as method of initial rates. The approach taken in the above method can also be varied slightly. This variation is illustrated here:

An Alternative Approach

We can also use a simple algebraic approach to find the exponents in a rate-law expression. Consider the set of rate data given here for the hypothetical reaction

$$A + 2B \longrightarrow AB_2$$

Experiment	Initial [A]	Initial [B]	Initial Rate of Formation of AB. $(M \cdot s^{-1})$
1	$1.0 \times 10^{-2} M$	$1.0 \times 10^{-2} M$	1.5×10^{-4}
2	$1.0 \times 10^{-2} M$	$2.0 \times 10^{-2} M$	1.5×10^{-4}
3	$2.0 \times 10^{-2} M$	$3.0 \times 10^{-2} M$	6.0×10^{-4}

Because we are describing the same reaction in each experiment, all the experiment are governed by the same rate-law expression,

$$\text{Rate} = k[A]^x[B]^y$$

The initial concentration of A is the same in experiments 1 and 2, so any change in the initial rates for these experiments would be due to different initial concentrations of B. To evaluate y, we solve the ratio of the rate-law expressions of these two experiments for y. We divide the first rate-law expression by the corresponding terms in the second rate-law expression.

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{k[A]_1^x[B]_1^y}{k[A]_2^x[B]_2^y}$$

The value of k always cancels from such a ratio because it is constant at a particular temperature. The initial concentrations of A are equal, so they too cancel. Thus, the expression simplifies to

$$\frac{\text{rate}_1}{\text{rate}_2} = \left(\frac{[B]_1}{[B]_2}\right)^y$$

The only unknown in this equation is y. We substitute data from experiments 1 and 2 in the equation, which gives us

$$\frac{1.5 \times 10^{-4} M \cdot s^{-1}}{1.5 \times 10^{-4} M \cdot s^{-1}} = \left(\frac{1.0 \times 10^{-2} M}{2.0 \times 10^{-2} M}\right)^y$$

$$1.0 = (0.5)^y \qquad \text{so} \qquad y = 0$$

Because the units of rate_1 and rate_2 are identical, they cancel. The units of $[B]_1$ and $[B]_2$ are identical, and they too cancel. Thus far, we know that the rate-law expression

$$\text{rate} = k[A]^x[B]^0 \qquad \text{or} \qquad \text{rate} = k[A]^x$$

Next we evaluate x. In experiments 1 and 3, the initial concentration of A is double and the rate increases by a factor of four. We neglect the initial concentration of B because we have just shown that it does *not* affect the rate of the reaction.

$$\frac{\text{rate}_3}{\text{rate}_1} = \frac{k[A]_3^x}{k[A]_1^x} = \left(\frac{[A]_3}{[A]_1}\right)^x$$

$$\frac{6.0 \times 10^{-4} M \cdot s^{-1}}{1.5 \times 10^{-4} M \cdot s^{-1}} = \left(\frac{2.0 \times 10^{-2} M}{1.0 \times 10^{-2} M}\right)^x$$

$$4.0 = (2.0)^x \qquad \text{so} \qquad x = 2$$

The power to which [A] is raised in the rate-law expression is 2, so the rate-law expression for this reaction is

$$\text{rate} = k[A]^2[B]^0 \qquad \text{or} \qquad \text{rate} = k[A]^2$$

We illustrate this approach taking one more example:

Example – 3

Use the following initial rate data to determine the form of the rate-law expression for the reaction

$$3A + 2B \longrightarrow 2C + D.$$

Experiment	Initial [A]	Initial [B]	Initial Rate of Formation of D
1	$1.0\times10^{-2}\,M$	$1.0\times10^{-2}\,M$	$6.00\times10^{-3}\,M\cdot\text{min}^{-1}$
2	$2.0\times10^{-2}\,M$	$3.0\times10^{-2}\,M$	$1.44\times10^{-1}\,M\cdot\text{min}^{-1}$
3	$1.0\times10^{-2}\,M$	$2.0\times10^{-2}\,M$	$1.20\times10^{-2}\,M\cdot\text{min}^{-1}$

Critical thinking

The rate law is of the form; rate = $k[A]^x[B]^y$. *Let's use the alternative approach presented just now to evaluate x and y.*

Solution: The initial concentration of A is the same in experiments 1 and 3. We divide the third rate-law expression by the corresponding terms in the first one.

$$\frac{\text{rate}_3}{\text{rate}_1} = \frac{k[A]_3^x[B]_3^y}{k[A]_1^x[B]_1^y}$$

The initial concentrations of A are equal,. so they cancel, as does k. Simplifying and then substituting known values of rates and $[B]$,

$$\frac{\text{rate}_3}{\text{rate}_1} = \frac{[B]_3^y}{[B]_1^y} \quad \text{or} \quad \frac{1.20\times10^{-2}\,M\cdot\text{min}^{-1}}{6.00\times10^{-3}\,M\cdot\text{min}^{-1}} = \left(\frac{2.0\times10^{-2}\,M}{1.0\times10^{-2}\,M}\right)^y$$

$$2.0 = (2.0)^y \quad \text{so} \quad y = 1 \quad \text{(The reaction is first order in [B].)}$$

No two of the experimental runs have the same concentrations of B, so we must proceed somewhat differently. Let us compare experiments 1 and 2. The observed change in rate must be due to the *combination* of the changes in [A] and [B]. We can divide the second rate-law expression by the corresponding terms in the first one, cancel the equal k values, and collect terms.

$$\frac{\text{rate}\,2}{\text{rate}\,1} = \frac{k[A]_2^x[B]_2^y}{k[A]_1^x[B]_1^y} = \left(\frac{[A]_2}{[A]_1}\right)^x\left(\frac{[B]_2}{[B]_1}\right)^y$$

Now let's insert the known values for rates and concentrations and the known [B] exponent of 1.

$$\frac{1.44\times10^{-1}\,M\cdot\text{min}^{-1}}{6.00\times10^{-3}\,M\cdot\text{min}^{-1}} = \left(\frac{2.00\times10^{-2}\,M}{1.00\times10^{-2}\,M}\right)^x\left(\frac{3.00\times10^{-2}\,M}{1.00\times10^{-2}\,M}\right)^1$$

Now, let's insert the known values for rates and concentrations and the known [B] exponent of 1.

$$24.0 = (2.00)^x (3.00)$$

$$8.00 = (2.00)^x \text{ or } \qquad x = 3 \qquad \text{(The reaction is third order in [A].)}$$

The rate-law expression has the form rate = $\boxed{\text{rate } k[A]^3[B].}$

Important Points.

1. Reactions are categorised according to their orders of reaction because the mathematics for dealing with a rate law is the same for a given order.

2. The units of k depend on the overall order of the reaction, consistent with converting the product of concentrations on the right to concentration/time on the left. For any reaction that is second order overall, the units of k are $M^{-1} \cdot time^{-1}$ or $L/(mol \cdot time)$. Can you deduce the units of k for a zero-order and first order reactions also? (please do it now.)

3. Remember that the specific rate constant k does *not* change with concentration. Only a temperature change or the introduction of a catalyst can change the value of k.

Before we move further ahead please attempt the following problems before seeing their solutions:

*   Consider the reaction $Q + R \longrightarrow S + T$ and the rate law for the reaction: Rate = $K[Q]^0[R]^2$. You run the reaction three times, each time starting with $[R] = 2.0$ M. For each run you change the starting concentration of $[Q]$: run 1, $[Q] = 0.0$ M; run 2, $[Q] = 1.0$ M; run 3, $[Q] = 2.0$ M. Rank the rates of the three reactions using each of these concentrations.

    The way the rate law is written in this problem is not typical for expressions containing reactants that are zero order in the rate law. Write the rate law in the more typical fashion.

Solution: (a) Keeping in mind that all reactant species must be present in some concentration for a reaction to occur, the reaction with $[Q] = 0$ is the slowest since no reaction occurs. The other two reactions are equal in rate because the reaction is zero order with respect to $[Q]$: as long as there is some amount of Q present, the reaction rate depends on the $[R]$ which is constant in this case.

(b) Since $[Q]^0 = 1$, you can rewrite the rate law as follows: Rate = $k[R]^2$.

*   Given the reaction $2A + B \rightarrow C + 3D$, can you write the rate law for this reaction? If so, write the rate law; if not, why?

Solution: You cannot write the rate law for this reaction from the information given. The rate law can only be determined by experiment, not by the stoichiometry of the reaction.

- You perform some experiments for the reaction $A \rightarrow B + C$ and determine the rate law has the form: Rate $= k[A]^x$. Calculate the value of the exponent x for each of the following cases.

  (a) [A] is tripled and you observe no rate change.

  (b) [A] is doubled and the rate doubles.

  (c) [A] is tripled and the rate goes up by a factor of 27.

Solution: (a) If the concentration is tripled but there is no effect on the rate, the order of the reaction must be zero. Thus, $x = 0$.

(b) If the concentration is doubled and the rate doubles, it is a first order reaction. Thus, $x = 1$.

(c) If the concentration is tripled and the rate goes up by a factor of 27, it is a third order reaction. Thus, $x = 3$.

- Given the hypothetical plot shown here for the concentration of compound Y versus time, answer the following questions.
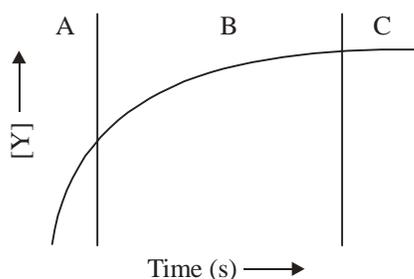

(a) In which region of the curve does the rate have a constant value (A, B, or C)?

(b) In which region of the curve is the rate the fastest (A, B, or C)?

Solution: (a) The rate has a constant value in region C, since the slope of the curve is constant (flat) in this region.

(b) The rate is the fastest in region A, since the slope of the curve is steepest in this region.

- You carry out the following reaction by introducing N_2O_4 into an evacuated flask and observing the concentration change of the product over time.

$$N_2O_4(g) \rightarrow 2NO_2(g)$$
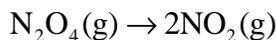
Which one of the curves shown here reflects the data collected for this reaction?

Curve A

Curve B
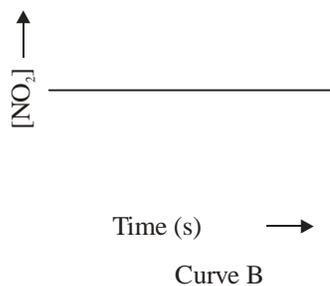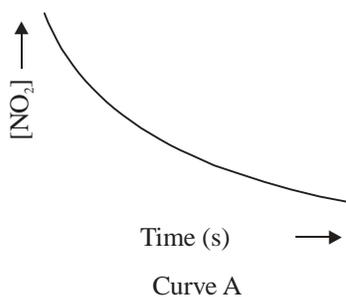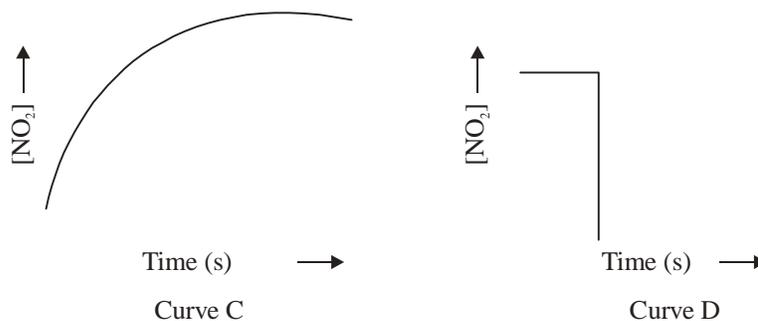
Curve C

Curve D

Solution: Since NO_2 is a product in the reaction, its concentration must increase with time. The only graph that has $[NO_2]$ increasing with time is curve C.

•   You are running the reaction $2A + B \rightarrow C + 3D$. Your lab partner has conducted the first two experiments to determine the rate law for the reaction. He has recorded the initial rates for these experiments in another data table. Come up with some reactant concentrations for Experiment 3 that will allow you to determine the rate law by measuring the initial rate.

Experiment Number	Concentration of A (*M*)	Concentration of B (*M*)
1	1.0	1.0
2	2.0	1.0
3		

Solution: A number of answers will work as long as you match one of the existing concentrations of A or B. For example: $[A] = 2.0\ M$ with $[B] = 2.0\ M$, or $[A] = 1.0\ M$ with $[B] = 2.0\ M$.

Example – 4

A second order reaction takes places at 0°C. All its reactants and products are in gaseous state. Its rate constant is found to be $k = 7 \times 10^{-6}\ s^{-1}\ atm^{-1}$. Express this rate constant in terms of molarity.

Critical thinking

We know that the partial pressures are directly proportional to the concentration of the respective gases. This can be observed from the ideal gas law:

$$PV = nRT$$

$$\Rightarrow \quad P = \left(\frac{n}{V}\right)RT \quad \text{...(i)}$$

pressure   concentration

We see that pressure is indeed directly proportional to concentration of the gas.

Now, in the conversion that we have to make, we see that $s^{-1}\ atm^{-1}$ has to be converted to $L\ mol^{-1}\ s^{-1}$ (which is the unit for the rate constant of second order reaction.). In both the units s^{-1} is common. So, we have only got to convert atm^{-1} to $L\ mol^{-1}$ (or) atm to mol/L. This can be achieved by using (i) above. Can you see how?

Solution: To make the conversion of atm to mol/L we would like to know so as to how many atm make up 1 mol/L or how may mol/L make up 1 atm (they are both equivalent.). Lets solve the problem by using both the conversions.

(a) 1 atm to ? moles/L

We will use equation (i) in critical thinking box to get to our answer. Since, P is in atm and n and V are in moles and litres we will take the value of R in same units i.e.

$$R = 0.082 \text{ lt-atm/mol/K}$$
$$T = 273 \text{ K } (given)$$
$$P = 1 \text{ atm } (assumed)$$

$$\frac{n}{V} = ? \text{ (to be calculated).}$$

Substituting the values in (1) we get

$$1 \text{ atm} = \left(\frac{n}{V}\right). (0.082 \text{ lt-atm/mol/K}) (273 \text{ K})$$

$$\Rightarrow \quad \frac{n}{V} \approx 0.045 \text{ mol/L}$$

So,

$$k \text{ (in mol/L/s)} = \frac{7 \times 10^{-6}}{s \text{ atm}} \times \frac{1 \text{ atm}}{0.045 \text{ mol/L}} \qquad ....(ii)$$

$$= \frac{7 \times 10^{-6}}{0.045} \cdot \frac{1}{s} \cdot \frac{1}{mol/L}$$

$$= 1.55 \times 10^{-4} . \text{ L mol}^{-1} \text{ s}^{-1}$$

(b) 1 mol/L to ? atm

Here,

$$R = 0.082 \text{ l-atm/mol/K}$$
$$T = 273 \text{ K}$$
$$P = ?$$

$$\frac{n}{V} = 1 \text{ mol/L}$$

Substituting the values in (i) again we get

$$P = (1 \text{ mol/L}) (0.082 \text{ l-atm/mol/K}) (273 \text{ K})$$

$$= 22.4 \text{ atm.}$$

So, 1 mol/L corresponds to 22.4 atm.

So, k (in mol/L/s) $\quad = \dfrac{7\times10^{-6}}{\text{s atm}}\times\dfrac{22.4\ \text{atm}}{1\ \text{mol/L}}$ ... (iii)

$$= \dfrac{(7\times22.4\times10^{-6})}{\text{s. atm}}\cdot\dfrac{\text{atm}}{\text{mol/L}}$$

$$= 156.8\times10^{-6}\ \text{L/mol/s}$$

$$= 1.56\times10^{-4}\ \text{L/mol/s}.$$

So, we see that we get the same answer from both the ways. Observe that the unit factors used in (ii) and (iii) are actually the same.

TRY YOURSELF - I

Q. 1 The rate constant of a reaction depends on
(a) temperature
(b) initial concentration of the reactants
(c) time of reaction
(d) extent of reaction

Q. 2 The rate constant of a first-order reaction depends on the
(a) concentration of the reactant
(b) concentration of the product
(c) time
(d) temperature

Q. 3 The rate law for the reaction $RCl + NaOH(aq) \rightarrow ROH + NaCl$ is given by, Rate $= k_1$ [RCl]. The rate of the reaction will be
(a) doubled on doubling the concentration of sodium hydroxide.
(b) halved on reducing the concentration of alkyl halide to one half.
(c) increased on increasing the temperature of the reaction.
(d) unaffected by increasing the temperature of the reaction.

Q. 4 The rate constant for the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$ is 3.0×10^{-5} s^{-1}. If the rate is 2.40×10^{-5} mol L^{-1} s^{-1}, then the concentration of N_2O_5 (in mol L^{-1}) is
(a) 1.4
(b) 1.2
(c) 0.04
(d) 0.8

Q. 5 Consider the chemical reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$. The rate of this reaction can be expressed in terms of time derivative of concentration of $N_2(g)$, $H_2(g)$ or $NH_3(g)$. Identify the correct relationship amongst the rate expressions.
(a) Rate $= - d[N_2]/dt = - 1/3d[H_2]/dt = 1/2d[NH_3]/dt$
(b) Rate $= - d[N_2]/dt = - 3d[H_2]/dt = 2d[NH_3]/dt$
(c) Rate $= d[N_2]/dt = 1/3d[H_2]/dt = 1/2d[NH_3]/dt$
(d) Rate $= - d[N_2]/dt = - d[H_2]/dt = d[NH_3]/dt$

Q. 6 Which one of the following statement for order of reaction is not correct?
(a) Order can be determined experimentally
(b) Order of reaction is equal to sum of the powers of concentration terms in differential rate law
(c) It is not affected with the stoichiometric coefficient of the reactants
(d) Order cannot be fractional

Q. 7 How many times must the concentration of substance B_2 in the system $2A_2(g) + B_2(g) \rightarrow 2A_2B(g)$ be increased for the rate of the forward reaction to remain unchanged when the concentration of substance A is lowered to one-fourth of its initial value? (The rate law for the reaction involves all reactants and their respective orders are same as stoichiometric coefficients in this case.)

Q. 8 In a certain time after the beginning of the reaction $3A + B \rightarrow 2C + D$, the concentrations of the substances were [A] = 0.03 mol/1, [B] = 0.01 mol/1, and [C] = 0.008 mol/1. What were the initial concentrations of reactants A and B?

Q. 9 Draw two axes of a graph. The vertical axis should be labelled 'rate of reaction'. The horizontal axis should be labelled 'concentration of reactant'. (The units and scales are unimportant.) On the graph, sketch lines that show how the rate varies with concentration for (i) a zeroth-order reaction, (ii) a first-order reaction, (iii) a second-order reaction.

Q. 10 In question no. 9, the graph of a first order reaction is a straight line. How will you determine the slope of this straight line?

Section - 2	INTEGRATED RATE EQUATION

Concentration versus time : The integrated rate equation

Often we wish to know the concentration of a reactant that would remain after some specification time, or how long it would take for some amount of the reactants to be used up.

> The equation that relates *concentration* and *time* is the **integrated rate equation**. We can also use it to calculate the half-life, $t_{1/2}$, of a reactant – the time it takes for half of that reactant to be converted into product. The integrated rate equation and the half-life are different for reactions of different order.

We shall look at relationships for some simple cases. (The derivation of the following results require calculus. If you have finished your calculus, then you may refer to the derivations given at the end of this section.)

First-Order Reactions

For reactions involving $a\,A \rightarrow$ products that are *first order in* A and *first order overall*, the integrated rate equation is

$$\ln\left(\frac{[A]_0}{[A]}\right) = akt \text{ or } \log\left(\frac{[A]_0}{[A]}\right) = \frac{akt}{2.303} \qquad \text{(first order)}$$

(a represents the coefficient of reactant A in the balanced overall equation)

$[A]_0$ is the initial concentration of reactant A, and $[A]$ is its concentration at some time, t, after the reaction begins. Solving this relationship for t gives

$$t = \frac{1}{ak}\ln\left(\frac{[A]_0}{[A]}\right) \qquad \text{or} \qquad t = \frac{2.303}{ak}\log\left(\frac{[A]_0}{[A]}\right)$$

We often wish to know so as to after how much time will half the reactants be converted into products. This time for a particular reaction is called its half life. Hence, we derive the half life (written as $t_{1/2}$) for the first order case:

By definition $[A] = \frac{1}{2}[A]_0$ at $t = t_{1/2}$ Thus (using the ln form),

$$t_{1/2} = \frac{1}{ak}\ln\frac{[A]_0}{\frac{1}{2}[A]_0} = \frac{1}{ak}\ln(2)$$

> Please note that the equations given in this section can also be written omitting "*a*" every where. In that case the k for the reaction would include the "*a*" term also implicitly. i.e. (new k) = *a*k

$$t_{1/2}\frac{\ln 2}{ak} = \frac{0.693}{ak} \quad \text{(first order)}$$

(This same expression for $t_{1/2}$ would be obtained using the base-10 log form above)

This relates the half-life of a reactant in a *first-order reaction* and its rate constant, k. In such reactions, the half-life *does not depend* on the initial concentration of A. This is not true for reactions having overall orders other than first order.

Example – 5

Compound A decomposes to form B and C in a reaction that is first order with respect to A and first order overall. At 25°C, the specific rate constant for the reaction is 0.0450 s^{-1}. What is the half-life of A at 25°C?

$$A \rightarrow B + C$$
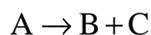
Critical thinking

We use the equation given above for $t_{1/2}$ for a first-order reaction. The value of k is given in the problem, the coefficient of reactant A is a = 1.

Solution: $t_{1/2} = \dfrac{\ln 2}{ak} = \dfrac{0.693}{1\left(0.0450 \text{s}^{-1}\right)} = 15.4 \text{ s}$

After 15.4 seconds of reaction, half of the original reactant remains, so that $[A] = \frac{1}{2}[A]_0$.

Example – 6

The reaction $2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$ obeys the rate law Rate $= k\,[N_2O_5]$, in which the specific rate constant is 0.00840 s^{-1} at a certain temperature. If 2.50 moles of N_2O_5 were placed in a 5.00-liter container at that temperature, how many moles of N_2O_5 would remain after 1.00 minute?

Critical thinking

We apply the first-order integrated rate equation.

$$\ln\left(\frac{[N_2O_5]_0}{[N_2O_5]}\right) = akt$$

First we must determine $[N_2O_5]_0$, the original molar concentration of N_2O_5. Then we solve for $[N_2O_5]$, the molar concentration after 1.00 minute. We must remember to express k and t using the same time units. Finally, we convert molar concentration of N_2O_5 to moles remaining.

Solution: The original concentration of N_2O_5 is

$$[N_2O_5]_0 = \frac{2.50 \text{ mol}}{5.00 \text{ L}} = 0.500\,M$$

The other quantities are

$$a = 2 \qquad k = 0.00840 \text{ s}^{-1} \qquad t = 1.00 \text{ min} = 60.0 \text{ s} \qquad [N_2O_5] = ?$$

The only unknown in the integrated rate equation is $[N_2O_5]$ after 1.00 minute. Let us solve for the unknown. Because $\ln x/y = \ln x - \ln y$.

$$\ln \frac{[N_2O_5]_0}{[N_2O_5]} = \ln[N_2O_5]_0 - \ln[N_2O_5] = akt$$

$$\ln[N_2O_5] = \ln[N_2O_5]_0 - akt$$

$$= \ln(0.500) - (2)(0.00840\,s^{-1})(60.0\,s) = -0.693 - 1.008$$

$$\ln[N_2O_5] = -1.701$$

Taking the inverse natural logarithm of both sides gives

$$[N_2O_5] = 1.82 \times 10^{-1}\ M.$$

Thus, after 1.00 minute of reaction, the concentration of N_2O_5 is 0.182 M. The number of moles of N_2O_5 left in the 5.00 –L container is

$$\text{amount of } N_2O_5 = 5.00\,L \times \frac{0.182\,mol}{L} = 0.910\ mol\ N_2O_5$$

Example – 7

A first order reaction is 20% complete in 10 minutes. Calculate (i) the rate constant of the reaction and (ii) the time taken for the reaction to go to 75% completion.

Critical thinking

(1) *Remember that the calculations here have to done in percentages and so, we don't need the actual concentration of the reactants as long as we have their ratios. This is an advantage that we have while using the integrated rate equation for first order reactions.*

Caution: The ratio of concentrations in the integrated rate equation for first order reactions can be expressed with Numerator and Denominator exchanged according to the form that one is using:

$$\ln \frac{[C]_t}{[C]_0} = -kt. \qquad \qquad ...(i)$$

$$\ln \frac{[C]_0}{[C]_t} = kt. \qquad \qquad ...(ii)$$

And so, you should be careful so as to which form you are using and use your data accordingly.

(2) *We have been given that 20% of the reaction is complete in 10 minutes. We have to find k for this reaction. We can see that we have to use the integrated rate equation. But remember that we cannot use $\frac{20}{100}$ in place of $\frac{[C]_t}{[C]_0}$ because $[C]_t$ denotes the concentration "remaining" after time, t, and not the concentration that has been used upto time, t.*

Solution: **(i)** For the first order reaction, we have,

$$ln\frac{[C]_0}{[C]_t} = kt \qquad ...(2)$$

Here,

$$\frac{[C]_0}{[C]_t} = \frac{100}{80} \text{ and } t = 10 \text{ minutes}$$

Substituting the values in (2) we get,

$$ln\frac{100}{80} = k \cdot (10 \text{ min})$$

$$\Rightarrow \quad ln(1.25) = k \cdot (10 \text{ min})$$

$$\Rightarrow \quad k = \frac{ln(1.25)}{10 \text{ min}}$$

$$\Rightarrow \quad k = 0.0223 \text{ min}^{-1}$$

(ii) Since the reaction is 75% complete, the remaining concentration is 25%. Using (ii) and obtained value of k in (i) above, we get,

$$ln\frac{100}{25} = (0.0223 \text{ min}^{-1})(t)$$

$$\Rightarrow \quad t = \frac{ln\,4}{0.0223 \text{ min}^{-1}}$$

$$\Rightarrow \quad t = 62.18 \text{ minutes}$$

Example – 8

In a first order reaction the concentration of reactant decreases from 800 mol/dm³ to 50 mol/dm³ in 2×10^4 sec. What is the rate constant of the reaction in sec⁻¹?

Critical thinking

Method-1: *We have been given concentrations of the reactant at two points of time and we also have the duration between the two points of time. We can easily calculate the k for this reaction using the integrated rate equation.*

Method-2: *If we observe the initial and final concentrations we can see that the reaction has undergone four half lives form the initial to final concentration:*

$$800M \xrightarrow{\ t_{1/2}\ } 400M \xrightarrow{\ t_{1/2}\ } 200M \xrightarrow{\ t_{1/2}\ } 100M \xrightarrow{\ t_{1/2}\ } 50M$$

So, the given time (2×10^4 sec) represents four half lives of this reaction. Can you see so as to how we can use this information to get the rate constant much more efficiently as compared to the rigorous method 1 above?

Solution: Method 1:

$$[C]_0 = 800\ M$$

$$[C]_t = 50\ M$$

$$t = 2 \times 10^4\ \text{sec}$$

Substituting these data in the equation

$$k = \frac{2.303}{t} \log \frac{[C]_0}{[C]_t}, \text{we get,}$$

$$k = \frac{2.303}{2 \times 10^4} \log \frac{800}{50}$$

$$= 1.386 \times 10^{-4}\ \text{sec}^{-1}.$$

Method 2: The reaction undergoes four half lives to go from $[C]_0 (= 800\ M)$ to $[C]_t (= 50\ M)$. So, the time taken to go from $[C]_0$ to $[C]_t$ $(2 \times 10^4\ \text{sec})$ is four times the half life of the reaction, i.e.,

$$2 \times 10^4\ \text{sec}. = 4 \times t_{1/2}$$

$$\Rightarrow \quad t_{1/2} = \frac{2 \times 10^4}{4} = 0.5 \times 10^4\ \text{sec}.$$

We know that,

$$t_{1/2} = \frac{0.693}{k} \quad \text{(for a first order reaction)}$$

$$\Rightarrow \quad k = \frac{0.693}{t_{1/2}}$$

$$\Rightarrow \quad k = \frac{0.693}{0.5 \times 10^4}$$

$$\Rightarrow \quad k = 1.386 \times 10^{-4}\ \text{sec}^{-1}$$

Example – 9

The rate of a first order reaction is 0.04 mol litre^{-1} s^{-1} at 10 minutes and 0.03 mol litre^{-1} s^{-1} at 20 minutes after initiation. Find the half-life of the reaction.

Critical thinking
We have been given rates at two instants of time of a first order reaction. From this we have to find the half life which can be easily done if we know the half life which can be easily done if we know the rate   constant, k.
Now, just using rate laws won't give us the rate constant and neither will the integrated rate equations. But the both when applied combined in the given question have the potential to give us the solution. Can you see how ?

Solution: If reactant is A(say), them the rate law for the given first order reaction is:

$$\text{rate} = k[A] \text{ (where } k \text{ is the rate constant)}$$

Now, according to the given data we can write:

$$(\text{rate})_{10 \text{ mins}} = k[A]_{10 \text{ mins}}. \qquad \ldots (i)$$

$$\Rightarrow \quad 0.04 \text{ mol litre}^{-1} \text{ s}^{-1} = k[A]_{10 \text{ mins}}. \qquad \ldots (ii)$$

and

$$(\text{rate})_{20 \text{ mins}} = k[A]_{20 \text{ mins}} \qquad \ldots (iii)$$

$$\Rightarrow \quad 0.03 \text{ mol l}^{-1} \text{ s}^{-1} = k[A]_{20 \text{ mins}}. \qquad \ldots (iv)$$

Dividing (ii) by (iv) we get,

$$\frac{0.04 \text{ mol L}^{-1} \text{ s}^{-1}}{0.03 \text{ mol L}^{-1} \text{ s}^{-1}} = \frac{k[A]_{10 \text{ mins}}}{k[A]_{20 \text{ mins}}}$$

$$\Rightarrow \quad \frac{4}{3} = \frac{[A]_{10 \text{ mins}}}{[A]_{20 \text{ mins}}} \qquad \ldots (v)$$

The point now is can we use this ratio in the integrated rate equation because there the ratio of concentrations is between the initial concentration and concentration after time t. Whereas in (v) the ratio is between concentrations at $t = 10$ min and $t = 20$ min (and none of them is the initial concentration.).

Actually, the integrated rate equation that we have derived is a special case of the integrated rate equation we derive here:

Let $aA \rightarrow$ products be a first order reaction.

Then, its rate law can be written as

$$-\frac{1}{a}\left(\frac{d[A]}{dt}\right) = k[A]$$

$$\Rightarrow \quad -\frac{d[A]}{[A]} = ak \, dt \qquad \ldots(1)$$

Now, if $[A]_1$ and $[A]_2$ are the concentrations of the reactants at times t_1 and t_2 respectively, then, we can integrate (1) above as:

$$-\int_{[A]_1}^{[A]_2} \frac{d[A]}{[A]} = \int_{t_1}^{t_2} ak \, at$$

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$$\Rightarrow \quad -ln[A]\Big|_{[A]_1}^{[A]_2} = ak\ t\Big|_{t_1}^{t_2}$$

$$\Rightarrow \quad -\left(ln[A]_2 - ln[A]_1\right) = ak\ (t_2 - t_1)$$

$$\Rightarrow \quad \boxed{ln\ \frac{[A]_1}{[A]_2} = ak\ \Delta t} \qquad\qquad ...(2)$$

i.e. the above equation can be used for concentrations at **any** two instants of time for a reaction. (Note that the integrated rate equation used earlier is a special case of the above equation. Also remember that in the above case also, there are two forms of equation :

$$ln\ \frac{[A]_1}{[A]_2} = ak\ (t_2 - t_1)$$

and

$$-ln\ \frac{[A]_2}{[A]_1} = ak\ (t_1 - t_2)$$

and you should be careful so as to which one you are using.)

So, we can now use (v) and (2) to solve the given problem.

We can write,

$$ln\ \frac{[A]_{10\,mins}}{[A]_{20\,mins}} = k(20-10)\,min \quad (\text{assuming } a \text{ is included in } k).$$

$$ln\ \frac{4}{3} = 10\ k$$

$$\Rightarrow \quad 2.303 \log \frac{4}{3} = 10\ k$$

$$\Rightarrow \quad k = 0.0287\ min^{-1}$$

$$\therefore\ ,$$

$$t_{1/2} = \frac{0.693}{k}$$

$$= \frac{0.693}{0.0287\ min^{-1}}$$

$$= 24.14\ min.$$

Although our syllabus does not require us to study second-order reactions, we take up its study hence, just so that we are able to compare it with corresponding results for first order reactions and appreciate the difference and the uniqueness of the first order reactions.

Second-Order Reactions

For reactions involving $aA \rightarrow$ products that are *second order with respect* to A *and second order overall*, the integrated rate equation is

$$\frac{1}{[A]} - \frac{1}{[A]_0} = akt \qquad \text{(second order in } A \text{, second order overall)}$$
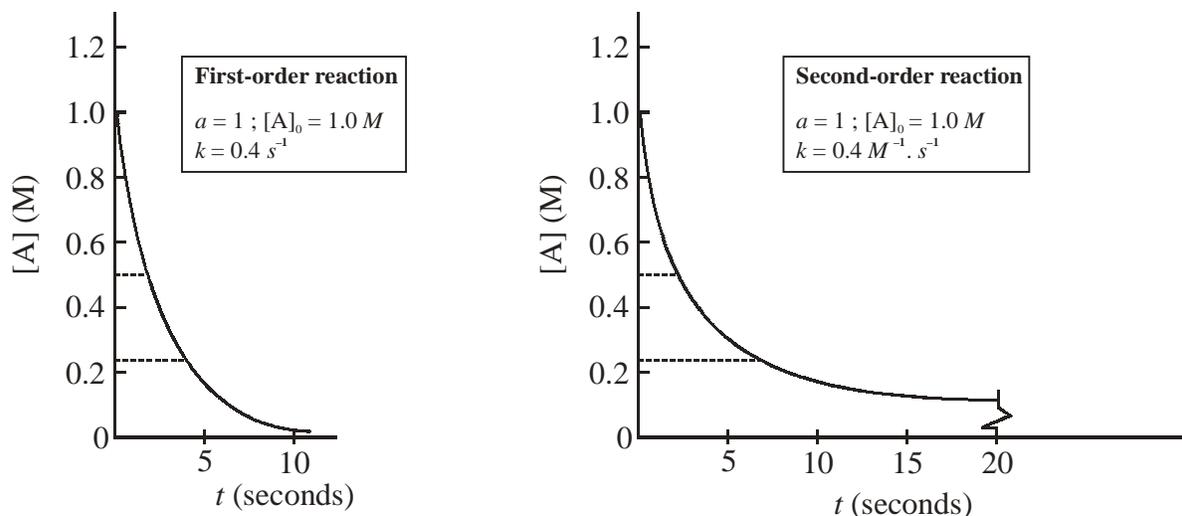
For $t = t_{1/2}$, we have $[A] = \frac{1}{2}[A]_0$, so

$$\frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0} = akt_{1/2}$$

Simplifying and solving for $t_{1/2}$, we obtain the relationship between the rate constant and $t_{1/2}$.

$$t_{1/2} = \frac{1}{ak[A]_0} \qquad \text{(second order in A, second order overall)}$$

In this case $t_{1/2}$ *depends on the initial concentration of A.* Figure 3 illustrates the different behaviour of half-life for first- and second- order reactions.

Figure - 3 (a) Plot of concentration versus time for a first-order reaction. During the first half-life, 1.73 seconds, the concentration of A falls from 1.00 M to 0.50 M. An additional 1.73 seconds are required for the concentration to fall by half again, from 0.50 M to 0.25 M, and so on. For a first-order reaction $t_{1/2} = \dfrac{\ln 2}{ak} = \dfrac{0.693}{ak}$; $t_{1/2}$ does not depend on the concentration at the beginning of that time period. (b) Plot of concentration versus time for a second-order reaction. The same values are used for a, $[A]_0$, and k as in part (a). During the first-half life, 2.50 seconds, the concentration of A falls from 1.00 M to 0.50 M. The concentration falls by half again from 2.50 to 7.50 seconds, so the second half life is 5.00 seconds. The half-life beginning at 0.25 M is 10.00 seconds. For a second-order reaction,

$$t_{1/2} = \frac{1}{ak[A]_0}$$

$t_{1/2}$ is inversely proportional to the concentration at the beginning of that time period.

Example – 10	

The gas phase decomposition of NOBr is second order in [NOBr], with $k = 0.810\,M^{-1}.\,s^{-1}$ at 10°C. We start with $4.00 \times 10^{-3}\,M$ NOBr in a flask at 10°C. How many seconds does it take to use up $1.50 \times 10^{-3}\,M$ of this NOBr?

$$2NOBr\,(g) \rightarrow 2NO\,(g) + Br_2\,(g) \qquad Rate = k\,[NOBr]^2$$

Critical thinking

We first determine the concentration of NOBr that remains after 1.50×10^{-3} M is used up. Then we use the second-order integrated rate equation to determine the time required to reach that concentration.

Solution: M NOBr remaining $= (0.00400 - 0.00150)\,M = 0.00250\,M = [NOBr]$

We solve the integrated rate equation $\dfrac{1}{[NOBr]} - \dfrac{1}{[NOBr]_0} = akt$ for t.

$$t = \frac{1}{ak}\left(\frac{1}{[NOBr]} - \frac{1}{[NOBr]_0}\right) = \frac{1}{(2)(0.810\,M^{-1}\cdot s^{-1})}\left(\frac{1}{0.00250\,M} - \frac{1}{0.00400\,M}\right)$$

$$= \frac{1}{1.62\,M^{-1}\cdot s^{-1}}\left(400\,M^{-1} - 250\,M^{-1}\right) \qquad \text{(The coefficient of NOBr is } a = 2)$$

$$= 92.6\,s\ (\text{or } 1.54\ \text{min})$$

Zero-Order Reaction

For a reaction $aA \rightarrow$ products that is zero order, we can write the rate-law expression as

$$-\frac{1}{a}\left(\frac{\Delta[A]}{\Delta t}\right) = k$$

The corresponding integrated rate equation is

$$[A] = [A]_0 - akt \qquad \text{(zero order)}$$

and the half-life is

$$t_{1/2} = \frac{[A]_0}{2ak} \qquad \text{(zero order)}$$

The following table summarises the relationships that we have presented so far in this section:

| Table - 1 | Summary of Relationships for Various Orders of the Reaction $aA \rightarrow Products$ |

Order

	Zero	First	Second
Rate-law expression	rate = k	rate = k [A]	rate = k [A]^2
Integrated rate equation	[A]=[A]$_0$– akt	$\ln\dfrac{[A]_0}{[A]} = akt$	$\dfrac{1}{[A]} - \dfrac{1}{[A]_0} = akt$
		or	
		$\log\dfrac{[A]_0}{[A]} = \dfrac{akt}{2.303}$	
Half-life, $t_{1/2}$	$\dfrac{[A]_0}{2ak}$	$\dfrac{\ln 2}{ak} = \dfrac{0.693}{ak}$	$\dfrac{1}{ak[A]_0}$

| *Thinking critically* : Which Equation should be used? |

How can you tell which equation to use to solve a particular problem?

1. You must decide whether to use the rate-law expression or the integrated rate equation. Remember that

    the *rate-law expression* **relates** *rate and concentration*

    whereas

   the *integrated rate equation relates time and concentration*.

    When you need to find the rate that corresponds to particular concentrations, or the concentrations needed to give a desired rate, you should use the rate-law expression. When the problem at hand involves the *time* required to reach a stated concentration, or the concentration that remains or that has been consumed after a stated time, you should use the integrated rate equation.

2. You must choose the form of the rate-law expression or the integrated rate equation–zero, first, or second order – that is appropriate to the order of the reaction. These are summarised in Table - 1. One of the following usually helps you decide.

    a. The statement of the problem may state explicitly what the order of the reaction is.

    b. The rate-law expression may be given, from which you can tell the order of the reaction from the exponents in that expression.

    c. The units of the specific rate constant, k, may be given; you can interpret these stated units to tell you the order of the reaction. The units of k for a zero-order reaction are M time^{-1}; those for a first-order reaction are time^{-1}; those for a second-order reaction are M^{-1}. time^{-1}.

    One method of assessing reaction order is based on comparing successive half-lives. As we have seen, $t_{1/2}$ for a first-order reaction does not depend on initial concentration. We can measure the time required for different concentrations of a reactant to fall to half of their original values. If this time remains constant, it is an indication that the reaction is first order for that reactant and first order overall (Figure 3a). By contrast, for other orders of reaction, $t_{1/2}$ would change depending on initial concentration. For a second-order reaction, successively measured $t_{1/2}$ values would increase as $[A]_0$ decreases (Figure 3(b)). $[A]_0$ is measured at the *beginning of each particular measurement period.*

Calculus Derivation of Integrated Rate Equations

The derivation of the integrated rate equation is an example of the use of calculus in chemistry. The following derivation is for a reaction that is assumed to be first order in a reactant A and first order overall. If you do not know calculus, you can still use the results of this derivation, as we have already shown in this section. For the reaction

$$aA \rightarrow products$$
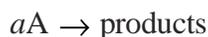
the rate is expressed as

$$rate = -\frac{1}{a}\left(\frac{\Delta[A]}{\Delta t}\right)$$

For a first-order reaction, the rate is proportional to the first power of [A].

$$-\frac{1}{a}\left(\frac{\Delta[A]}{\Delta t}\right) = k[A]$$

In calculus terms, we express the change during an infinitesimally short time dt as the derivative of [A] w.r.t. time,

$$-\frac{1}{a}\frac{d[A]}{dt} = k[A]$$

Separating variables, we obtain

$$-\frac{d[A]}{[A]} = (ak)dt$$

We integrate this equation to get

$$-\ln[A] = akt + C$$

We evaluate C, the constant of integration, by setting $t = 0$. This refers to the beginning of the reaction. At that time, the concentration of A is $[A]_0$, its initial value, so $C = -\ln [A]_0$.

$$\ln[A] = akt - \ln[A]_0$$

We now rearrange the equation, remembering that $\ln (x) - \ln(y) = \ln (x/y)$.

$$\ln[A]_0 - \ln[A] = akt$$

$$\ln\frac{[A]_0}{[A]} = akt \qquad \text{(first order)}$$

This is the integrated rate equation for a reaction that is first order in reactant A and first order overall.

Integrated rate equations can be derived similarly from other simple rate laws. For a reaction $aA \rightarrow$ products that is second order in reactant A and second order overall, we can write the rate equation as

$$-\frac{d[A]}{adt} = k[A]^2$$

Again, using the methods of calculus, we can separate variables, integrate, and rearrange to obtain the corresponding second-order integrated rate equation.

$$\frac{1}{[A]} - \frac{1}{[A]_0} = akt \qquad \text{(second order)}$$

For a reaction $aA \rightarrow$ products that is zero order overall, we can write the rate equation as

$$-\frac{d[A]}{adt} = k$$

In this case, the calculus derivation already described leads to the zero-order integrated rate equation

$$[A] = [A]_0 - akt \quad \text{(zero order)}$$

(You are requested to provide the missing steps in the derivations of the second- and zero- order integrated rate equations).

Using Integrated Rate Equations to Determine Reaction Order

The integrated rate equation can help us to analyse concentration-versus-time data to determine reaction order. A graphical approach is often used. We can rearrange the first-order integrated rate equation

$$\ln \frac{[A]_0}{[A]} = akt$$

as follows. Remembering that the logarithm of a quotient, $\ln (x/y)$, is equal to the difference of the logarithms, $\ln x - \ln y$, we can write

$$\ln [A]_0 - \ln [A] = akt \quad \text{or} \quad \ln [A] = -akt + \ln [A]_0$$

Recall that the equation for a straight line may be written as

$$y = mx + b$$

where y is the variable plotted along the ordinate (vertical axis), x is the variable plotted along the abscissa (horizontal axis), m is the slope of the line, and b is the intercept of the line with the y axis (figure 4). If we compare the last two equations, we find that $\ln [A]$ can be interpreted as y, and t as x.

$$\underbrace{\ln [A]}_{y} \quad = \quad \underbrace{-akt}_{m\ x} \quad + \quad \underbrace{\ln[A]_0}_{b}$$
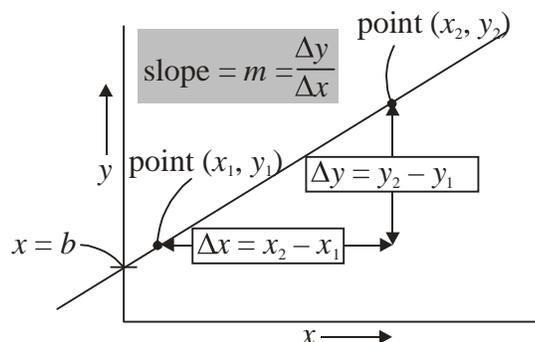
Figure 4: *Plot of the equation $y = mx + b$, where m and b are constant. The slope of the line z(positive in this case) is equal to m; the intercept on the y axis is equal to b.*

The quantity $-ak$ is a constant as the reaction proceeds, so it can be interpreted as m. The initial concentration of A is fixed, so $\ln [A]_0$ is a constant for each experiment, and $\ln [A]_0$ can be interpreted as b. Thus, a plot of $\ln[A]$ versus time for a first-order reaction would be expected to give a straight line (Figure 5) with the slope of the line equal to $-ak$ and the intercept equal to $\ln [A]_0$.

$$\frac{1}{[A]} - \frac{1}{[A]_0} = akt \text{ to read } \frac{1}{[A]} = akt + \frac{1}{[A]_0}$$

Again comparing this with the equation for a straight line, we see that a plot of $1/[A]$ versus time would be expected to give a straight line (Figure 6). The line would have a slope equal to ak and an intercept equal to $1/[A]_0$.

For a zero-order reaction, we can rearrange the integrated rate equation

$$[A]_0 - [A] = akt \quad \text{to} \quad [A] = -akt + [A]_0$$
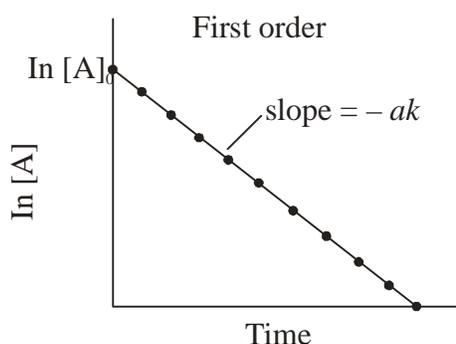
Figure 5: Plot of ln [A] versus time for a reaction aA $\rightarrow$ products that follows first-order kinetics. The observation that such a plot gives a straight line would confirm that the reaction is first order in [A] and first order overall, i.e., rate $= k[A]$. The slope is equal to $-ak$. Because a and k are positive numbers, the slope of the line is always negative.

Logarithms are dimensionless, so the slope has the units $(\text{time})^{-1}$. A plot of (base-10) log [A] for a first-order reaction would give a straight line with slope equal to $-ak/2.303$. The logarithm of a quantity less than 1 is negative, so data points for concentrations less than 1 molar would appear below the time-axis.
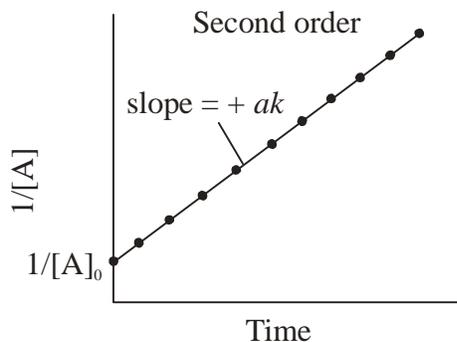
Figure 6: Plot of 1/[A] versus time for a reaction aA $\rightarrow$ products that follows second-order kinetics. The observation that such a plot gives a straight line would confirm that the reaction is second order in [A] and second order overall, ie., rate $= k[A]^2$. The slope is equal to ak. Because a and k are positive numbers, the slope of the line is always positive. Because concentrations cannot be negative, 1/[A] is always positive, and the line is always above the time-axis.

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Comparing this with the equation for a straight line, we see that a straight-line plot would be obtained by plotting concentration versus time, [A] versus t. The slope of this line is $-ak$, and the intercept is $[A]_0$.

This discussion suggests another way to deduce an unknown rate-law expression from experimental concentration data. The following approach is particularly useful for any decomposition reaction, one that involves only one reactant.

$$aA \rightarrow products$$
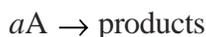
We plot the data in various ways as suggested above. *If* the reaction followed zero order kinetics. *then* a plot of [A] versus t would give a straight line. But *if* the reaction followed first-order kinetics, then a plot of ln[A] versus t would give a straight line whose slope could be interpreted to derive a value of k. *If* the reaction were second order in A and second order overall, *then* neither of these plots would give a straight line, but a plot of 1/[A] versus t would. If none of these plots gave a straight line (within expected scatter due to experimental error), we would know that none of these is the correct order (rate law) for the reaction. Plots to test for other orders can be devised, as can graphical tests for rate-law expressions involving more than one reactant, but those are subjects for more advanced courses. The graphical approach that we have described is illustrated in the following example.
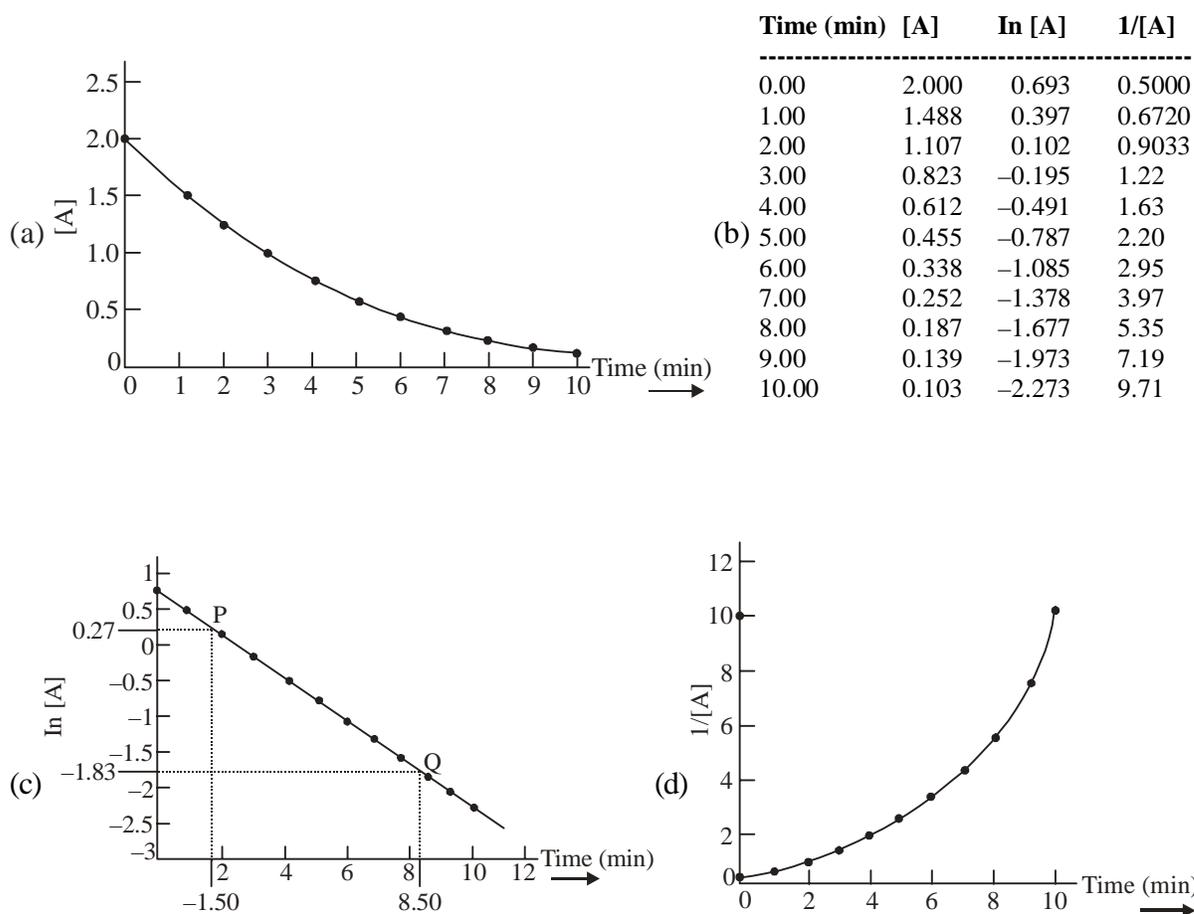
Example – 11

We carry out the reaction A $\rightarrow$ B + C at a particular temperature. As the reaction proceeds, we measure the molarity of the reactant, [A], at various times. The observed data are tabulated in the table below. (a) Plot [A] versus time. (b) Plot ln [A] versus time. (c) Plot 1/[A] versus time. (d) What is the order of the reaction? (e) Write the rate-law expression for the reaction. (f) What is the value of k at this temperature?

Time (min)	[A] (mol/L)
0.00	2.000
1.00	1.488
2.00	1.107
3.00	0.823
4.00	0.612
5.00	0.455
6.00	0.338
7.00	0.252
8.00	0.187
9.00	0.139
10.00	0.103

Critical thinking

For parts (a)–(c), we use the observed data to make the required plots, calculating related values as necessary. (d) We can determine the order of the reaction by observing which of these plots gives a straight line. (e) Knowing the order of the reaction, we can write the rate-law expression. (f) The value of k can be determined from the slope of the straight-line plot.

Solution: **(a)** The plot of [A] versus time is given in Figure 7 (a)

Time (min)	[A]	In [A]	1/[A]
0.00	2.000	0.693	0.5000
1.00	1.488	0.397	0.6720
2.00	1.107	0.102	0.9033
3.00	0.823	–0.195	1.22
4.00	0.612	–0.491	1.63
5.00	0.455	–0.787	2.20
6.00	0.338	–1.085	2.95
7.00	0.252	–1.378	3.97
8.00	0.187	–1.677	5.35
9.00	0.139	–1.973	7.19
10.00	0.103	–2.273	9.71

Figure 7: Plots and data conversion for Example. (a) Plot of [A] versus time using the data given. (b) The data are used to calculate the two columns ln [A] and 1/[A]. (c) Plot of ln [A] versus time. The observation that this plot gives a straight line indicates that the reaction follows first-order kinetics. (d) Plot of 1/[A] versus time. If the reaction had followed second-order kinetics, this plot would have resulted in a straight line, and the plot in Figure 7 (c) would not.

(a) The plot of [A] versus time is given in Figure 7(a).

(b) We first use the given data to calculate the ln[A] column in Figure 7b. These data are then used to plot ln[A] versus time, as shown in Figure 7(c).

(c) The given data are used to calculate the 1/[A] column in Figure 7b. Then we plot 1/[A] versus time, as shown in Figure 7(d)

(d) It is clear from the answer to part (b) that the plot of ln[A] versus time gives a straight line. This tells us that *the reaction is first order in [A]*.

(e) Putting our answer to part (d) in the form of a rate-law expression, we write rate $= k[A]$.

(f) We use the straight-line plot in Figure 7(c) to find the value of the rate constant for this first-order reaction from the relationship

$$\text{slope} = - ak \quad \text{or} \quad k = - \frac{\text{slope}}{a}$$

To determine the slope of the straight line, we pick any two points, such as P and Q, on the line. From their coordinates, we calculate

$$\text{slope} = \frac{\text{change in ordinate}}{\text{change in abscissa}} = \frac{(-1.83)-(0.27)}{(8.50-1.50)\,\text{min}} = -0.300\,\text{min}^{-1}$$

$$k = -\frac{\text{slope}}{a} = -\frac{-0.300\,\text{min}^{-1}}{1} = 0.300\,\text{min}^{-1}$$

You may wish to confirm that a straight line would also be obtained by plotting log [A] versus time and that the proper interpretation of its slope would give the same value.

(PS: Remember that the ordinate is the vertical axis and the abscissa is the horizontal one. If you are not careful to keep the points in the same order in the numerator and denominator, you will get the wrong sign for the slope.)

_____

The Graphical interpretations of concentration-versus-time data for some common reaction orders are summarised in the following table.

| **Table - 2** | Graphical Interpretations for Various Orders of the Reaction $aA \rightarrow$ Products |

	Order		
	Zero	**First**	**Second**
Plot that gives straight line	[A] vs. t	ln [A] vs. t	$\dfrac{1}{[A]}$ vs. t
Direction of straight-line slope	Down with time	Down with time	Up with time
Interpretation of slope	$-ak$	$-ak$	ak
Inerpretation of intercept	$[A]_0$	ln $[A]_0$	$\dfrac{1}{[A]_0}$

Please attempt the following problems before seeing their solutions:

- A reaction believed to be either first or second order has a half-life of 20 s at the beginning of the reaction but a half-life of 40 s some time later. What is the order of the reaction?

Solution: The half-life of a first-order reaction is constant over the course of the reaction. The half-life of a second-order reaction depends on the initial concentration and becomes larger as time elapses. Thus, the reaction must be second order because the half-life increases from 20 s to 40 s after time has elapsed.

- The reaction $2A(g) \rightarrow A_2(g)$ is being run in each of the following containers. The reaction is found to be second order with respect to A.
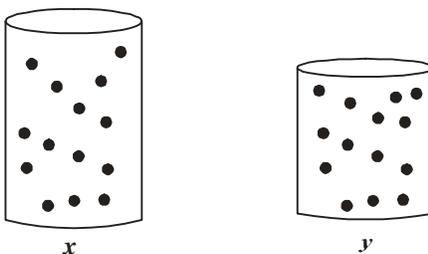
(a) Write the rate law for the reaction.
(b) Which reaction container will have a faster reaction rate?
(c) In which container will the reaction have a shorter half-life?
(d) What are the relative rates of the reactions in each container?
(e) After a set amount of time has elapsed, which container will contain fewer A atoms?

Solution: (a) The rate law for a second-order reaction is Rate $= k[A]^2$.

(b) The faster reaction rate will correspond to the container with the higher concentration of A. Both containers contain the same number of A particles, but the volume of container y is only one-half the volume of container x. Therefore, the initial concentration of A in container y is double the initial concentration of A in container x. Thus, the reaction will be faster in container y.

(c) For a second-order reaction, the relationship between the half-life, rate constant, and initial concentration of A is

$$t_{1/2} = \frac{1}{k[A]_0}$$

Since the half-life is inversely proportional to the initial concentration, the shorter half-life will correspond to the higher initial concentration of A, which is container y.

(d) The relative rates of the reaction can be determined as follows. Since the initial concentration of A in container y is double the initial concentration of A in container x, the ratio of the rate in container y to that in container x is

$$\frac{\text{Rate}_y}{\text{Rate}_x} = \frac{k[A]_{0,y}^2}{k[A]_{0,x}^2} = \left(\frac{[A]_{0,y}}{[A]_{0,x}} \right)^2 = \left(\frac{2[A]_0, x}{[A]_0, x} \right)^2 = 2^2 = 4$$

Thus, the reaction rate in container y is four times the reaction rate in container x.

(c) Since both containers start with the same number of A particles, and the reaction rate is faster in container y, more A particles will have reacted in container y than in container x, so container y will contain fewer atoms.

- When viewed from a molecular perspective, a particular reaction is written as:

$$\overset{\bullet\bullet}{A}\overset{\bullet\bullet}{B} \longrightarrow \overset{\bullet}{A} + \overset{\bullet}{B}$$

(a) If the reaction is first-order with a half-life of 10 seconds, complete the following pictures after 10 and 20 seconds have elapsed.

$t = 0s$ $t = 10s$ $t = 20s$
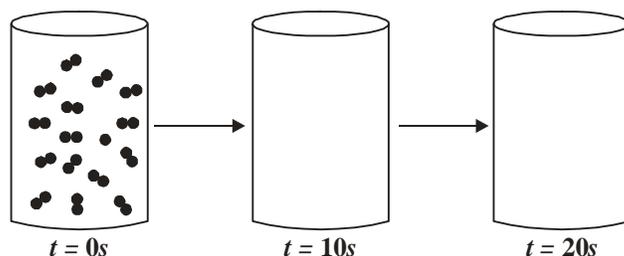
(b) How would the pictures from part (a) change if the reaction were second-order with the same half-life?

(c) For the first-order case, what are the relative reaction rates at the start of the reaction and after 10 seconds have elapsed?

(d) For the second-order case, what are the relative reaction rates at the start of the reaction and after 10 seconds have elapsed?

Solution: (a) The reaction is first-order with a half-life of 10 seconds. Starting with four particles in the container, after 10 seconds (one half-life), two of the particles will have reacted and two will remain unreacted. After 20 seconds (two half-lives), three of the particles will have reacted and one will remain unreacted. The pictures are

$t = 0s$ $t = 10s$ $t = 20s$
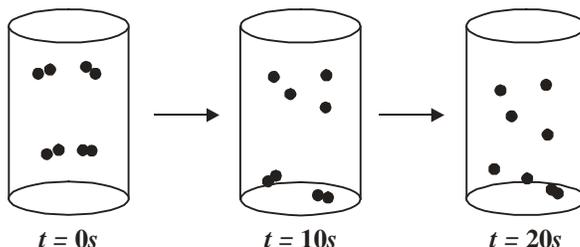
(b) If the half-life is the same for the second-order reaction, the pictures will be the same.
(c) After 10 seconds (one half-life), the concentration of the particles is one-half their initial value. If we call the particles A, then for the first-order case the relative reaction rates at the start and after 10 seconds are

$$\frac{\text{Rate}_0}{\text{Rate}_{10}} = \frac{k[A]_{o,0}}{k[A]_{o,10}} = \frac{[A]_{o,0}}{[A]_{o,10}} = \left(\frac{[A]_o}{1/2[A]_o}\right) = 2$$

Thus, for the first-order case, after 10 seconds, the rate is one-half the initial rate.
(d) After 10 seconds (one half-life), the concentration of the particles is one-half their initial value. If we call the particles A, then for the second-order case the relative reaction rates at the start and after 10 seconds are

$$\frac{\text{Rate}_0}{\text{Rate}_{10}} = \frac{k[A]_{o,0}^2}{k[A]_{o,10}^2} = \left(\frac{[A]_{o,0}}{[A]_{o,10}}\right)^2 = \left(\frac{[A]_o}{1/2[A]_o}\right)^2 = 2^2 = 4$$

Thus, for the second-order case, after 10 seconds, the rate is four times the initial rate.

Example – 12

The gas phase decomposition of dimethyl ether follows first-order kinetics

$$CH_3OCH_3(g) \rightarrow CH_4(g) + CO(g) + H_2(g)$$

The reaction is carried out at constant volume container at 500 °C and has a half-life of 14.5 minutes. Initially only dimethyl ether is present at a pressure of 0.40 atmosphere. What is the total pressure of the system after 12 minutes? (Assume ideal gas behaviour)

Critical thinking

Please remember that for questions involving gases,, we often have to deal with the partial pressure of the reactions. In such cases remember that the concentrations are directly proportional to the partial pressures (Example - 4) and this fact can be used to substitute for concentrations with partial pressures if ratio of concentrations are involved as the constant term would cancel out. For example, suppose that we have a homogenous mixture of two gases 1 and 2. Then their respective ideal gas equations are:

$$P_1 V_1 = n_1 RT \qquad\qquad ... (1)$$

$$and \qquad P_2 V_2 = n_2 RT \qquad \text{(R is universal constant and T is same for both the gases at an instant)}$$

$$... (2)$$

We can rewrite (1) and (2) as :

$$P_1 = \left(\frac{n_1}{V_1}\right)RT \quad and \quad P_2 = \left(\frac{n_2}{V_2}\right)RT.$$
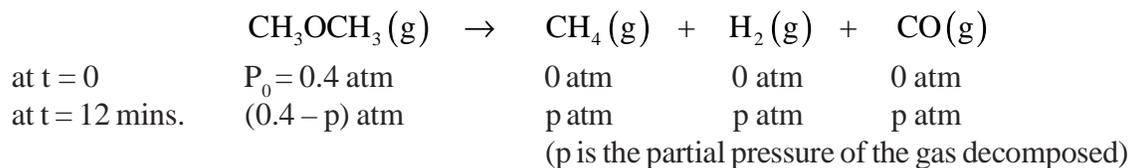
Dividing them we get:

$$\frac{P_1}{P_2} = \frac{\left(\frac{n_1}{V_2}\right)RT}{\left(\frac{n_2}{V_2}\right)RT}$$

$$\Rightarrow \qquad \frac{P_1}{P_2} = \frac{C_1}{C_2} \qquad\qquad \text{(where } C_1 \text{ and } C_2 \text{ are concentrations of the respective gases.)}$$

So, we see that we can substitute $\dfrac{P_1}{P_2}$ for $\dfrac{C_1}{C_2}$

Having this concept in your hands, you can easily solve this question using the integrated rate equation

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Solution: We are given

$$CH_3OCH_3(g) \quad \rightarrow \quad CH_4(g) \quad + \quad H_2(g) \quad + \quad CO(g)$$

at t = 0	$P_0 = 0.4$ atm	0 atm	0 atm	0 atm
at t = 12 mins.	(0.4 – p) atm	p atm	p atm	p atm

(p is the partial pressure of the gas decomposed)

Now, according to the integrated rate equation,

$$\log \frac{[A]_t}{[A]_0} = \left(\frac{-k}{2.303} \right) t$$

Since, concentration is directly proportional to partial pressure,

we get,

$$\log \frac{(0.4 - P)}{(0.4)} = \frac{-k}{2.303} \cdot t \qquad \ldots (A)$$

k can be obtained by $\quad k = \dfrac{0.693}{t_{1/2}}$

$$= \frac{0.693}{14.5} \, min^{-1}$$

∴   (A) becomes,

$$\log \frac{(0.4 - p)}{(0.4)} = -\frac{0.693}{14.5 \times 2.303} \times (12 \, mins.)$$

$$\Rightarrow \quad \log \left(\frac{0.4 - p}{0.4} \right) = -0.249$$

$$\frac{0.4 - p}{0.4} = -0.564$$

$$0.4 - p = 0.4 \times 0.564$$

$$p = 0.4 \, (1 - 0.564)$$

$$p = 0.1744 \, atm.$$

At t = 12 mins. the partial pressure of the four gases are:

CH₃OCH₃(g)	(0.4 – p) = 0.2256 atm
CH₄ (g)	P = 0.1744 atm
H₂ (g)	P = 0.1744 atm
CO(g)	P = 0.1744 atm
Total pressure	= 0.7488 atm

Chemistry / Chemical Kinetics

TRY YOURSELF - II

Q. 1 Substance A reacts according to a first-order rate law with $k = 5.0 \times 10^{-5}\,s^{-1}$. (a) If the initial concentration of A is 1.0 M, what is the initial rate and the rate after 1.0 hour?

Q. 2 For a first-order reaction, the ratio of times to complete 99.9% and half of the reaction is
(a) 8   (b) 9
(c) 10   (d) 12

Q. 3 The reaction $X \rightarrow$ products, follows first order kinetics. In 40 minutes the concentration of X changes from 0.1 M to 0.025 M. The rate of reaction, when concentration of X is 0.01 M is
(a) $1.73 \times 10^{-4}\,M\,min^{-1}$ (b) $3.47 \times 10^{-5}\,M\,min^{-1}$
(c) $3.47 \times 10^{-4}\,M\,min^{-1}$ (d) $1.73 \times 10^{-5}\,M\,min^{-1}$

Q. 4 The first-order reaction has $k = 1.5 \times 10^{-6}\,s^{-1}$ at 200° C. If the reaction is allowed to run for 10 hours, what percentage of the initial concentration would have changed into the product? What is the half-life of this reaction?

Q. 5 The rate constant for an isomerisation reaction $A \rightarrow B$ is $4.5 \times 10^{-3}\,min^{-1}$. If the initial concentration of A is 1 M, calculate the rate of the reaction after 1 hour.

Q. 6 The decomposition of N_2O_5 according to the equation $2N_2O_5(g) \rightarrow 4\,NO_2(g) + O_2(g)$ is a first-order reaction. After 30 min from the start of decomposition in a closed vessel, the total pressure developed is found to be 284.5 mmHg and on complete decomposition, the total pressure is 584.5 mmHg. Calculate the rate constant of the reaction.