

Section - 4

THE ARRHENIUS EQUATION

Temperature: The Arrhenius Equation

The average kinetic energy of a collection of molecules is proportional to the absolute temperature. At a particular temperature, T_1 , a definite fraction of the reactant molecules have sufficient energy, E_a , to react to form product molecules upon collision. At a higher temperature, T_2 a greater fraction of the molecules possess the necessary activation energy, and the reaction proceeds at a faster rate. This is depicted in Figure 11.

From experimental observations, Svante Arrhenius developed the mathematical relationship among activation energy, absolute temperature, and the specific rate constant of a reaction, k , at that temperature. The relationship, called the Arrhenius equation, is

$$k = Ae^{-E_a/RT}$$

or, in logarithmic form,

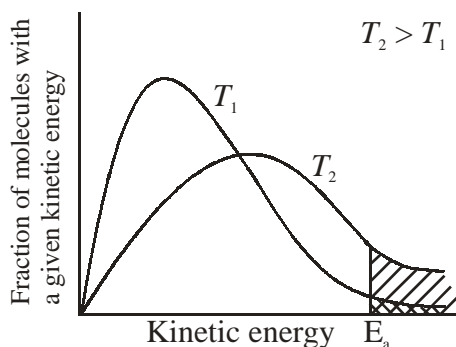
$$\ln k = \ln A - \frac{E_a}{RT} \quad \text{or} \quad \log k = \log A - \frac{E_a}{2.303 RT}$$

In this expression, A is a constant having the same units as the rate constant. It is proportional to the frequency of collisions between reacting molecules.

Actually A (called frequency factor or pre-exponential factor) is equal to $Z\rho$ i.e. $A = Z\rho$ where Z is the number of collisions of the molecules per second in a unit volume and ρ is the steric factor. The necessity of introducing the factor ρ in the Arrhenius equation is explained by the fact that the collisions even between active molecules (i.e. molecules with sufficient energy to bring about reaction) do not always result in a reaction, but only when the molecules have a definite orientation. (Refer figure – 8 of section – 3 for an example). The factor ρ is proportional to the ratio of the ratio of the number of ways of the mutual orientation of the molecules favourable for proceeding of a reaction to the total number of possible ways of orientation: the greater this ratio, the more rapidly will a reaction proceed. The steric factor ρ is usually much smaller than unity; it has an especially great influence on the rate of reactions proceeding with the participation of complex molecules (for example, glucose and proteins), when the total number of various possible orientations is very great, and the number of orientations favourable for proceeding of a reaction is very limited.

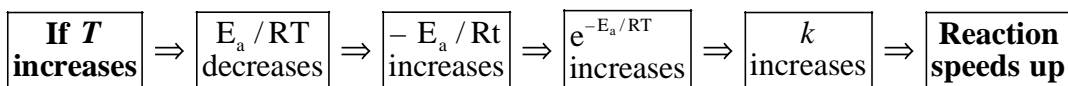
R is the universal gas constant, expressed with the same energy units in its numerator as are used for E_a . For instance, when E_a is known in J/mol, the value $R = 8.314 \text{ J/mol} \cdot \text{K}$ is appropriate. Here the unit “mol” is interpreted as “mole of reaction,” as described the unit on thermodynamics. One important point is the following: The greater the value of E_a , the smaller the value of and the slower the reaction rate (other factors being equal). This is because fewer collisions take place with sufficient energy to get over a high energy barrier.

The Arrhenius equation predicts that increasing T results in faster reaction for the same E_a and concentrations.



The area between the distribution curve and the horizontal axis in Figure is proportional to the total number of molecules present. The total area is the same at T_1 and T_2 . The shaded areas represent the number of particles that exceed the energy of activation, E_a .

Figure 11: The effect of temperature on the number of molecules that have kinetic energies greater than E_a . At T_2 , a higher fraction of molecules possess at least E_a , the activation energy.



Let's look at how the rate constant varies with temperature for a given single reaction. Assume that the activation energy and the factor A do not vary with temperature. We can write the Arrhenius equation for two different temperatures. Then we subtract one equation from the other, and rearrange the result to obtain, in natural logarithm (ln) form,

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

In base-10 logarithm (log) form this equation is written as

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Let's substitute some typical values into this equation. The activation energy for many reactions that occur near room temperature is about 50 kJ/mol (or 12 kcal/mol). For such a reaction, a temperature increase from 300 K to 310 K would result in

$$\ln \frac{k_2}{k_1} = \frac{50,000 \text{ J/mol}}{(8.314 \text{ J/mol} \cdot \text{K})} \left(\frac{1}{300 \text{ K}} - \frac{1}{310 \text{ K}} \right) = 0.647$$

$$\frac{k_2}{k_1} = 1.91 \approx 2$$

Chemists sometimes use the rule of thumb that near room temperature the rate of a reaction approximately doubles with a 10° C rise in temperature. Such a "rule" must be used with care, however, because it obviously depends on the activation energy.

Example – 13

The specific rate constant, k , for the following first-order reaction is $9.16 \times 10^{-3} \text{ s}^{-1}$ at 0.0° C. The activation energy of this reaction is 88.0 kJ/mol. Determine the value of k at 2.0° C.



Critical thinking

First we tabulate the values, remembering to convert temperature to the Kelvin scale.

$$E_a = 88,000 \text{ J/mol}$$

$$R = 8.314 \text{ J/mol} \cdot \text{K}$$

$$k_1 = 9.16 \times 10^{-3} \text{ s}^{-1}$$

at

$$T_1 = 0.0^\circ \text{C} + 273 = 273 \text{ K}$$

$$k_2 = ?$$

at

$$T_2 = 2.0^\circ \text{C} + 273 = 275 \text{ K}$$

We use these values in the "two-temperature" form of the Arrhenius equation.

Solution:

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \left(\frac{k_2}{9.16 \times 10^{-3} \text{ s}^{-1}} \right) = \frac{88,000 \text{ J/mol}}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}} \left(\frac{1}{273 \text{ K}} - \frac{1}{275 \text{ K}} \right) = 0.282$$

Taking inverse (natural) logarithms of both sides.

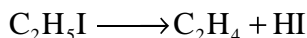
$$\frac{k_2}{9.16 \times 10^{-3} \text{ s}^{-1}} = 1.32$$

$$k_2 = 1.32 (9.16 \times 10^{-3} \text{ s}^{-1}) = 1.21 \times 10^{-2} \text{ s}^{-1}$$

We see that a very small temperature difference, only 2°C, causes an increase in the rate constant (and hence in the reaction rate for the same concentrations) of about 32%. Such sensitivity of rate to temperature change makes the control and measurement of temperature extremely important in chemical reactions.

Example – 14

The gas-phase decomposition of ethyl iodide to give ethylene and hydrogen iodide is a first-order reaction.



At 600 K, the value of k is $1.60 \times 10^{-5} \text{ s}^{-1}$. When the temperature is raised to 700 K, the value of k increases to $6.36 \times 10^{-3} \text{ s}^{-1}$. What is the activation energy for this reaction?

Critical thinking

We know k at two different temperatures. We solve the two-temperature form of the Arrhenius equation for E_a and evaluate

Solution:

$$k_1 = 1.60 \times 10^{-5} \text{ s}^{-1} \text{ at } T_1 = 600 \text{ K} \quad k_2 = 6.36 \times 10^{-3} \text{ s}^{-1} \text{ at } T_2 = 700 \text{ K}$$

$$R = 8.314 \text{ J/mol} \cdot \text{K}$$

$$E_a = ?$$

We arrange the Arrhenius equation for E_a .

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{so} \quad E_a = \frac{R \ln \frac{k_2}{k_1}}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)}$$

Substituting,

$$E_a = \frac{\left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right) \ln\left(\frac{6.36 \times 10^{-3} \text{s}^{-1}}{1.60 \times 10^{-5} \text{s}^{-1}}\right)}{\left(\frac{1}{600 \text{ K}} - \frac{1}{700 \text{ K}}\right)} = \frac{\left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right)(5.98)}{2.38 \times 10^{-4} \text{ K}^{-1}}$$

$$E_a = 2.09 \times 10^5 \text{ J/mol} \quad (\text{i.e. } 209 \text{ kJ/mol})$$

The determination of E_a in the manner illustrated in the last Example may be subject to considerable error, because it depends on the measurement of k at only two temperatures. Any error in either of these k values would greatly affect the resulting value of E_a . A more reliable method that uses many measured values for the same reaction is based on a graphical approach. Let us rearrange the single-temperature logarithmic form of the Arrhenius equation and compare it with the equation for a straight line.

$$\underbrace{\ln k}_{y} = -\underbrace{\left(\frac{E_a}{R}\right)}_m \underbrace{\left(\frac{1}{T}\right)}_x + \underbrace{\ln A}_b$$

The value of the collision frequency factor, A , is very nearly constant over moderate temperature changes. Thus, $\ln A$ can be interpreted as the constant term in the equation (the intercept). The slope of the straight line obtained by plotting $\ln k$ versus $1/T$ can be interpreted as $-E_a/R$. This allows us to determine the value of the activation energy from the slope (Figure 12).

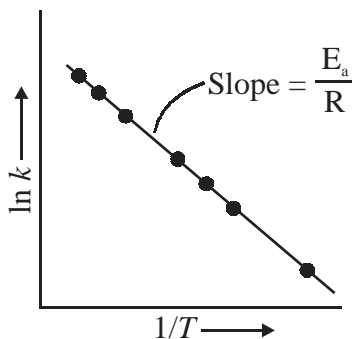


Figure 12: A graphical method for determining activation energy, E_a . At each of several different temperatures, the rate constant, k , is determined by methods such as those in Section 2. A plot of $\ln k$ versus $1/T$ gives a straight line with negative slope. The slope of this straight line is $-E_a/R$. Alternatively, a plot of $\log k$ versus $1/T$ gives a straight line whose slope is $-E_a/2.303 R$. Use of this graphical method is often desirable, because it partially compensates for experimental errors in individual k and T values.

Please attempt the following problem before seeing its solution:

- The chemical reaction $A \rightarrow B + C$ has a rate constant that obeys the Arrhenius equation. Predict what happens to both the rate constant k and the rate of the reaction if the following were to occur:
 - a. a decrease in temperature.
 - b. an increase in the activation energy of the forward and reverse reactions.
 - c. an increase in both activation energy and temperature.

Solution: The Arrhenius equation is $k = Ae^{-E_a/RT}$

- When the temperature is decreased, the rate constant, k , will also decrease. When k decreases, the rate also decreases.
- When the activation energy is increased, the rate constant, k , also decreases. When k decreases, the rate also decreases.
- Since the activation energy is in the numerator and the temperature is in the denominator, you cannot predict the effect without knowing the magnitude of the changes.

Catalysts

Catalysts are substances that can be added to reacting systems to increase the rate of reaction. They allow reactions to occur via alternative pathways that increase reaction rates by lowering activation energies. The catalyst causes unstable intermediates (called activated complexes) to appear as a new transition state which has a lower energy as compared to the transition state corresponding to activated complexes of the uncatalysed reactions. Since, the new transition state has lower energy, a much greater number of reacting species have the required energy to reach this new transition state. This increases the rate of the reaction. Once this transition state is attained, its decomposition leads to the formation of the products.

The activation energy is lowered in all catalysed reactions, as depicted in Figures 13 and 14. A catalyst does take part in the reaction, but all of it is regenerated in later steps. Thus a catalyst does not appear in the balanced equation for the reaction.

For constant T and the same concentrations,

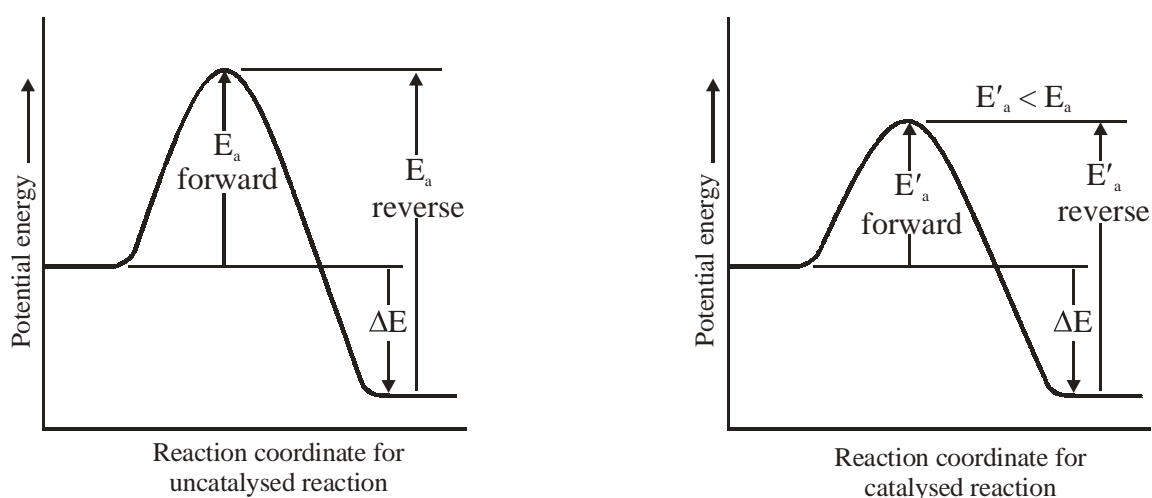
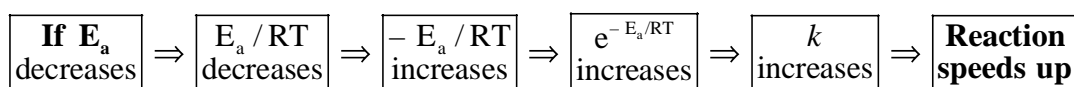


Figure 13: Potential energy diagrams showing the effect of a catalyst. The catalyst provides a different, lower-energy mechanism for the formation of the products. A catalysed reaction typically occurs in several steps, each with its own barrier, but the overall energy barrier is lower than the uncatalysed reaction. ΔE has the same value for each path. The value of ΔE depends only on the states of the reactants and products.

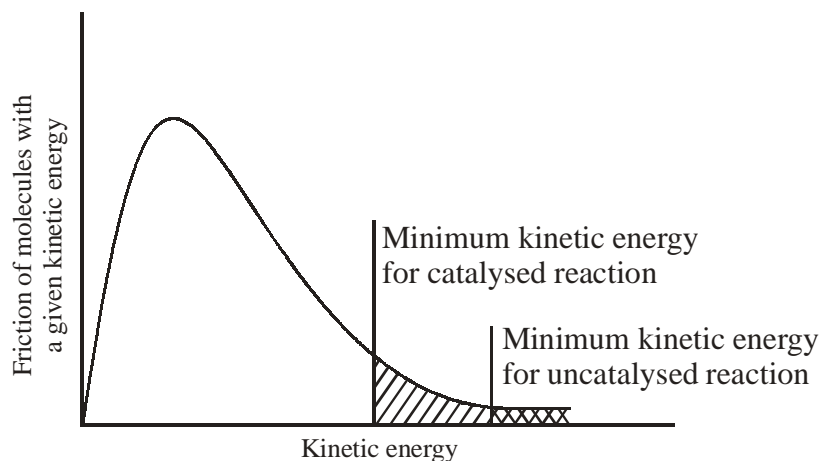
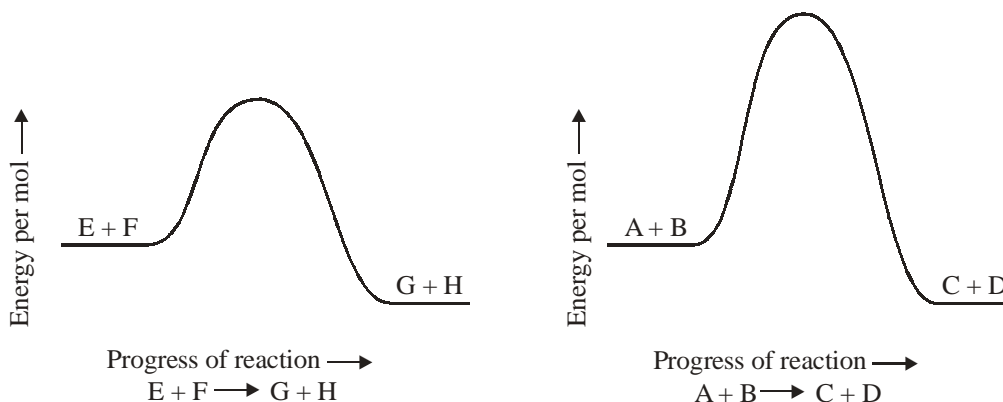


Figure 14: When a catalyst is present, the energy barrier is lowered. Thus, more molecules possess the minimum kinetic energy necessary for reaction. This is analogous to allowing more students to pass a course by lowering the requirements.

Please attempt the following problem before seeing its solution:

- Considering the potential energy curves for two different reactions:



- Which reaction has higher activation energy for the forward reaction?
- If both reactions were run at the same temperature and have the same orientation requirements to react, which one would have the larger rate constant?
- Are these reactions exothermic or endothermic?

Solution:

- Since the “hump” is larger, the $A + B$ reaction has a higher activation energy.
- Since the activation energy is lower, the $E + F$ reaction would have the larger rate constant. Keep in mind the inverse relationship between the activation energy, E_a , and the rate constant, k .
- Since in both cases energy per mole of the reactants is greater than the products, both reactions are exothermic.

Example – 15

The activation energy of a reaction is 75.24 kJ/mol in the absence of a catalyst, and 50.14 kJ/mol with a catalyst. How many times will the rate of the reaction grow in the presence of a catalyst if the reaction proceeds at 25° C?

Critical thinking

*When the reaction is catalysed, the rate constant of the reaction increases and E_a decreases. However A remains constant. We can use this information to calculate the **ratio** of rate constants between two alternative paths. This ratio shall give us the relative rates quite successfully.*

Solution: Let the activation energy of the reaction without a catalyst be E_a , and with one, E'_a , let k and k' be the respective rate constants of the reaction. Using the Arrhenius equation, we find:

$$\frac{k'}{k} = \frac{\exp(-E'_a/RT)}{\exp(-E_a/RT)} = \exp\left(\frac{E_a - E'_a}{RT}\right)$$

hence

$$\ln \frac{k'}{k} = 2.303 \log \frac{k'}{k} = \frac{E_a - E'_a}{RT}, \quad \text{and} \quad \log \frac{k'}{k} = \frac{E_a - E'_a}{2.303RT}$$

Introducing the data of the example into the last equation, expressing the activation energy in joules, and taking into account that

$T = 298$ K, we get:

$$\log \frac{k'}{k} = \frac{(75.24 - 50.14) \times 10^3}{2.30 \times 8.314 \times 298} = \frac{25.1 \times 10^3}{2.30 \times 8.314 \times 298} = 4.40$$

We finally obtain $k'/k = 2.5 \times 10^4$. Hence, a decrease in the activation energy by 25.1 kJ resulted in the reaction rate growing 25000 times.

Example – 16

From the following data for the reaction between A and B, calculate (i) the order of the reaction with respect to A and with respect to B, (ii) the rate constant at 300 K, (iii) the energy of activation, and (iv) the pre-exponential factor.

[A]/mol L ⁻¹	[B]/mol L ⁻¹	Initial rate/mol L ⁻¹ s ⁻¹ at	
		300 K	320 K
2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}	2.0×10^{-3}
5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}	–
1.0×10^{-3}	6.0×10^{-2}	1.6×10^{-2}	–

Critical thinking

Sub-questions (i) and (ii) are left for you as an exercise. The answers are provided for cross-checking.

In sub-question (iii), we cannot calculate E_a by the “one-temperature form” of the Arrhenius equation as we don't have A (called some times as pre-exponential factor). So, the other alternative is to see for the possibility of the two temperature form of Arrhenius equation to give us the solution. In such a case we would need **ratio** of the rate constants of the same reaction at two different temperatures. But so far in (i) and (ii) we have only got the value of rate constant at one particular temperature (300 K). So, what do we do? Please go back to Example – 12 and note that in cases where ratio of two quantities are involved we can substitute it with ratio of two other quantities which are directly proportional to the ratio of the first two quantities.

Here, we know that the rate of a reaction at a particular temperature is proportional to the rate constant at that particular temperature. Note also that the data given in table has two rates of reaction at two different temperatures for first choice of concentrations of A and B. Can you use this information to find your substitute for $\frac{k_1}{k_2}$?

Solution: The two temperature form of the Arrhenius equation is:

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \dots \text{(i)}$$

But, we know that,

$$(\text{rate})_2 = k_2 [A]^2 [B]^1 \quad \dots \text{(ii)}$$

and

$$(\text{rate})_1 = k_1 [A]^2 [B]^1 \quad \dots \text{(iii)}$$

Dividing (ii) by (iii) to get:

$$\frac{(\text{rate})_2}{(\text{rate})_1} = \frac{k_2 [A]^2 [B]^1}{k_1 [A]^2 [B]^1} \quad \dots \text{(iv)}$$

Hence, if we substitute A and B at the same instant, we get:

$$\frac{(\text{rate})_2}{(\text{rate})_1} = \frac{k_2}{k_1} \quad (\text{for the first choice of concentrations of A and B})$$

$$\Rightarrow \frac{k_2}{k_1} = \frac{2.0 \times 10^{-3}}{5.0 \times 10^{-4}} \quad \dots \text{(v)}$$

Substituting (v) in (i), we get,

$$\log\left(\frac{2.0 \times 10^{-3}}{5.0 \times 10^{-4}}\right) = \frac{E_a}{(2.303)(8.314 \text{ J/K/mol})\left(\frac{1}{300 \text{ K}} - \frac{1}{320 \text{ K}}\right)}$$

$$\Rightarrow E_a = \frac{(2.303)(8.314)(300)(320) \log 4}{(320 - 300)}$$

$$= 5.53 \times 10^4 \text{ J/mol}$$

$$= 55.33 \text{ kJ/mol.}$$

(iv) To calculate the pre-exponential factor A, it is easier if we take logarithm of the Arrhenius equation. Hence,

$$\log A = \log k + \frac{E_a}{2.303RT} \quad \dots (A)$$

Here, $k = 2.67 \times 10^8$ (at 300 K) (You should have calculated it in sub-question (ii) above)

$$E_a = 5.53 \times 10^4 \text{ J/mol}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T = 300 \text{ K}$$

Substituting these values in (A) we get

$$\log A = \log(2.67 \times 10^8) + \frac{5.53 \times 10^4 \text{ J mol}^{-1}}{(2.303)(8.314 \text{ J/K/mol})(300 \text{ K})}$$

$$\Rightarrow \log A = 8.43 + 9.63 = 18.06$$

$$\Rightarrow A = 1.145 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}.$$

Answer (i) order w.r.t. A = 2 order w.r.t. B = 1

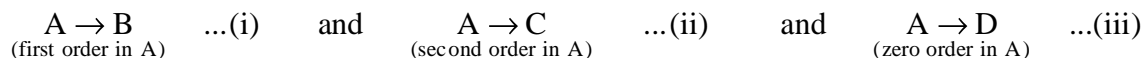
Answer (ii) $k = 2.67 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$.

Example – 17

A first-order reaction, $A \rightarrow B$, requires activation energy of 70 kJ mol^{-1} . When a 20% solution of A was kept at 25°C for 20 minutes, 25% decomposition took place. What will be percent decomposition in the same time in a 30% solution maintained at 40°C ? Assume that activation energy remains constant in this range of temperature.

Critical thinking

First of all we need to understand an important characteristic of first order reactions. Consider the reactions:



We have seen that the integrated rate equation for the reaction (i), (ii) and (iii) are:

$$\ln \frac{[A]_0}{[A]_t} = akt \quad \text{(first order)} \quad \dots \text{(iv)}$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = akt \quad \text{(second order)} \quad \dots \text{(v)}$$

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

Suppose we have two initial concentrations for A, say, 2M and 5M respectively. And we want to know the time after which a certain percentage of the reactants have reacted (say, 25%). Then in the first order case, we will see:

$$\ln \frac{2M}{1.5M} = akt \quad \text{and} \quad \ln \frac{5M}{3.75M} = akt$$

(1.5 M and 3.75M is what is left after 25% decomposition in the respective cases)

$$\Rightarrow \ln 1.33 = akt \quad \text{and} \quad \ln 1.33 = akt$$

$$\Rightarrow t = \frac{\ln(1.33)}{ak} \quad \text{and} \quad t = \frac{\ln(1.33)}{ak}$$

We see that, in both the cases, the time required is same and observing closely we can realise, that the extent of reaction in a first order reaction is independent of the initial concentration.

You may use the same two concentrations in second order and zero order case to see that the extent of reaction is dependent upon the initial concentration.

Zero order case is shown:

$$2M - 1.5M = akt \quad \text{and} \quad 5M - 3.75M = akt$$

$$\Rightarrow t = \frac{0.5M}{ak} \quad \text{and} \quad t = \frac{1.25M}{ak}$$

Since, the time required for 25% decomposition is different in both the cases, we can see that the extent of reaction in the same time period is different too and is dependent upon the initial concentration in this case.

Solution: We know that the fraction of reactants reacted in a first order reaction is independent of initial concentration. So, we need not worry about the terms 20% solution and 30% solution.

Now, it is given that 25% of A is decomposed in 20 minutes at 25° C. And we need to find the percent decomposition in the same time at 40° C for the same reaction.

Quite obviously, the rate constants of this reaction at two temperatures are different. We can also see that the rate constant for the first reaction can be calculated using the integrated rate equation and then this can be used in the “two-temperature” form to get the rate constant of the reaction at 40°C. This rate constant at 40°C can then be used in the integrated rate equation to obtain the required data.

We illustrate the above methodology we have planned over here:

We know that,

$$\log \frac{[A]_0}{[A]_t} = \frac{akt}{2.303} \dots(\text{vii})$$

Here, at 25°C,

$$a = 1$$

$$k_1 = ?$$

$$t = 20 \text{ min.}$$

$$\frac{[A]_0}{[A]_t} = \frac{100}{75} \quad (\text{as 25\% decomposition has taken place})$$

Substituting these values in (vii), we get,

$$\log \frac{100}{75} = \frac{1 \cdot k_1 \cdot (20 \text{ min})}{2.303}$$

$$\Rightarrow k_1 = 1.44 \times 10^{-2} \text{ min}^{-1}$$

Now, letting k_2 be the rate constant of this reaction at 40°C, we can use the two temperature form of Arrhenius equation as:

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\Rightarrow \log \frac{k_2}{(1.44 \times 10^{-2})} = \frac{70 \times 10^3 \text{ J/mol}}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \left(\frac{1}{298 \text{ K}} - \frac{1}{313 \text{ K}} \right)$$

Solving for k_2 , we will get,

$$k_2 = 5.56 \times 10^{-2} \text{ min}^{-1}$$

Finally,

$$\log \frac{[A]_t}{[A]_0} = - \left(\frac{k_2}{2.303} \right) t$$

$$= - \left(\frac{5.56 \times 10^{-2} \text{ min}^{-1}}{2.303} \right) (20 \text{ min})$$

$$\Rightarrow \frac{[A]_t}{[A]_0} = 0.33 = \frac{33}{100}$$

This remains 20 min. because we have been asked to find the percentage decomposition at 40°C in the same time interval as the first reaction (at 25°C) during which 25% decomposition took place.

i.e.,

percentage of A remaining at ($t = 20 \text{ min}$) = 33%

percentage of A reacted till ($t = 20 \text{ min}$) = $(100 - 33) = 67\%$

TRY YOURSELF - III

- Q. 1** For a first-order reaction
- the degree of dissociation is equal to $(1 - e^{-kt})$
 - a plot of reciprocal concentration of the reactant versus time gives a straight line
 - the time taken for the completion of 75% reaction is thrice that of $t_{1/2}$ of the reaction
 - the pre-exponential factor in the Arrhenius equation has the dimension of time T^{-1}
- Q. 2** In the Arrhenius equation, $k = A \exp(-E_a/RT)$, A may be termed as the rate constant at..... .
- Q. 3** A catalyst is a substance which
- increases the equilibrium concentration of the product
 - changes the equilibrium constant of the reaction
 - shortens the time to reach equilibrium
 - supplies energy to the reaction
- Q. 4** A catalyst
- increases the average kinetic energy of reacting molecules
 - decrease the activation energy
 - alters the reaction mechanism
 - increases the frequency of collisions of reacting species
- Q. 5** For an endothermic reaction where ΔH represents the enthalpy of the reaction, the minimum value for the energy of activation will be
- | | |
|--------------------------|-------------------------|
| (a) less than ΔH | (b) zero |
| (c) more than ΔH | (d) equal to ΔH |
- TRUE or FALSE (Q. 6 - Q. 8)**
- Q. 6** Catalyst makes a reaction more exothermic.
- Q. 7** Catalyst does not affect the energy of activation in a chemical reaction.
- Q. 8** The rate of an exothermic reaction increases with increasing temperature.
- Q. 9** In the Arrhenius equation for a certain reaction, the value of A and E_a (activation energy) are $4 \times 10^{13} \text{ s}^{-1}$ and 98.6 kJ mol^{-1} , respectively. If the reaction is of first-order, at what temperature will its half-life period be ten minutes?
- Q. 10** A first-order reaction is 50 percent completed in 30 min at 27° C and in 10 min at 47° C . Calculate the reaction rate constant at 27° C and the energy of activation of the reaction.
- Q. 11** The trans \rightarrow cis isomerisation of 1, 2-dichloroethylene proceeds with $E_a = 231 \text{ kJ/mol}$ and $\Delta H = 4.2 \text{ kJ/mol}$. What is E_a for the cis \rightarrow trans isomerisation?

- Q. 12** Will the value of the rate constant of a reaction change (a) when one catalyst is replaced with another one, and (b) when the concentrations of the reactants and products are changed?
- Q. 13** Does the heat effect of a reaction depend on its activation energy? Substantiate your answer.
- Q. 14** For which reaction—the forward or the reverse one—is the activation energy greater if the forward reaction proceeds with the liberation of heat?
- Q. 15** How many times will the rate of a reaction proceeding at 298 K grow if its activation energy is lowered by 4 kJ/mol?
- Q. 16** What is the activation energy of a reaction if its rate doubles when the temperature is raised from 290 K to 300 K?
- Q. 17** What is the value of the activation energy for a reaction whose rate at 300 K is ten times greater than at 280 K?
- Q. 18** Which of the following procedures will lead to a change in the rate constant of a reaction? (a) A change in the pressure; (b) a change in the temperature; (c) a change in the volume of the reaction vessel; (d) the introduction of a catalyst into the system; (e) a change in the concentration of the reactants and products.
- Q. 19** The increase in a reaction rate with temperature is due chiefly to: (a) an increase in the average kinetic energy of the molecules; (b) a growth in the number of active molecules; (c) a growth in the number of collisions.
- Q. 20** The first-order gaseous decomposition of N_2O_4 into NO_2 has a k value of $4.5 \times 10^3 \text{ s}^{-1}$ at 1°C and an energy of activation of 58 kJ mol^{-1} . At what temperature its half-life would be $6.93 \times 10^{-5} \text{ s}$?