ACTIVATION ENERGY (E_a) Section - 4

A mixture of magnesium and oxygen does not react at room temperature. But if a burning splinter is introduced to the mixture, it burns vigorously. Similarly a mixture of methane and oxygen does not react at room temperature, but if a burning match-stick is put in the mixture, it burns rapidly. *Why it happen like this, that some external agents has to be introduced in order to initiate the reaction* ?

According to the theory of reaction rates "*for a chemical reaction to take place, reactant molecules must make collisions among themselves*". Now in actual, only a fraction of collisions are responsible for the formation of products, i.e., not all collisions are *effective* enough to give products. So the collisions among reactant molecules are divided into two categories :

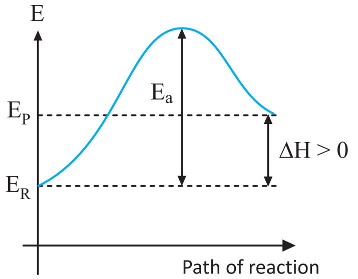
Effective collisions and *In-effective collisions*

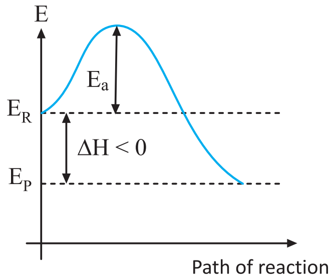
Effective collisions are collisions between the molecules which have energies equal to or above a certain minimum value. This minimum energy which must be possessed by the molecules in order to make an effective collision (i.e., to give a molecule of products) is called as *threshold energy*. So it is the effective collisions which bring about the occurrence of a chemical reaction.

Ineffective collisions are the collisions between the molecules which does not posses the *threshold energy*. These can not result in a chemical reaction.

Now most of the times, the molecules of reactants do not possess the threshold energy. So in order to make effective collisions (i.e., to bring about the chemical reaction), an additional energy is needed to be absorbed by the reactant molecules. This additional energy which is absorbed by the molecules so that they achieve the threshold energy is called as *energy of activation* or simply *activation energy*. It is represented as E_a.

Note :
- The progress of the reaction can studied in a graph with energy of the reacting system. You can find ΔH and E_a from graph below.
- All the colliding molecules must collide at a proper orientation for a collision to be effective, other than "sufficient energy" factor. A reaction having more number of reactants (high molecularity) is expected to be slower because it is less probable that all the reactant molecules, with energy greater than activation energy collide simultaneously at proper orientation.





A reaction which needs higher activation energy is slow at a given temperature.

For example : $NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g)$ is faster at ordinary temperature whereas the following reaction :

$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$ is slower at the same temperature as the value of E_a for the second reaction is much higher.

Arrhenius Equation :

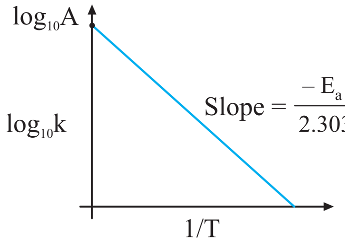
Arrhenius proposed the following equation for the determination of activation energy (E_a) at a given temperature T.

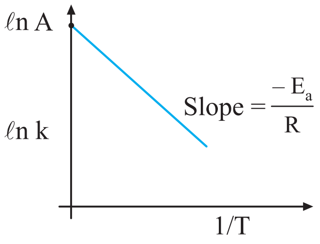
$$k \propto e^{-E_a/RT} \quad \Rightarrow \quad k = A\,e^{-E_a/RT}$$

where E_a = activation energy, A = frequency factor and k = rate constant

Simplifying the equation :

$$\log_{10} k = \frac{-E_a}{2.303\,RT} + \log_{10} A$$

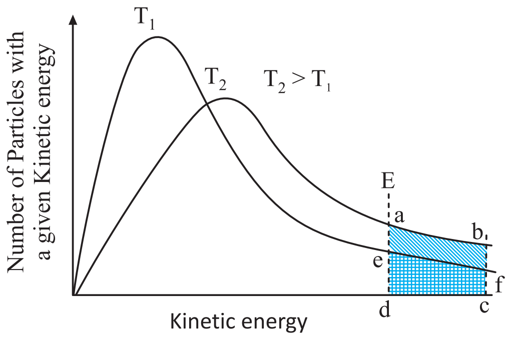




Now a plot of $\log_{10}k$ or ℓn k vs 1/T will be a straight line whose equation is given above. If k_1 is the value of the rate constant at T_1 K and k_2 is the value of rate constant at T_2 K for a reaction whose energy of activation is E_a, then

$$\left.\begin{aligned} k_1 &= A\,e^{-Ea/RT_1} \\ \text{and}\quad k_2 &= A\,e^{-Ea/RT_2} \end{aligned}\right\} \text{Divide and take } \log_e \text{ on both sides to get : } \log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

This equation is called as *Integrated Arrhenius equation*. This equation is very useful in determining the value of E_a of a reaction by knowing the values of k_1 and k_2 at different temperatures T_1 and T_2.



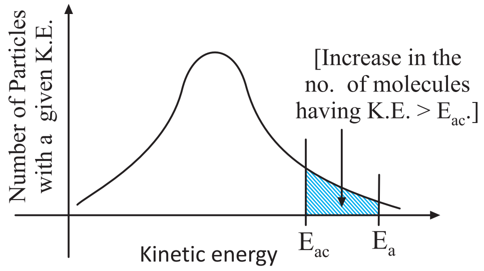
Note : ➤ For most of the reactions, a 10° C rise near the room temperature, the rate constant is almost doubled i.e. $\frac{k_{35°C}}{k_{25°C}} \approx 2$.

This can be explained by the fact that the number of molecules possessing energy greater than the *threshold energy* increases tremendously as shown by the shaded area (a–b–f–e–a) in the figure.

- The fraction of molecules having internal energy greater than or equal to E_a is equal to $e^{-E_a/RT}$. This shows that as temperature increases, the number of molecules crossing this energy barrier increases tremendously, accounting for the increase in the rate constant.

- Rate constant 'k' can also be increased by reducing 'E_a' to 'E_{ac}' through the addition of a catalyst in the system.

$$k_1 = Ae^{-E_a/RT} \text{ and } k_2 = Ae^{-E_{ac}/RT}$$



$$\Rightarrow \qquad \log_{10}\frac{k_2}{k_1} = \frac{E_a - E_{ac}}{2.303RT}$$

Note : $$\log_{10}\frac{(k_2)_f}{(k_1)_f} = \frac{(E_a)_f - (E_{ac})_f}{2.303RT} \quad \ldots.\text{(i)} \qquad \text{and} \qquad \log_{10}\frac{(k_2)_b}{(k_1)_b} = \frac{(E_a)_b - (E_{ac})_b}{2.303RT} \quad \ldots.\text{(ii)}$$

$$\log_{10}\frac{(k_2)_f}{(k_1)_f} = \frac{(E_a)_f}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \ldots.\text{(iii)} \qquad \log_{10}\frac{(k_2)_b}{(k_1)_b} = \frac{(E_a)_b}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \ldots.\text{(iv)}$$

where $(E_a)_f$ and $(E_a)_b$ are the activation energies of the reaction in forward and backward reaction, and $(E_{ac})_f$ and $(E_{ac})_b$ are the activation energies of catalysed reaction in forward and backword reaction.

Illustration - 6 *The activation energy of the reaction : A + B* $\longrightarrow$ *products is* 105.73 *kJ/mol. At* 40°C, *the products are formed at the rate of* 0.133 *mol/L/min. What will be rate of formation of products at* 80°C ?

SOLUTION :

Let the rate law be defined as

At T_1 : $r_1 = k_1[A]^x[B]^y$

At T_2 : $r_2 = k_2[A]^x[B]^y$

$$\Rightarrow \qquad r_2 = r_1\left(\frac{k_2}{k_1}\right)$$

Using Arrhenius equation, find k at 40°C.

$$\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left(\frac{T_2 - T_1}{T_1\,T_2}\right)$$

$$\Rightarrow \qquad \log_{10}\frac{k_2}{k_1} = \frac{105.73\times10^3}{2.303\times8.31}\left(\frac{40}{313\times353}\right)$$

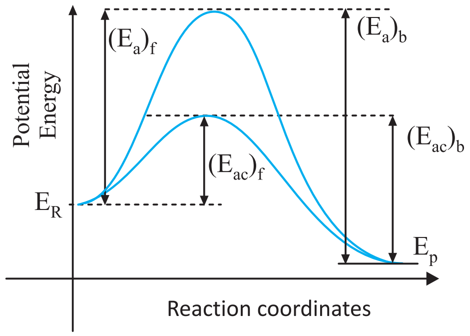
$$\Rightarrow \qquad \log_{10}\frac{k_2}{k_1} = 2.0$$

$$\Rightarrow \qquad \frac{k_2}{k_1} = 100$$

$$\Rightarrow \qquad r_2 = 0.133\times100 = 13.3 \text{ mol/L/min}$$

Illustration - 7 *The activation energy of a non-catalysed reaction at 37°C is 200 kcal/mol and the activation energy of the same reaction when catalysed decreases to only 60.0 kcal/mol. Calculate the ratio of rate constant of the two reactions.*

SOLUTION :



$$\Rightarrow \log_{10}\frac{k_c}{k} = \frac{1}{2.303\,R\,T}(E_a - E_{ac})$$

$$\Rightarrow \log_{10}\frac{k_c}{k} = \frac{1}{2.303\times2\times310}(200\times10^3 - 60\times10^3)$$

$$\Rightarrow \log_{10}\frac{k_c}{k} = 98.0 \qquad \Rightarrow \qquad \frac{k_c}{k} = 10^{98}$$

Note : Decrease in the activation energy in forward and backward direction by the addition of catalyst is same. i.e. $(E_a)_f - (E_{ac})_f = (E_a)_b - (E_{ac})_b$ .Thus rate constant in forward and backward directions increases by same factor. Since, for a reaction $A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B : K_{eq} = \frac{k_f}{k_b}$, adding catalyst will not alter K_{eq} of the reaction.

IN-CHAPTER EXERCISE - B

1. *Radioactive decay is first order reaction. Radioactive carbon in a wood sample decays with a half life of 5770 yrs. What fraction would remain after 11540 yrs ?*

2. *The half-life of a radioactive isotope is 3.0 hrs. What mass of it remains undecayed in 15 hours if the initial mass of the isotope was 100 gm ?*

3. *For a particular first order reaction, the time for half reaction is 5×10^3 sec at 27°C and 1×10^3 sec at 37°C. Find the energy of activation of the reaction.*

4. *Show that for a first order reaction, the time required to complete 99.9 % of the reaction is 10 times that required for the half of the reaction.*

5. *A first order reaction is 40% complete after 8 minutes. How long will it be before it is 90% complete ? Also find the value of rate constant.*

6. *The energy of activation of a first order reaction is 187.06 kJ/mol at 750 K and the value of pre-exponential factor A is $1.97 \times 10^{12}\ s^{-1}$. Calculate the rate constant and the half life. [Use $e^{-30} = 9.35 \times 10^{-14}$]*

7. *If temperature of a reaction is increased from 27°C to 37°C, find by what factor the rate of reaction increases, if energy of activation E_a is :*

(a) 12.85 *kcal* mol^{-1} **(b)** 17.13 *kcal* mol^{-1}

8. *A first order reaction is 20% complete in 10 min. Calculate*

(a) *specific reaction rate* **(b)** *time taken for the reaction to go to 75%*

Choose the correct option. Only one choice is correct.

9. *Graph between* $\log_{10} k$ *and* $\left(\frac{1}{T}\right)$ *is linear of slope S (magnitude) Hence* E_a *is :*

(A) $R \times S$ **(B)** S / R **(C)** R / S **(D)** $2.303\,RS$

10. *The activation energy for a simple chemical reaction* $A \longrightarrow B$ *is* E_a *in forward direction. The activation energy for reverse reaction :*

(A) *can be less than or more than* E_a

(B) *is always double of* E_a

(C) *is negative of* E_a

(D) *is always less than* E_a

11. *A particular reaction increases by a factor of* 2 *when the temperature is increased from* 27°C *to* 37°C. *Hence activation energy of the reaction is :*

(A) $12.9\ kcal\ mol^{-1}$ **(B)** $0.14\ kcal\ mol^{-1}$

(C) $1.1\ kcal\ mol^{-1}$ **(D)** *None of these*

12. *If in the fermentation of sugar in an enzymatic solution that is* $0.12\ M$, *the concentration of the sugar is reduced to* $0.06\ M$ *in* $10\ Hr$ *and to* $0.03\ M$ *in* $20\ Hr$. *What is the order of the reaction ?*

(A) 1 **(B)** 2 **(C)** 3 **(D)** 0

13. *Reaction rates are determined by all of the following factors except :*

(A) *the number of collisions between molecules*

(B) *the force of collisions between molecules*

(C) *the orientation of collisions between molecules*

(D) *the spontaneity of the reaction*

14. *The plot of* $\ln \frac{C_0}{C_0 - x}$ *against t is a straight line, showing the reaction to be a :*

(A) *zero-order reaction*

(B) *first-order reaction*

(C) *second-order reaction*

(D) *half-order reaction*

15. *For a first-order reaction, the units of Arrhenius Factor (A) will be :*

(A) $JK^{-1}s^{-1}$ **(B)** s^{-1} **(C)** $mol\ L^{-1}s^{-1}$ **(D)** $JK^{-1}\ L^{-1}\ s^{-1}$

16. *The half-life periods of a reaction at initial concentrations* $0.1\ mol\ L^{-1}$ *and* $0.5\ mol\ L^{-1}$ *are* 200s *and* 40s *respectively. The order of the reaction is :*

(A) 1 **(B)** 1/2 **(C)** 2 **(D)** 0

17. *Rate constant k of a reaction is dependent on temperature :* $k = Ae^{-E_a/RT}$

k has the least value at :

(A) *high T and high* E_a **(B)** *high T and small* E_a

(C) *low T and low* E_a **(D)** *low T and high* E_a

18. *The reaction* $A \longrightarrow B$ *follows first order kinetics. The times taken for* 0.8 *mol of A to produce* 0.6 *mol of B is* 1 *hour. What is the time taken for conversion of* 0.9 *mol of A to produce* 0.675 *mol of B ?*

(A) 0.25 *hour* **(B)** 2 *hours* **(C)** 1 *hour* **(D)** 0.5 *hour*

FACTORS AFFECTING RATE OF REACTIONS Section - 5

Factors Affecting Rate of Reactions :

The rate of reaction depends upon following factors :

1. **Concentration :**

   In general the rate of a reaction is directly proportional to the concentration of reactants, i.e., the rate increases as the concentration of reactant(s) increases. For gaseous reaction, rate is proportional to the *partial pressures* of reactant(s).

2. **Nature of Reactants :**

   - The rate of reactions in which complex molecules are taking part is slower than those in which simple molecules take part. A chemical reaction involves the rearrangement of atoms (i.e., breaking and reforming of bonds), hence the rearrangement of molecules involving many bonds is rather slow process and consequently the rate of a reaction is slower.
   - Physical state of reactants also play key role in determining reaction rates. The greater is the surface area of a solid surface, the faster is the rate of reaction involving solid molecules. For example, the burning of wood is slower than the burning of a pulverized wood (due to increased surface area).

3. **Effect of Catalyst :**

   The catalyst in general enhances the rate of reactions without actually taking part in the reaction. The catalyst is used up during the reaction but at the end of reaction it is recovered as such. The phenomenon of increase in the rate of a reaction with the help of a catalyst is known as *catalysis*. Catalysts generally lower the activation energy which enables more reacting molecules to cross the energy barrier and hence increased rate of reaction.

4. **Effect of Temperature :**

   The rate of a reaction increases by increasing the temperature. It is quite clear from Arrhenius equation $\left(k = A\,e^{-E_a/RT}\right)$, that for small rise in temperature rate of reaction increases tremendously (increases exponential). In fact it is one of most significant factors that affects the rate most strongly. *A 10°C rise in temperature, for most of the reactions, doubles the rate of reaction.* On increasing the temperature, the number of molecules possessing activation energy increases (i.e, effective collisions) by a large quantity, as compared to the total increase in molecular collisions.