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Physical Chemistry/ Theories of Chemical Reactions   المرحلة الثالثة

Theories of Chemical Reactions

The main questions that were raised in the course of the development of the theory of chemical reactions were as follows:

1) Why don't all chemical reactions proceed if they are thermo-dynamically possible?
2) Why does the reaction speed increase along the exponent with the increase of temperature?
3) Why is it that in reactions proceeding with bond breaking, the activation (additional) energy is usually much smaller than that necessary to break the bond thermally?

Indeed, why is it that reactions proceed with the breaking of the chemical bond in normal conditions, while we need a temperature of more than 4,000° C to break such bonds thermally? Examples of such reactions are interactions of radicals and ions with molecules, catalytic and photochemical reactions.

Collision Theory of Reaction Rates

According to this theory, **a chemical reaction takes place only by collisions between the reacting molecules.** But not all collisions are effective.

Only a small fraction of the collisions produce a reaction.

The two main conditions for a collision between the reacting molecules to be productive are :

1. The colliding molecules must posses sufficient kinetic energy to cause a reaction.

2. The reacting molecules must collide with proper orientation.

Postulates of the Collision Theory

(1) **The molecules must collide with sufficient kinetic energy**

Let us consider a reaction

$$A-A + B-B \longrightarrow 2A-B$$

A chemical reaction occurs by breaking bonds between the atoms of the reacting molecules and forming new bonds in the product molecules.

The **energy** for the breaking of bonds comes from the **kinetic energy** possessed by the reacting molecules before the collision. **Fig. 1** shows the energy of molecules A_2 and B_2 as the reaction $A_2 + B_2 \rightarrow 2AB$ progresses.
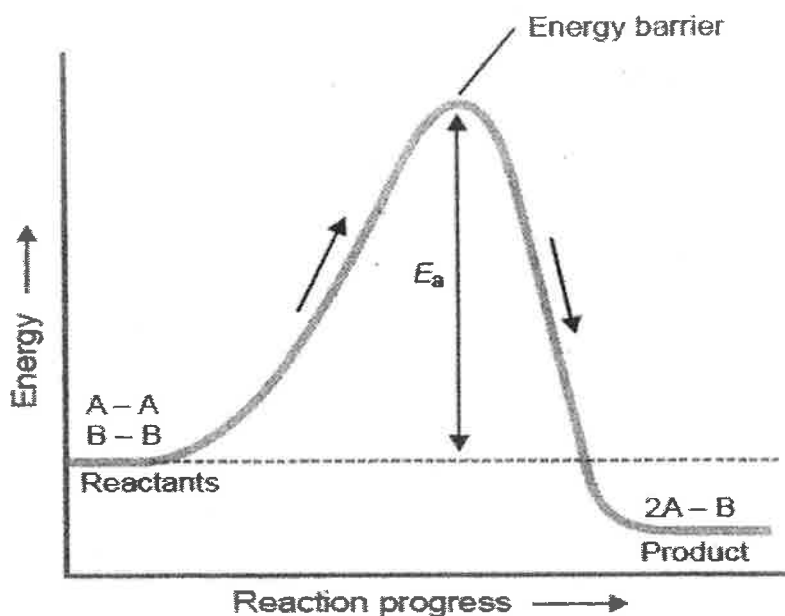
Figure 1

The energy of the collision

Activation Energy

Even if the species are orientated properly, you still won't get a reaction unless the particles collide with a certain minimum energy called the *activation energy* of the reaction.

Activation energy is the minimum energy required before a reaction can occur. You can show this on an *energy profile* for the reaction. For a simple over-all exothermic reaction, the energy profile looks like this:
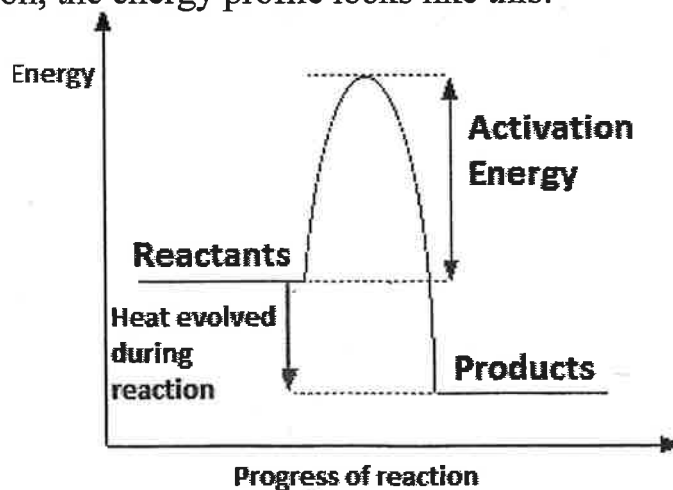
If the particles collide with less energy than the activation energy, nothing important happens. They bounce apart. You can think of the activation energy as a barrier to the reaction. Only those collisions which have energies equal to or greater than the activation energy result in a reaction.

Any chemical reaction results in the breaking of some bonds (needing energy) and the making of new ones (releasing energy). Obviously some bonds have to

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be broken before new ones can be made. **Activation energy** is involved in **breaking** some of the original bonds.

Where collisions are relatively gentle, there isn't enough energy available to start the bond-breaking process, and so the particles don't react.

The Maxwell-Boltzmann Distribution

Because of the key role of activation energy in deciding whether a collision will result in a reaction, it would obviously be useful to know what sort of proportion of the particles present have high enough energies to react when they collide.
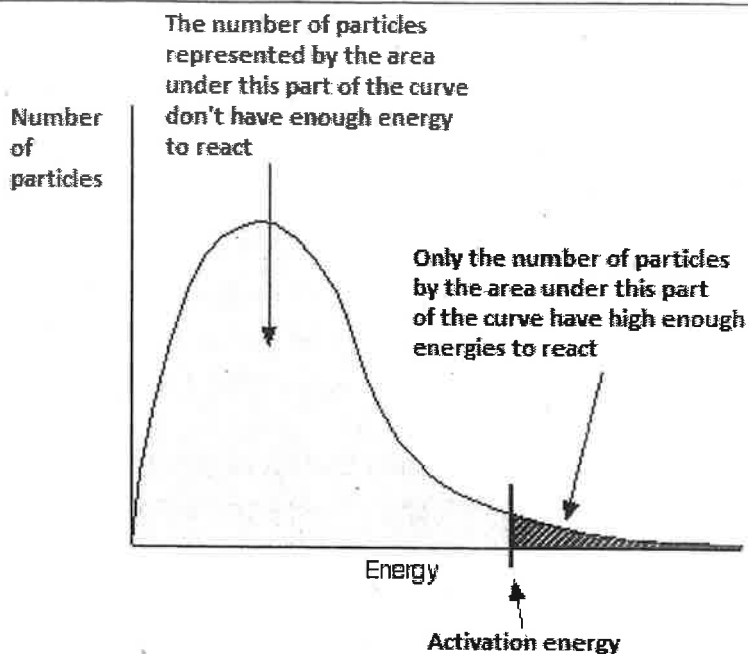
In any system, the particles present will have a very wide range of energies. For *gases*, this can be shown on a graph called the Maxwell-Boltzmann Distribution which is a plot of the number of particles having each particular energy.
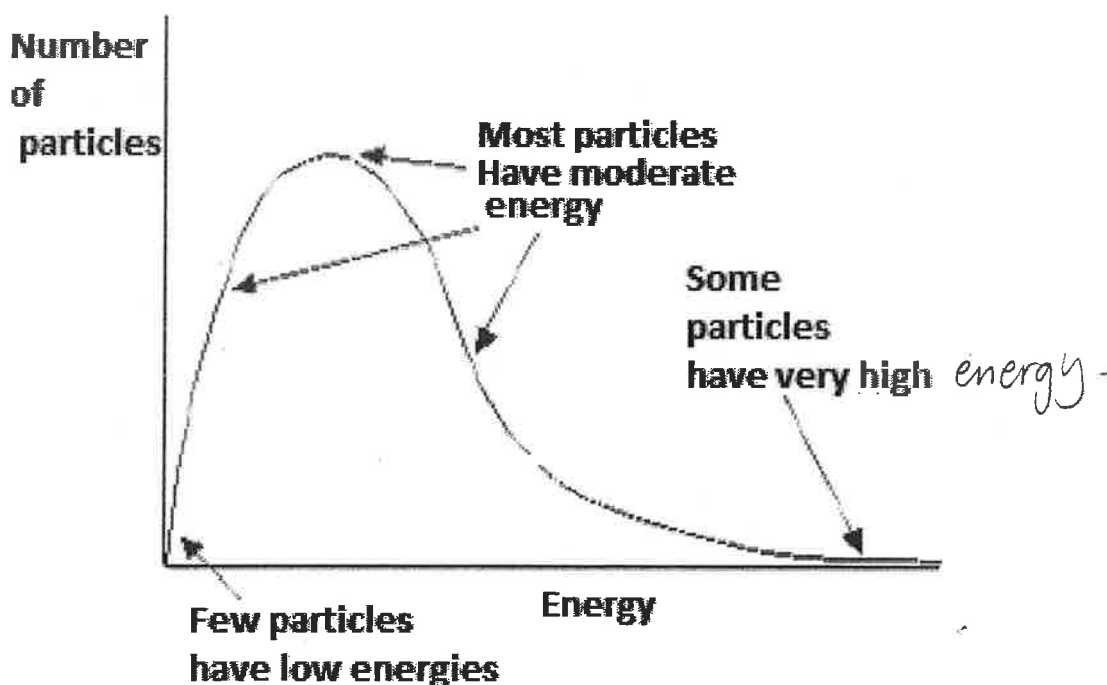
The area under the curve is a measure of the total number of particles present.

The Maxwell-Boltzmann Distribution and activation energy

Remember that for a reaction to happen, particles must collide with energies equal to or greater than the activation energy for the reaction. We can mark the activation energy on the Maxwell-Boltzmann distribution:

Number of particles

The number of particles represented by the area under this part of the curve don't have enough energy to react

Only the number of particles by the area under this part of the curve have high enough energies to react

Energy

Activation energy

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Notice that the large majority of the particles don't have enough energy to react when they collide. To enable them to react we either have to **change the shape of the curve**, or **move the activation energy further to the left**. This is described on other pages.

(2) The molecules must collide with correct orientation

The reactant molecules must collide with favourable orientation (relative position). **The correct orientation is that which ensure direct contact between the atoms involved in the breaking and forming of bonds.**

From the above discussion it is clear that : **Only the molecules colliding with kinetic energy greater that E_a and with correct orientation can cause reaction.**
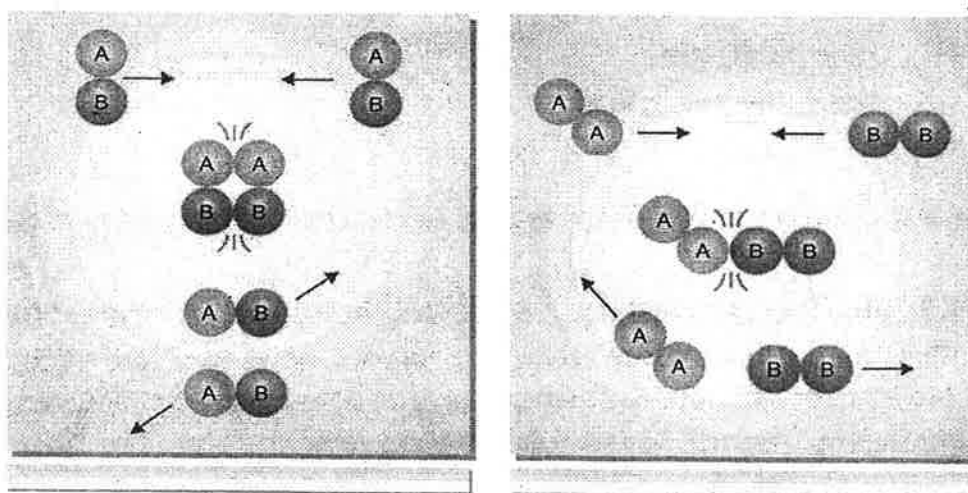
Orientations of reacting molecules A2 and B2 which lead to an effective and ineffective collision.

Collision Theory and Reaction Rate Expression

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Taking into account the two postulates of the collision theory, the reaction rate for the elementary process.
is given by the expression

$$A + B \longrightarrow C + D$$

$$\text{rate} = f \times p \times z$$

where
f = fraction of molecules which possess sufficient energy to react;
p = probable fraction of collisions with effective orientations, and
z = collision frequency.

Effect of Increase of Temperature on Reaction Rate
It has been found that generally an increase of temperature increases the rate of reaction. As a rule, an **increase** of temperature by **10°C doubles** the reaction rate. Thus the ratio of rate constants of a reaction at two different temperatures differing by 10 degree is known as

Temperature Coefficient.

$$\textit{i.e., Temperature Coefficient} \quad = \frac{k_{35°}}{k_{25°}} = \frac{k_{308}}{k_{298}}$$

$$= 2 \text{ to } 3$$

It has been found that **generally an increase of temperature increases the rate of reaction.** As a rule, an increase of temperature by 10°C doubles the reaction rate.

Temperature Dependence of Reaction Rate and Arrhenius Equation
We know that the kinetic energy of a gas is directly proportional to its temperature. Thus as the temperature of a system is increased, more and more molecules will acquire necessary energy greater that E_a to cause productive collisions. This increases the rate of the reaction.
In 1889, Arrhenius suggested as simple relationship between the rate constant, k, for a reaction and the temperature of the system.

$$k = A \, e^{-Ea/RT}$$

This is called the **Arrhenius equation** in which A is an experimentally determined quantity, E_a is the activation energy, R is the gas constant, and T is Kelvin temperature.

$$\ln k = -\frac{E_a}{RT} + \ln A$$

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

Taking natural logs of each side of the Arrhenius equation, it can be put in a more useful form

If k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively, we can derive

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Arrhenius equation is **valuable** because it can be used to **calculate** the activation energy, E_a if the experimental value of the rate constant, k, is known.

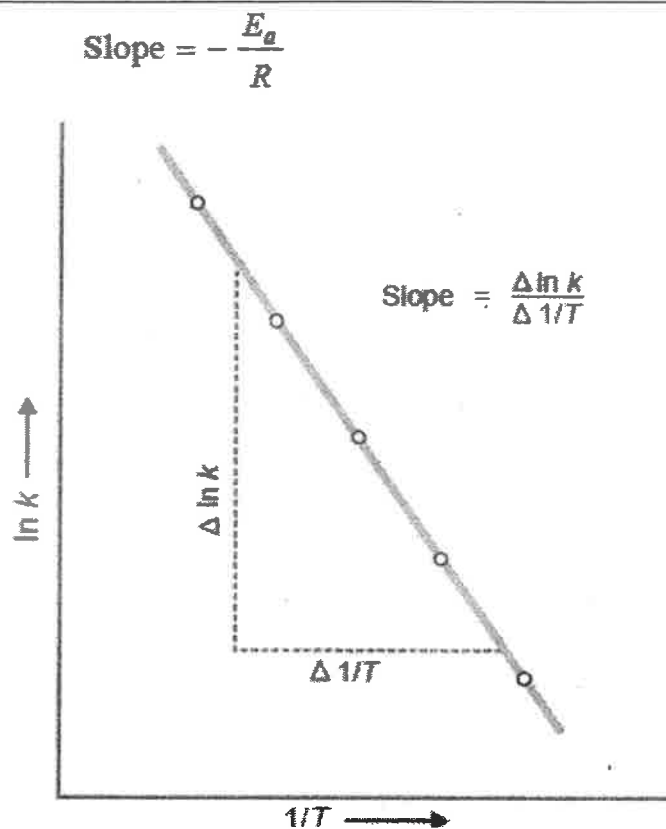## Calculation of E_a Using Arrhenius Equation

In slightly rearranged form Arrhenius equation (2) can be written as

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

$$\uparrow \qquad\qquad \uparrow \qquad\qquad \uparrow$$

$$y \quad = \quad mx \quad + \quad b$$

You can see that the equation (3) is that of a straight line, $y = mx + b$. The two variables in this equation are $\ln k$ and $1/T$.

Thus if we plot the natural logarithm of k against $1/T$, we get a straight line (Fig. 20.11). From the slope of the line, we can calculate the value of E_a.

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$$\text{Slope} = -\frac{E_a}{R}$$

$$\text{Slope} = \frac{\Delta \ln k}{\Delta 1/T}$$

The plot of In k versus I/T gives a straight line. The slope of line Δ In k /Δ I/T gives Ea using the expression given above.

The Effect of Temperature on Reaction Rates

The explanation
Increasing the collision frequency

Particles can only react when they collide. If you heat a substance, the particles move faster and so collide more frequently. That will speed up the rate of reaction.

That seems a fairly straightforward explanation until you look at the numbers! It turns out that the frequency of two-particle collisions in gases is proportional to the square root of the kelvin temperature. If you increase the temperature from 293 K to 303 K (20°C to 30°C), you will increase the collision frequency by a factor of:
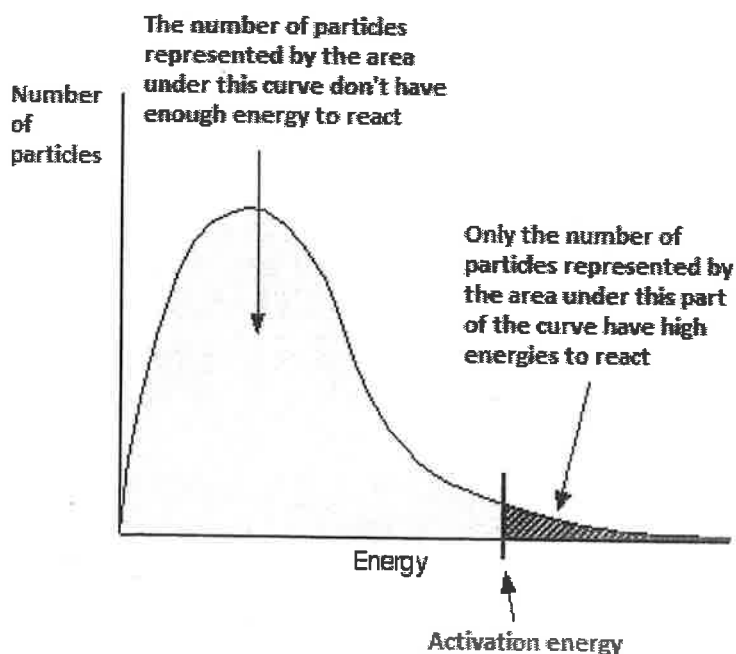
$$\sqrt{\frac{303}{293}} = 1.017$$

That's an increase of 1.7% for a 10° rise. The rate of reaction will probably have doubled for that increase in temperature - in other words, an increase of about 100%. The effect of increasing collision frequency on the rate of the reaction is *very* minor. The important effect is quite different . . .

The key importance of activation energy

Collisions only result in a reaction if the particles collide with enough energy to get the reaction started. This minimum energy required is called the activation energy for the reaction.

You can mark the position of activation energy on a Maxwell-Boltzmann distribution to get a diagram like this:

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Only those particles represented by the area to the right of the activation energy will react when they collide. The great majority don't have enough energy, and will simply bounce apart.

To speed up the reaction, you need to increase the number of the very energetic particles - those with energies equal to or greater than the activation energy. Increasing the temperature has exactly that effect - it changes the shape of the graph.

In the next diagram, the graph labelled **T** is at the original temperature. The graph labelled **T+t** is at a higher temperature.
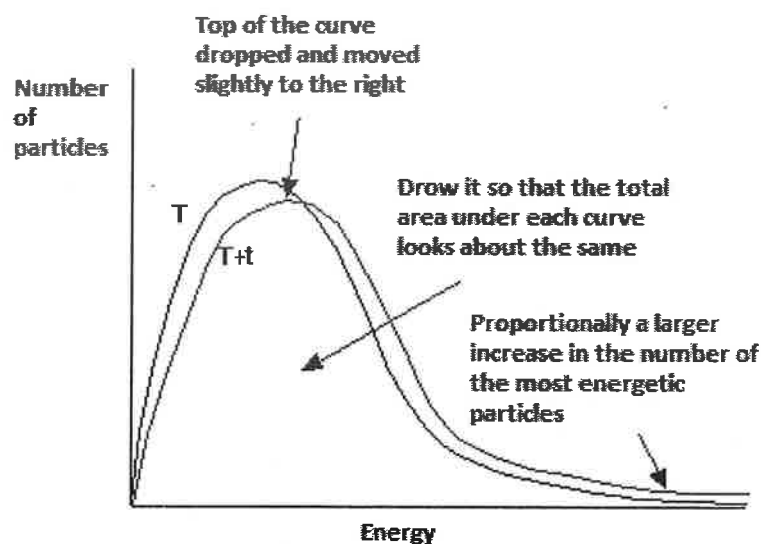
If you now mark the position of the activation energy, you can see that although the curve hasn't moved very much overall, there has been such a large increase in the number of the very energetic particles that many more now collide with enough energy to react.

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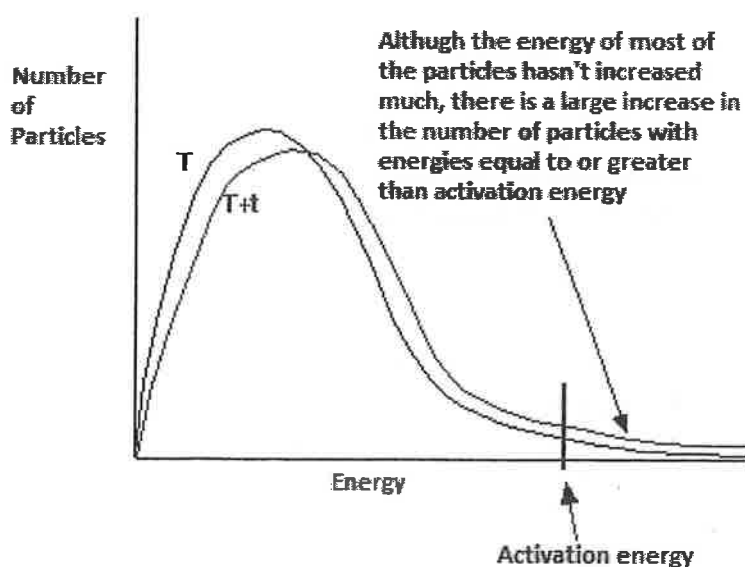
Remember that the area under a curve gives a count of the number of particles. On the last diagram, the area under the higher temperature curve to the right of the activation energy looks to have at least doubled - therefore at least doubling the rate of the reaction.

Summary

Increasing the temperature increases reaction rates because of the disproportionately large increase in the number of high energy collisions. It is only these collisions (possessing *at least* the activation energy for the reaction) which result in a reaction.

Calculation of E_a from the Values of k at Two Temperatures

The rate constant, k, is measured at two temperatures. E_a, is then calculated using the formula that can be derived as follows from equation (3) above.
At temperature T_1, where the rate constant is k_1,

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A$$ ...(1)

At temperature T_2, where the rate constant is k_2,

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A$$ ...(2)

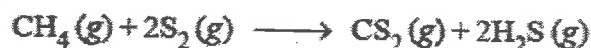Subtracting the equation (1) from the equation (2), we have

$$\ln k_2 - \ln k_1 = \left(-\frac{E_a}{RT_2} + \ln A\right) - \left(-\frac{E_a}{RT_1} + \ln A\right)$$

$$= -\frac{E_a}{RT_2} + \frac{E_a}{RT_1}$$

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

Thus the values of k_1 and k_2 measured at T_1 and T_2 can be used to find E_a.

SOLVED PROBLEM. The gas-phase reaction between methane (CH_4) and diatomic sulphur (S_2) is given by the equation

$$CH_4(g) + 2S_2(g) \longrightarrow CS_2(g) + 2H_2S(g)$$

At 550°C the rate constant for this reaction is 1.1 l mol^{-1} sec and at 625°C the rate constant is 6.4 1 mol^{-1} sec. Calculate E_a for this reaction.

SOLUTION

Here
$$k_1 = 1.1 \text{ litre mol}^{-1} \text{ sec.} \quad T_1 = 550 + 273 = 823 \text{ K}$$
$$k_2 = 6.4 \text{ litre mol}^{-1} \text{ sec.} \quad T_2 = 625 + 273 = 898 \text{ K}$$

Substituting the values in the equation

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

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$$\ln\left(\frac{6.4}{1.1}\right) = \frac{E_a}{8.3145\,J\,K^{-1}\,mol^{-1}}\left(\frac{1}{823\,K} - \frac{1}{898\,K}\right)$$

Solving for E_a, gives

$$E_a = \frac{(8.3145\,J\,K^{-1}\,mol^{-1})\,\ln\left(\frac{6.4}{1.1}\right)}{\left(\frac{1}{823\,K} - \frac{1}{898\,K}\right)}$$

$$= 1.4 \times 10^5\ J/mol$$

Limitations of the Collision Theory

The collision theory of reaction rates is logical and correct. However, it has been oversimplified and suffers from the following weaknesses.

1. **The theory applies to simple gaseous reactions only.**
   It is also valid for solutions in which the reacting species exist as simple molecules.
2. The values of rate constant calculated from the collision theory expression (Arrhenius equation) are in agreement with the experimental values only for simple bimolecular reactions.
   For reactions involving complex molecules, the experimental rate constants are quite different from the calculated values.
3. There is no method for determining the steric effect (p) for a reaction whose rate constant has not been determined experimentally.
4. In the collision theory it is supposed that only the kinetic energy of the colliding molecules contributes to the energy required for surmounting the energy barrier. There is no reason why the rotational and vibrational energies of molecules should be ignored.
5. **The collision theory is silent on the cleavage and formation of bonds involved in the reaction.**

The various drawbacks in the simple collision theory do not appear in the modern transition-state theory.
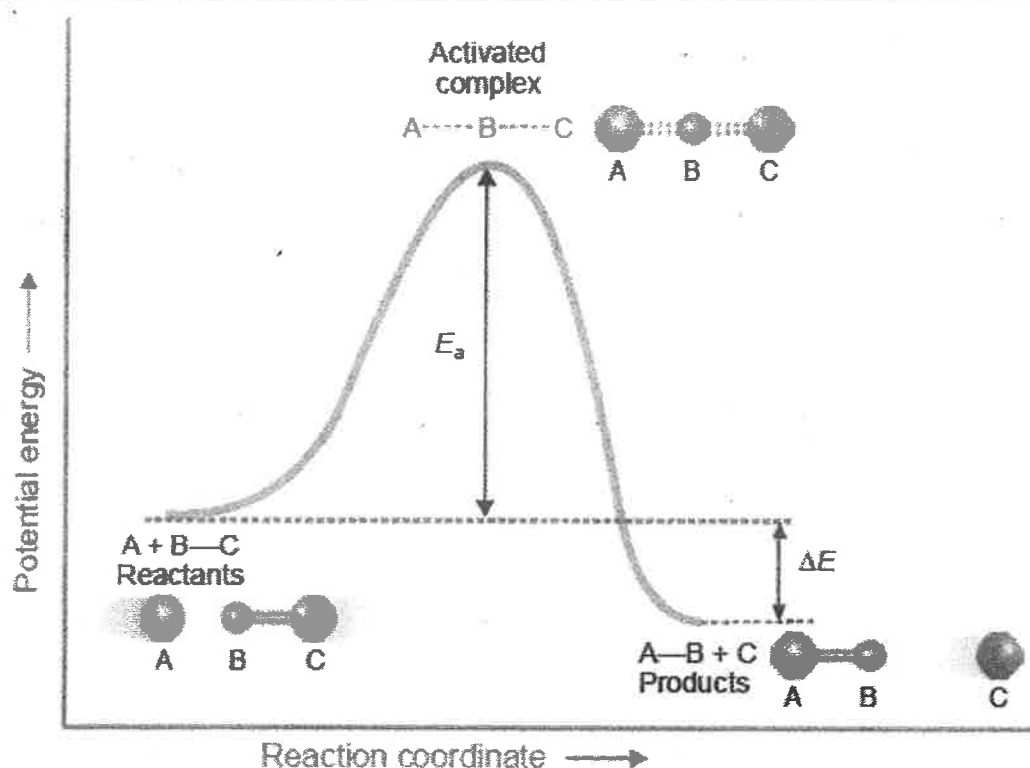
TRANSITION STATE THEORY

The **transition state** or **activated complex theory** was developed by Henry Erying (1935). This theory is also called the **absolute rate theory** because with its help it is possible to get the absolute value of the rate constant. The transition state theory assume that simply a collision between the reactant molecules does not really causes a reaction. During the collision, **the reactant molecules form a transition state or activated complex which decomposes to give the products.** Thus,

$$\underbrace{A + B\!-\!C}_{\text{Reactants}} \longrightarrow \underset{\substack{\text{Activated}\\\text{complex}}}{ABC^{\ddagger}} \longrightarrow \underbrace{A\!-\!B + C}_{\text{Products}}$$

The double dagger superscript ( ) is used to identify the activated complex. The transition state theory may be summarised as follows :

(1) In a collision, the fast approaching reactant molecules (A and BC) slow down due to gradual repulsion between their electron clouds. In the process **the kinetic energy of the two molecules is converted into potential energy.**

(2) As the molecules come close, **the interpenetration of their electron clouds occurs which allows the rearrangement of valence electrons.**

(3) A partial bond is formed between the atoms A and B with corresponding weakening of B − C bond. This leads to formation of an **activated complex** or **transition state.** The activated complex is momentary and decomposes to give the products (A–B + C)

The activated complex theory may be illustrated by the **reaction energy diagram**

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Change of potential energy during a collision between the reactant molecules for an exothermic reaction.

Change of potential energy during a collision between the reactant molecules for an exothermic reaction.

Here the potential energy of the system undergoing reaction is plotted against the **reaction coordinate** (the progress of the reaction). The difference in the potential energy between the reactants and the activated complex is the **activation energy,** E_a. The reactants must have this minimum energy to undergo the reaction through the transition state.

As evident from the energy diagram, energy is required by the reactants to reach the transition state. Also, the energy is obtained in passing from the transition state to the products. If the potential energy of the products is less than that of the reactants (Fig. 20.14) the energy obtained in going from the activated complex to products will be more than the activation energy (E_a). Thus such a reaction will be **exothermic**
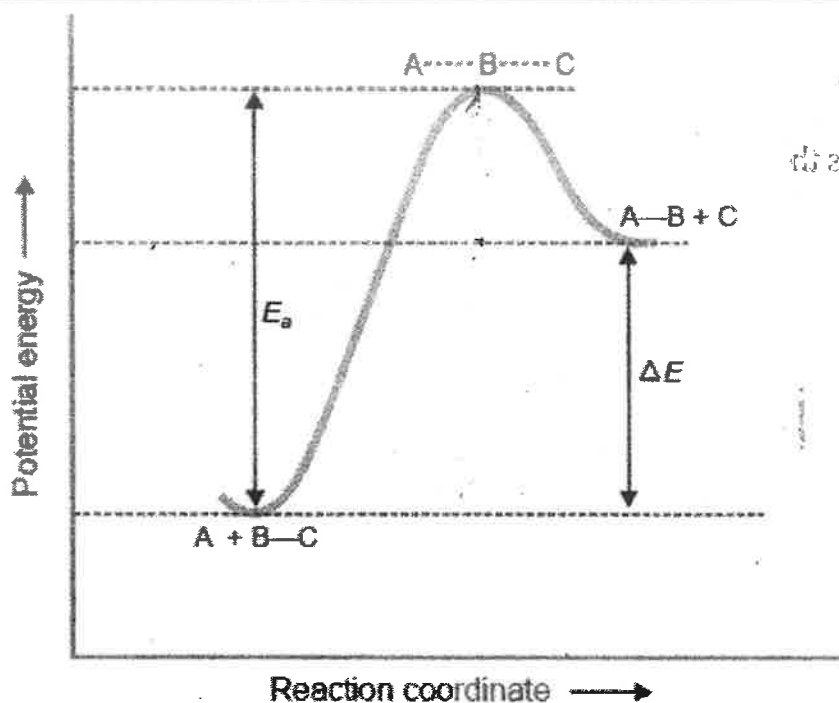
A potential energy diagram for an endothermic reaction.

On the other hand, if the potential energy of the products is greater than that of the reactants, the energy released in going from the activated complex to products will be less than the activation energy and the reaction will be **endothermic.**

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ACTIVATION ENERGY AND CATALYSIS

We know that for each reaction a certain energy barrier must be surmounted. As shown in the energy diagram shown in Fig. 20.15, the reactant molecules possess the activation energy, E_a, for the reaction to occur.
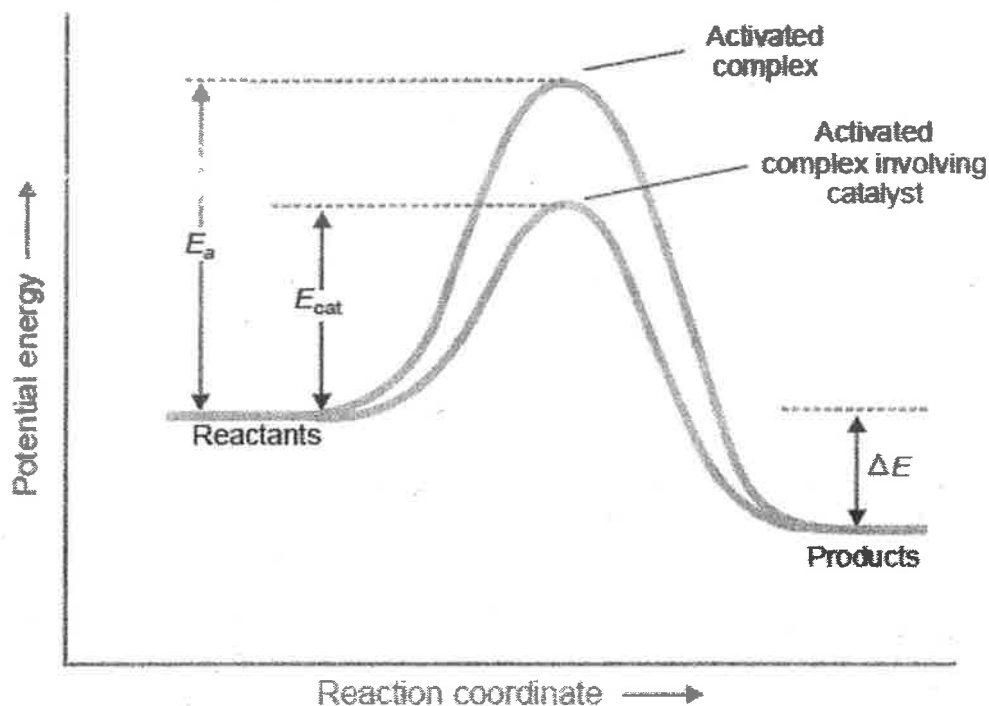

Energy diagram for a catalysed and uncatalysed reaction showing a lowering of activation energy by a catalyst.

The catalyst functions by providing another pathway with lower activation energy, E_{cat}. Thus a much large number of collisions becomes effective at a given temperature. Since the rate of reaction is proportional to effective collisions, the presence of a catalyst makes the reaction go faster, other conditions remaining the same. It may be noted from the above diagram that although a catalyst
lowers the activation energy, the energy difference, ΔE, between products and reactants remains the same.
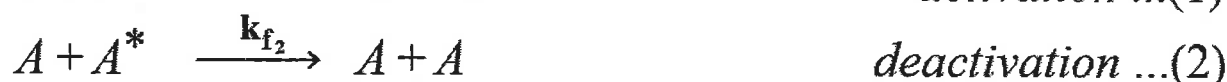
Unimolecular Reactions

many reactions are unimolecular reactions, for example,

$$2N_2O_{5\,(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$$
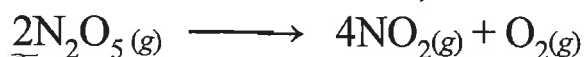
are found to be of the first order.

It is difficult to account for such reactions using the collision theory and the absolute reaction rate theory. If two molecules must collide in order to provide necessary activation energy, a second order rate law should result.

In 1922, Lindeman explained this anomaly by assuming that **there existed a time lag between activation and reaction of molecules.** During this time lag, the activated molecules could either react or be deactivated. Thus,

$$A + A \xrightarrow{\ \ k_f\ \ } A + A^* \qquad\qquad activation \,...(1)$$

$$A + A^* \xrightarrow{\ \ k_{f_2}\ \ } A + A \qquad\qquad deactivation \,...(2)$$

$$A^* \xrightarrow{\ \ k_b\ \ } products \qquad\qquad reaction \,...(3)$$

If the time lag is long, step (3) is slow, the reaction should follow first order kinetics. However, if A reacts as soon as formed, step (2) is the slow step, then the reaction should be second order.

rate constants being k_f for forward reaction & k_b for backward reaction and A*→P has the rate constant =kf_2 .

Here A* is the energized A molecule which has acquired sufficient vibrational energy to enable it to isomerize or decompose. In other words, the vibrational energy of A exceeds the threshold energy for the overall reaction A→P . It must be borne in mind that A* is simply a molecule in a high vibrational energy level and not an activated complex. In the first step, the energized molecule A* is produced by collision with another molecule A. What actually happens is that the kinetic energy of the second molecule is transferred into the vibrational energy of the first. In fact, the second molecule need not be of the same species; it could be a product molecule or a foreign molecule present in the system which, however, does not appear in the overall stoichiometric reaction A→P . The rate constant for the energization step is k_f . After the production of A*, it can either be de-energized back to A (in the reverse step) by collision in which case it vibrational energy is transferred to the kinetic energy of an A molecule or be decomposed or isomerized to products (in the second step above) in which case the excess vibrational energy is used to break the appropriate chemical bonds.

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In the Lindemann mechanism, a time lag exists between the energization of A to A* and the decomposition (or isomerization) of A* to products. During the time lag, A* can be de-energized back to A .

Mathematical Treatment

According to the steady state approximation (s.s.a.), whenever a reactive (i.e. Short lived) species is produced as an intermediate in a chemical reaction, its rate of formation is equal to its rate of decomposition. Here, the energized species A* is short lived.

$$\text{Its rate of formation} = k_f \times [A]^2$$

and its

$$\text{rate of decomposition} = k_b \times [A][A^*] + k_{f2} \times [A^*]$$

Thus

$$d[A*]/dt = k_f \times [A]^2 - (k_b \times [A][A^*] + k_{f2} \times [A^*]) = \dots\dots\dots\dots(1)$$

so that

$$[A^*] = \frac{k_f \times [A]^2}{k_b \times [A] + k_{f2}} \dots\dots\dots\dots\dots (2)$$

The rate of the reaction is given by

$$r = - d[A]/dt = k_{f2}[A^*]\dots\dots\dots\dots\dots\dots(3)$$

Substituting Eq.2 in Eq.3,

$$r = \frac{k_f k_{f2} \times [A]^2}{k_b \times [A] + k_{f2}} \dots\dots\dots\dots\dots\dots (4)$$

The rate law given by Equation 4 has **no definite order**.
We can, however consider two limiting cases, depending upon which of the two terms in the denominator of Equation 4 is greater.
If kb [A]>>k_{f2} , then the k_{f2} term in the denominator can be neglected giving:

$$r = \frac{k_f k_{f2}}{k_b} [A] \dots\dots\dots\dots\dots\dots. (5)$$

which is the rate reaction for a first order reaction.
In a gaseous reaction, this is the high pressure limit because at very high pressures. [A] is very large so that $k_f[A]$>>k_{f2} .
If k_{f2}>>$k_b[A]$, then the $k_b[A]$ term in the denominator of equation 4 can be neglected giving

$$r = k_f[A]^2 \dots\dots\dots\dots\dots\dots. (6)$$

which is the rate equation of a second order reaction. This is the low pressure

limit.

The experimental rate is defined as

$$r = k_{uni}[A] \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (7)$$

where k_{uni} is unimolecular rate constant. Comparing Eqs.4 & 7 we have the rate constant of <u>Unimolecular</u> reaction:

$$k_{uni} = \frac{k_f k_{f2} \times [A]}{k_b \times [A] + k_{f2}}$$

or

$$k_{uni} = \frac{k_f k_{f2}}{k_b + \frac{k_{f2}}{[A]}}$$

QUESTIONS

1. Explain Arrhenius equation. Discuss Arrhenius concept of activation energy. Give graphical representation of activation energy diagram.

2. Explain briefly the collision theory of reaction rates. What are its limitations?

3. The energy of activation for a reaction is 105 kJ mol^{-1}. Calculate the specific reaction rate for the reaction at 300 K, if the frequency factor is 2.5×10^{15} sec^{-1}.

Answer. 1.3×10^{-3} sec^{-1}

4. Explain the term collision frequency. On what factors does it depend? What is meant by collision diameter?

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Eyring equation

Transition state theory provides a more accurate alternative to the previously used Arrhenius equation and the collision theory. The transition state theory attempts to provide a better understanding of activation energy, Ea, and the thermodynamic properties involving the transition state.

In 1935, Henry Eyring helped develop a new theory called the transition state theory to provide a more accurate alternative to the previously used Arrhenius equation and the collision theory.
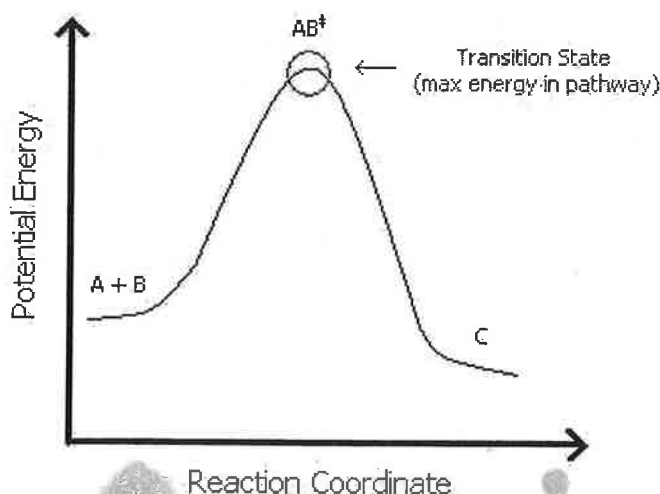
The Eyring equation involves the statistical frequency factory, v, which is fundamental to the theory.

Derivation

Consider the following reaction:

$$A + B \rightleftharpoons X^{\ddagger} \rightarrow C + D$$

here A and B are reactants, $X^{\ddagger}$ is the activated complex or the transition state, and C and D are the products. A quasiequilibrium between the reactants and the activated complex ($\ddagger$) is assumed.

The equilibrium constant, $K^{\ddagger}$, for the transition state and the reactants can thus be written:

$$K^{\ddagger} = \frac{[X]^{\ddagger}}{[A][B]}$$

Considering just the forward reaction gives:

$$A + B \rightleftharpoons X^{\ddagger} \xrightarrow{k} C + D$$

The rate of the overall reaction is the following:

$$rate = k[A][B]$$

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However, the rate of the overall reaction can also be thought of as the concentration of the transition state complex , X at the top of the barrier (shown at the peak of the graph below), multiplied by the frequency, v, of crossing the barrier. Therefore,

$$rate = v[X]^{\ddagger}$$

Because: $[X]^{\ddagger} = K^{\ddagger}[A][B]$

$$rate = v[A][B]K^{\ddagger}$$

Comparing this to the original rate for the overall reaction, it can be written:

$$k = vK^{\ddagger}$$

This equation is called the Eyring equation.

It is important to note here that the equilibrium constant $K^{\ddagger}$ can be calculated by absolute, fundamental properties such as bond length, atomic mass, and vibration frequency. This gives the transition rate theory the alternative name absolute rate theory, because the rate constant, k, can be calculated from fundamental properties

Thermodynamics of Transition State Theory

To reveal the thermodynamics of the theory, $K^{\ddagger}$ must be expressed in terms of $\Delta G^{\ddagger}$. $\Delta G^{\ddagger}$ is simply

$$\Delta G^{o\ddagger} = G^{o}(transition state) - G^{o}(reactants)$$

By definition, at equilibrium, $\Delta G^{\ddagger}$ can be expressed as:

$$\Delta G^{\ddagger} = -RT \ln K^{\ddagger}$$

Rearrangement gives:

$$[K]^{\ddagger} = e^{-\frac{\Delta G^{\ddagger}}{RT}}$$

From the Eyring equation, $k = vK^{\ddagger}$,

$$k = ve^{-\frac{\Delta G^{\ddagger}}{RT}}$$

Statistical Frequency Factor (v)

Statistical mechanics provides that the frequency, v, is equivalent to the thermal energy. $k_B T$, divided by Planck's constant

$$v = \frac{k_B T}{h}$$

Inserting into the equation derived from the Eyring Equation above yields.

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^{\ddagger}}{RT}} M^{1-m}$$

where h is Planck's constant (6.626×10^{-34}) and k_B is the Boltzmann constant (1.38×10^{-23} J K^{-1}).

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Thermodynamic Properties Extended ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$)

It is also possible to obtain terms for the change in enthalpy and entropy for the transition state. Because

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

it follows that the derived equation becomes,

$$k = \frac{k_B T}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT} M^{1-m}$$

Application of the Eyring Equation

The linear form of the Eyring Equation is given below.

$$\ln\frac{k}{T} = \frac{-\Delta H^{\ddagger}}{R}\frac{1}{T} + \ln\frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R} \tag{17}$$

The values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ can be determined from kinetic data obtained from a $\ln\frac{k}{T}$ vs. $\frac{1}{T}$ plot. The equation is a straight line with negative slope, $\frac{-\Delta H^{\ddagger}}{R}$, and a y-intercept, $\frac{\Delta S^{\ddagger}}{R} + \ln\frac{k_B}{h}$.