

Effect of Temperature on Reaction Rates

It has been found that an increase in temperature generally increases the rate of a reaction. In majority of cases it has been seen that the rate of a reaction increases by a factor of 2 or 3 for every 10⁰C rise in temperature. This is empirically given by the relation

$$\frac{k_{t+10}}{k_t} \approx 2 \text{ or } 3$$

However, more correct dependence of k on temperature is given by Arrhenius equation

$$\frac{d \ln k}{dt} = \frac{E_a}{RT^2} \quad \dots\dots\dots (65)$$

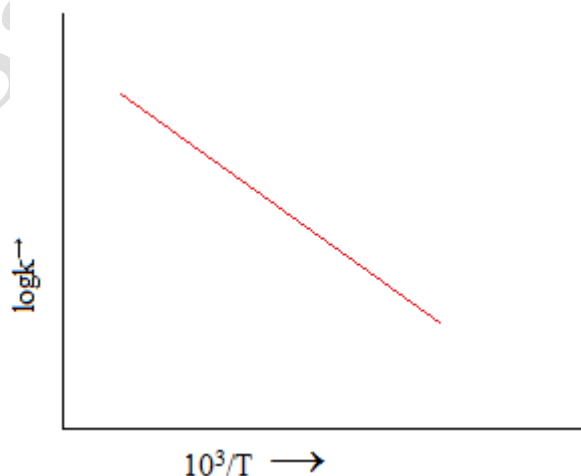
Where E_a is called the *activation energy* of the reaction and is characteristic of the reaction. It is the threshold energy that the reactant molecules must have in order to react. Integration of Eq.(65) yields

$$\ln k = -E_a/RT + I \quad \dots\dots\dots (66)$$

$$\log k = -E_a/2.303RT + I' \quad \dots\dots\dots (67)$$

$$k = A e^{-E_a/RT} \quad \dots\dots\dots (68)$$

where I is the integration constant. The factor A is called the pre-exponential factor or the frequency factor. Equation (67) suggests that a plot of log k versus 1/T should be a straight line for many reactions as shown in Fig .9



Chemical Kinetics

Figure 9: Plot of $\log k$ versus $1/T$

The slope of the plot is equal to $-E_a/2.303R$ and the intercept equal to I' . From the slope of this plot the activation energy can be evaluated. However, if we integrate eq.(65) between the limits $k=k_1$ at $T=T_1$ and $k=k_2$ at $T=T_2$, then

$$\begin{aligned} \ln \frac{k_2}{k_1} &= \frac{E_a}{R} \left[-\frac{1}{T} \right]_{T_1}^{T_2} \\ &= \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \\ &= \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \end{aligned}$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \quad \dots\dots\dots (69)$$

or

From this equation it is evident that the activation energy, E_a , can be obtained from the value of the rate constant at two different temperatures.

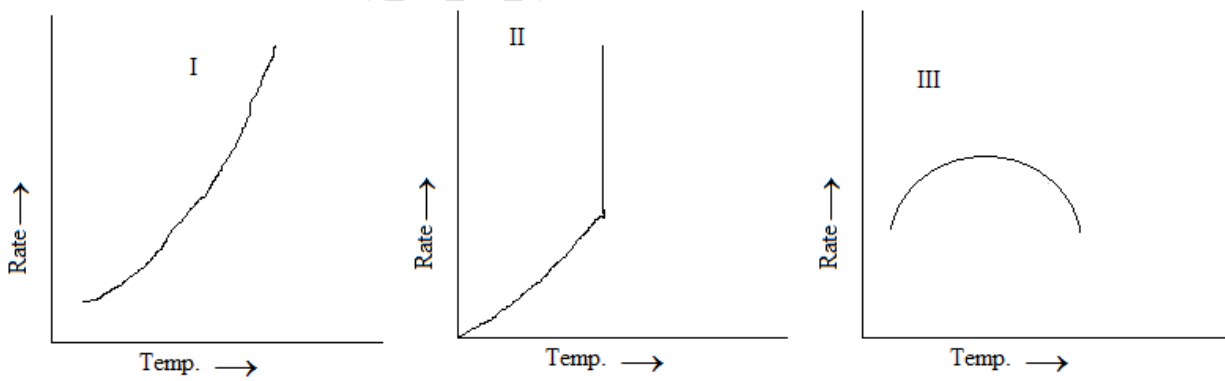


Figure 10: Various types of curves showing variation of rate with temperature

Arrhenius equation shows that the rate of a reaction increases exponentially with rise in temperature (fig.10). Curve of type I is generally obtained for most of the reaction. For explosive reaction, curve of type II is obtained whereas curve III is obtained for enzyme catalysed reactions.

The energy of Activation:

In Arrhenius equation appearance of E_a suggests that molecule must acquire a certain amount of energy before they could undergo chemical reactions. This means that before the chemical reaction to occur the molecules must be activated, i.e., they must be raised to a higher energy state. *The minimum energy which the reacting molecules must possess before the reaction to occur is known as the energy of activation.* According to the concept of activation, the transformation of the reactions into the products does not take place directly. The reacting molecules, however, must acquire sufficient energy to cross an activation energy barrier. This idea may be made clear with the help of a schematic diagram as shown in the **fig. 11** for the reaction $A \rightarrow B$.

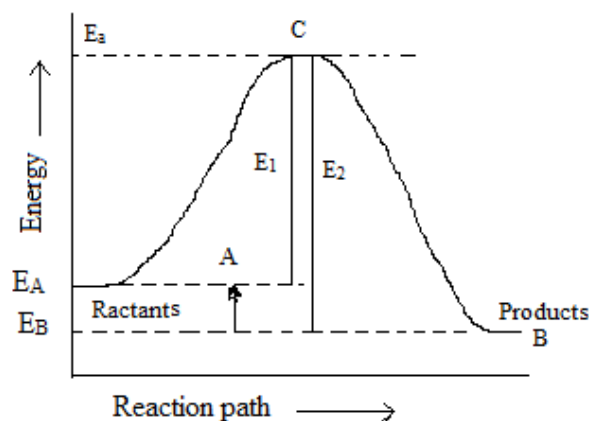


Figure 11: Energy of activation

Let E_A represent the average energy of the reactants and E_B those of the products. Even if E_A is greater than E_B , the reactants A will not be directly converted into the products B . The reacting molecules must first attain the minimum energy E_a , for the reaction to occur. Molecules at C having energy E_a , are said to be in an activated state. The excess energy $(E_a - E_A)$, which the reactant molecules must absorb in order to become activated and react, is the energy of activation E_1 for the forward direction, i.e., $A \rightarrow C$

Energy of activation = Energy of the activated state - Energy of the reactants

$$E_1 = E_a - E_A$$

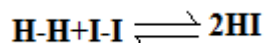
When the activated complex decomposes into the products, energy (E_2) is given out. This can be taken as the energy of activation of the process $B \rightarrow C$, i.e.,

$$E_2 = E_a - E_B$$

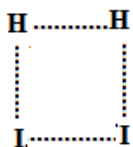
Thus, the difference ΔE , between E_A and E_B is given as, $\Delta E = E_1 - E_2 = (E_a - E_A) - (E_a - E_B) = E_B - E_A$. ΔE is simply the difference in energy between the products and reactant and is known as the enthalpy of the reaction at constant volume. This means that when the activated complex decomposes into the products, it gives out an energy E_2 which is equal to the energy absorbed by the reactant molecules from A to C plus the enthalpy of the reaction. If $E_2 > E_1$, the reaction is evidently exothermic, whereas if $E_2 < E_1$, the reaction is endothermic.

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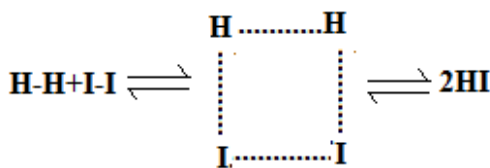
Application of the idea of activation of energy to the reaction:



When two molecules (H_2 and I_2) are far apart and the total energy of the system is equal to the potential energy of H_2 and I_2 , this part of the reaction is represented by the horizontal portion of the curve in fig. 11. As the molecules approach each other, H-H and I-I bonds begin to stretch and HI bonds begin to form. The energy starts increasing and is represented by the rising portion of the curve. HI bond formation increases and that of H-H and I-I bonds breakage increases, a point is reached when the energy is maximum (point C). At this point the activated complex of the type shown below is formed:



The point C in the curve is called the transition state. A slight distortion of the bond in the form of compression of HI bond and stretching of H-H and I-I bonds results in the activated complex to pass through the transition state yielding the products as follows:



❖ Collision Theory of Reaction Rates

The collision theory attempts to account for the observed kinetics of reactions in terms of kinetic molecular theory. This theory has been found to be satisfactory for gaseous reactions and postulates that the reacting molecules must collide. If collision is the only requirement for a reaction to occur then the rate of the reaction should be proportional to the number of collisions between the reacting molecules. In order to explain this discrepancy, it is assumed that molecules are activated and only those molecules possessing energy equal to or greater than the activation energy are able to form the products. Furthermore, in many cases it is assumed that molecules must be properly oriented so that rearrangements of atoms can occur with minimum expenditure of energy and time.

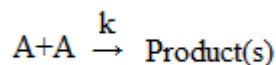
Thus, in collision theory the essential requirements for reactions to occur are :

- i) Collision between the reactant molecules.
- ii) Activated of molecules and

Chemical Kinetics

iii) Proper orientation of the reacting molecules at the time of collision.

For a bimolecular gaseous reaction



The rate of the reaction is given by

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

If the concentration of A is 1 mol dm⁻³, we get

$$-\frac{d[A]}{dt} = k \quad \dots\dots\dots (70)$$

According to the collision theory the rate of the reaction is given by

$$-\frac{d[A]}{dt} = k = Z_{11}q \quad \dots\dots\dots (71)$$

Where Z_{11} is the number of collision between the reacting molecules per second per dm³ and q is the fraction of the total number of molecules which are activated. The values of Z_{11} and q can be calculated from the kinetic theory of gases. Z_{11} is given by

$$Z_{11} = \frac{1}{2} \sqrt{2} \pi \sigma^2 (n')^2 C_{av} \quad \dots\dots\dots (72)$$

$$q = \frac{n^*}{n} e^{-E_a/RT} \quad \dots\dots\dots (73)$$

Where σ is the collision diameter and C_{av} the average velocity of the molecules in dm per second, n^* the number of molecules per dm³ having energy equal to or more than the activation energy E_a and n' is the total number of molecules per dm³. Substituting the value of C_{av} in eq (72)

, we get

$$Z_{11} = \frac{1}{2} \sqrt{2} \pi \sigma^2 (n')^2 \sqrt{\frac{8RT}{\pi M}} \quad \dots\dots\dots (74)$$

Chemical Kinetics

$$=2\sigma^2(n')^2 \cdot \sqrt{\frac{\pi RT}{M}} \dots\dots\dots(75)$$

The number of collisions per second between two unlike molecules 1 and 2 is given by

$$Z_{12} = n_1' n_2' \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2 \cdot \sqrt{\frac{8\pi kT}{\mu}} \dots\dots\dots(76)$$

Where n_1' and n_2' are the number of molecules per dm^3 of reactants 1 and 2, σ_1 and σ_2 are the collision diameters of the molecules 1 and 2 and μ is the reduced mass given by

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

Hence the expression for the rate of a reaction involving identical molecules is given by

$$\text{Rate} = qZ_{11} = 2\sigma^2(n')^2 \cdot \sqrt{\frac{\pi RT}{M}} e^{-E_a/RT} \dots\dots\dots(77)$$

And for different reactant molecules

$$\text{Rate} = qZ_{12} = n_1' n_2' \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2 \cdot \sqrt{\frac{8\pi kT}{\mu}} e^{-E_a/RT} \dots\dots\dots(78)$$

Comparison of Eq.(77) and (68) shows that the pre-exponential factor A in the Arrhenius equation is equal to Z_{11} .

The results predicted by Eq.(77) and (78) can be compared with the experimental values of the rate constants.

Discrepancy between experimental and calculated value of k –introduction of steric factor:

Take the example of dissociation of a mole of HI per dm^3 at 556K. The value of activation energy for the reaction has been found to be 185.0 kJ, the collision diameter for HI is 3.5×10^{-9} dm, the molar mass is $1.28 \times 10^{-1} \text{kg mol}^{-1}$ and the number of molecules per dm^3 is 6.023×10^{23} . Substituting these values in eq. (75), we obtain

$$Z_{11} = 2\sigma^2(n')^2 \cdot \sqrt{\frac{\pi RT}{M}}$$

Chemical Kinetics

$$\begin{aligned}
 &= 2 \times (3.5 \times 10^{-9} \text{ dm})^2 (6.023 \times 10^{23} \text{ dm}^{-3}) \left(\frac{3.14 \times 8.314 \times 10^2 \text{ kg dm}^2 \text{ s}^{-2} \text{ K}^{-1} \text{ mol}^{-1} \times 556 \text{ K}}{1.28 \times 10^{-1} \text{ kg mol}^{-1}} \right)^{1/2} \\
 &= 2.99 \times 10^{34} \text{ s}^{-1} \text{ dm}^{-3}
 \end{aligned}$$

The number of colliding molecules per second per dm^3 is twice the value of Z_{11} , i.e. 5.98×10^{34} .

The fraction of total number of molecules, q , is given by

$$\begin{aligned}
 q &= e^{-E_a/RT} \\
 &= \exp[-(185 \times 10^3)/(8.314 \times 556)] = 5.2 \times 10^{-18}
 \end{aligned}$$

$$\text{Hence } k = qZ_{11} = 5.98 \times 10^{34} \times 5.2 \times 10^{-18} = 3.12 \times 10^{17} \text{ molecules/dm}^3/\text{sec}$$

If this value is divided by Avogadro constant, we get the rate constant in units of $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

$$\text{Therefore, } k = 5.2 \times 10^{-7} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

The experimental value of k has been found to be $3.5 \times 10^{-7} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

The agreement between these values is quite satisfactory indicating the validity of the theory. However, the agreement between the calculated and the observed values has been found to hold only for simple bimolecular gaseous reactions and in solutions where the reacting molecules are simple. For reaction involving complex molecules, the experimental rates are quite different from the calculated values. In order to account for the observed discrepancy it is further postulated that the molecules must be properly oriented at the time of the collision and an additional term is introduced in expression for the rate of the reaction i.e.,

$$k = PZ_{11}e^{-E_a/RT} \dots\dots\dots (79)$$

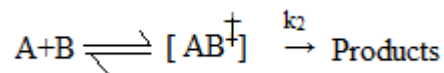
where P is referred to as *the probability* or *steric factor* and is related to the geometry of the molecule. It is a measure of the deviation from the calculated value. It can have values ranging from unity to about 10^{-9} for slow reactions.

The Transition State Theory or The Theory of Absolute Reaction Rates

The collision theory of reaction rates suffers from the following drawback: (i) It is difficult to calculate the steric factor from molecular geometry for complex molecules; (ii) the theory is applicable essentially to gaseous reactions. An alternate theory called absolute reaction rate theory or frequently known as transition state theory of reaction rates has been developed by Eyring in 1935. This theory attempts to treat the reaction rates from thermodynamic considerations. It is assumed that an equilibrium is established between the reactions and the activated complex. The activated complex is treated formally as a molecule in spite of its transitory existence and the laws of thermodynamics can be applied to it. As stated previously that all the reactions proceeds through an activated or transition state which has energy higher than the reactants or the products. The rate of reaction depends upon two factors, viz, (i) the

Chemical Kinetics

concentration of the transition state species and (ii) the rate at which the activated complex decomposes. Consider a simple bimolecular reaction between molecules A and B as



The rate of such a reaction = [concentration of activated complex molecule] X [Frequency of decomposition of the activated complex into the products]

In order to calculate the concentration of activated complex it is assumed that the complex is in equilibrium with the reactant molecules. Hence the equilibrium constant K_{eq}^\ddagger is given as

$$K_{eq}^\ddagger = \frac{[AB^\ddagger]}{[A][B]}$$

$$[AB^\ddagger] = K_{eq}^\ddagger [A][B] \quad \dots\dots\dots (80)$$

The activated complex is an aggregate of atoms and is assumed to be similar to an ordinary molecule except that it breaks up into products at a special vibration at which it is unstable. The frequency of such a vibration is something like the rate at which the activated complex decomposes. If ν is the frequency of such a vibration, then the rate of decomposition of the activated complex is given as

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k_2 [A][B]$$

$$= [AB^\ddagger] \nu = K_{eq}^\ddagger [A][B] \nu \quad \dots\dots\dots (81)$$

Since an activated complex is an unstable species and is held together by loose bonds, therefore the vibration of low frequency will decompose the activated complex. The average energy of such a vibrational degree of freedom is given by kT (where k is the Boltzmann constant and is equal to R/N where N is the Avogadro constant). The energy of E of this vibration is given by Planck's expression, $E=h\nu$.

$$\nu = E/h = kT/h = RT/N_A h$$

Substituting this value of ν in Eq.(81), we get

$$k_2 [A][B] = K_{eq}^\ddagger [A][B] \frac{RT}{N_A h}$$

$$k_2 = K_{eq}^\ddagger \frac{RT}{N_A h} \quad \dots\dots\dots (82)$$

Thermodynamic Aspects:

The result given by expression eq.(82) is of importance when the equilibrium constant is interpreted thermodynamically by introducing the terms, free energy of activation, ΔG^\ddagger , the enthalpy of activation, ΔH^\ddagger and the entropy of activation, ΔS^\ddagger . These quantities represent the difference between the values of the respective thermodynamic functions between the activated complex and the reactants, all substances being in their standard state, i.e., activity being unity.

Since we have

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

$$\ln K_{eq}^\ddagger = -\Delta G^\ddagger / RT \quad \dots\dots\dots (83)$$

and

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad \dots\dots\dots (84)$$

Putting the value of ΔG^\ddagger in Eq. (83), we get

$$\ln K_{eq}^\ddagger = -\frac{\Delta H^\ddagger - T\Delta S^\ddagger}{RT}$$

$$K_{eq}^\ddagger = \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \exp\left(\frac{\Delta S^\ddagger}{R}\right) \quad \dots\dots\dots (85)$$

Substituting this value of K_{eq}^\ddagger in Eq. (82) gives

$$k_2 = \frac{RT}{N_A h} \left[\exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \exp\left(\frac{\Delta S^\ddagger}{R}\right) \right] \quad \dots\dots\dots (86)$$

Equation (86) can be expressed in a form which involves the experimental activation energy E_a instead of enthalpy of activation ΔH^\ddagger . The variation of K_{eq}^\ddagger with temperature is given by

$$\frac{d \ln K_{eq}^\ddagger}{dT} = \frac{\Delta E^\ddagger}{RT^2} \quad \dots\dots\dots (87)$$

Where ΔE^\ddagger represents the increase in energy when the reactants go from the initial state to the activated state. Taking logarithm of Eq. (82), we get

$$\ln k_2 = \ln T + \ln K_{eq}^\ddagger + \ln \frac{R}{N_A h} \quad \dots\dots\dots (88)$$

Differentiating the above equation with respect to the temperature, we obtain

$$\frac{d \ln k_2}{dT} = \frac{1}{T} + \frac{d \ln K_{eq}^\ddagger}{dT} \quad \dots\dots\dots (89)$$

Substituting the value $d \ln K_{eq}^\ddagger / dT$ from Eq. (87)

$$\frac{d \ln k_2}{dT} = \frac{1}{T} + \frac{\Delta E^\ddagger}{RT^2}$$

$$= \frac{RT + \Delta E^\ddagger}{RT^2} \quad \dots\dots\dots (90)$$

Chemical Kinetics

Comparison of Eq.(90) with Eq.(65) leads to

$$\frac{d \ln k}{dT} = E_a / RT^2 \dots (65)$$

Since $E_a = \Delta E^\ddagger + RT$
 Therefore $\Delta E^\ddagger = \Delta H^\ddagger - P\Delta V^\ddagger$
 $E_a = \Delta H^\ddagger + RT - P\Delta V^\ddagger \dots (91)$

For ideal gases, Eq. (91) reduces to $E_a = \Delta H^\ddagger + RT - \Delta n^\ddagger RT$ (as $P\Delta V^\ddagger = \Delta n^\ddagger RT$)(92)

Where ΔV^\ddagger is the change in volume and Δn^\ddagger is the change in number of molecules passing from the initial state to the activated state. For a unimolecular reaction, there is no change in the number of molecules as the activated complex is formed. Therefore, ΔV^\ddagger is zero and Eq.(91) reduces to

$$E_a = \Delta H^\ddagger + RT \dots (93)$$

and the rate Eq. (86) becomes

$$k_2 = \frac{RT}{N_A h} \left[\exp\left(-\frac{E_a - RT}{RT}\right) \exp\left(\frac{\Delta S^\ddagger}{R}\right) \right]$$

$$= \frac{RT}{N_A h} \left[\exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{E_a}{RT}\right) e \right] \dots (94)$$

For a bimolecular reaction $\Delta n^\ddagger = -1$ and Eq. (92) becomes

$$E_a = \Delta H^\ddagger + 2RT \dots (94)$$

The rate Eq. (86) now becomes

$$k_2 = \frac{RT}{N_A h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{E_a - 2RT}{RT}\right)$$

$$= \frac{RT}{N_A h} \left[\exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{E_a}{RT}\right) e^2 \right] \dots (95)$$

The entropy of activation can be calculated from the experimental values of rate constant and activation energy. It has been found that the difference between ΔH^\ddagger and E_a is small and in fact, for reactions in solutions and for unimolecular reaction $\Delta H^\ddagger \approx E_a$. In other cases involving gases, an additional term $\Delta n^\ddagger RT$ has been included. Hence without much error, we may write

$$k_2 = \frac{RT}{N_A h} \left[\exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{E_a}{RT}\right) \right] \dots (96)$$

$$= \frac{RT}{N_A h} \left[\exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \right] \dots (97)$$

The expression resembles the Arrhenius equation except that ΔH^\ddagger appears instead of E_a . The quantity ΔH^\ddagger is often called the enthalpy of activation. A comparison of Eq. (97) with Eq. (68) shows that the pre-exponential factor A is related to the entropy of activation as

$$k = A e^{-E_a/RT} \dots (68)$$

Chemical Kinetics

$$A = \frac{RT}{N_A h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \dots\dots\dots(98)$$

An exact calculation of A needs the evaluation of ΔS^\ddagger . A negative value of ΔS^\ddagger means that the activated complex is more ordered than the reactants. A more negative value of ΔS^\ddagger indicates that A will have smaller value which means the reaction will be slower. A positive value of activation entropy ΔS^\ddagger means that the entropy of the complex is greater than the entropy of the reactants. A loosely bound complex has a higher entropy than a tightly bound one. More often there is a decrease in entropy in passing through the activated complex. The steric (probability) factor used in the collision theory is more or less analogous to the entropy of activation in the transition state theory. It should be noted that the quantity $RT/N_A h$ does not depend on the nature of the reactant or activated complex and, therefore, will be same for all reactions at the same temperature.

From the collision theory, $k_2 = P Z_{11} \exp(-E_a/RT)$ i.e., the activation energy determines k_2 , while in transition state theory it is determined by the free energy of activation, ΔG^\ddagger . For slower reactions, a higher value of ΔG^\ddagger will be observed at a given temperature. Since

$$k_2 = P Z_{11} \exp(-E_a/RT) \quad \text{(from collision theory) } \dots\dots\dots (99)$$

and
$$k_2 = \frac{RT}{N_A h} \left[\exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \right] \quad \text{(from transition state theory) } \dots\dots\dots (100)$$

Hence the orientation factor P is related to ΔS^\ddagger , i.e., the entropy of activation. The steric (probability) factor A in the Arrhenius equation is equal to Z_{11} of the collision theory and is equal to $RT/N_A h \exp(\Delta S^\ddagger/R)$.

For simple molecules these values are identical. For more complex reactant molecules where the collision theory fails the transition state theory still gives satisfactory value of A.