

SUBJECT – CHE GE 404, SEMESTER- 1V,

CHEMICAL KINETICS

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THEORIES OF REACTION RATES

Arrhenius theory increases our standing of reaction process, but it neither it gives information about Energy of activation (E) nor give information about Frequency factor (A). The two theories have been proposed to predict the reaction rates in terms of molecular collision which allow better interpretation of E and A.

The macroscopic discussion of kinetics can be now expanded into a more microscopic picture in terms of molecular level properties (e..g, mass and velocities) involving two important theories: (1) collision theory and (2) transition-state theory.

Collision theory and transition state theory are two theories that are used to explain the reaction rates of different chemical reactions at the molecular level. Collision theory describes the collisions of gas molecules in gas-phase chemical reactions. Transition state theory explains the reaction rates by assuming the formation of intermediate compounds in transition states.

Collision Theory

The collision theory explains that gas-phase chemical reactions occur when molecules collide with sufficient kinetic energy. This theory is built based on the kinetic theory of gases (the kinetic theory of gases describe that gases contain particles having no defined volumes but with defined masses and there are no intermolecular attractions or repulsions between these gas particles).

If two molecules need to collide in order for a reaction to take place, then factors that influence the ease of collisions will be important. The more energy there is available to the molecules, the faster they will move around, and the more likely they are to bump into each other. Higher temperatures ought to lead to more collisions and a greater frequency of reactions between molecules.

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

- (i) Collision between the reactant molecules
- (ii) Activation of molecules and
- (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

$$-d[A]/dt = k[A]^2$$

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

$$-d[A]/dt = k$$

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

$$-d[A]/dt = k = Z_{11}q$$

Where Z_{11} is the number of collisions between the reacting molecules per second per liter 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 is given by

$$Z_{11} = \sqrt{2} \pi \sigma^2 (n')^2 C_{av} / 2 \text{ -----(!)}$$

$$\text{and } q = n^*/n = e^{-E_a/RT}$$

where σ is the collision diameter and C_{av} the average velocity of the molecules in meter/sec, n^* the total number of molecules per litre having energy equal to or more than the activation energy E_a and n' is the total number of molecules per litre. Putting the value of C_{av} in equation (1), we get

$$\begin{aligned} Z_{11} &= \sqrt{2} \pi \sigma^2 (n')^2 \sqrt{8RT/\pi M} / 2 \\ &= 2 \sigma^2 (n')^2 \sqrt{\pi RT/M} \end{aligned}$$

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

$$Z_{12} = n_1' n_2' (\sigma_1 + \sigma_2)^2 / 2 \sqrt{8\pi kT/\mu} \text{ -----(2)}$$

Where n_1' and n_2' are the number of molecules per litre 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

$$\mu = m_1 m_2 / m_1 + m_2 \text{ -----(3)}$$

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

$$\text{Rate} = qZ_{11} = 2 \sigma^2 (n_1')^2 \sqrt{\pi RT/M} \times e^{-E_a/RT} \text{-----(4)}$$

And for different molecules

$$\text{Rate} = qZ_{12} = n_1' n_2' (\sigma_1 + \sigma_2)^2 / 2 \sqrt{8\pi kT/\mu} \times e^{-E_a/RT} \text{-----(5)}$$

Now comparing equation with Arrhenius equation $k = A e^{-E_a/RT}$

$$K = qZ_{11} = A e^{-E_a/RT} = 2 \sigma^2 (n_1')^2 \sqrt{\pi RT/M} \times e^{-E_a/RT}$$

$$A = 2 \sigma^2 (n_1')^2 \sqrt{\pi RT/M} \text{-----(6)}$$

The results predicted by equation (4) and (5) can be compared with experimental values of the rate constants. The agreement between these two values is quite satisfactory indicating the validity of the theory. However, this theory fails for bigger and complicated molecules. 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 the expression for the rate of the reaction, i.e.,

$$K = PZ_{11} e^{-E_a/RT} \text{-----(7)}$$

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

Transition-state theory (activated complex theory)

Transition state theory (TST) provides a more accurate alternative to the previously used Arrhenius equation and the collision theory. The transition state theory attempts to provide a greater understanding of activation energy, E_a , and the thermodynamic properties involving the transition state. Collision theory of reaction rate, although intuitive, lacks an accurate method to predict the probability factor for the reaction. The theory assumes that reactants are hard spheres rather than molecules with specific structures. 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 factor, ν , which is fundamental to the theory.

According to TST, between the state where molecules are reactants and the state where molecules are products, there is a state known as the transition state. In the transition state, the reactants are combined in a species called the activated complex. The theory suggests that there are three major factors that determine whether a reaction will occur:

1. The concentration of the activated complex
2. The rate at which the activated complex breaks apart
3. The way in which the activated complex breaks apart: whether it breaks apart to reform the reactants or whether it breaks apart to form a new complex, the products.

Collision theory proposes that not all reactants that combine undergo a reaction. However, assuming the stipulations of the collision theory are met and a successful collision occurs between the molecules, transition state theory allows one of two outcomes: a return to the reactants, or a rearranging of bonds to form the products.

Consider a bimolecular reaction:



$$K = [C] / [A][B]$$

where K is the equilibrium constant. In the transition state model, the activated complex AB^\ddagger is formed:



$$K^\ddagger = [AB^\ddagger] / [A][B]$$

There is an energy barrier, called activation energy, in the reaction pathway. A certain amount of energy is required for the reaction to occur. The transition state, AB^\ddagger , is formed at maximum energy. This high-energy complex represents an unstable intermediate. Once the energy barrier is overcome, the reaction is able to proceed and product formation occurs.

The rate of a reaction is equal to the number of activated complexes decomposing to form products. Hence, it is the concentration of the high-energy complex multiplied by the frequency of it surmounting the barrier.

$$\text{rate} = \nu[\text{AB}^\ddagger] = \nu[\text{A}][\text{B}] K^\ddagger \text{-----}(1)$$

The rate can be rewritten:

$$\text{rate} = [\text{A}][\text{B}]K \text{-----}(2)$$

Combining Equations

$$k[\text{A}][\text{B}] = \nu[\text{A}][\text{B}]K^\ddagger$$

$$K = \nu K^\ddagger \text{-----}(3)$$

where

- ν is the frequency of vibration,
- k is the rate constant and
- K^\ddagger is the thermodynamic equilibrium constant.

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

$$\nu = E/h = kT/h = RT/Nh \text{-----}(4)$$

Substituting the value of ν from (4) in (3), we get

$$K = K^\ddagger RT/Nh \text{-----}(5)$$

Conclusion

This equation is more reliable than either the Arrhenius equation and the equation for the Collision Theory. However, it has its limitations, especially when considering the concepts of quantum mechanics. Quantum mechanics implies that tunneling can occur, such that particles can bypass the energy barrier created by the transition state. This can especially occur with low activation energies, because the probability of tunneling increases when the barrier height is lowered.

In addition, transition state theory assumes that an equilibrium exists between the reactants and the transition state phase. However, in solution non-equilibrium situations can arise, upsetting the theory. Several more complex theories have been presented to correct for these and other discrepancies. This theory still remains largely useful in calculating the thermodynamic properties of the transition state from the overall reaction rate. This presents immense usefulness in medicinal chemistry, in which the study of transition state analogs is widely implemented.

Collision Theory vs Transition State Theory

The collision theory explains that the gas-phase chemical reactions occur when molecules collide with sufficient kinetic energy.

Transition state theory indicates that, in between the state where molecules are reactants and the state where molecules are products, there is a state known as the transition state.

Principle

Collision theory states that chemical reactions (in the gas phase) occur due to collisions between reactants.

Transition state theory states that chemical reactions occur via going through a transition state.

Requirements

According to the collision theory, only successful collisions cause chemical reactions to occur.

According to transition state theory, a chemical reaction will progress if the reactants can overcome the activation energy barrier.