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Class : Semester-2
Paper: C4T: Organic Chemistry
Topic : General Treatment of Reaction Mechanism II (Reaction kinetics)

Comments: Read the notes thoroughly. This part is very important for final examination.

References: Wikipedia

General Tratment of Reaction Mechanism II

Reaction Kinetics: Part-1

Chemical kinetics is the branch of physical chemistry which deals with a study of the speed of chemical reactions. Such studies also enable us to understand the mechanism by which the reaction occurs. Thus, in chemical kinetics we can also determine the rate of chemical reaction.

From the kinetic stand point the reactions are classified into two groups:

a) homogeneous reactions which occur entirely in one phase b) heterogeneous reactions where the transformation takes place on the surface of a catalyst or the walls of a container.

Rate of reaction

The rate of reaction i.e. the velocity of a reaction is the amount of a chemical change occurring per unit time.

The representation of rate of reaction in terms of concentration of the reactants is known as **rate law**. It is also called as rate equation or rate expression.The rate is generally expressed as the decrease in concentration of a reactant or as the increase in concentration of the product. If C the concentration of a reactant at any time t is, the rate is expressed by -dC/dt or if the concentration of a product be x at any time t, the rate would be dx/dt . The time is usually expressed in seconds. The rate will have units of concentration divided by time. The concentrations are taken in gm-moles/litre, hence rate is moles/litre/second.

Factors influencing the rate of reaction:

Rate of a chemical reaction is influenced by the following factors:

(i) Temperature (ii) Concentration of the reactants (iii) Nature of reactants (iv) Catalysts (v) Radiation

(i) Temperature:

In most cases, the rate of a reaction in a homogeneous reaction is approximately doubled or tripled by an increase in temperature of only 100 C. In some cases the rise in reaction rates are even higher.

(ii) Concentration of the reactants

At a fixed temperature and in the absence of catalyst, the rate of given reaction increases with increased concentration of reactants. With increasing concentration of the reactant the number of molecules per unit volume is increased, thus the collision frequency is increased, which ultimately causes increased reaction rate.

(iii) Nature of reactants

A chemical reaction involves the rearrangement of atoms between the reacting molecules to the product. Old bonds are broken and new bonds are formed. Consequently, the nature and the strength of the bonds in reactant molecules greatly influence the rate of its transformation into products. The reaction in which involve lesser bond rearrangement proceeds much faster than those which involve larger bond rearrangement.

(iv) Catalysts

The rate of a chemical reaction is increased in presence of a catalyst which ultimately enhanced the speed of a chemical reaction.

(v) Radiation

The rate of a number of chemical reactions increases when radiations of specific wave length are absorbed by the reacting molecules. Such reactions are called photochemical reactions. For example, chlorine may be mixed safely with hydrogen in dark, since the reaction between the two is very slow. However when the mixture is exposed to light, the reaction is explosive.

$$H_2 + Cl_2 \xrightarrow{h\nu} 2HCl + 188\,KJ$$

Consider a general reaction

$aA + bB \rightarrow cC + dD$

where a, b, c and d are the stoichiometric coefficients of reactants and products.

The rate expression for this reaction is Rate $\propto [A]^x [B]^y$

where exponents *x and y may or may not be* equal to the stoichiometric coefficients (a and b) of the reactants. The x and y indicate how sensitive the rate is to the change in concentration of A and B. Sum of these exponents, i.e., x + y in (4.4) gives the overall order of a reaction whereas x and y represent the order with respect to the reactants A and B respectively. Hence, **the sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction**.

Order of a reaction can be 0, 1, 2, 3 and even a fraction. A zero order reaction means that the rate of reaction is independent of the concentration of reactants.

Another property of a reaction called molecularity helps in understanding its mechanism. **The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction**. The reaction can be unimolecular when one reacting species is involved, for example, decomposition of ammonium nitrite.

$NH_4NO_2 \rightarrow N_2 + 2H_2O$

Bimolecular reactions involve simultaneous collision between two species, for example, dissociation of hydrogen iodide.

$2HI \rightarrow H_2 + I_2$

Trimolecular or termolecular reactions involve simultaneous collision between three reacting species, for example,

$2NO + O_2 \rightarrow 2NO_2$

The probability that more than three molecules can collide and react simultaneously is very small. Hence, reactions with the molecularity three are very rare and slow to proceed.

	Order	**Molecularity**
1	The number of concentration terms on which the reaction rate depends is called the order of a reaction.	The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.
2	It is a experimentally determined quantity.	It is a theoretically predicted quantity.
3	Order may be integer, fraction etc.	Molecularity always will be integer.
4	Order cannot be predicted from the stoichiometry of the balanced reaction equation.	Order can be predicted from the stoichiometry of the balanced reaction equation.

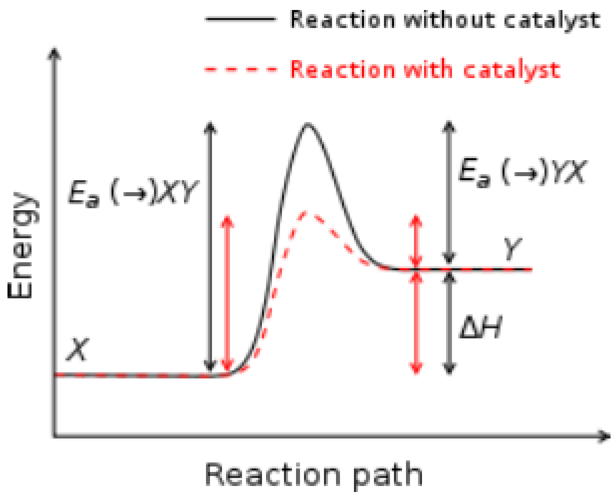
Free energy profile for one-step, two-step and three-step reactions

The Arrhenius equation gives the quantitative basis of the relationship between the activation energy and the rate at which a reaction proceeds. From the equation, the activation energy can be found through the relation

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

where A is the pre-exponential factor for the reaction, R is the universal gas constant, T is the absolute temperature (usually in kelvins), and k is the reaction rate coefficient. Even without knowing A, E can be evaluated from the variation in reaction rate coefficients as a function of temperature (within the validity of the Arrhenius equation).

At a more advanced level, the net Arrhenius activation energy term from the Arrhenius equation is best regarded as an experimentally determined parameter that indicates the sensitivity of the reaction rate to temperature. There are two objections to associating this activation energy with the threshold barrier for an elementary reaction. First, it is often unclear as to whether or not reaction does proceed in one step; threshold barriers that are averaged out over all elementary steps have little theoretical value. Second, even if the reaction being studied is elementary, a spectrum of individual collisions contributes to rate constants obtained from bulk ('bulb') experiments involving billions of molecules, with many different reactant collision geometries and angles, different translational and (possibly) vibrational energies—all of which may lead to different microscopic reaction rates.



The relationship between activation energy (E_a) and enthalpy of formation (Δ*H*) with and without a catalyst, plotted against the reaction coordinate. The highest energy position (peak position) represents the transition state. With the catalyst, the energy required to enter transition state decreases, thereby decreasing the energy required to initiate the reaction.

Catalysts: A substance that modifies the transition state to lower the activation energy is termed a catalyst; a catalyst composed only of protein and (if applicable) small molecule cofactors is termed an enzyme. A catalyst increases the rate of reaction without being consumed in the reaction. In addition, the catalyst lowers the activation energy, but it does not change the energies of the original reactants or products, and so does not change equilibrium. Rather, the reactant energy and the product energy remain the same and only the *activation energy* is altered (lowered).

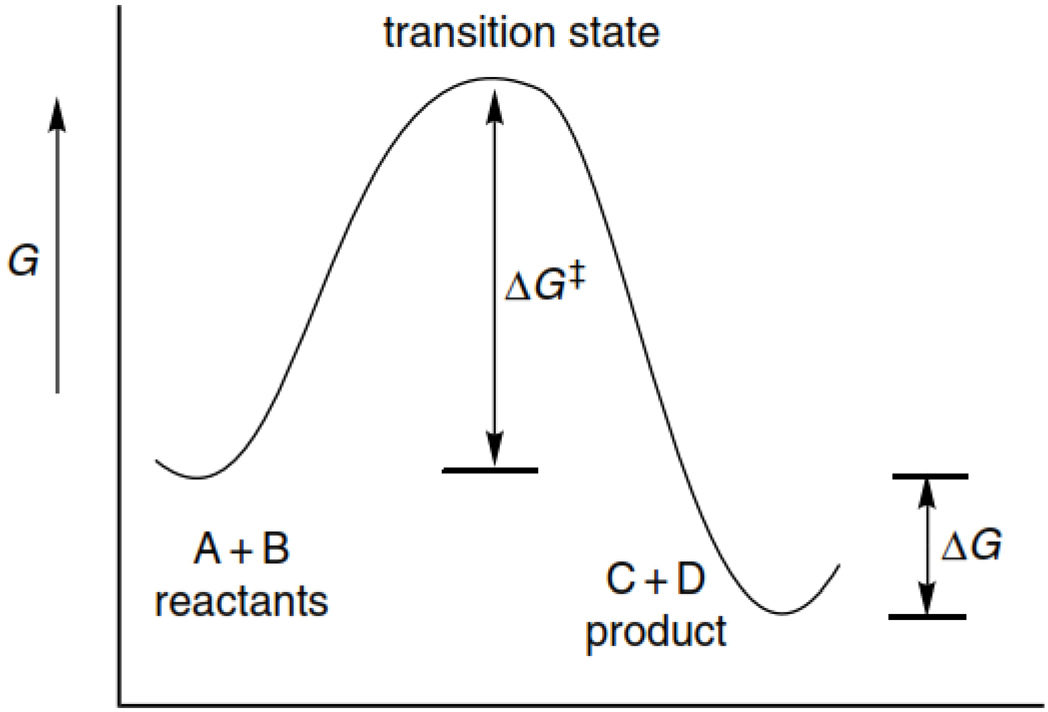
A catalyst is able to reduce the activation energy by forming a transition state in a more favorable manner. Catalysts, by nature, create a more "comfortable" fit for the substrate of a reaction to progress to a transition state. This is possible due to a release of energy that occurs when the substrate binds to the active site of a catalyst. This energy is known as Binding Energy. Upon binding to a catalyst, substrates partake in numerous stabilizing forces while within the active site (i.e. Hydrogen bonding, van der Waals forces). Specific and favorable bonding occurs within the active site until the substrate forms to become the high-energy transition state. Forming the transition state is more favorable with the catalyst because the favorable stabilizing interactions within the active site *release* energy. A chemical reaction is able to manufacture a high-energy transition state molecule more readily when there is a stabilizing fit within the active site of a catalyst. The binding energy of a reaction is this energy released when favorable interactions between substrate and catalyst occur. The binding energy released assists in achieving the unstable transition state. Reactions otherwise without catalysts need a higher input of energy to achieve the transition state. Non-catalyzed reactions do not have free energy available from active site stabilizing interactions, such as catalytic enzyme reactions.

Relationship with Gibbs energy of activation:

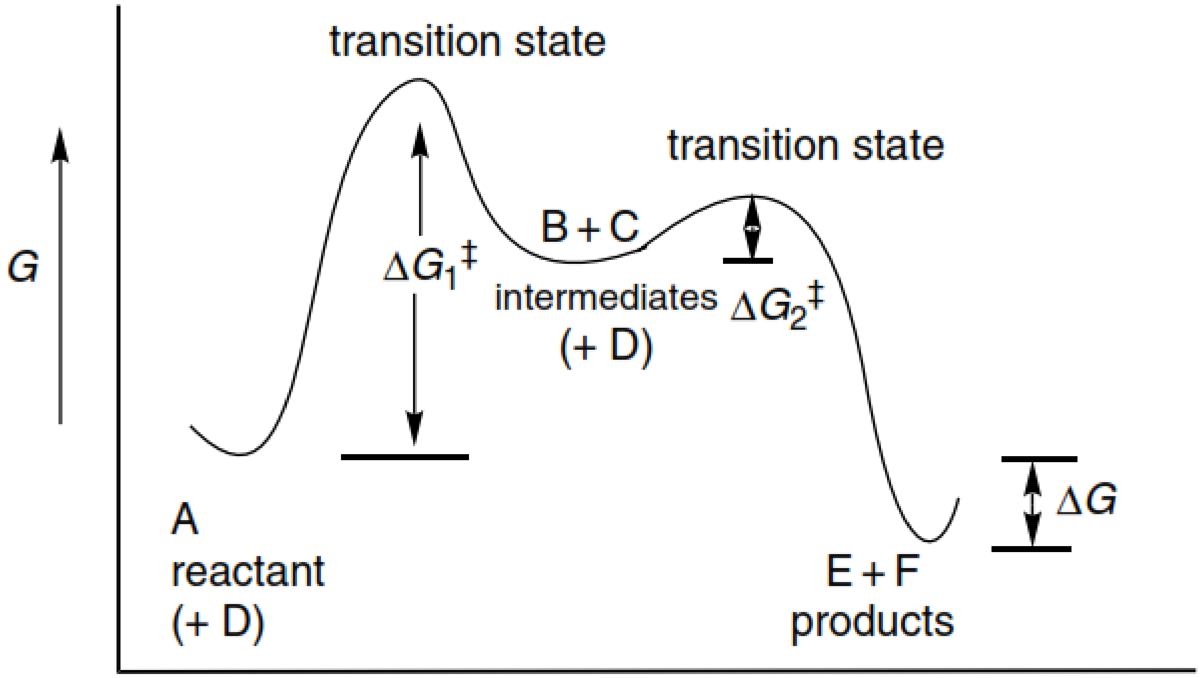
In the Arrhenius equation, the term activation energy (Ea) is used to describe the energy required to reach the transition state, and the exponential relationship $k = A\ \exp(-Ea/RT)$ holds. In transition state theory, a more sophisticated model of the relationship between reaction rates and the transition state, a superficially similar mathematical relationship, the Eyring equation, is used to describe the rate of a reaction: $k = (kT/h)\ \exp(-\Delta G^{\ddagger} / RT)$. However, instead of modeling the temperature dependence of reaction rate phenomenologically, the Eyring equation models individual elementary step of a reaction. Thus, for a multistep process, there is no straightforward relationship between the two models. Nevertheless, the functional forms of the Arrhenius and Eyring equations are similar, and for a one-step process, simple and chemically meaningful correspondences can be drawn between Arrhenius and Eyring parameters.

Instead of also using Ea, the Eyring equation uses the concept of Gibbs energy and the symbol G to denote the Gibbs energy of activation to achieve the transition state. In the equation, k and h are the Boltzmann and Planck constants, respectively. Although the equations look similar, it is important to note that the Gibbs energy contains an entropic term in addition to the enthalpic one. In the Arrhenius equation, this entropic term is accounted for by the pre-exponential factor A. More specifically, we can write the Gibbs free energy of activation in terms of enthalpy and entropy of activation: $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\ \Delta S$. Then, for a unimolecular, one-step reaction, the *approximate* relationships $E\text{a} = \Delta H^{\ddagger} + RT$ and $A = (kT/h)\ \exp(1 + \Delta S^{\ddagger}/R)$ hold. Note, however, that in Arrhenius theory proper, *A* is temperature independent, while here, there is a linear dependence on *T*. For a one-step unimolecular process whose half-life at room temperature is about 2 hours, $\Delta G^{\ddagger}$ is approximately 23 kcal/mol. This is also the roughly the magnitude of *E* for a reaction that proceeds over several hours at room temperature. Due to the relatively small magnitude of $T\Delta S$ and *RT* at ordinary temperatures for most reactions, in sloppy discourse, *E*a, , $G^{\ddagger}$, and $\Delta H^{\ddagger}$ are often conflated and all referred to as the "activation energy".

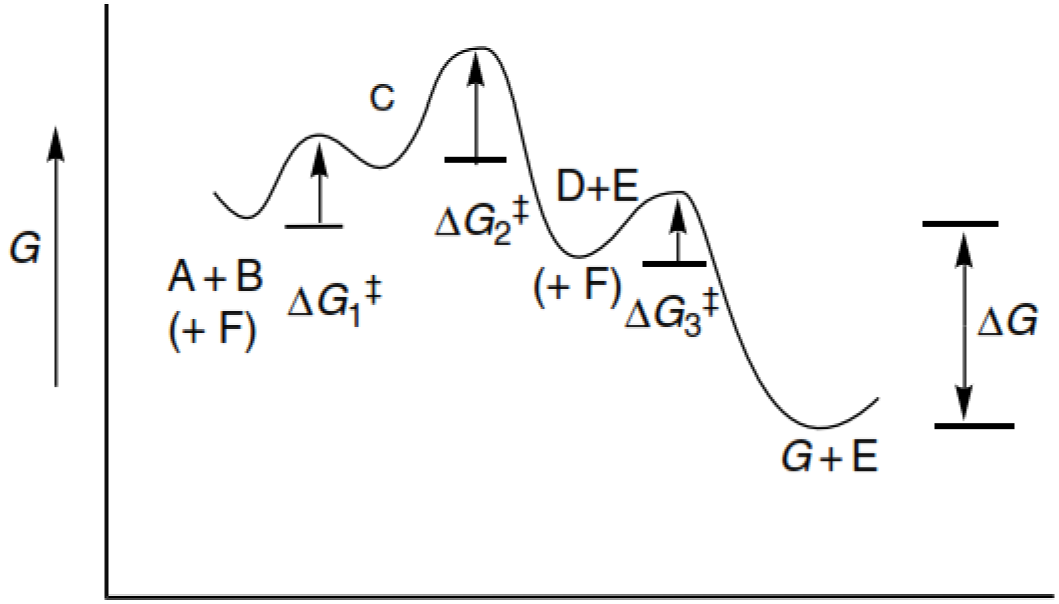
The total free energy change of a reaction is independent of the activation energy however. Physical and chemical reactions can be either exergonic or endergonic, but the activation energy is not related to the spontaneity of a reaction. The overall reaction energy change is not altered by the activation energy.



(a) Energy diagram for a single-step reaction.



(b) Energy diagram for a two-step reaction.



(c) Energy diagram for a three-step reaction.

Reaction energy profiles for one-, two-, and three-step reactions showing successive transition states and intermediates.

Negative activation energy: In some cases, rates of reaction *decrease* with increasing temperature. When following an approximately exponential relationship so the rate constant can still be fit to an Arrhenius expression, this results in a negative value of *E*. Elementary reactions exhibiting these negative activation energies are typically barrierless reactions, in which the reaction proceeding relies on the capture of the molecules in a potential well. Increasing the temperature leads to a reduced probability of the colliding molecules capturing one another (with more glancing collisions not leading to reaction as the higher momentum carries the colliding particles out of the potential well), expressed as a reaction cross section that decreases with increasing temperature. Such a situation no longer leads itself to direct interpretations as the height of a potential barrier.

Hammond's Postulate

Hammond's postulate states that the transition state of a reaction resembles either the reactants or the products, to whichever it is closer in energy. In an exothermic reaction, the transition state is closer to the reactants than to the products in energy (Fig. 1). Therefore, according to Hammond's postulate, in an exothermic reaction, the transition state resembles the reactants.

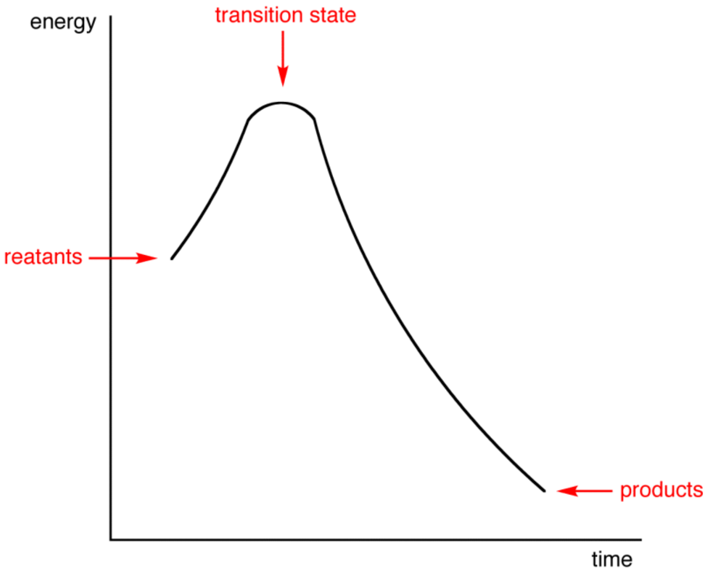


Fig. 1

In an endothermic reaction, the transition state is closer to the products than to the reactants in energy (Fig. 2). Therefore, according to Hammond's postulate, in an endothermic reaction, the transition state resembles the products.

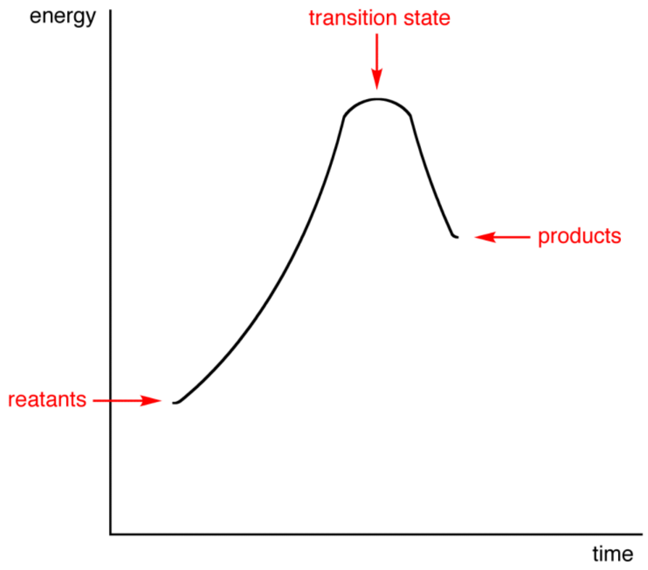


Fig. 2