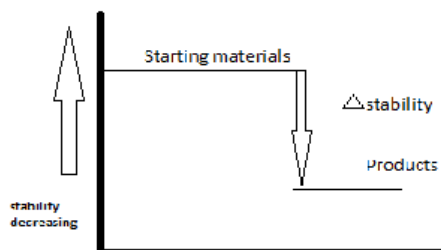


Energetics of Reaction

The most important information that we want to about a reaction is that how much of the products are converted into products (that is called percentage yield). This question can be answered from the value of equilibrium constant K . All the systems want to move towards stability, which means more stable are the products, more will be the equilibrium moves towards products formation.

In following diagram, larger the $\Delta_{\text{stability}}$ is, greater the expected conversion into products.



Enthalpy change (ΔH) is the heat of reaction that can be measured as simple energy change as going from reactants to products. It means that (ΔH) can give an important clue about the value of K . simply more will be the heat of reaction, more will be the value of K , and faster will reaction move towards products. However the observations are not in favor of this theory. Many exothermic reactions with large ΔH value are known with very small value of K and many endothermic reactions are known which have large K . It means that some factor other than enthalpy is also involved in deciding the equilibrium constant.

A measure of the degree of disorder of the system is called **entropy (S)**. For a system to be in most stable condition, it must have the minimum energy (minimum enthalpy, H) and maximum disorder (maximum entropy, S). Thus to attain a maximum stability, a system must have to compromise between the enthalpy and entropy, as given by the Gibb's free energy, G , as defined by

$$G = H - TS$$

Where T is the absolute temperature. The free energy change during a reaction at a particular temperature is thus given by:

$$\Delta G = \Delta H - T\Delta S$$

The relationship between the change in free energy and equilibrium constant k , of a reaction, is given below:

$$-\Delta G = 2.303RT \log k$$

It shows that the negative value of ΔG is directly proportional to the equilibrium constant K . Larger the decrease in free energy, larger the value of k , means that further over the equilibrium lies over towards the products.

For example in a reaction where there is no free energy change with ($\Delta G=0$) and $k=1$ corresponds to a 50% conversion of starting materials into products. Increasing positive value of ΔG shows rapidly decreasing value of k (extremely little conversion to products) and increasing negative value of ΔG shows an increasing value of k (high conversion rate to products). Thus a ΔG value of -42 kJ corresponds to an equilibrium constant of almost 10^7 shows an almost complete conversion into products. Thus an exact value of free energy change of reactants and products give us valuable information about prediction of extent of the reaction.

Enthalpy factor calculation:

The ΔH value of the reaction can be calculated from the difference of energies between the bonds of starting materials and the bonds of the products.

Entropy calculation:

However the entropy factor cannot be explained so easily. Simply we can say that the reaction in which total number of molecules are increasing in going from reactants to products for example in a reaction



There is likely to be an increase in entropy due to more crowding.

An increase in value of entropy increases the term $-T\Delta S$. This will make ΔG value negative even if the term ΔH is positive for an endothermic reaction. So the equilibrium lies in favor of the products. For an exothermic reaction $-\Delta H$ value makes the ΔG value more negative and the equilibrium constant K still remains large.

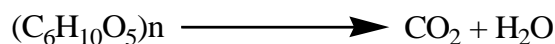
However in reactions where participating species decrease on going from reactants to products, entropy decreases (ΔS will be positive).



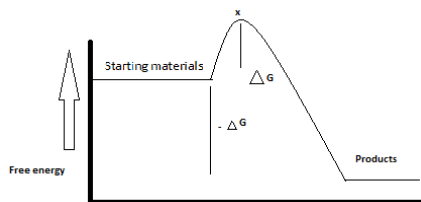
So if the reaction is exothermic and ΔH value is large and negative then the products are formed. But if the ΔH value is not negative (endothermic reactions) then ΔG becomes positive and equilibrium lies on the reactant side and no product will be formed.

Kinetics of reaction

The negative value of free energy of reaction ($-\Delta G$) tells us clearly that the reaction will move towards product formation or not. However still it is unable to give some other important information. For example it is unable to tell that how fast the reaction will take place and within how much time the reactants will be converted into products (Rate of reaction). Thus for oxidation of cellulose:

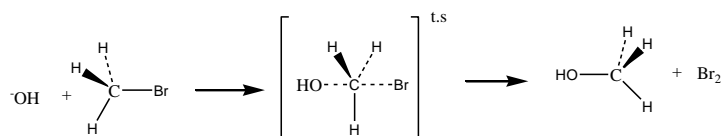


The value of ΔG is large and negative. So the reaction should remain towards CO_2 and H_2O . But we know that a news paper made up of cellulose is not converted into CO_2 and H_2O even present in air. The rate of reaction is very low at normal temperature although it can be increased at elevated temperatures. It means that even having a large negative value of ΔG , there is generally a barrier in conversion of reactants to products as shown below:



Reaction rate and free energy of activation

The position x in the energy profile diagram is called **activated complex or transition state**. It is defined as the least stable configuration through which starting materials pass during their conversion into products. It should be emphasized that it is highly unstable state and is not discrete molecular specie or intermediate and it cannot be actually detected or isolated. An example is the transition state in alkaline hydrolysis of bromomethane in which $\text{HO}-\text{C}$ bond is being formed at the same time as the $\text{C}-\text{Br}$ bond is being broken.



The height of the barrier i.e. ΔG^\ddagger is called Free energy of activation for the reaction. The high it is, slower the reaction will be. It is thought to being made up of enthalpy ΔH^\ddagger and entropy $T\Delta S^\ddagger$ terms.

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

Here ΔH^\ddagger is called enthalpy of activation for T.S., which is defined as the energy necessary for stretching or even breaking of the bonds. This is the basic requirement for reaction to take place. **Another important terminology is energy of activation (E_{act}) which is also related to ΔH^\ddagger . It is defined as the minimum threshold of energy which the reactant molecule must bring with them before collision to make reaction possible.** This is the reason that an increase in temperature increases the rate of reaction as the proportion of the molecules having this threshold energy increases.

The value of E_{act} for a reaction can be calculated form values of k, determined experimentally at two different temperatures T_1 and T_2 using Arrhenius equation which relates k to T, the absolute temperature.

$$K = Ae^{-E_a/RT} \quad \text{or}$$

$$\log_{10}k = E_{\text{act}}/2.303RT + \log_{10}A$$

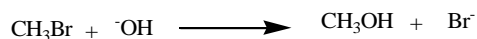
Where R is the gas constant and A is the constant for the reaction, independent of temperature, and is related to successful number of collisions between reactant molecules to products. The value of E_{act} can be calculated graphically by plotting values of $\log_{10}k$ against $1/T$ as given below:

$$\log_{10}k_1/k_2 = -E_{\text{act}}/2.303RT [1/T_1 - 1/T_2]$$

ΔS^\ddagger term here also relates to randomness. It is the measure of change in organization in going from reactants to transition state. ΔS^\ddagger is related to the "A" factor in Arrhenius equation. If formation of the transition state requires high degree of organization in the way reactant molecules must approach each other, so the transition state require a sizeable decrease in entropy, so the probability of its formation will be decreased.

Kinetics and rate limiting step

Rate of the reaction can be measured by investigating the rate at which reactants appear or products disappear at a particular temperature. Then the rate is related with the concentration of one or all of the reactants. Reaction can be monitored by variety of ways e.g., directly by removing the reaction materials followed by their titrimetric determination or indirectly by observation of conductimetric or spectroscopic changes.

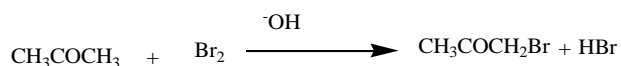


Thus for the above reaction, the reaction rate equation is

$$\text{Rate} = K[\text{CH}_3\text{Br}][\text{}^-\text{OH}]$$

Here K is the rate constant for the reaction. Reaction is said to be a second order reaction overall, first order with respect to CH_3Br and first order with respect to $\text{}^-\text{OH}$.

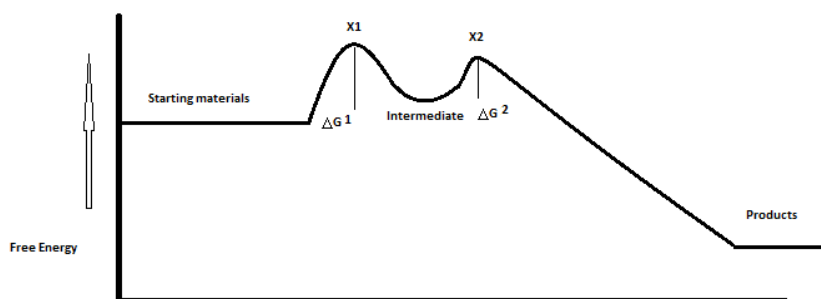
Now consider another reaction; base catalyzed bromination of propanone:



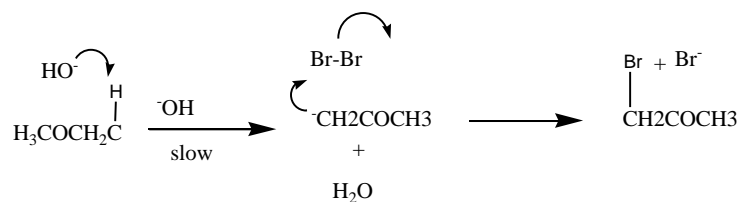
We find the rate equation as

$$\text{Rate} = k\{\text{CH}_3\text{COCH}_3\}[\text{}^-\text{OH}]$$

It shows that bromine is not involved in the reaction rate equation instead $\text{}^-\text{OH}$ is involved. It shows that reaction has two steps. In one step bromine is involved in the reaction but we are not measuring the rate of that step. In other step bromine is not involved whose rate we are measuring. Actually very few organic reactions are completed in one step but actually they are completed in more than one steps. Out of all these steps, we are only interested in the slowest step whose rate we measure, because the overall rate of reaction depends upon the rate of the slowest step.



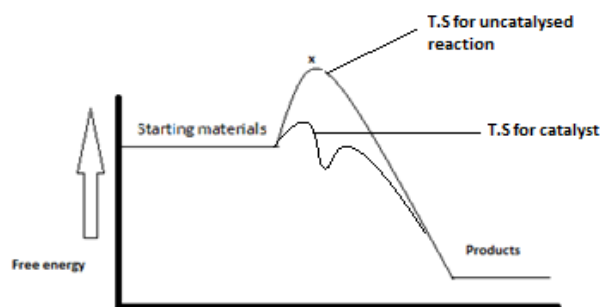
In above diagram, starting materials are converted via a transition state "x1" into an intermediate, which then decomposes into products via a second transition state "x2". As clear from the diagram that formation of intermediate x1 is more energy demanding ($\Delta G_1 > \Delta G_2$) than the intermediate X2 and hence will be slower among the two steps. So the rate of this slow step will control the overall rate of reaction.



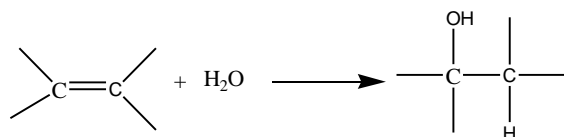
In above bromination reaction of propanone, slow rate limiting removal of proton by base results in the formation of carbanion which undergoes rapid non rate-limiting attack by Br₂ to yield bromopropanone and bromide ion as products. Our experimentally determined rate equation will not only give us information about the molecular species that are involved but also about the rate limiting step of the reaction.

Effect of catalyst:

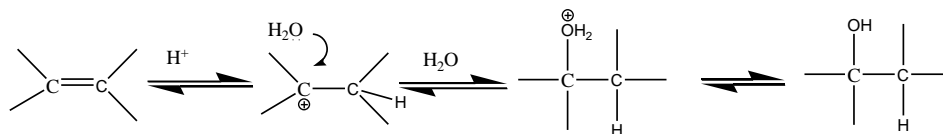
The effect of a catalyst is to increase the rate of reaction: so catalyst creates a new path with less free energetic demand, often through the formation of a new and more stable intermediate:



Thus the rate of hydration of alkene directly with water is often very slow:



But can be speed up with a catalytic amount of an acid. In this alternative path way, first the alkene is protonated to a carbocationic intermediate, which is then followed by an easy attack on positive carbon by a water molecule acting as a nucleophile. Finally the proton is liberated which again can act as a catalyst.



Kinetic versus thermodynamic control

When a starting material is converted into two or more alternative products, the proportions of both products in which they are formed is controlled by their relative rate of formation. The faster a product is formed the more of it will be in the final product mixture. This is called kinetic control.

This is not the case always: if one of more of the alternative reactions is reversible or if products are readily convertible to each other under the reaction conditions, the composition of the final product mixture is not dictated by the rate of reaction but their relative thermodynamic stabilities under the reaction system. This is called thermodynamic or equilibrium control. **Thus the nitration of methyl benzene is found to be kinetically controlled.** But the Friedel-Crafts alkylation of the same specie is thermodynamically controlled. Some time the control can be influenced by the reaction conditions. For example the sulphonation of naphthalene by concentrated sulphuric acid is kinetically controlled at 80° but at 160° it is thermodynamically controlled.