

## Classification of Reactions – by:

- 1) Functional group
- 2) Kind
  - a) Addition:  $A + B \longrightarrow C$
  - b) Elimination:  $A \longrightarrow B + C$
  - c) Substitution:  $A-B + C-D \longrightarrow A-C + B-D$
  - d) Rearrangement:  $A \longrightarrow B$ ,  
where B is a constitutional isomer of A
- 3) Mechanism
  - a) General Type
  - b) Specific Details

### General Mechanism Type

Three common reaction types ---

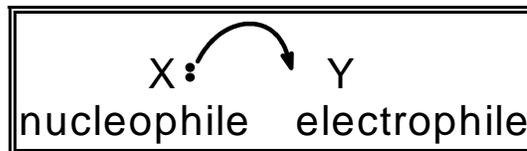
± Polar

☯ Free Radical

⬡ Pericyclic

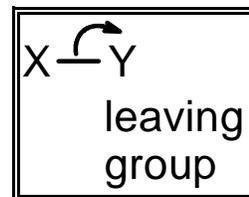
Polar--- most important.

Bonds are formed *heterogenically*: an electron rich moiety (molecule or part of a molecule) called a *nucleophile* donates a pair of electrons to an electron poor moiety, an *electrophile*.

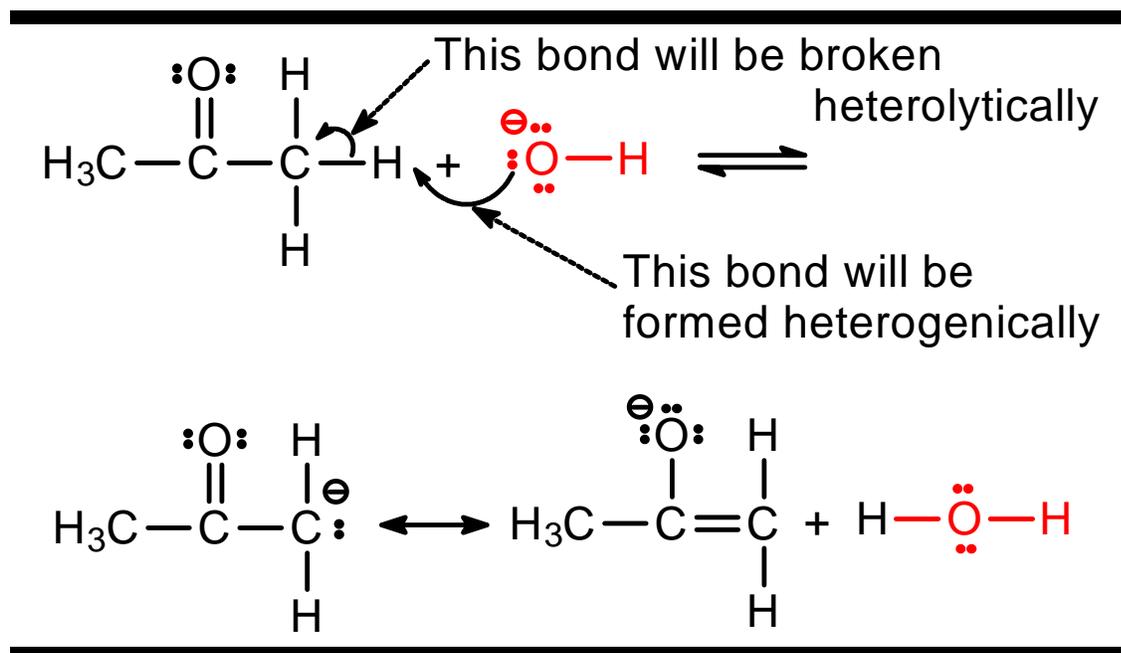


Bonds are broken *heterolytically*: one part of a molecule accepts both electrons in bond.

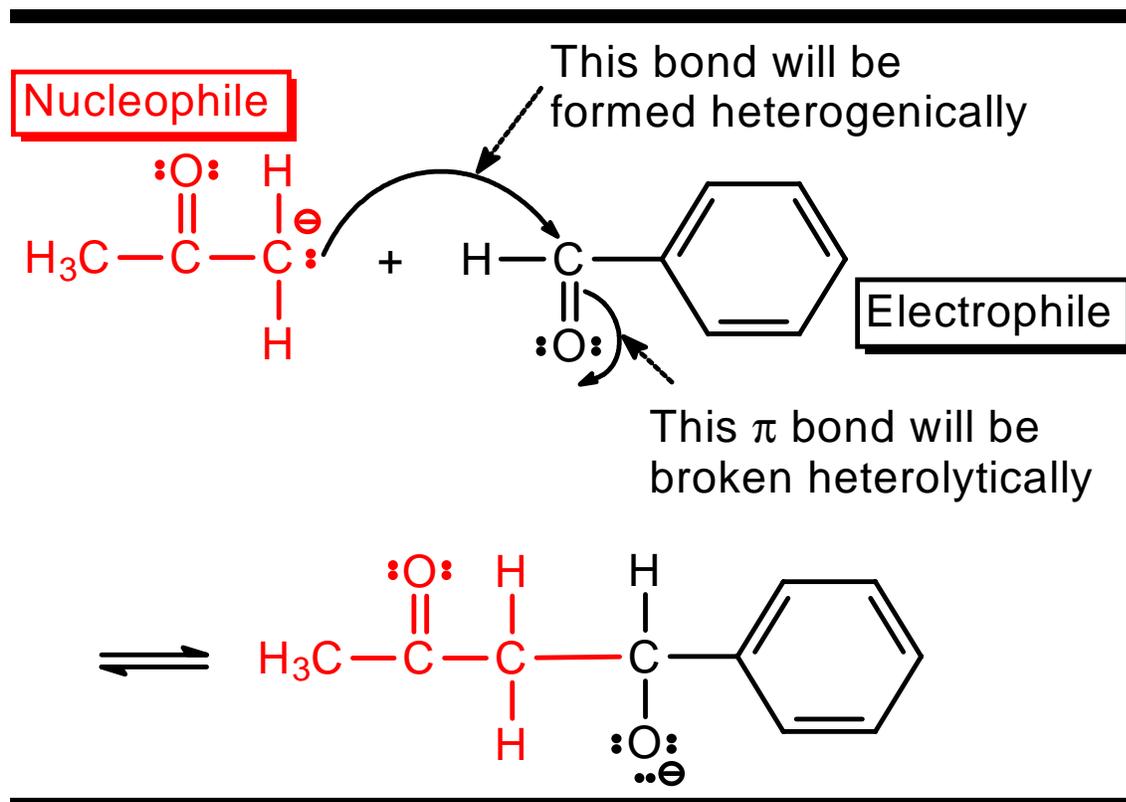
When a single bond is broken the departing moiety is called the *leaving group*.



Examples of polar reactions:



When C is site of attack,  
Lewis base = *nucleophile*  
Lewis acid = *electrophile*



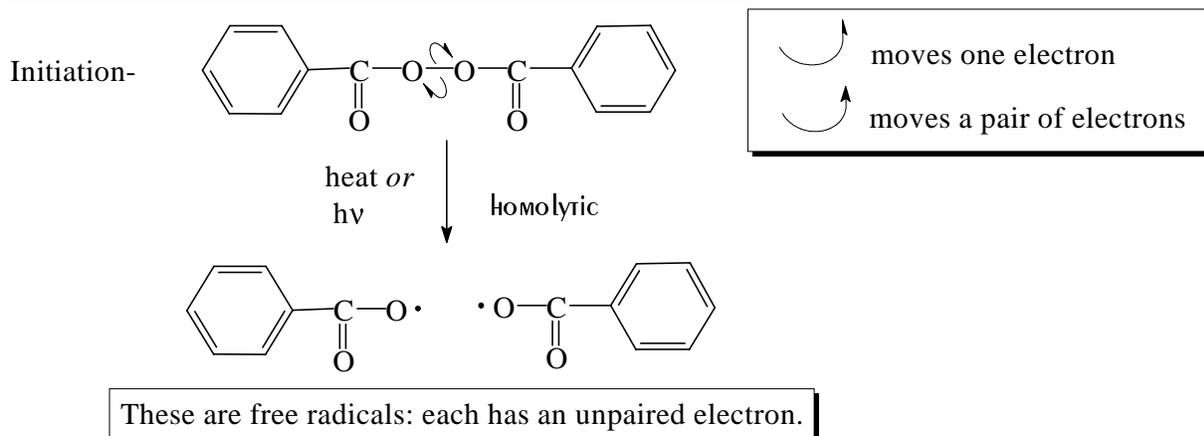
(Free) Radical ---

Reaction involves a (*free*) *radical* --- a chemical species with an unpaired electron.

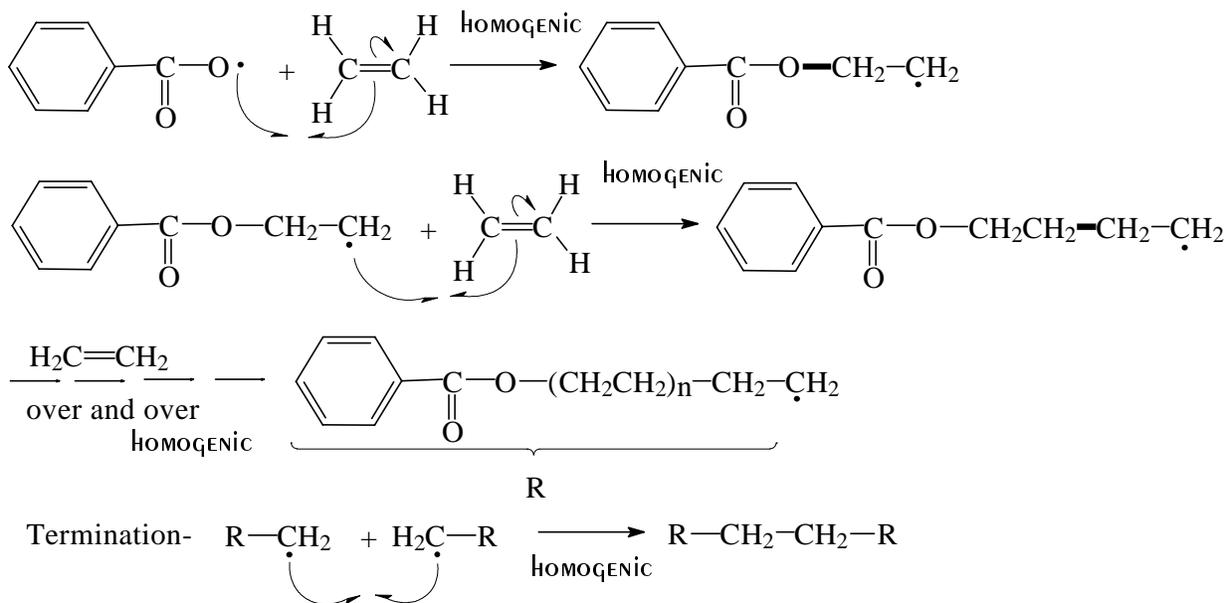
Bonds form *homogenically*: radical and moiety with which it reacts each provide **one** electron.

Bonds break *homolytically*: atom on each side of bond takes **one** electron from bond.

## Example: Polymerization of Ethylene to Form Polyethylene



Propagation steps-



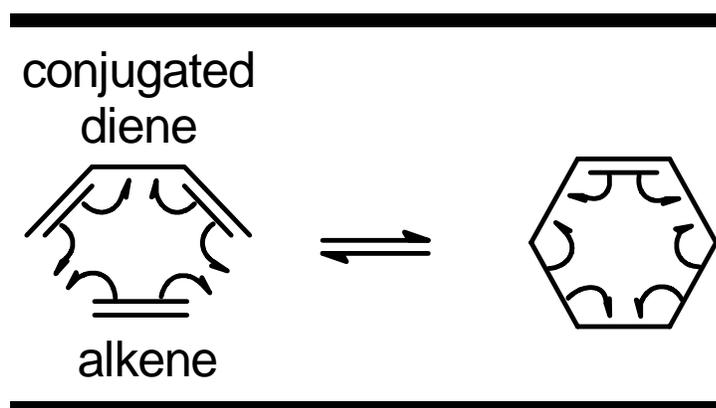
This is a *chain reaction*. The product of each step, a free radical, is a reactant in a subsequent step. This is a variation on the theme for free radical chain reactions seen earlier – in those cases the product of a subsequent step was a reactant in a previous step.

## Pericyclic ---

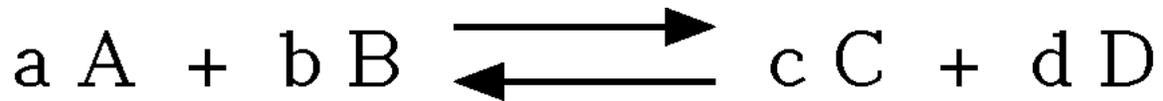
These reactions involve a redistribution of bonding electrons in a *concerted, cyclic* manner.

Example:

The cycloaddition reaction between a conjugated (alternating double and single bonds) diene (two double bonds) and an alkene known as the Diels-Alder reaction.



## Reaction Equilibrium



$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$K_{eq} = \exp -\Delta G^\circ/RT = 1/\exp \Delta G^\circ/RT,$$

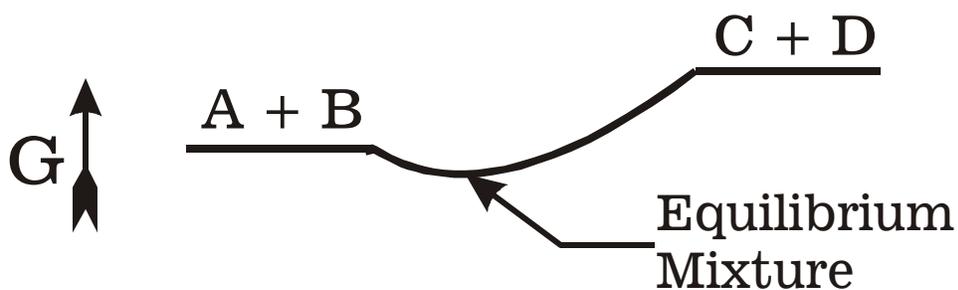
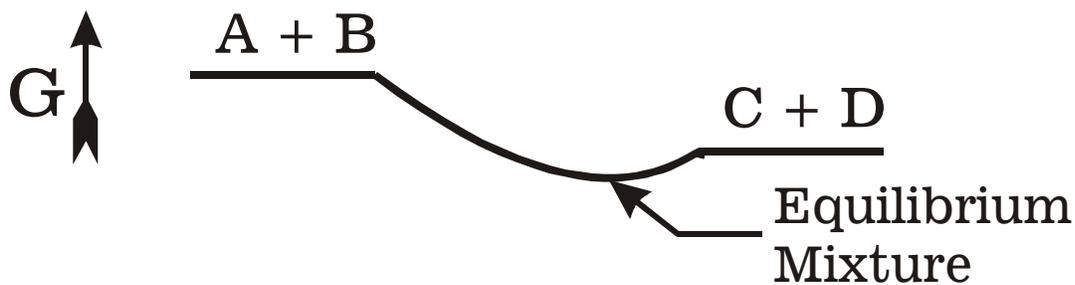
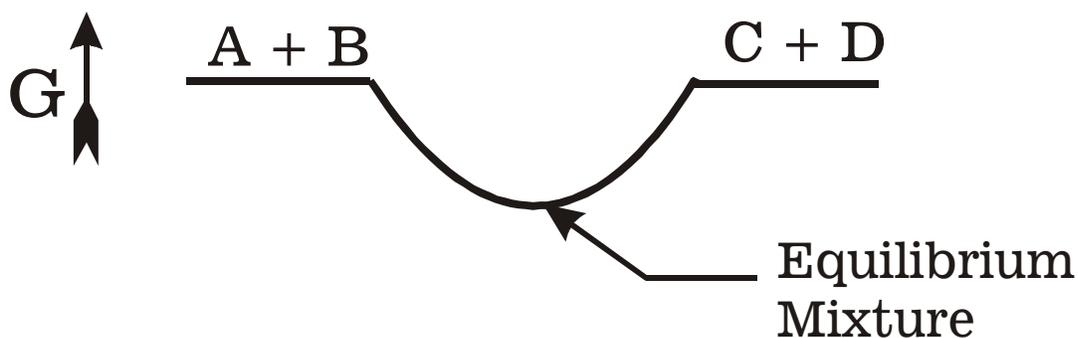
where,  $R = 1.99 \text{ cal/degree-mole}$   
 $T = \text{temperature in } ^\circ\text{K}$

$\Delta G^\circ = \text{the standard Gibbs free energy change}$   
 $= \text{free energy of products} - \text{free energy of reactants}$

If  $\Delta G^\circ = 0$ ,  $K = 1$ . The larger  $\Delta G^\circ$  is, the smaller  $K$  is; the smaller or more negative  $\Delta G^\circ$  is, the larger  $K$  is.

(If  $G^\circ_{\text{products}} > G^\circ_{\text{reactants}}$ ,  $K < 1$ , reactants favored at equilibrium;

if  $G^\circ_{\text{products}} < G^\circ_{\text{reactants}}$ ,  $K > 1$ , products favored at equilibrium.)



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

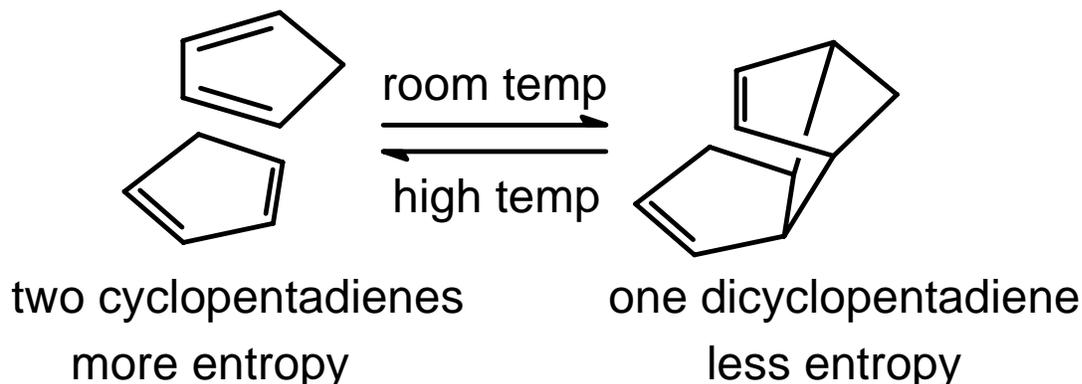
$\Delta H^\circ$  = standard heat of reaction;  
if negative: exothermic;  
if positive: endothermic.

$\Delta H^\circ$  is a measure of the change in total bonding energy (total bond energy of products - total bond energy of reactants), but calculations can be simplified by looking only at bonds which break or are formed (to a first approximation the energy of the others does not change).

$\Delta S^\circ$  = standard change in entropy and is a measure of the amount of "disorder" or "randomness" caused by a reaction.  $\Delta S^\circ = +$  if there are more product molecules than reactant molecules and/or if the product molecules are more flexible than the reactant molecules.  $\Delta S^\circ = -$  if the converse is true.

In many cases, especially at room temperature,  $T\Delta S^\circ$  is small compared to  $\Delta H^\circ$ . In these cases,  $\Delta G^\circ \approx \Delta H^\circ$ .

A double edged example: cyclopentadiene  $\rightleftharpoons$  dicyclopentadiene



In this case, at low temperature H controls ( $\sigma$  bonds are stronger than  $\pi$  bonds); two  $\pi$  bonds are converted to two  $\sigma$  bonds in going from left to right.

However, at high temperature, S controls because of the  $T\Delta S$  term in  $\Delta G$ ; two molecules have more entropy than one because they can each move independently.

## Reaction Rate

Reaction rate refers to how fast or slow a reaction is: how fast a product forms or a reactant disappears.

Mathematically the rate is:  $d[\text{product}]/dt$  or  $-d[\text{reactant}]/dt$ , where [ ] is concentration and t is time.

It is often the case that reactions with a favorable equilibrium constant are fast, but not always. It is almost always the case that reactions with unfavorable equilibrium constants are slow.

An overall reaction – reactants  $\rightleftharpoons$  products – may comprise several steps or only one. The rate of the overall reaction cannot be faster than the slowest step – the *rate limiting step*. The rate of any step, including the rate limiting step is the product of 3 factors: molecular collision frequency, energy exchange in collision, and a probability factor.

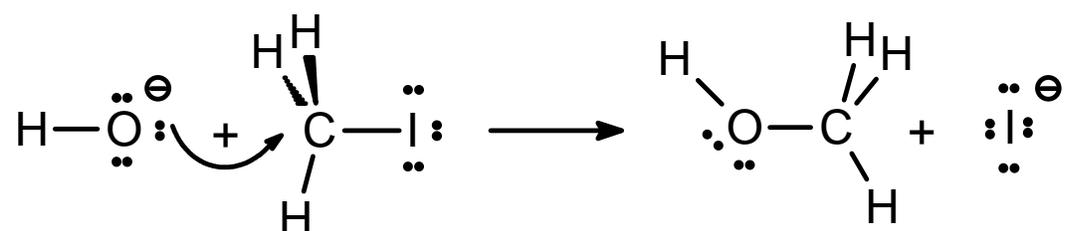
Molecular collision frequency – Molecules (or atoms or ions) have to collide in order to react with each other; the more collisions per unit time, other things being equal, the faster the reaction. In most cases not every collision will result in reaction; this is where the other two factors come into play.

Energy factor – To react, colliding molecules must usually exchange some energy, which means they must bang into each other with a certain amount of force. For example, if a reaction involves breaking one bond (#1) and forming another (#2), the energy required to break #1 will come partly from the energy released by formation of #2. However, kinetic energy is needed from the collision because bond breaking (#1) and bond formation (#2) are not perfectly synchronized or because bond #2 is weaker than #1.

The minimum energy required from the collision for

reaction to occur is called  $e_{\text{act}}$  or  $\Delta H^\ddagger$ .

Probability factor – This depends on the orientation of the molecules when they collide and on the change in “randomness” at collision. The orientation part is pretty straightforward. Consider the following reaction:



The fact is, for this reaction to occur, the oxygen of the OH group must hit the carbon of the iodomethane on the side away from the iodine. If the collision occurs in any other orientation – the oxygen of the OH hits a hydrogen or the iodine, or the H of the OH hits any of the atoms in the iodomethane – the reaction will not take place.

The “randomness” part of this factor is a little esoteric and we will not consider it further.

$$\text{Rate} = \underbrace{\text{Collision Frequency}} \times \underbrace{\text{Energy Factor}} \times \underbrace{\text{Probability Factor}}$$

Depends on concentration and temp.

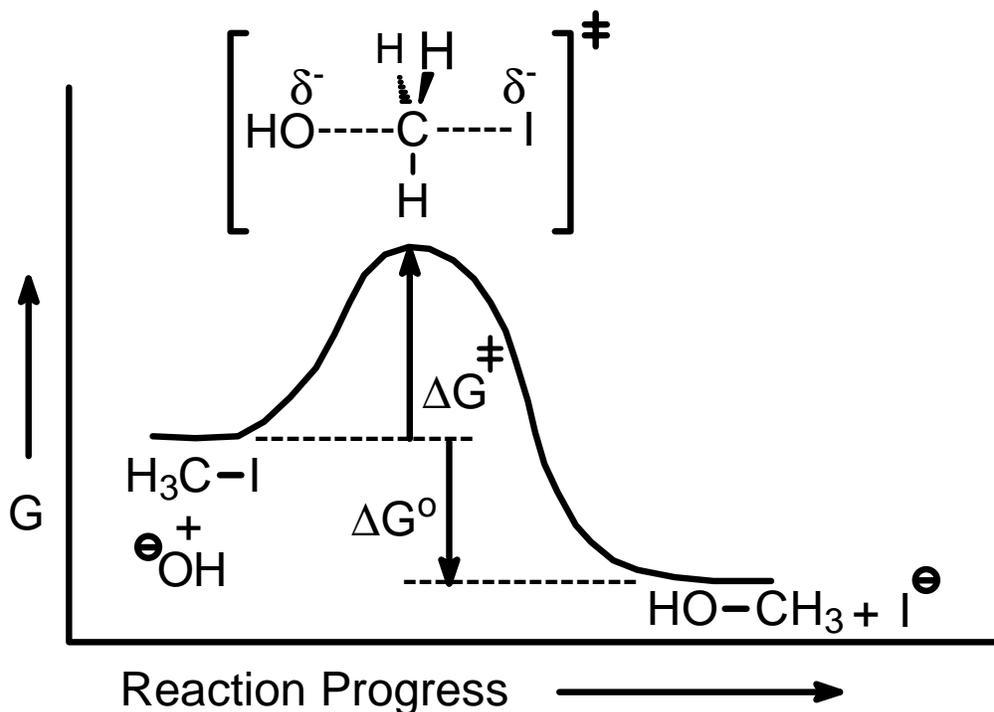
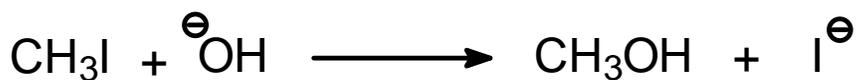
Most important; depends on  $\Delta H^\ddagger$  ( $\sim e_{\text{act}}$ ) and T; fraction of collisions with  $e \geq e_{\text{act}} = \exp -e_{\text{act}}/RT$ .

Depends on orientation and "randomness":  $\Delta S^\ddagger$



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

Consider –



This is a fairly simple reaction. The reactants, iodomethane and hydroxide ion, form the products, methanol and iodide ion, in one step. Since the C-O bond is stronger than the C-I bond more energy is released than consumed, so  $\Delta H^{\circ}$  is negative – the reaction is exothermic. Since  $\Delta G^{\circ} \sim \Delta H^{\circ}$ , it, too, is negative. Note, in the reaction energy diagram, that the products are below the reactants in terms of  $G$ , the free energy.

Note, also, in the reaction energy diagram that the colliding molecules must change enough kinetic energy from the collision into potential energy to “get over” the  $\Delta G^\ddagger$  barrier. The molecular structure at the highest point in the energy curve, shown in brackets with a double dagger ( $\ddagger$ ), is called the *transition state*. This is not a stable (or even an unstable) molecule. It is the highest energy arrangement of atoms through which the reactants pass on their way to forming products. At this point in the reaction the C-I bond is partially broken and the C-O bond is partially formed. As the reaction continues, the C-I bond is broken and the C-O bond is formed, giving the products.

Some reactions are more complicated than this one. As an (important) example, some reactions follow the path: reactants  $\rightarrow$  [transition state 1] $^\ddagger$   $\rightarrow$  intermediate  $\rightarrow$  [transition state 2] $^\ddagger$   $\rightarrow$  products. An instance of this would be the reaction between an alkene and HBr to give an alkyl bromide. The reaction energy diagram in this case will exhibit two “humps” – the two transition states – and a high-energy valley between them – the *carbocation* intermediate. This case is discussed at length in McMurry.