Marcus Hush Theory

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Marcus Hush Theory

- Marcus theory for ETR was originally developed by Rudolph A. Marcus in 1956 & due to this theory received Nobel Prize in chemistry in 1992.
- This theory is widely used in chemistry as well as biology to explain the rate of ETR. Firstly it was formulated to explain OSETR then Hush extended to ISETR. So it is also known as MH Theory.
- This theory based upon the TST which gives idea about structural changes in a reaction.

Marcus Hush Theory

This theory based upon the following consideration:

- The charge may be transferred in any portion from one body to another.
- It depends upon different fast electron polarization P_e and the slow atom and orientation polarization P_u of the solvent.
- Marcus separates the inner sphere (reactant + tightly bound solvent molecules, in
- complexes + ligands) and the outer sphere (free solvent)
- It must be confined to calculating the outer sphere energy of the non-equilibrium polarization of the "transition state". The outer sphere energy is often much larger than the inner sphere contribution because of the far reaching electrostatic forces.

Suppose, as a special case, we have a redox reaction where the electron donor, D, and the acceptor A, reversibly form an encounter complex; where the rate determining step is the electron transfer step; and where break up of the successor complex is fast.

$$\mathrm{D} + \mathrm{A} \xrightleftharpoons{K_{\mathrm{DA}}} \mathrm{DA}$$

$$\mathrm{DA} \xrightarrow{k_{\mathrm{ET}}} \mathrm{D}^{+}\mathrm{A}^{-}$$

$$\mathrm{D}^{+}\mathrm{A}^{-} \xrightarrow{\textit{fast}} \mathrm{D}^{+} + \mathrm{A}^{-}$$

Marcus theory: ET from a donor (D) to an acceptor (A)

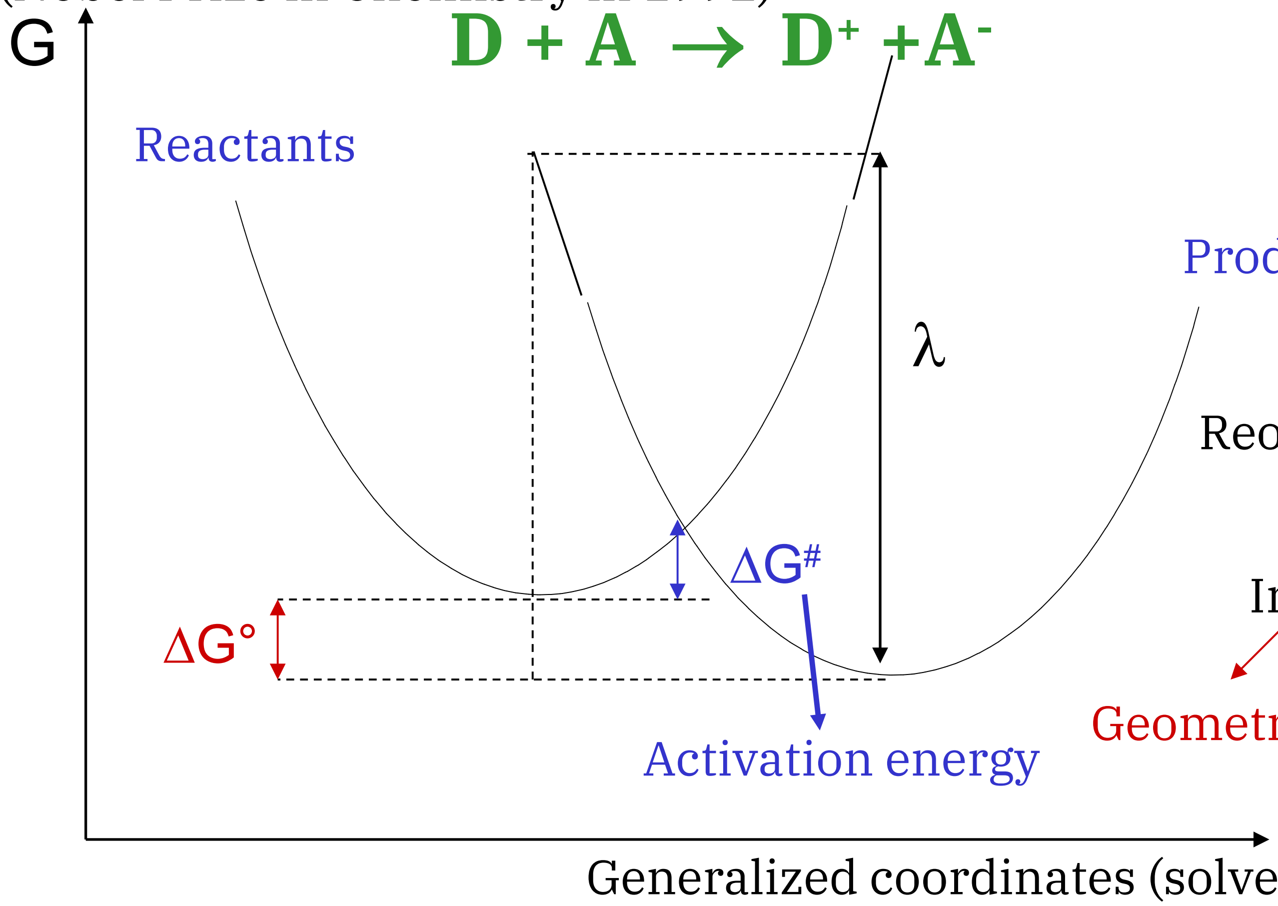
This theory mathematically & graphically developed by following way:

(Nobel Prize in Chemistry in 1992)

G= Gibbs energy

$\Delta G = \Delta H + T\,\Delta S$

$D + A \rightarrow D^+ + A^-$



Reorganization energy λ

λ_i λ_s

Internal + External

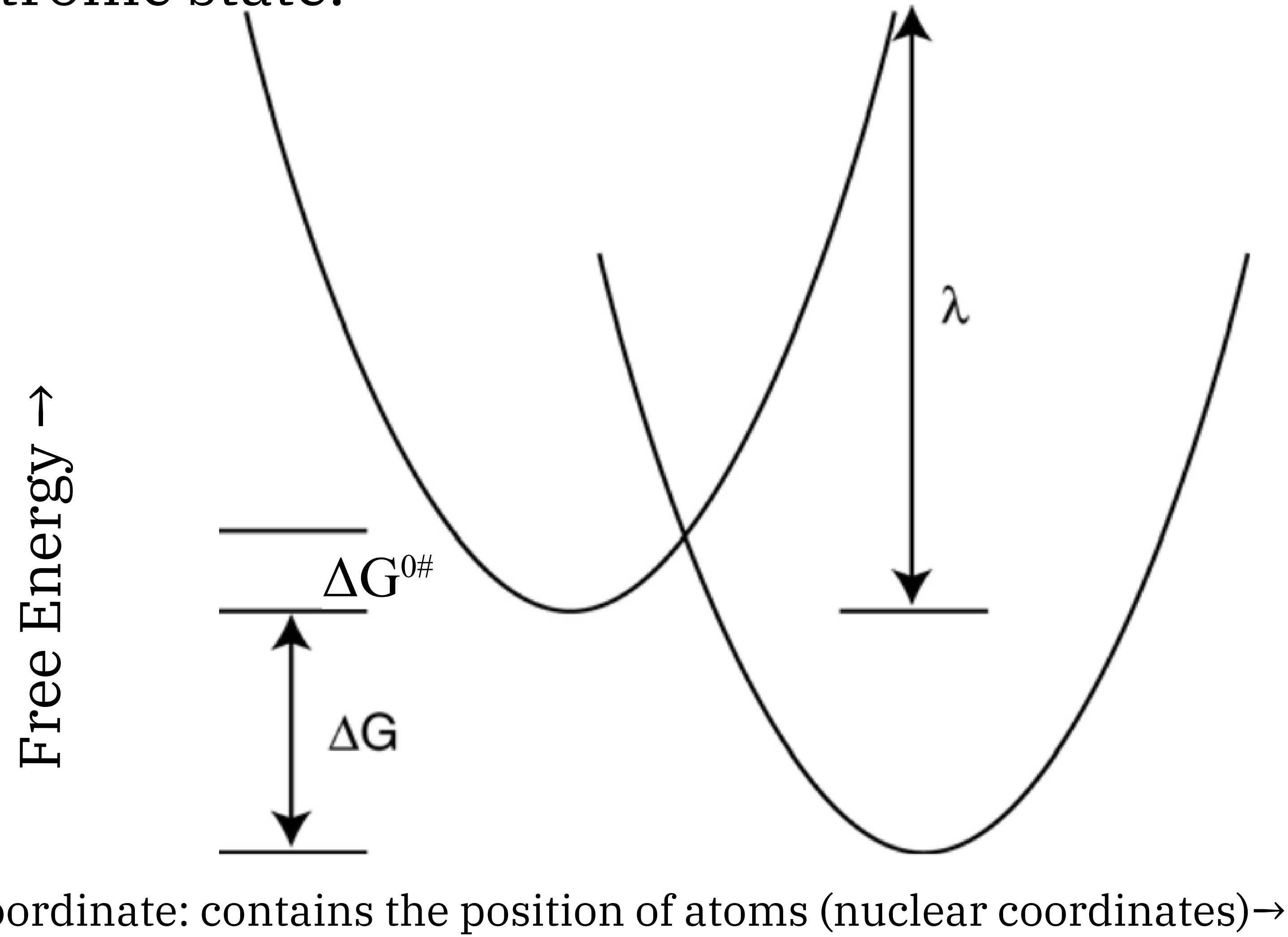
Geometry

Solvent

$$k_{et} = A\exp^{-\Delta G^{\#}/kT} = (4\pi^2/h)\,H_{RP}^2\,(4\pi\lambda kT)^{-1/2}\exp^{-(\Delta G^\circ + \lambda)^2/4\lambda kT}$$

K_{et} is the rate of electron transfer

The Reorganization Energy λ is defined as the energy required to “reorganize” the structure from initial to final coordinates, without changing the electronic state.



1. For a reaction to take place D and A must diffuse together. They form the precursor complex, usually a kinetic, unstable, solvated encounter complex, which by electron transfer is transformed to the successor complex, and finally this separates by diffusion. For a one electron transfer the reaction is

$$\mathrm{D} + \mathrm{A} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} [\mathrm{D}\cdots\mathrm{A}] \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} [\mathrm{D}^{+}\cdots\mathrm{A}^{-}] \xrightarrow{k_{30}} \mathrm{D}^{+} + \mathrm{A}^{-}$$

(D and A may already carry charges). Here k_{12}, k_{21} and k_{30} are diffusion constants, k_{23} and k_{32} rate constants of activated reactions.

The total reaction may be diffusion controlled (the electron transfer step is faster than diffusion, every encounter leads to reaction) or activation controlled (the "equilibrium of association" is reached, the electron transfer step is slow, the separation of the successor complex is fast).

Redox reactions are preferably run in polar solvents. Donor and acceptor then have a solvent shell and the precursor and successor complexes are solvated also.

The closest molecules of the solvent shell, or the ligands in complexes, are tightly bound and constitute the "inner sphere".

Reactions in which these participate are called inner sphere redox reactions. The free solvent molecules constitute the "outer sphere".

Outer sphere redox reactions do not change the inner sphere, neither formation of bond nor breaking of bond takes place.