

### ❖ Hammond's Postulate

*Hammond's postulate states when a transition state gives rise to an unstable reaction intermediate (or product) it will have comparable energy to that intermediate, and both will be interconvertible by a very minute reorganization of molecular structure.*

This hypothesis was first proposed by George Hammond in 1955 to correlate the transition states with intermediates and products. Nevertheless, besides Hammond's postulate, another chemist J. E. Leffler also gave an assumption that the transition state will have a greater resemblance to the less stable species (i.e., reactant, or intermediate, or product). Since many teachers or textbooks state 'Leffler assumption' but refer to the statement as 'Hammond's postulate' due to their similar arguments, it is better to use 'Hammond- Leffler postulate' to give the credit where it is due.

Therefore, the geometric structure of a state can be predicted by comparing its energy to the species neighboring it along with the reaction coordinate. For instance, the geometry of the transition state resembles reactants in an exothermic reaction; whereas the endothermic reactions will have transition states closer to products. This kind of assessment is very useful especially when most transition states cannot be analyzed experimentally.

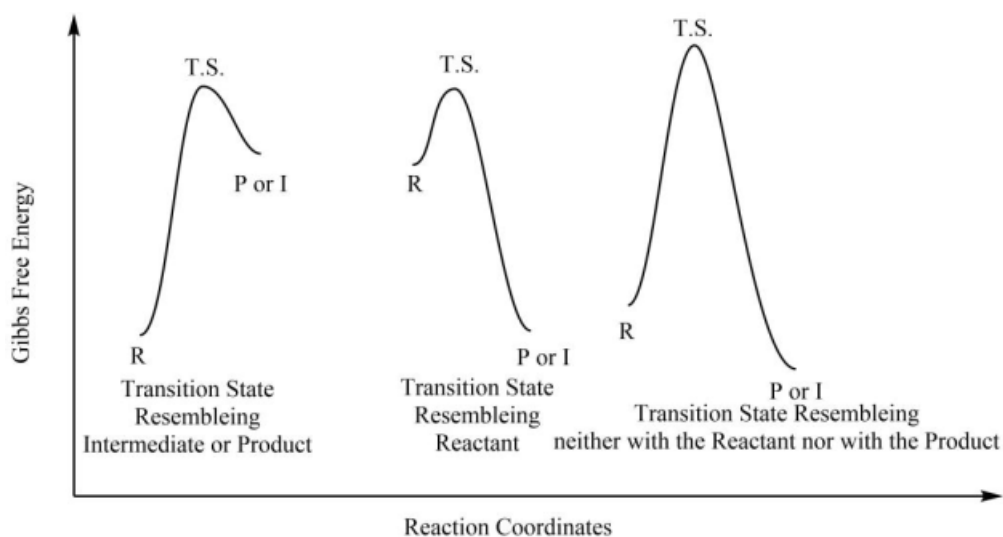


Figure 5. Three cases of according to Hammond's postulate.

Hammond's postulate can also be used to rationalize the Bell-Evans-Polanyi principle describes the experimental observation that the rate of a reaction (and so the activation energy) is influenced by the enthalpy of that reaction. Hammond's postulate describes this observation by explaining how does enthalpy variation results in the structure change of the transition state; which in turn, would change the energy of the transition state, and so the reaction rate as well (via changing activation energy).

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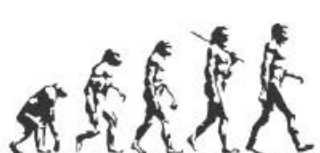
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# A TEXTBOOK OF ORGANIC CHEMISTRY

**Volume I**

**MANDEEP DALAL**



*First Edition*

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