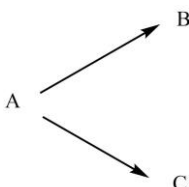


### ❖ Kinetic and Thermodynamic Control

The thermodynamic or the kinetic control in a chemical reaction can dictate the composition in the final product mixture when two or more competing pathways giving rise to different products and the selectivity or stereoselectivity is influenced by the reaction conditions. Consider a typical reaction in which reactant A can transform into product B and C i.e.



Now, will discuss the two cases of thermodynamic and kinetic control of the overall reaction depending upon the nature of the product.

#### ➤ *Different Products from Thermodynamic and Kinetic Control*

The difference will be obvious when product C forms at a faster rate than product B because the activation energy for product C is lower than that for product B (even if B is more stable than A). In such a scenario, C is favored kinetically and called as the kinetic product; whereas B is favored thermodynamically controlled and is called as the thermodynamic product. The exact nature of the final product (thermodynamic or kinetic) will be dictated by many reaction conditions like temperature, pressure, solvent, or any other factor which might affect the reaction pathway. Also, it must be kept in mind that the above-mentioned statement is true only if the activation energy of the two routes are different; with dominating yield for the pathway having lower activation energy ( $E_a$ ) than the other.

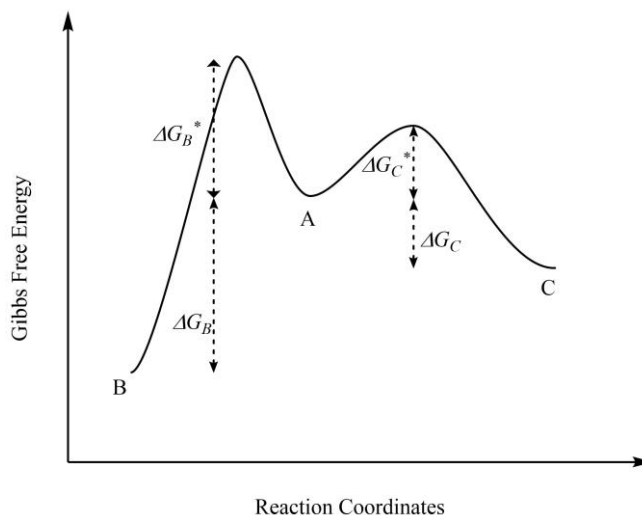


Figure 3. Energy profile diagram for kinetic versus thermodynamic product reaction.

➤ **Same Products from Thermodynamic and Kinetic Control**

In this case, product B forms at a faster rate than product C because the activation energy for product B is lower than that for product C. Also, since  $\Delta G_B > \Delta G_C$ , B is more stable thermodynamically than C. Therefore, the thermodynamic as well kinetic control of the reaction will favor the formation of product B. The activation of thermodynamic or kinetic control dictates the composition of the end product when these competing pathways give rise to different products influencing the selectivity of the reaction.

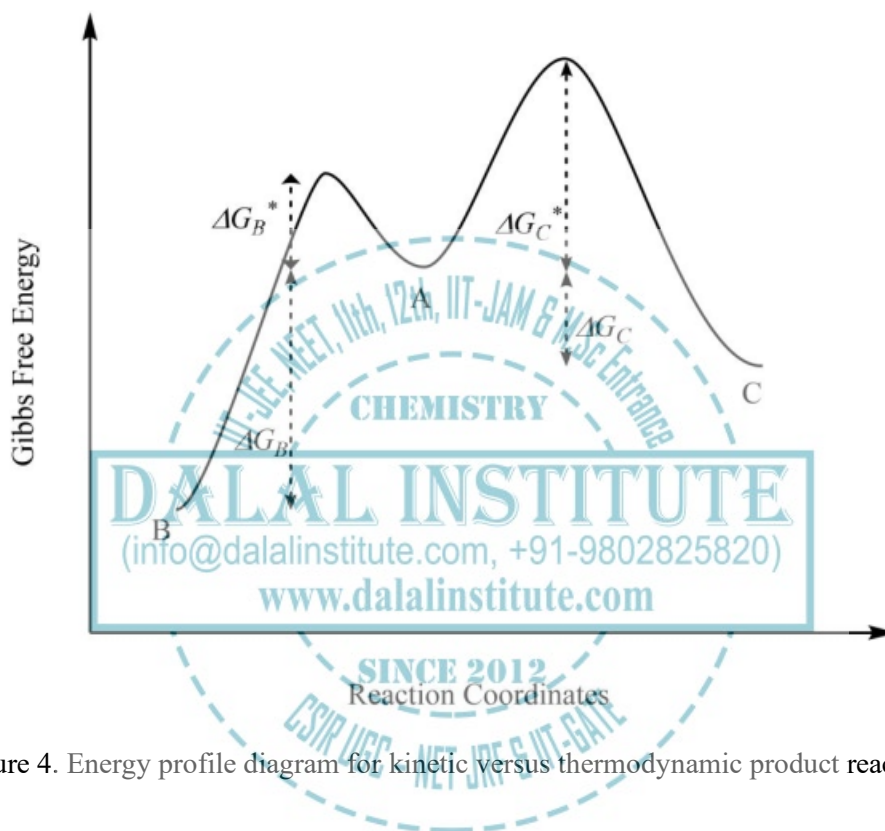


Figure 4. Energy profile diagram for kinetic versus thermodynamic product reaction.

The selectivity arising from kinetic vs thermodynamic control is extremely important in the case of asymmetric synthesis. This can be attributed to the fact that the pairs of enantiomers have the same Gibbs free energy; and therefore, the thermodynamic control will yield a racemic mixture by obligation. So, any catalytic reaction that gives the product with enantiomeric excess different than zero must be under some kind of kinetic control. Several stoichiometric asymmetric syntheses occur giving enantiomeric products due to a chiral substrate i.e., the reaction is actually a diastereoselective type; and therefore, even if such transformations are kinetically controlled, thermodynamic control is at least theoretically possible.

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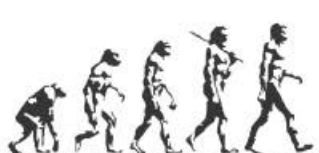
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# A TEXTBOOK OF ORGANIC CHEMISTRY

**Volume I**

**MANDEEP DALAL**



*First Edition*

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