

❖ Curtin-Hammett Principle

The Curtin–Hammett principle in chemical kinetics was proposed by David Yarrow Curtin and Louis Plack Hammett to predict the relative ratio of the products obtained from a conformational equilibrium.

It states that the relative ratio of the products obtained from a conformational equilibrium is independent of the relative concentration of participating conformers and is a function of the free-energy-gap of the corresponding transition states provided that the rate of conformational-interconversion is much larger than the rate of formation of products.

To understand the Curtin-Hammett principle in perspective, consider a typical reaction in which products C and D are formed from two conformers A and B as



Since the enthalpy of activation for most of the organic reactions is greater than the equilibrium between participating conformers ($\Delta G_A^* > \Delta G^o$ and $\Delta G_B^* > \Delta G^o$), the reactants A and B are will remain abundant.

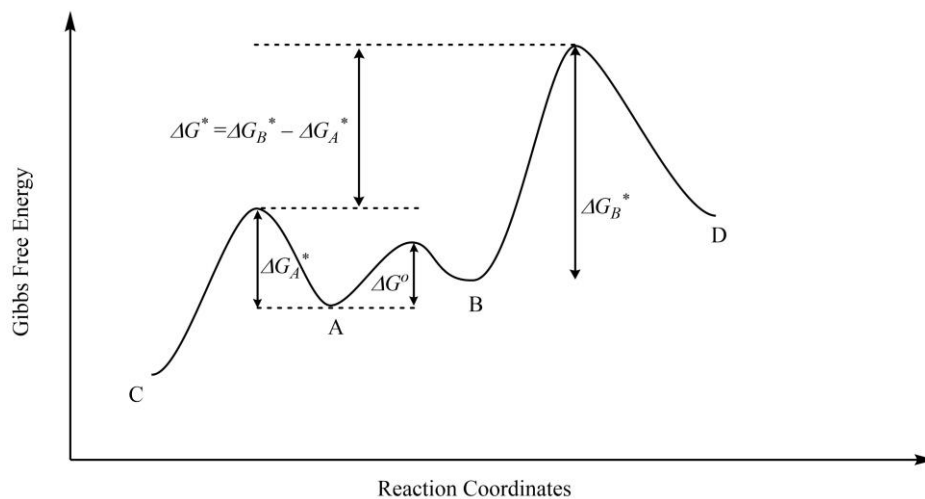


Figure 6. Potential energy diagram for Curtin-Hammett principle.

For the conformational equilibrium, the equilibrium constant (K) will be

$$K = \frac{B}{A} \quad (5)$$

The formation rate for C can be given as

$$\frac{dC}{dt} = k_C[A] \quad (6)$$

$$\frac{dD}{dt} = k_D[B] \quad (7)$$

Now considering the reaction is first-order or pseudo-first-order in nature, the ratio of the products can simply be obtained by dividing equation (7) by equation (6) i.e.

$$\frac{dD}{dt} \times \frac{dt}{dC} = \frac{k_D[B]}{k_C[A]} \quad (8)$$

$$\frac{dD}{dC} = \frac{k_D[B]}{k_C[A]} \quad (9)$$

Using the value of $[B]/[A]$ from equation (5), we get

$$\frac{dD}{dC} = \frac{k_D}{k_C} K \quad (10)$$

But we know from chemical kinetics that

$$K = e^{-\Delta G^0/RT} \quad (11)$$

$$k_C = \frac{RT}{Nh} e^{-\Delta G_A^*/RT} \quad (12)$$

$$k_D = \frac{RT}{Nh} e^{-\Delta G_B^*/RT} \quad (13)$$

Using equations (11–13) in equation (10), we get

$$\frac{dD}{dC} = \frac{\frac{RT}{Nh} e^{-\Delta G_B^*/RT}}{\frac{RT}{Nh} e^{-\Delta G_A^*/RT}} e^{-\Delta G^0/RT} \quad (14)$$

$$\frac{dD}{dC} = \text{Products Ratio} = e^{-\Delta G_B^*/RT} e^{+\Delta G_A^*/RT} e^{-\Delta G^0/RT} \quad (15)$$

$$\text{Products Ratio} = e^{-\frac{\Delta G_B^* + \Delta G_A^* - \Delta G^0}{RT}} \quad (16)$$

However, it is obvious from Figure 5 that $-\Delta G_B^* + \Delta G_A^* - \Delta G^0 = -\Delta G^*$; therefore, we have

$$\text{Products Ratio} = e^{-\frac{\Delta G^*}{RT}} \quad (17)$$

Hence, the product ratio is governed by the energy gap between the transition states rather than ΔG^0 , which is the famous Curtin-Hammett principle.

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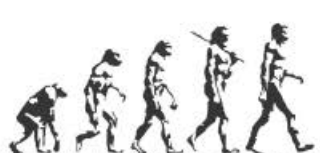
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Volume I

MANDEEP DALAL



First Edition

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