

How is the rate constant for product formation expressed in terms of thermodynamic parameters?

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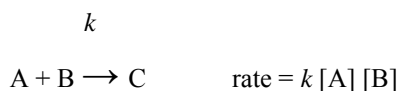
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Abstract: The prime purpose of this article is to express the rate constant for product formation in terms of thermodynamic parameters.

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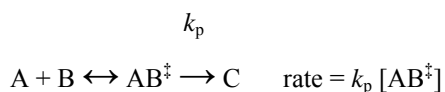
Key words: bimolecular reaction; transition state theory; collision theory; thermodynamic parameters.

The bimolecular reaction



is considered by transition state theory.

According to the transition state model, the reactants are getting over into an unsteady intermediate state on the reaction pathway



It can be shown that

$$k / k_p = [AB^\ddagger] / [A] [B]$$

In this equation, k is the bimolecular rate constant for conversion of A and B to C and k_p is the unimolecular rate constant for decomposition of the activated complex AB^\ddagger to form C.

The Gibbs energy of activation (ΔG) is given by the equation

$$\Delta G = \Delta G^0 + RT \ln (k / k_p)$$

where R is the gas constant, T is the temperature in Kelvin and ΔG^0 is the standard Gibbs activation energy.

The Gibbs activation energy (ΔG), in turn, can be broken into component parts, as shown in the equation below:

$$\Delta G = \Delta H + T (-\Delta S)$$

In this equation, ΔH is the activation enthalpy and ΔS is the activation entropy.

If these two expressions for ΔG are compared, we find that

$$\text{When } \Delta H = \Delta H^0 - T\Delta S^0 \text{ then } R \ln (k / k_p) = (-\Delta S)$$

Or, alternatively,

$$\text{When } E = \Delta H + T\Delta S^0 \text{ then } \ln (k / k_p) = (-\Delta S/R)$$

Or, alternatively,

$$\text{When } T = [E - \Delta H] / \Delta S^0 \text{ then } k = k_p \exp (-\Delta S/R)$$

The rate constant for a bimolecular reaction, as predicted by collision theory is:

$$k = P Z \exp (-E / RT)$$

where P is the steric factor, Z is the collision frequency and E is the activation energy of the reaction.

Further if we substitute

$$k = k_p \exp (-\Delta S/R)$$

then we have to substitute

$$T = [E - \Delta H] / \Delta S^0$$

Substituting $k = k_p \exp (-\Delta S/R)$ we obtain

$$k_p \exp (-\Delta S/R) = P Z \exp (-E / \Delta S^0 / R [E - \Delta H])$$

Or, alternatively,

$$k_p = P Z \exp (\Delta S/R) \exp (\Delta S^0 / R [\Delta H/E] - R)$$

"We have thus expressed the rate constant for product formation in terms of thermodynamic parameters".

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