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

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Abstract: This paper outlines how the rate constant for product formation is expressed in terms of thermodynamic parameters.

If we consider the bimolecular reaction A +B →Products and if C_A, C_B be the molar concentrations of reactants, A and B at any time t, then the reaction rate

$V = k\, C_A\, C_B$

where k = velocity or rate constant. Velocity constant is defined as the rate of reaction when the molar concentration of each reactant is unity. It is known as specific reaction rate.

If two reactants A and B react to give products, then according to the transition theory the following steps take place: $A + B \rightleftharpoons AB^{\neq} \rightarrow$ Products

According to transition state theory, the reactant molecules before reacting form an activated complex in quasi equilibrium with the reactants. The activated complex has the property of an ordinary molecule but its existence is only transient. It then decomposes to give the products. The reaction rate is given by the rate of decomposition of this activated complex.

If $k_P\, C^{\neq}$ is the rate of rate of decomposition of the activated complex, then the reaction rate

$V = k_P\, C^{\neq}$

where k_P = rate constant for product formation and $C^{\neq}$ = concentration of activated complex.

For conversion of reactant into products,

Rate of reaction $(V) = k\, C_A\, C_B = k_P\, C^{\neq}$

Or $k\, C_A\, C_B = k_P\, C^{\neq}$

Separating the constants from the variables:

$C_A\, C_B / C^{\neq} = k_P / k$

In thermodynamic terms the Gibbs activation energy $\Delta G_{\neq}$ is related to the standard Gibbs activation energy $\Delta G_{\neq}^0$ by the equation

$\Delta G_{\neq} = \Delta G_{\neq}^0 + RT\, l\,n\, (C^{\neq} / C_A\, C_B)$

Or

$\Delta G_{\neq} = \Delta G_{\neq}^0 - RT\, l\,n\, (C_A\, C_B / C^{\neq})$

where R = ideal gas constant (8.314 J/mol·K) and T = absolute temperature.

Since $C_A\, C_B / C^{\neq} = k_P / k$, therefore,

$\Delta G_{\neq} = \Delta G_{\neq}^0 - RT\, l\,n\, (k_P / k)$

Furthermore $\Delta G_{\neq}^0$ is given by

$\Delta G_{\neq}^0 = \Delta H_{\neq}^0 - T\, \Delta S_{\neq}^0$

where $\Delta H_{\neq}^0$ = standard activation enthalpy and $\Delta S_{\neq}^0$ = standard activation entropy.

Substituting this in above equation, we get

$\Delta G_{\neq} = (\Delta H_{\neq}^0 - T\, \Delta S_{\neq}^0) - RT\, l\,n\, (k_P / k)$

It has been experimentally found that the difference between $(\Delta H^0)*$ and E is very small and in fact, for reactions in solution, $\Delta H_{\neq}^0 = E_a$. So, we can therefore write

$\Delta G_{\neq} = (E_a - T\, \Delta S_{\neq}^0) - RT\, l\,n\, (k_P / k)$

where E_a, in units of KJ/mol, is called the activation energy.

Additionally, thermodynamics gives a further description of the Gibbs activation energy:

$$\Delta G_{\neq} = \Delta H_{\neq} - T\, \Delta S_{\neq}$$

where $\Delta H_{\neq}$ = activation enthalpy and $\Delta S_{\neq}$ = entropy of activation.

Comparing the last two expressions, we can draw the following conclusion:

$E_a - T\, \Delta S_{\neq}^0 = \Delta H_{\neq}$ when $R\, l\,n\, (k_P / k) = \Delta S_{\neq}$

Or

$k = k_P \exp [-\Delta S_{\neq} / R]$ when $T = (E_a - \Delta H_{\neq}) / \Delta S_{\neq}^0$

In 1884, van't Hoff showed that the value of equilibrium constant varies with temperature. On this basis, Arrhenius (1889) proposed a simple rate equation describing the dependence of the rate constant k of chemical reactions on the temperature T (in absolute temperature kelvins) and activation energy E_a, as shown below:

$k = A \exp [-E_a / RT]$

where A is the pre-exponential factor or simply the prefactor. Alternatively, the equation may be expressed as

$k = B \, T^n \exp[-E_a / RT]$

This is called the modified Arrhenius equation in which n is a constant and B is a temperature - independent constant.

When $k = k_P \exp[-\Delta S_{\neq} / R]$, $T = (E_a - \Delta H_{\neq}) / \Delta S_{\neq}^0$ then from above equation, we have

$k_P \exp[-\Delta S_{\neq} / R] = B \, (E_a - \Delta H_{\neq})^n \, (\Delta S_{\neq}^0)^{-n} \exp[-E_a \Delta S_{\neq}^0 / R \, (E_a - \Delta H_{\neq})]$

Or

$k_P = B \, (E_a - \Delta H_{\neq})^n \, (\Delta S_{\neq}^0)^{-n} \exp[\Delta S_{\neq} / R] \exp[\Delta S_{\neq}^0 / R - R \, (\Delta H_{\neq} / E_a)]$

The rate constant for product formation k_P is thus expressed in terms of thermodynamic parameters.

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