Transition State Theory 2

Transition state theory provides a more accurate alternative to the previously used Arrhenius equation and the collision theory. The transition state theory attempts to provide a better understanding of activation energy, $E_a$, and the thermodynamic properties involving the transition state.

Introduction

The collision theory of reaction rate, although intuitive, lacks an accurate method to predict the probability factor for the reaction. The theory assumes that reactants are hard spheres rather than molecules with specific structures. In 1935, Henry Eyring helped develop a new theory called the transition state theory to provide a more accurate alternative to the previously used Arrhenius equation and the collision theory. The Eyring equation involves the statistical frequency factory, $v$, which is fundamental to the theory.

Derivation

Consider the following reaction:

\[(A + B \rightleftharpoons X^\ddagger \rightarrow C + D)\]

here A and B are reactants, $X^\ddagger$ is the activated complex or the transition state, and C and D are the products. A quasi-equilibrium between the reactants and the activated complex($('\{\ddagger\}$)) is assumed.

The equilibrium constant, $K$, for the transition state and the reactants can thus be written:

\[\dfrac{[X^\ddagger]}{[A][B]}\]

Considering just the forward reaction gives:

\[(A + B \rightleftharpoons X^\ddagger \rightarrow C + D)\]
The rate of the overall reaction is the following:

\[
\text{rate} = k[A][B]
\]

However, the rate of the overall reaction can also be thought of as the concentration of the transition state complex, \(X^{\ddagger}\) at the top of the barrier (shown at the peak of the graph below), multiplied by the frequency, \(v\), of crossing the barrier. Therefore,

\[
\text{rate} = v[X]^{\ddagger}
\]

Because \([X]^{\ddagger} = K^{\ddagger}[A][B]\)

\[
\text{rate} = v[A][B]K^{\ddagger}
\]

Comparing this to the original rate for the overall reaction, it can be written:

\[
k = vK^{\ddagger}
\]

This equation is called the Eyring equation.

It is important to note here that the equilibrium constant \(K^{\ddagger}\) can be calculated by absolute, fundamental properties such as bond length, atomic mass, and vibration frequency. This gives the transition rate theory the alternative name absolute rate theory, because the rate constant, \(k\), can be calculated from fundamental properties.
Thermodynamics of Transition State Theory

To reveal the thermodynamics of the theory, $K^{\ddagger}$ must be expressed in terms of $\Delta G^{\ddagger}$. $\Delta G^{\ddagger}$ is simply,

$$\Delta G^{\ddagger} = G^o (\text{transitionstate}) - G^o (\text{reactants})$$

By definition, at equilibrium, $\Delta G^{\ddagger}$ can be expressed as:

$$\Delta G^{\ddagger} = -RT \ln K^\ddagger$$

Rearrangement gives:

$$[K]^\ddagger = e^{-\frac{\Delta G^{\ddagger}}{RT}}$$

From the Eyring equation, $k = vK^\ddagger$,

$$k = ve^{-\frac{\Delta G^{\ddagger}}{RT}}$$
**Statistical Frequency Factor** \( (v) \)

Statistical mechanics provides that the frequency, \( v \), is equivalent to the thermal energy, \( k_B T \), divided by Planck's constant, \( h \).

\[
v = \frac{k_B T}{h}
\]

Inserting into the equation derived from the Eyring Equation above yields,

\[
k = \frac{k_B T}{h} e^{-\frac{\Delta G}{RT}} M^{1-m}
\]

where \( h \) is Planck's constant \((6.626 \times 10^{-34})\) and \( k_B \) is the Boltzmann constant \((1.38 \times 10^{-23} \text{ J K}^{-1})\).

**Thermodynamic Properties Extended** \((\Delta H^\ddagger)\) and \((\Delta S^\ddagger)\)

It is also possible to obtain terms for the change in enthalpy and entropy for the transition state. Because

\[
\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger
\]

it follows that the derived equation becomes,

\[
k = \frac{k_B T}{h} e^{\frac{\Delta S^\ddagger}{R}} e^{-\frac{\Delta H^\ddagger}{RT}} M^{1-m}
\]

**Conclusion**

In this article, the complete thermodynamic formulation of the transition state theory was derived. This equation is more reliable than either the Arrhenius equation and the equation for the Collision Theory. However, it has its limitations, especially when considering the concepts of quantum mechanics. Quantum mechanics implies that tunneling can occur, such that particles can bypass the energy barrier created by the transition state. This can especially occur with low activation energies, because the probability of tunneling increases when the barrier height is lowered.

In addition, transition state theory assumes that an equilibrium exists between the reactants and the transition state phase. However, in solution non-equilibrium situations can arise, upsetting the theory. Several more complex theories have been presented to correct for these and other discrepancies. This theory still remains largely useful in calculating the thermodynamic properties of the transition state from the overall reaction rate. This presents immense usefulness in medicinal chemistry, in which the study of transition state analogs is widely implemented.

**References**


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