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Introduction to the Transition State Theory

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Abstract

The transition state theory (TST), which is also known as theory of absolute reaction rates (ART) and the theory of activated state (complex), is essentially a refined version of crude collision theory, which treats the reacting molecules as the rigid spheres without any internal degree of freedom. The theory explains the rate of chemical reaction assuming a special type of chemical equilibrium (quasi-equilibrium) between the reactants and activated state (transition state complex). This special molecule decomposes to form the products of reaction. The rate of this reaction is then equal to the rate of decomposition of activated complex. This chapter also explains the limitation of TST theory and deals with the kinetics isotope effect.

Keywords: transition state theory, theory of absolute reaction rates, activated complex, equilibrium constant, reaction rate, kinetics, activation energy, frequency factor, partition function, thermodynamics of activated state, kinetics isotope effect

1. Introduction

"Two major findings have, however, stood the test of time. First, there was the unmistakable evidence that molecular collisions play the all-important role in communicating the activation energy to the molecules which are to be transformed and, second, there was the recognition of the activation energy (derivable for the Arrhenius Law of the temperature dependence) as a dominant, though by no means the sole, factor determining reactivity in general."—C.N. Hinshelwood [1]

The transition state method in chemical kinetics dates back to the important article of French physical chemist René Marcelin (1885–1914) [2, 3] who laid the foundation of the concept of potential energy surface (PES). The transition state theory (TST), which is widely accepted

today, describes the rates of elementary reactions[1] on molecular scale. The theory was formulated by Erying and Polanyi in 1935 (The calculation of absolute reaction rates [4]) in order to explain bimolecular reactions based on the relationship between kinetics and thermodynamics [5, 6]. Based on their original assumption that the reaction rates can be calculated absolutely, the theory is also called as the theory of absolute reaction rates (ART) [7].

> "I showed that rates could be calculated using quantum mechanics for the potential surface, the theory of small vibrations to calculate the normal modes, and statistical mechanics to calculate the concentration and rate of crossing the potential energy barrier. This procedure provides the detail picture of the way for reactions that still dominates the field" [8].

In other words, TST (ART) theory states that [9]:

> "Atoms and molecules can collide and combine to form an unstable, high energy complex. When the molecules fall out of this high energy state, they may do so as new and different molecules, or in their original states. The energy required to reach the activated state must be available if the molecules are to change into something new."

As was introduced in the previous chapter, the term "transition state" was suggested by M. Polanyi and M.G. Evans, who also made a significant contribution to this theory. Today, the TST theory becomes the paradigm for interpretation of the rates of chemical processes[2] as well as their dependence on temperature, medium, structure, and other parameters [10].

The basic assumption of STS theory is the existence of activated state (activated complex[3]), which is formed via the activation of reactants, i.e. the collision between reactant molecules does not form the product of reaction directly. Eyring wrote [4]:

> "The activated state is because of its definition always a saddle point with positive curvature in all degrees of freedom except the one which corresponds to crossing the barrier for which it is of course negative."

Since the kinetic energy of colliding molecules[4], possessing sufficient energy and having proper orientation, is transformed into potential energy the energetic state of activated complex is characterized by positive molar Gibbs energy. The standard Gibbs energy of activation (standard free energy of activation) is the difference between the transition state of a reaction and the ground state of reactants [5, 7, 11, 12].

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[1] Single step reactions, which proceed without intermediates, that is, an elementary reaction is assumed to pass through a single transition state [11].

[2] Despite the fact that the formation of transition state was originally developed for chemical reactions, the theory of thermally activated processes is the key factor for any transport phenomena, for example, the thermally activated jump of atom from one interstitial position to another.

[3] From this reason the TST is also known and more appropriately termed as the activated complex theory (ACT) [6].

[4] Hinshelwood [12] shows that the molecular collisions could both activate and deactivate the reactant molecule.

Activated state is then formed as highly energized and then unstable intermediate[5], which has transient existence and decomposes to form the products of reaction. The rate of reaction is given by the definite rate of decomposition of activated complex [5]. The other most important assumption of STS theory is the existence of chemical equilibrium[6] [6, 13] (quasi-equilibrium) between reactants and activated state (complex) [6]. Despite the fact that this equilibrium is different from classical chemical equilibrium, it can be described by the same thermodynamic treatment [14]. It can be then summarized that TST theory assumes that chemical reaction (or any other activated process[2] proceeds as two-stage process:

1. Formation of activated complex;

2. Decomposition of activated complex into the products of reaction;

as is shown in example in **Figure 1**. (Notes: The representation of energetic pathway derived from the intersection of the PES associated with the reaction.) (Since the catalysts provide an alternative reaction mechanism with lower E_a (**Figure 1(d)**), the rate of reaction increases (Eq. 7 in Chapter 1). This demonstration of significant effect of mechanism on the value of activation energy emphasizes the necessity to know the whole kinetic triplet (E_a, A and n) to complete the characterization of reaction kinetics.)

A general stoichiometric equation for the chemical reaction between R_i chemical species (individuals, that is, atoms, molecules, ions, etc.) in the state marked by the appending (f)[7]:

---

[5]Activated state is then less stable state than any other occurring during the reaction [6].

[6]Chemical equilibrium is the state in which both, reactants and products are present in the concentrations which have further tendency to change with time [13]. The concept of chemical equilibrium was developed after French chemist Claude Louis Berthollet (1748–1822, elected FRS in 1789) found that some chemical reactions are reversible. Josiah Willard Gibbs (1839–1903) suggested that the equilibrium is attained when the Gibbs free energy of the reaction system under constant temperature and pressure reaches its minimum value (the rate of process in both directions is identical):

$$\Delta_r G = \Delta_r G^\circ + RT \ln K = 0. \tag{a}$$

The relation between the standard Gibbs free energy and the equilibrium constant is given by the equation:

$$\Delta_r G^\circ = -RT \ln K; \tag{b}$$

(please refer also to Eq. 26), at the equilibrium of reaction $\Delta_r G^\circ = 0$, that is, $K = 1$. The idea regarding the behavior of an equilibrium system when the changes to its reaction conditions occur is given by "Le Châtelier's principle" (Henry Louis Le Châtelier, 1850–1936), which is also known as "The equilibrium law." The equilibrium constant for the process of formation of activated state cannot be measured experimentally [6].

[7]This appending usually refers to solid (s), liquid (ℓ), gas (g) or kind of solvent, the most aqueous solution (aq). An example to the general formula Eq. 1, that is, the reaction of formation of carbon monoxide is presented below:

$$C(s) + \frac{1}{2}O_2(a) \Longleftrightarrow CO(g) \Longrightarrow 0 = CO(g) - C(s) - \frac{1}{2}O_2(g) \Longrightarrow \sum_i \nu_i R_i(f) = 0.$$
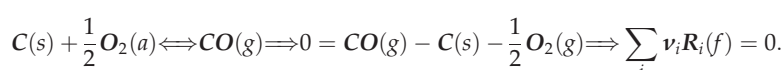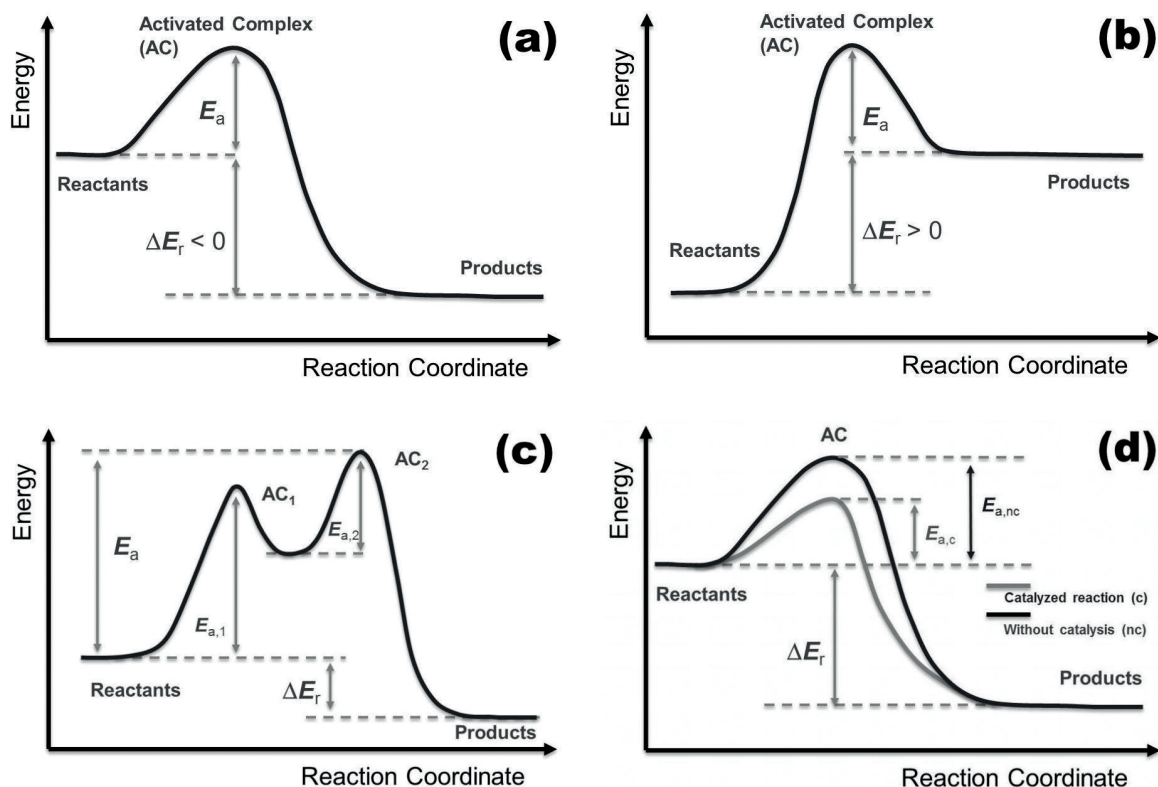
Figure 1. Potential energy diagram (potential energy profile or reaction coordinate diagram for exothermic (a) endothermic (b) multistep process (c) and catalyzed reaction (d).

$$\sum_i \nu_i R_i(f) = 0 \quad \Rightarrow \quad a A(f) + b B(f) + \ldots \Leftrightarrow s S(f) + t T(f) + \ldots \tag{1}$$

where A, B… and S, T… are reactants and products (reaction products), respectively. Integers[8] ν_i = a, b, s, t… are the stoichiometric coefficients[9], i.e. the degree to which a chemical species participates in a reaction, that is conventionally negative for reactants and positive for products.

For the selected case of the three-atom bimolecular reaction of the type:

$$AB + C \leftrightarrow A + BC. \tag{2}$$

It is possible to write:

$$AB + C \leftrightarrow A \ldots B \ldots C \rightarrow A + BC; \tag{3}$$

where $A \cdots B \cdots C$ is an activated complex. The energy difference between the energy of activated complex and reactants is termed as the activation energy (E_a).

---

[8] From the Latin word "integer" that means "whole."

[9] The term stoichiometry, which was first used in 1792 by German chemist Jeremias Benjamin Richter (1762–1807), is derived from Greek words "stoicheion" and "metron", that is, "element" and "measure," respectively.

Since the equilibrium of activated complex with reactant is assumed, it is possible to define the equilibrium constant of activation:

$$AB + C \leftrightarrow A...B...C; \tag{4}$$

as follows:

$$K^{\#} = \frac{[C^{\#}]}{[AB][C]} = \frac{[C^{\#}]}{\prod_i [C_i]^{v_i}}; \tag{5}$$

where $[C^{\#}] = K^{\#}[AB][C]$ denotes the concentrations of activated complexes. The rate of the reaction is then given by the activated complex decomposition rate, i.e.:

$$A...B...C \rightarrow A + BC; \tag{6}$$

which is proportional to $[C^{\#}]$, so that the relation can be written:

$$r = v^{\#}[C^{\#}] = v^{\#}K^{\#}[AB][C]; \tag{7}$$

where $v^{\#}$ is the activated complex decomposition frequency.

According to the statistical thermodynamics, the value of equilibrium constant (Eq. 5) in the reaction 3 is given by the formula:

$$K^{\#} = \frac{Q_0^{\#}}{Q_{AB}Q_C} \exp \left(-\frac{E_0}{RT} \right); \tag{8}$$

where E_0 is an energetic difference between the energy of activated state (product) and reactants that is given as relative to the energy of atoms in gaseous state at the temperature of 0 K. So in this particular case the value of $E_0 = E_a$. The quantities $Q_0^{\#}$, Q_{AB}, and Q_C are the partition functions of activated state and reactant molecules.

2. Formulation of partition function

The partition function of molecule Q, which consists of multiple quantum microstates j (index for the microstate of the system[10]) [15] which share the same energy ε_j, i.e. the energy levels of the system, which are degenerated, can be expressed by the following formula:

---

[10]In statistical mechanics, a microstate is a specific microscopic configuration of a thermodynamic system that the system may occupy with a certain probability in the course of its thermal fluctuation. In contrast, the macrostate of the system refers to its macroscopic properties, such as its temperature and pressure. A macrostate is characterized by a probability distribution of possible states across a certain statistical ensemble of all microstates [15].

$$Q = \sum_j g_j \, \exp\left(-\frac{\varepsilon_j}{k_B T}\right) = \sum_j g_j \, \exp\left(-\beta \varepsilon_j\right); \tag{9}$$

where g_j is the number of allowed equimolar quantum microstates (degeneracy factor) and k_B is the Boltzmann constant[11]. The value of thermodynamic beta is defined as:

$$\beta = \frac{1}{k_B T} = \frac{1}{\tau} = \frac{1}{k_B} \frac{dS}{dE} = \frac{\partial \ln g_j}{\partial \varepsilon_j}; \tag{10}$$

and the exponential factor $\exp\left(-\beta \varepsilon_j\right)$ is known as the Boltzmann factor, S is the entropy and E is the energy. τ in Eq. 10 is termed as the fundamental temperature that has a unit of energy, i.e. the joule ($J = kg \cdot m^2/s^2$). The denominator $k_B T$, i.e. the product of the Boltzmann's constant and thermodynamic temperature, that expresses an energy on molecular scale, is also termed as the constant of distribution.

The partition function is then the summation of terms $exp\left(-\varepsilon_j/k_B T\right)$ for all allowed quantum states (j) of the system, which can be considered for the sum of energy of independent moves, such as [16]:

• Translation: the translational energy for one-dimensional motion is usually given by the following equation:

$$Q_{trans} = \frac{1}{2} m \bar{v}^2 = \frac{\bar{p}^2}{2m}; \tag{11}$$

where m is the mass and $\bar{p}$ is the momentum of particle.

• Rotation: the rotational (angular) kinetic energy around the axis of rotation is given by the formula:

$$Q_{rot} = \frac{1}{2} I \omega^2; \tag{12}$$

where ω is the angular velocity and I is the moment of inertia around the axis of rotation. The comparison of Eqs. (11) and (12) shows that the moment of inertia in rotating system is the parameter analogical to mass and the angular velocity is a quantity, which is analogical to the velocity.

• Vibration: the reactants, e.g, the species AB, C in Eqs. 2–4, have 3 N-6 or 3 N-5 vibrational degrees of freedom (n_{VDF}, please refer also to footnote 16) as they are non-linear or linear, respectively. The same can also be extended to the activated complex ($A \cdots B \cdots C$) that possesses

_____

[11]Heat (energy), which is required to increase the temperature by 1 K for one gas particle, i.e. $k_B = R/N_A = (1.380648\ 52 \pm 0000000\ 79) \cdot 10^{-23}$ J·K^{-1}, where $N_A = (6.022140857 \pm 0000000\ 074) \cdot 10^{23}$ mol^{-1} is Avogadro constant (Lorenzo Romano Amedeo Carlo Avogadro, 1776–1856). The constant was named after Austrian physicist Ludwig Eduard Boltzmann (1844–1906).

$3 \cdot (N_{AB} + N_C) - 6$ or $3 \cdot (N_{AB} + N_C) - 5$ vibrational degrees of freedom if it is non-linear or linear, respectively.

• Energy of the electron states.

So it is possible to write the formula:

$$Q = Q_{trans} \ Q_{rot} \ Q_{vibr} \ Q_{el}. \tag{13}$$

The calculation of this energy then requires the information about allowed energetic levels and their degeneration in the molecule, which can be determined via the methods of quantum mechanics from the structure of this molecule, i.e., the molecular parameters.

As was already mentioned, the activated complex moving along one-dimensional reaction pathway, which is known as the reaction coordinate (collective variable), is decomposed to the product of the reaction. That enables to split the partition function into two parts:

1. Contribution (one particular degree of freedom) that corresponds to the shift (vibration) along the reaction coordinate (Q_{rk}), which leads to the decomposition of activated complex;

2. Contribution corresponding to another molecular degree of freedom (Q_{oth}); so it can be written:

$$Q^{\#} = Q_{rk} \ Q_{oth}. \tag{14}$$

The allowed energetic state for quantum oscillator vibrating along the reaction coordinate results from the solution of Schrödinger equation:

$$\varepsilon_n = \frac{nh\nu}{k_B T}; \tag{15}$$

where $n = 0, 1, \ldots \infty$, ν is the oscillator frequency and h is the Planck constant. The Q_{rk} partition function can be then expressed by the formula:

$$Q_{rk} = \sum_{n=0}^{\infty} \exp\left(-\frac{nh\nu}{k_B T}\right). \tag{16}$$

Using the following substitution:

$$\frac{nh\nu}{k_B T} = x; \tag{17}$$

in order to solve this geometric series (Eq. 16), the relation can be written:

$$Q_{rk} = \frac{1}{1 - \exp\left(-\frac{h\nu}{k_B T}\right)}. \tag{18}$$

A small value of ν means that the product $h\nu \gg k_B T$ and the denominator in Eq. 18 should be developed in every convergent Taylor[12] (Maclaurin[13]) series (expansion or polynomial):

$$
\begin{aligned}
\exp\left(-\frac{h\nu}{k_B T}\right) &= 1 - \frac{h\nu}{k_B T} + \frac{1}{2}\left(\frac{h\nu}{k_B T}\right)^2 - \frac{1}{6}\left(\frac{h\nu}{k_B T}\right)^3 + \frac{1}{24}\left(\frac{h\nu}{k_B T}\right)^4 - \cdots \\
&= 1 - \frac{h\nu}{k_B T}
\end{aligned}
\tag{19}
$$

It is then possible to write that[14]:

$$
Q_{rk} \cong \frac{1}{1 - 1 + \frac{h\nu}{k_B T}} = \frac{k_B T}{h\nu}.
\tag{20}
$$

<hr>

[12]The power series of infinite sum of term calculated from the values of the function's derivatives at a single point (p):

$$
f(x) = \sum_{n=0}^{\infty} f^{(n)}(p)\frac{(x-p)^n}{n!}.
$$

[13]The Maclaurin series (polynomial), that is, the Taylor series[14] expansion of a function $f(x)$ around $x = 0$, is an infinite sum:

$$
f(x) = \sum_{n=0}^{\infty} f^{(n)}(x)\frac{x^n}{n!} = f(0)\frac{x^0}{0!} + f'(0)\frac{x^1}{1!} + f''(0)\frac{x^2}{2!} + f'''(0)\frac{x^3}{3!} + f^{(4)}(0)\frac{x^4}{4!} + \cdots
\tag{a}
$$

Since:

$$
f(x) = \exp(-x) \Longrightarrow f(0) = 1.
\tag{b}
$$

$$
f'(x) = -\exp(-x) \Longrightarrow f'(0) = -1.
\tag{c}
$$

$$
f''(x) = \exp(-x) \Longrightarrow f''(0) = 1.
\tag{d}
$$

$$
f'''(x) = -\exp(-x) \Longrightarrow f'''(0) = -1, \text{etc.};
\tag{e}
$$

The series (a) is then expanded:

$$
e^{-x} = 1 - x + \frac{x^2}{2} - \frac{x^3}{6} + \frac{x^4}{24} - \frac{x^5}{120} + \frac{x^6}{720}\cdots;
\tag{f}
$$

That is, the series that is equal to Eq. 19. The series is named after Scottish mathematician Colin Maclaurin (1698–1746).

[14]This particular vibrational degree of freedom, which corresponds to the vibration along the reaction coordinate (Q_{rk} contribution to the partition function), disappears, when the activated complex becomes dissociated into products (Eq. 6), so:

$$
Q_{rk} = \lim_{n_{VDF}^{rk}} \frac{1}{1 - \exp\left(-\frac{h\nu}{k_B T}\right)} = \frac{1}{1 - \left(1 - \frac{h\nu}{k_B T}\right)} = \frac{k_B T}{h\nu}
$$

Since the frequency of this vibration means the frequency of decomposition of activated state into the product ($\nu^{\#}$), the combination with Eq. 5 and substitution to Eq. 7 enable to formulate the rate of reaction as follows:

$$r = \nu^{\#} \left[C^{\#} \right] = \nu^{\#} K^{\#} [AB][C] =$$
$$\nu^{\#} \frac{kT}{h\nu^{\#}} \frac{Q_{oth}}{Q_{AB} Q_C} \exp \left(-\frac{E_a}{RT} \right) [AB][C]^{'} \tag{21}$$

and then:

$$r = \frac{k_B T}{h} \frac{Q_{oth}}{Q_{AB} Q_C} \exp \left(-\frac{E_a}{RT} \right) [AB][C]. \tag{22}$$

3. Calculation of the reaction rate

Since the kinetic equation for the reaction 2 can be written as follows[15]:

$$r = k \, [AB] \, [C]; \tag{23}$$

where k is the rate constant, the combination of Eqs. (8) and (22) then leads to the formula:

$$k = \frac{k_B T}{h} \frac{Q_{oth}}{Q_{AB} Q_C} \exp \left(-\frac{E_a}{RT} \right); \tag{24}$$

which enables to calculate the reaction rate from the properties of activated complex and reactants. Unfortunately, the evaluation of partition function of the activated state is usually difficult due to the lack of information about its structure. Therefore, the following formula is often used:

$$k = \frac{k_B T}{h} K^{+}; \tag{25}$$

where K^{+} is the equilibrium constant of activation (Eq. 4), which does not include particular part of partition function that corresponds to the vibration along the reaction coordinate. Assuming the parity $K^{+} = K^{\#}$, the following relation can be written:

$$-RT \, \ln K^{\#} = \Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \tag{26}$$

---

[15]Eq. 23 expresses a fundamental approach of empirical kinetics, which is based on experimental experiences with reactions, which occur in homogenous phase. The rate of reaction is the product of two functions:

$$r = k(T)f(c_i)$$

One of them is the function of temperature only ($k(T)$, Eq. 20 in Chapter 1) and the second depends on concentrations of reactants in the reaction (Eq. 1).

The combination of above introduced Eqs. 24–26 then leads to the expression of general form of so-called Eyring-Polanyi equation[16]:

$$k = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\#}}{R}\right) \exp\left(-\frac{\Delta H^{\#}}{RT}\right) = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^{\#}}{RT}\right) = \nu^{\#} K^{\#};$$

(27)

where term $\nu^{\#} = k_B T/h$ is known as the universal frequency (frequency factor). The combination of Eq. 27 with universal frequency of activated complex ($\nu_{AC}^{\#}$, please refer to Eq. 115 in Chapter 3) enables to solve the relation between the Arrhenius (Eq. 20 in Chapter 1) and Eyring (Eq. 27) rate constants as follows:

$$k_{Arrhenius} = A \cdot exp\left(-E_a/RT\right) = k_{Eyring}/e = \left(\nu^{\#} K^{\#}\right)/e \Longrightarrow k_{Arrhenius}/k_{Eyring} = 1/e.$$

Since every vibration does not necessarily result in the decomposition of activated complex into the products, the proportionality constant (transmission coefficient) κ can be introduced into the Eyring equation (Eq. 27) to get the relation[17] [17, 18]:

$$k = \kappa \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\#}}{R}\right) \exp\left(-\frac{\Delta H^{\#}}{RT}\right) =$$
$$\kappa \frac{k_B T}{h} \exp\left(-\frac{\Delta G^{\#}}{RT}\right) = \kappa \nu^{\#} K^{\#} = k^{\#} K^{\#}$$

;

(28)

where k is assumed to be directly proportional to the frequency of the vibrational mode, which is responsible for the decomposition of the activated complex into products. Furthermore, the transmission coefficient (κ) is in most cases considered to be close to unity, so Eq. 28 comes to Eq. 27. Since $k^{\#} \geq k$ the value of transmission coefficient is then $0 \leq \kappa \leq 1$.

The temperature dependence of the rate constant k is then given by the Arrhenius law (Eq. 20) introduced in Chapter 1. The comparison of this equation (Eq. 27) to Arrhenius enables to derive that for the processes occurring in the condensed phases $E_a \approx \Delta H^{\#}$[18] [6, 19]:

$$\Delta H^{\#} = E_a - RT;$$

(29)

and the frequency factor can be considered as independent on temperature. The entropy of activation can be calculated from the relation:

$$\Delta S^{\#} = R \ln\left(\frac{hA}{k_B T}\right);$$

(30)

and:

---

[16] The formulation of this equation resembles the van't Hoff-Arrhenius Equation (Eq. 7 in Chapter 1).

[17] The term $\kappa(k_B T/h)$ in Eq. 28 is close to 10^{12} s^{-1} for many bond vibrations [17].

[18] The term is usually not to be higher than 10 kJ·mol^{-1}, while the activation energy is mostly higher than 100 kJ·mol^{-1}. Therefore, the final difference should be below 10%.

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}. \tag{31}$$

The linearized (logarithmic) form of Eq. 27, which can be written as follows:

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^{\#}}{R}\frac{1}{T} + \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\#}}{R}; \tag{32}$$

enables to determine the enthalpy (ΔH) and the entropy of activation ($\Delta S^{\#}$) from the investigation of reaction rate (kinetics) of reaction at different temperatures. The plot (so-called Eyring plot) of $ln\ (k/T)$ versus reciprocal temperature ($1/T$) provides straight line with the slope of $-\Delta H^{\#}/R$ and the intercept $ln\ (k_B/h) + \Delta S^{\#}/R$.

The examples of Arrhenius (a) and Eyring plot (b) for the process of thermal decomposition of calcite[19], i.e. the trigonal polymorph of $CaCO_3$, in an inert atmosphere of N_2:

$$CaCO_3(s_1) \overset{T}{\leftrightarrow} CaO(s_2) + CO_2(g); \tag{33}$$
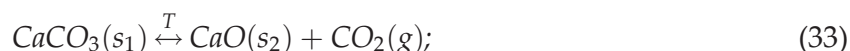
are introduced in **Figure 2**.

The slope of Arrhenius plot (($-E_a/R$), please refer to Eq. 20 in Chapter 1) is used to write the relation for the activation energy (Arrhenius activation energy) as follows:

$$E_a = -R\left(\frac{\partial \ln k(T)}{\partial (1/T)}\right)_p = -p\ \left(\frac{\partial \ln k(T)}{\partial (1/V_m(T))}\right)_p; \tag{34}$$

where $V(T)$ is the volume of ideal gas at temperature T. That means that:

$$\ln\ k(T) = \ln\ A - \frac{E_a}{pV_m(T)} \quad \Rightarrow \quad k(T) = A\ \exp\ \left(-\frac{E_a}{pV_m(T)}\right). \tag{35}$$

The isobaric character of the process means that the relation between Eqs. 20, 34 and 35 is given by the Charles's Law[20] [20]:

$$\frac{V_m}{T} = \text{const.} = \frac{R}{p}; \tag{36}$$

which is also known as the law of volumes.

---

[19]This example uses the data of original thermogravimetric (TGA, please refer to Footnote[2] in Chapter 3) kinetic experiments (TG-DTA analyzer, SDT Q600, Thermal Instruments) performed for the purpose of this book with transparent variety of calcite, that is, optical calcite or "Iceland Spar," from Leping, China. Please compare also the slope of both plots in **Figure 2** with respect to the discussion on Eq. 29, that is, the fact that $E_a \approx \Delta H^{\#}$. Furthermore, the plot $\Delta H^{\#}$ vs. T is straight line with the slope-R and the intercept E_a.

[20]French inventor and scientist Jacques Alexandre César Charles (1746–1823). The law was formulated by Joseph Louis Gay-Lussac (1778–1850) in 1802 [20], who gave credit to unpublished work by J. Charles.
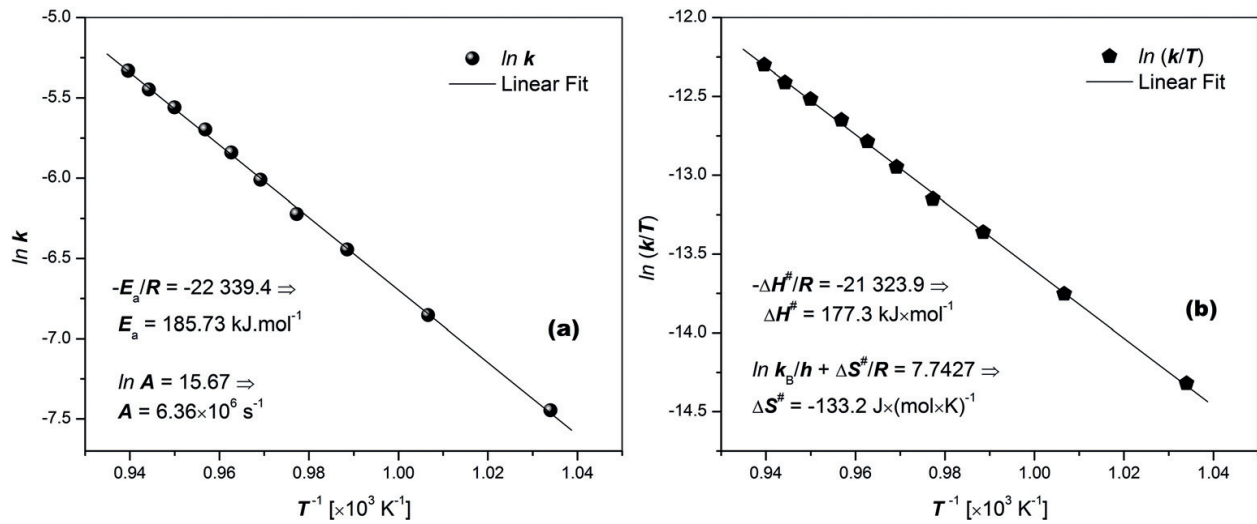
Figure 2. An example of calculation of enthalpy and entropy of activation for the process of thermal decomposition of calcite: the temperature dependence of the rate constant presented in the form of Arrhenius plot (a) and Eyring plot (b).

4. Frequency factor as the function of temperature

The temperature dependence for experimental (marked by subscript *exp*), i.e. usual form of the Arrhenius equation (Eq. 20 in Chapter 1), and theoretically calculated (*th*) reaction rate constants can be written as follows:

$$k_{\exp} = A_{\exp} \, \exp\left(-\frac{E_{a,\exp}}{RT}\right); \tag{37}$$

and

$$k_{th} = B(T) \, \exp\left(-\frac{W}{RT}\right); \tag{38}$$

where the pre-exponential factor $B(T)$ is the function of temperature and W is the difference between energy of reactants and activated complex in the basic state. According to the transition state theory, the value of $B(T)$ is approximately proportional to the temperature.

The equations for the experimental and calculated (theoretical) activation energy can be then written as follows:

$$E_{a,\exp} = RT^2 \, \frac{d\ln k_{\exp}}{dT}; \tag{39}$$

and:

$$E_{a,th} = RT^2 \, \frac{d\ln k_{th}}{dT} = RT^2 \, \frac{d\ln B(T)}{dT} + W = \Theta \, RT + W; \tag{40}$$

where:

$$\Theta = T \; \frac{d\ln\, B(T)}{dT}.$$

(41)

The substitution to Eq. 38 then leads to the formula:

$$k_{th} = B(T) \; \exp{(\Theta)}\exp\left(-\frac{E_{th}}{RT}\right).$$

(42)

In the case that:

$$B(T) = CT;$$

(43)

where C is a constant, it can be written that:

$$\Theta = T\frac{d\ln B(T)}{dT} = 1;$$

(44)

and then:

$$k_{th} = B(T)\exp\left(-\frac{E_{th}}{RT}\right).$$

(45)

That also means the parity:

$$E_{th} = E_{\exp};$$

(46)

and:

$$A_{th} = B(T) = CT.$$

(47)

Since the value of Θ is close to one, the pre-exponential (frequency) factor can be considered as independent of temperature[21].

5. Limitations of transition state theory (TST)

As was mentioned above, the universality of the transition state theory provides a conceptual foundation for understanding the course and rate of elementary reaction on molecular scale. On the other hand, the TST theory can fail in some cases, for example [21, 22]:

1. If applied to each elementary step of multistep reactions (**Figure 1c**).

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[21]Please refer also to the discussion on Eq. 8 in Chapter 1. This equation considers the frequency factor as proportional to T^m.

2. When the intermediates are very short-living, so that the Boltzmann distribution[22] of energies is not reached before the process continues to the next step.

3. The transition state theory also fails for some reactions at high temperatures due to the more complex motions of molecules or at very low temperatures due to the quantum tunneling.

Furthermore, the TST is also based on the assumption that atomic nuclei behave according to the classic mechanics. It is assumed that unless atoms or molecules collide with enough energy to form the transition structure (activated complex), the reaction does not occur. However, according to the quantum mechanics, for any barrier with a finite amount of energy, there is a possibility that particles can still tunnel across the barrier [21].

6. Kinetic isotope effect

The discovery of isotopes[23] [23, 24] of the elements resulted from a thorough study of the properties of radioactive substances during the first years of the twentieth century.

> *"The word isotope signifies 'the same place' in allusion to isotopes occupying the same place in the Periodic Table"* [24].

The conclusion that certain species of atom have identical chemical properties but different radioactive properties comes from chemical studies, which accompanied the study of radioactivity. The fundamental theory of the chemical isotope effect was established in 1947 by Urey [25] and Bigeleisen and Mayer who stated [26]:

> *"It is pointed out that the possibility of chemical separation of isotopes is a quantum effect. This permits a direct calculation of the difference in the free energies of two isotopic molecules."*

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[22]The Boltzmann distribution (F), which is also called the Gibbs distribution, is a probability distribution which expresses the probability that the system is in a certain state for given energy and temperature of the system. The ratio of Boltzmann distribution for two energetic states is known as the Boltzmann factor that depends on the energy difference between these states:

$$\frac{F(state\ 2)}{F(state\ 1)} = \exp\left(\frac{E_1 - E_2}{kT}\right).$$

[23]The history of isotopes fittingly commences with the discovery of radiothorium, a new product in the thorium disintegration series, by Sir William Ramsay (1852–1916) and Otto Hahn (1879–1968) in 1905 [24]. The isotopes were discovered and proved by English radiochemist Frederick Soddy (1877–1956, Nobel Prize for chemistry in 1921) and physical chemist Kasimir Fajans (1887–1975). Together with Ernest Rutherford (1871–1937), F. Soddy provided the base towards the understanding of radioactivity:

"…radioactive substances were transformed from one element to another."

The word isotope was first suggested by Scottish doctor Margaret Todd (1859–1918) in 1913, a family friend of F. Soddy. The experimental method that first revealed the existence of isotopes among the successive products of radioactive change had been applied in 1907.

The kinetic isotope effect (KIE) is the effect of isotopic substitution on the reaction rate[24]. Early research on the effect of the difference in mass between isotopes upon the rate of chemical transformation has been limited entirely to the very lightest elements, especially hydrogen; although the effect of isotopic mass upon the rate of many physical properties has been extend throughout the periodic table [3, 27, 28]. The heavy atom kinetic isotope effect studies became possible after the Second World War with the availability of radioactive isotopes and mass spectrometers for the measurement of stable isotope ratios [29].

The origin of all isotope effects lies in the differences of various vibrational modes of a molecule which arise when one isotope is substituted with another [17]. There are two kinds of KIE recognized [30, 31]:

1. Primary kinetics isotope effect, i.e. the effect of isotopic substitution on the rate constant of transformation of isotopologues. Isotopologues are molecules which differ only in their isotopic composition (the number of isotopic substitutions or also isotopic identities), for example, protium containing water (H_2O[25]) and deuterium (please refer to Footnote[36] in Chapter 1) **bearing semiheavy (HDO) or heavy water (D_2O)**. Other examples are CH_4 and CH_3D, or $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, and $^{12}C^{18}O^{16}O$, and so on.

For the multiple isotopic substitution (two or more rare isotopes) in isotopologues, the name "clumped" isotopologues are used. If isomers have the same number of each isotopic atoms but they occupy different symmetrically non-equivalent positions, e.g. $^{14}N^{15}N^{16}O$ and $^{15}N^{14}N^{16}O$, they are termed as isotopomers, i.e. isotopic isomers [30, 31].

For heavy atoms (heavy atoms isotope effects), the maximum reaction rate constant ration is proportional to the square root of inverse isotopic masses:

$$\frac{k_x}{k_y} = \sqrt{\frac{M_y}{M_x}}. \tag{48}$$

2. Secondary kinetics isotope effect (steric isotope effect), which is attributed to different vibrational amplitudes of isotopologues, e.g. the mean-square of amplitudes of vibration of C-H bonds is greater than that of C-D bonds

One of the other early studies of KIE was the work of Beeck et al. [32] and the ^{14}C effect in the decarboxylation of malonic acid (propanedioic acid, $CH_2(COOH)_2$) and bromomalonic acid by Yankwich and Calvin [28]. The effect of isotopic mass on certain chemical equilibria was used to separate the isotopes. From this point of view, the classic theory (formulated in 1947 [25, 26]), i.e. the mass-dependent theory, assumes that at a constant temperature, the isotope enrichment factor is proportional to the isotopic mass difference and inversely proportional to the product of masses of two isotopes. For as long as four decades after the formulation of the mass-dependent theory, a failure of the isotope effect in chemical exchange equilibria to follow

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[24]It should also be pointed that isotopic composition of material contains a lot of information regarding its origin and history [25, 31].

[25]With regard to oxygen, there are isotopologues $H_2^{18}O$ and $H_2^{16}O$.

the theory has not been reported [33]. The mass-independent isotope fractionations were first observed for O and S in 1983 [34].

Also, the course of crystallization could be affected by isotopic composition hence rapidly grown crystals could have a disequilibrium elemental and isotopic concentrations, which result from the diffusion limitation and diffusivity differences in the growth medium [35]. The isotopic composition is also affected by the presence of simple organic molecules and could be a crystal-face-dependent [36]. The variations in oxygen ($^{18}O/^{16}O$) and hydrogen ($^{2}H/^{1}H$) isotope ratios of water and ice are powerful tools in hydrology and ice core studies [37]. The fractionation of Cu, Fe, and Zn isotopes during the oxidative weathering of sulfide-rich rocks could also have an impact on the distributions of stable Fe, Cu, and Zn isotopes in natural waters [38].

Historically, the isotope techniques came into use in catalysis in 1960s with the investigation of oxygen and other molecules reactivity [39]. The study of dynamics of isotope transfer under steady-state reaction conditions, the so-called Steady-State Isotopic Transient **Kinetic** Analysis (SSITKA), is successfully employed in the investigation of mechanism of heterogeneous catalytic reactions [40, 42–45] and to estimate the surface concentrations of intermediates and reaction rate coefficients [40].

SSITKA method was initially developed by Happel [41, 46], Bennett [47], and Biloen [42, 48].

> "…proper understanding of heterogeneous catalysis is linked to understanding of transient effects. The interpretation requires a model based on elementary steps, and various steps may be rate-determining as the conversion and temperature vary." [47].

The basic idea of the isotope dynamic experiment is as follows. When the reaction under study achieves the steady state, the initial feed gas flow is stepwise replaced by another flow differing in the isotope composition, but absolutely identical in a chemical one. The composition of feed gas and reaction products is continuously measured using a quadrupole mass spectrometer [40, 45].

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