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Article

Teaching and Learning Dialectical Relationship between Thermodynamic Equilibrium and Reaction Rate Constant

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Abstract

The development of science and technology in the present era has an urgent demand for the training of innovative thinking of undergraduates. This requirement actively promotes research and teaching of basic theories, beneficial to the career development of students. This study clarified the dialectical relation between thermodynamic equilibrium constant and reaction rate constant through the contrast thinking method. Findings reveal that both isobaric Van't Hoff equation and Arrhenius equation had four similar forms, and the change in the trend of both constants showed a similar law. By the derivation of the formation rate constant of product (K_Y) and the consumption rate constant of the reactant (K_A), the ratio of both constants at the end state indicated the nature of equilibrium state in agreement with that of thermodynamic equilibrium constant ($K^{\theta}(T)$). This study has thus presented that the thermodynamic equilibrium constant contained the characteristics of microscopic dynamics based on the analysis of the reaction mechanism, and both constants are organically connected and unified. The reaction enthalpy and activation energy are closely related to each other with the same connotation.

Keywords

Thermodynamic equilibrium constant · Reaction rate constant · PBL teaching · Dialectical relation · Innovative thinking

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Problem-Based Learning (PBL) is a set of teaching methods for designing learning situations based on problems. In 1969, Barrows, an American neurologist, pioneered the PBL teaching method at McMaster University in Canada, and it has become a popular teaching method in the world. PBL teaching is a student-centered teaching method based on the real world. Under the guidance of teachers, the student-centered and problem-based teaching can be carried out through group discussions; data collection by students independently about problems, finding and solving problems, and cultivating the autonomous learning ability and innovative ability. PBL is very different from the traditional subject-based teaching method, and it emphasizes the active learning of students, rather than the teaching in the traditional way.

In order to improve the teaching effect, PBL method is also used in physical chemistry course at present. Physical chemistry is an important basic course, and it is also recognized as a difficult course to learn and teach due to aa very strong logicality and abstractness. Physical chemistry comprises theoretical basis of medicine, biology, chemical engineering, materials and other disciplines, and is called the soul of chemistry (Carter & Brickhouse, 1989; Mack & Towns, 2016; Sözbilir, 2004). This course plays a very important role in cultivating students' creative ability and improving their comprehensive quality. In addition, the development of economy, science and technology needs more and more innovative talents. Therefore, the educational researchers are more responsible for being in research of knowledgeable theories of learning. These efforts of the educational faculty deepen the research awareness of teaching and learning in higher education, which is related to discipline-specific subject matter and practices (Mack & Towns, 2016). Moreover, the adoption and persistence of research-based instructional strategies will make faculty to improve the quality of teaching and learning in undergraduate education and resolve the difficulties faced by learners.

Less research has been reported about the training of philosophical thinking method, and the introduction of philosophical ideas and thinking methods for studying physical chemistry. In the process of learning the basic theories and some concepts, undergraduate students generally cannot completely understand the relevant chemistry theories and their connotation nor can they accurately grasp the essential property of the concept. Moreover, a great deal of formulas, strong abstractness and logicality of concept are also vital reasons why students face difficulty in understanding them exactly. Besides, physical chemistry contains strong philosophical ideas, accompanied by distinctive theoretical and abstract characteristics.

A study of the influencing factors and basic principles of thermodynamics help analyze the thermodynamic equilibrium constant in detail. This also helps to understand fully some factors that affect the rate of production efficiency as with the decrease of petrochemical energy, the improvement of production efficiency is seen more urgent. Therefore, a new perspective of how to study effectively knowledge was required for students to understand the relationship between activation energy and reaction enthalpy For this purpose, in this work, the isobaric Van't Hoff equation and Arrhenius equation were taken as examples to illustrate the teaching beliefs because the two equations are widely used in the fields of material preparation (Kohout, 2021), organic synthesis (Asnin & Stepanova, 2018; Nuernberg, 2020), chemical reaction engineering (Batiot et al., 2021; Kohout, 2021; Koutek et al., 2020), geotechnical engineering (Kim et al., 2014), and so on. These equations therefore ideally suited to measure the students' learning difficulties.

The study discussed similarities and differences of isobaric Van't Hoff and Arrhenius equations; and how to derive the consistency of thermodynamic equilibrium constant and reaction rate constant. The mathematical principles and formula characteristics of isobaric Van't Hoff equation and Arrhenius equation were also discussed in order to comprehensively understand the differences in the related theories and connotation of the involved concepts. The difference of the connotation between thermodynamic equilibrium constant and reaction rate constant Liu et al. (2019); Villanueva-Cab et al. (2010) were also clarified using contrast thinking method. In addition, the dialectics relation of two physical quantities were also further expounded, revealing a consistency in the nature or meaning.

This work is expected to provide a reference for students to learn other similar problems by contrast thinking. The main objective of this study was to develop a rich belief which is beneficial to improve the teaching and learning quality when faculty talk about their teaching method and practice, especially in the more difficult basic curriculum in undergraduate education.

Literature review

Several studies (Carter & Brickhouse, 1989; Sözbilir, 2004) have reported the causes of learning difficulties faced by students in physical chemistry. Their findings were based on data collected through a developed questionnaire on variables like student-controlled factor, course-related factor, and domain specific factor of chemistry. In addition, these studies focused on understanding of specific concepts in physical chemistry, whose results indicated that the learning difficulties in physical chemistry were quite different from each other. These results were based on students' views, which may be attributed to different levels of cognition, learning ability, and their own experiences.

Various types of problems can be applied in practical cases including thermodynamic calculation, and those involving in phase equilibrium models in geology, material science (Jin, Easton, Tang, et al., 2018; Jin, Easton, Yin, et al., 2018; Jin et al., 2015; Jin, Kong, et al., 2020) and chemical engineering (Junheng Fu et al., 2020) etc. With the development of social economy and industry, the higher utilization of raw materials inevitably is required and the yield will be of great concern for producers in order to strengthen the study of the theory of equilibrium movement. The thermodynamic equilibrium constant embodies exactly the composition of the system at the equilibrium state. In physical chemistry experiments, similar problems are often encountered. For example, sucrose hydrolysis is a commonly used experiment in biochemistry. It is a contradictory problem to increase simultaneously the hydrolysis reaction rate and conversion rate. Students do not know how to control the reaction conditions, because a higher reaction rate means that the concentration of the reactant is higher, and a larger conversion rate means that the concentration of the reactant is very low.

All such problems have a commonality of making use of the analyzing method, resolved through reproducible and repeatable methods such as Van't Hoff equation and Arrhenius equation. These two equations help in understanding the relationship between the reaction rate and equilibrium movement (the relationship between the reaction rate constant and the equilibrium constant). Although Arrhenius equation presents a more accurate relationship between the temperature and the reaction rate constant in most of elementary reactions, compared to that of Van't Hoff rule, a large amount of experiments has shown that the real elementary reactions are rare, and the relationship between chemical reaction rate and temperature is complicated. Some chemical reactions have almost no effect below a certain temperature. When the temperature reaches a certain value, the reaction is almost complete instantly, such as an explosion. The neutralization reaction is completed instantaneously at normal temperature, and no change in temperature is observed; some chemical reactions decrease with the increase of temperature, such as, NO and O_2 to form NO_2 (Jin et al., 2015; Jin et al., 2021; Jin, Xie, et al., 2019; Jin, Yin, et al., 2019).

Some reactants generate decomposition, gasification or other side reactions when reaction temperatures rise to a certain value. Especially, with the development of modern industry and science and technology, many reactions are often carried out under the catalysts or higher temperatures, and the relationship between the reaction rate and temperature is more complex. In summary, Arrhenius equation explains the effect of temperature on the reaction rate from a perspective of kinetics, compared with Van't Hoff rule, Arrhenius equation is more accurate due to the introduction of reaction activation energy. The isobaric Van't Hoff equation, on the other hand, explains the effect of temperature on the equilibrium constant from a perspective of thermodynamics, describing the effect of temperature on the reaction limit in essence. Obviously, there is one thing in common for Arrhenius equation and the isobaric Van't Hoff equation: both present an effect of temperature on the reaction rate, while one of the two equations is chemical thermodynamics and the other is chemical kinetics. Therefore, they have a dialectical relationship: unity and contradiction, and the further discussion is carried out by the establishment of reaction model and the proposal of kinetic mechanism of reaction.

Methodology

- *Research design*

The study adopted an experimental research design surrounding the investigations around isobaric Van't Hoff and Arrhenius equation. A learning difficulty diagnostic test was devised for this research with the objective to identify the actual learning difficulties in physical chemistry exhibited by students; and to find out ways how to improve their academic performance.

- *Research sample*

The sample of the study comprised 65 second-year university students of 2018-2019 (2 semester) who have been taught isobaric Van't Hoff and Arrhenius equation. The purposive sampling method was used to identify students with different grades.

- *Research instruments and procedure*

PBL method was used to find out the main problems through discussion and comparison. A questionnaire was designed to understand students' understanding of the knowledge points of thermodynamic equilibrium constant and reaction rate constant.

- *Data analysis*

The data was analyzed characteristically in the light of two equations Isobaric Van't Hoff Equation and Arrhenius Equation. These equations helped the derivation process, findings similarities and differences in the students' understanding of the knowledge points of thermodynamic equilibrium constant and reaction rate constant.

Theoretical framework

i. *Isobaric Van't Hoff Equation*

The isobaric Van't Hoff equation and the isotherm Van't Hoff equation were created by Jacobus Henricus van't Hoff (the Netherland Chemist, August 30, 1852-March 11, 1911, who won the first Nobel Prize in Chemistry in 1901). The isobaric Van't Hoff equation is mainly used to explore the effect of temperature on the thermodynamic equilibrium constant of chemical reaction, while the isotherm Van't Hoff equation evaluated the relation between Gibbs free energy of chemical reaction and thermodynamic equilibrium constant (Gilbert & Treagust, 2009; Kim et al., 2014; Simonson et al., 2019).

It is important to analyze the prerequisites of two equations to profoundly grasp the connotation and characteristics of thermodynamic equilibrium constant, the mathematical principle, the physical model. The analysis process is as follows: Closed system without volume work: aA → yY where a and y are the measurement coefficient of reactant (A) and product (Y), respectively. In this system, only ideal gas participates in the chemical reaction process, and all substance are in the standard state. Thus, Gibbs function of molar reaction can be expressed in equation (1).

$$\Delta_{\mathrm{r}}G_{\mathrm{m}} = \Delta_{\mathrm{r}}G_{\mathrm{m}}^{\theta} + RT\ln\frac{(C_{\mathrm{Y}})^{y}\cdot\left(C_{\mathrm{Y}}^{\theta}\right)^{-\mathrm{y}}}{(C_{\mathrm{A}})^{a}\cdot\left(C_{\mathrm{A}}^{\theta}\right)^{-\mathrm{a}}} \qquad (1)$$

The introduction of thermodynamic equilibrium constant ($K^{\theta}(\mathrm{T})$):

$$K^{\theta}(\mathrm{T}) = \frac{(C_{\mathrm{Y}})^{y}\cdot\left(C_{\mathrm{Y}}^{\theta}\right)^{-\mathrm{y}}}{(C_{\mathrm{A}})^{a}\cdot\left(C_{\mathrm{A}}^{\theta}\right)^{-\mathrm{a}}} = \frac{(C_{\mathrm{Y}})^{y}}{(C_{\mathrm{A}})^{a}} \quad (\theta\text{: standard pressure}, C_{\mathrm{Y}}^{\theta} = 1; C_{\mathrm{A}}^{\theta} = 1) \qquad (2)$$

When the reaction reaches equilibrium, $\Delta_{\mathrm{r}}G_{\mathrm{m}} = 0$

So, $\Delta_{\mathrm{r}}G_{\mathrm{m}}^{\theta} = -RT\ln K^{\theta}(\mathrm{T})$ (3)

Equation (3) is the isotherm Van't Hoff equation (Peter & Julio 2010, Fu & Shen 2005), which shows the relation between Gibbs function of standard molar reaction and thermodynamic equilibrium constant.

The standard chemical potential (μ_{B}^{θ}) is only a function of temperature, and Gibbs function of standard molar reaction ($\Delta_{\mathrm{r}}G_{\mathrm{m}}^{\theta} = \sum_{B} n_{B}\mu_{B}^{\theta}$), $\Delta_{\mathrm{r}}G_{\mathrm{m}}^{\theta}$ is also only a function of temperature. Similarly, thermodynamic equilibrium constant ($K^{\theta}(\mathrm{T})$) is only a function of temperature; moreover, this constant is a dimensionless constant (or the unit considered to be 1), which reflects the characteristics of compositions at equilibrium state, indicating the ratio of the concentration of product to the concentration of reactant. Therefore, to increase the yield or product concentration, the chemical equilibrium need shift towards the product or shift towards the right direction and understand how to change the related reaction conditions will be very important for the problem.

The known conditions: $K^{\theta}(T_0)$ or $\Delta_{r}G_{m}^{\theta}(T_0)$ and reaction enthalpy $\Delta_{r}H_{m}^{\theta}(T_0)$ at T_0 temperature is used to find out how find the constant $K^{\theta}(T_1)$ at T_1 temperature, and this problem can be solved by isobaric Van't Hoff equation (such as definite integral form).

The derivation process (to simplify the formula form, temporarily ignoring some conditions, such as θ, m (per moL) and r (reaction)) is as follows:

There is a certain T temperature in the above-mentioned system, $\Delta G = \Delta H - T(\Delta S)$
Or deformation:

$$-\Delta S = \frac{\Delta G - \Delta H}{T} \tag{4}$$

At isobaric condition, the fundamental equation of thermodynamics of Gibbs free energy:

$$dG = -sdT \tag{5}$$

At isobaric condition, a new relation is available from (5):

$$(\frac{\partial \Delta G}{\partial T})_p = -\Delta S \tag{6}$$

Combining (4) and (6):

$$(\frac{\partial \Delta G}{\partial T})_p = \frac{\Delta G - \Delta H}{T} \tag{7}$$

Then, $(\frac{\Delta G}{T})$ finds the partial derivative of T:

$$[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}]_p = \frac{T(\frac{\partial \Delta G}{\partial T})_p - \Delta G(\frac{\partial T}{\partial T})_p}{T^2} \tag{8}$$

Substituting (7) into (8):

$$[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}]_p = -\frac{\Delta H}{T^2} \tag{9}$$

Equation (9) is Gibbs-Helmholtz equation (Peter & Julio, 2010; Fu & Shen, 2005) (ΔG can be changed to $\Delta_r G_m^\theta$; ΔH can be changed to $\Delta_r H_m^\theta$ at per moL and standard pressure condition, as shown in equations from (10) to (13)).

This equation was devised by two renowned scientists: Josiah Willard Gibbs, American Physical Chemist, Mathematical Physicist (February 11, 1839-April 28, 1903) proposed the concepts of Gibbs free energy and chemical potential etc., and clarified the essence of phenomena such as chemical equilibrium, phase equilibrium, and surface adsorption etc. Gibbs was one of the founders of Chemical Thermodynamics. The second scientist, Hermann Von Helmholtz was a German Physicist, Physiologist, Biophysicist (October 31, 1821-September 8, 1894) who had first proposed the Law of conservation of energy mathematically.

Then, substituting (3) into (9): $[\frac{\partial(-R\ln K^\theta)}{\partial T}]_p = -\frac{\Delta_r H_m^\theta}{T^2}$;

Or deformation:

$$\frac{d(\ln K^\theta)}{dT} = \frac{\Delta_r H_m^\theta}{RT^2} \tag{10}$$

Therefore, equation (10) is the isobaric Van't Hoff equation (Acosta-Cabronero et al., 2010; Jinhong Fu et al., 2005), which shows the relation between the temperature and thermodynamic equilibrium constant, and the relation is obviously related to the reaction enthalpy of standard molar ($\Delta_r H_m^\theta$).

The equation can be explained thus:

When the change of heat capacities of all substance in the above-mentioned system is zero, that is to say, $\Delta_r C_{p,m} = \sum_B \nu_B C_{p,m}=0$, $\Delta_r H_m^\theta$ is a constant (when $\Delta_r C_{p,m} \neq 0$, $\Delta_r H_m^\theta$ is not a constant.

The definite integral, indefinite integral, and exponential forms can be obtained from equation (10), as shown in equations (11) to (13).

$$\ln\frac{K^\theta(T_1)}{K^\theta(T_0)} = -\frac{\Delta_r H_m^\theta}{R}(\frac{1}{T_1} - \frac{1}{T_0}) \tag{11}$$

$$\ln K^\theta(T) = -\frac{\Delta_r H_m^\theta}{RT} + C \quad \text{(C is a constant)} \tag{12}$$

$$K^\theta(T) = A \cdot e^{\frac{-\Delta_r H_m^\theta}{RT}} \quad \text{(A is a pre-exponential factor)} \tag{13}$$

In equation (13), $A > 0, R > 0$, derivation:

$$\frac{\partial K^\theta(T)}{\partial T} = Ae^{\frac{-\Delta_r H_m^\theta}{RT}} \frac{\Delta_r H_m^\theta}{R} \frac{1}{T^2} \tag{14}$$

Figure 1 indicates that the relationship (solid line curve) between thermodynamic equilibrium constant ($K^{\theta}(T)$) and temperature (T) is related to the reaction enthalpy. Here, $\Delta_r H_m^{\theta} > 0$ endothermic reaction, and the derivative is greater than zero, so $K^{\theta}(T)$ increases with the increase of temperature. However, when the temperature increases, the corresponding value of derivative decreases gradually and tends to become zero, so the change trend is firstly fast and then slow.

Subsequently, $\Delta_r H_m^{\theta} < 0$ exothermic reaction, $K^{\theta}(T)$ decreases with the increase of temperature, similarly, the change trend is also fast in the lower temperature range, subsequently, slow in the higher temperature range, as shown in Figure 1.

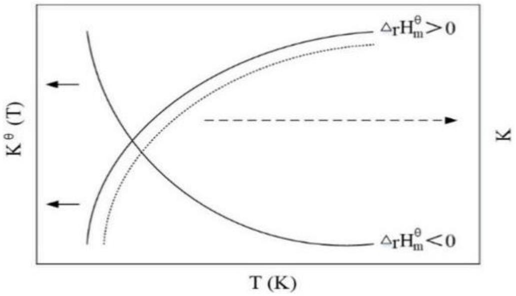

Figure.1. *The relation between reaction rate constant (K), thermodynamic equilibrium constant (*$\boldsymbol{K^{\theta}(T)}$*) and temperature (T)*

ii. *Arrhenius Equation*

Arrhenius equation was created by Svante August Arrhenius (Swedish chemist, February 19, 1859, October 2, 1927, who won the Nobel Prize in Chemistry in 1903). This equation mainly discusses the effect of temperature on the reaction rate constant (Jinhong Fu et al., 2005). Nevertheless, this effect relation was first summarized by Van't Hoff in 1884 based on a great number of experimental results: for most chemical reactions, the reaction rate increases with the increase of temperature. The effect of temperature on concentration is generally negligible, so the change of reaction rate with temperature is reflected in the change of rate constant with temperature. A large number of experiments show that the reaction rate becomes 2~4 times for every 10 K increase in the reaction temperature for a homogeneous thermochemical reaction: $\frac{K_{(T_0+10\,K)}}{K_{T_0}} \approx 2 \sim 4$. Although plentiful of experiments have shown that Van't Hoff rule is not accurate, especially, when data is lacking, it is still useful to roughly calculate the change in reaction rate with temperature. However only when the reaction temperature is not very high, or the change range of temperature is not very large too, the Van't Hoff rule provides the valuable results. In 1889, Arrhenius further analyzed the dependence of the reaction rate on temperature, and explained the equation from the perspective of principle, and proposed the existence of "energy barrier" in the reaction. E_a is the experimental activation energy and approximately constant independent of temperature, in fact, this experimental activation energy is in relation to the temperature:$E_a = E_c + \frac{1}{2}RT$ (E_c is the theoretically critical activation energy which is a fixed value independent of temperature, when the temperature T is not very high, $E_a \approx E_c$, and the activation energy of the reaction is relatively low (50-240 KJ·mol-1)).

Moreover, four forms of Arrhenius equation are similar to that of isobaric Van't Hoff equation, and the differential expression, definite integral, indefinite integral, and exponential forms can be shown from (15) to (18) equation.

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{E_a}{RT^2} \tag{15}$$

$$\ln\frac{K_1}{K_0} = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_0}\right) \tag{16}$$

$$\ln k = -\frac{E_a}{RT} + C^* \tag{17}$$

$$k = A^* \cdot e^{-\frac{E_a}{RT}} \tag{18}$$

For equation (18), derivation:

$$\frac{\partial K}{\partial T} = A^* \cdot e^{-\frac{E_a}{RT}} \cdot \frac{E_a}{R}\frac{1}{T^2} \tag{19}$$

Where E_a is usually constant greater than zero, and C^* is a constant, and A^* is a pre-exponential factor. Figure 1 indicates the relationship between reaction rate constant (K) and temperature (T). Thus, the change trend of reaction rate constant (K) with the increase of temperature is similar with that of $K^{\theta}(T)$, as shown in dotted line in Figure 1.

The change trend is also fast in the lower temperature range, subsequently, slow in the higher temperature range. Of course, when the change range of temperature is large, Arrhenius equation needs to be amended due to errors, such as the following formula is often used to modify the Arrhenius equation: $k = A^*(\frac{T_1}{T_0})^n \cdot e^{-\frac{E_a}{RT}}$, or $k = A^* \cdot e^{-(\frac{E_a}{RT})^{\beta}}$ (Peter & Julio, 2010; Fu & Shen, 2005) (The value of n is in the range of -1 and 1, when n=0, the equation is the unmodified Arrhenius equation; the dimensionless β is also constant, in addition, E_a is also an important factor affecting the reaction rate constant, generally, the higher activation energy is beneficial to the reaction at higher temperature, and lower activation energy is beneficial to the reaction at lower temperature. But we only discussed the constant activation energy too in this work).

Results and Discussion

- *Nature of Students' Learning Difficulty*

Table 1 reveals the nature of students' learning difficulty and the number of students with such a difficulty in isobaric Van't Hoff and Arrhenius equations. These percentage values were rounded off to the nearest whole number.

Table 1. *Nature of Students' Learning Difficulty Experienced by Students in Isobaric Van't Hoff and Arrhenius Equation, Total Number and Percentage (%) of Difficulties about 65 Students in 2018-2019 (2 Semester)*

Question number	Content of Isobaric Van't Hoff and Arrhenius equation	Nature of learning difficulties	Number and percentage of difficulties
1	Definition of isobaric Van't Hoff and Arrhenius equation	Inability to differentiate isobaric Van't Hoff and Arrhenius equation	31(48%)
		Inability to understand the relationship of thermodynamic equilibrium constant and reaction rate constant	36(55%)
2	Characteristics of Van't Hoff and Arrhenius equation	Inability to write various formula forms: differential, integral, and exponential form	30(46%)
		Inability to recognize the different role of temperature in both equations	33(51%)
		Inability to describe the difference of activation energy and reaction enthalpy	42(65%)
3	Effect factors of thermodynamic equilibrium constant and reaction rate constant	Inability to identify the effect of temperature on constants	36(55%)
		Inability to understand the production nature of activation energy at the level of atom (micro perspective)	37(57%)
4	Definition of thermodynamic equilibrium constant and reaction rate constant	Inability to understand the definition and unit of reaction rate constant in different grades	48(74%)
		Inability to write the formula of thermodynamic equilibrium constant in isothermal equation	35(54%)
		Inability to derive the process of isobaric Van't Hoff	54(83%)
5	Physical model of thermodynamic equilibrium constant and reaction rate constant	Inability to understand the dialectical relations of two equations	36(55%)
		Inability to understand the difference of reaction rate and rate constant	40(62%)
		Inability to understand the rate constant at per unit concentration	38(58%)
		Inability to understand the consistency of two constants in reversible process model at per unit concentration	54(83%)

The nature of learning difficulty and percentage of occurrence (in brackets) experienced by students in learning isobaric Van't Hoff and Arrhenius equations were obtained by use of the above test. As showed in Table 1, the difficulties were as below: inability to understand the relationship of thermodynamic equilibrium constant and reaction rate constant 36(55%); inability to describe the difference of activation energy and reaction enthalpy 42(65%); inability to understand the production nature of activation energy at the level of atom (micro perspective) 37(57%); inability to understand the definition and unit of reaction rate constant in different grades 48(74%); inability to derive the process of isobaric Van't Hoff 54(83%); Inability to understand the consistency of two constants in reversible process model at per unit concentration 54(83%), etc..

The percentage values of difficulties based on different questions were obviously different, due to all kinds of reasons, for example, the basic knowledge of mathematics was insufficient (inability to write the formula of thermodynamic equilibrium constant in isothermal equation, and inability to derive the process of isobaric Van't Hoff); and the basic knowledge of the previous chapters is insufficient (inability to understand the reversible process. Some basic concepts were also not understood clearly too (activation energy, reaction enthalpy, and reversible process, etc.).

- *Solving Problems through Group Discussion with Contrast Thinking Method*

In modern philosophical methodology, contrast thinking is a basic form of thinking, and it not only has important philosophical significance, but also has a great practical application value. Therefore, this kind of thinking training is also beneficial for students to improve their thinking ability. Table 2 shows the effect of the study of second-year university students with 71 in 2019-2020 (2 semester) and 59 in 2020-2021 (1 semester) after group discussion on the targeted problems.

Table 2. *Improvement of Students' Learning Experienced in Isobaric Van't Hoff and Arrhenius Equation, Total Number and Percentage (%) of Difficulties of Students with 71 students in 2019-2020 (2 Semester) and 59 students in 2020-2021 (1 Semester), respectively.*

Question number	Content of isobaric Van't Hoff and Arrhenius equation	Revealed reasons and nature corresponding to Table 1 through discussion by contrast method	Total number and percentage of improvement
1	Definition of isobaric Van't Hoff and Arrhenius equation	Isobaric Van't Hoff belongs to thermodynamic theory, the effect of enthalpy and temperature on equilibrium constant. Arrhenius equation belongs to kinetic theory, the effect of activation energy and temperature on rate constant	60(85%), 41(70%)
		Equilibrium constant has no time effect Reaction rate constant has time effect, but both can be derived at per unit concentrations	53(75%), 51(86%)
2	Characteristics of Van't Hoff and Arrhenius equation	Ability to write various formula forms: differential, integral, and exponential form	54(76%), 44(74%)
		The effect of temperature on equilibrium movement is essentially caused by the different effects on forward and reverse reaction rates.	50(71%), 43(73%)
		Ability to describe the relation of activation energy and reaction enthalpy	53(75%), 47(80%)
3	Effect factors of thermodynamic equilibrium constant and reaction rate constant	Ability to identify the acceleration effect essence of temperature on constants	60(85%), 47(80%)
		Ability to reveal the essence of activation energy at the level of atom (micro perspective)	60(85%), 48(81%)
4	Definition of thermodynamic equilibrium constant and reaction rate constant	Ability to write the definition and different unit of reaction rate constant in different grades	62(87%), 53(89%)
		Ability to reveal the origin of thermodynamic equilibrium constant in isothermal equation	67(95%), 59(100%)
		Ability to derive the process of isobaric Van't Hoff	52(73%), 41(70%)
5	Physical model of thermodynamic equilibrium constant and reaction rate constant	Ability to reveal the dialectical relations of two equations	53(75%), 44(74%)
		Ability to differentiate the difference of reaction rate and rate constant	65(92%), 59(100%)
		Reaction rate is the rate constant at per unit concentration	62(88%), 56(95%)
		Ability to understand the consistency of two constants in reversible process model at per unit concentration	53(75%), 44(74%)

The improvement of learning and percentage of occurrence (in brackets) experienced by students in learning isobaric Van't Hoff and Arrhenius equations, were obtained by use of the above test. As showed in Table 2, the obvious improvement was as follows:

Students can discern equilibrium constant with time effect and reaction rate constant without time effect, and the total number and percentage of improvement of students out of 71 students in 2019-2020 (2 semester) and 59 students in 2020-2021 (1 semester) are 53(75%) and 51(86%), respectively; these students (percentage of improvement) with 50(71%) and 43(73%) can reveal the essential effect of temperature on equilibrium movement, compared to 29(45%)) (obtained from 36(55%) in 65 students); these students (percentage of improvement) with 53(75%) and 44(74%) can understand the dialectical relations of two equations and the consistency of two constants in reversible process model at per unit concentration, compared to 11(17%) (obtained from 54(83%) in 65 students).

It can be seen that the designed main problems promoted the understanding through group discussion with contrast method. The problem-based learning method enabled students to grasp the main contradictions and explore the essence from the details. The contrast thinking created the concept of complementarity in the philosophical sense. In the basic principles of modern philosophy, the dialectics suggested that all opposites were interdependent, and their conflict will never end in the complete victory of one side, but always in the interaction of the two sides (Jin, Yin, et al., 2019; Jin, Zhang, et al., 2020).

Therefore, in the current study, both teachers and students were aware that comparison was multifactorial, and even considered the role of relative factors to establish comprehensive factors. If both teachers and students followed these basic principles of comparative philosophy, they could find differences in similarity, and find the similarity in different. This similarity of two equations included the form of equation, the effect of temperature, and the difference included the constant and activation energy and/or enthalpy.

Obviously, both teachers and students compared the main contradictions and differences in the main aspects of the contradiction, they could not only compare the related thinking methods in terms of philosophical basic principles such as function and methodology, but also compared some concrete and practical cases based on the actual problem-solving guidance, and then guide the students to summarize: the primary and secondary contradictions. "Core problems" and "Main characteristics" were often described as the main contradiction; in life practice, the primary problems were usually expressed as "grasp the mainstream", or "direction". Here, this mainstream of two equations was the definition and the origin of thermodynamic equilibrium constant and reaction rate constant. Only when students really knew the origin of these two constants could they truly understand their differences and similarities.

In short, in the education and training of students, schools and teachers not only paid attention to the development of students' physical and mental health, but also cultivated students' good thinking quality. Because, only when students faced good thinking habits, could they exert their creativity and subjective initiative in future work. Next, the comparison method was used to deduce these two equations and the consistency of these two constants based on the group discussions and the designed problems. A new perspective based on a reversible reaction model was also used to clarify the relationship between these two constants, reflecting innovative thinking.

• *Thermodynamic Equilibrium Constant and Reaction Rate Constant*

The above system aA→yY can still be used as an example, and the reaction conditions were the same as well. The reaction rate $\nu = -\frac{\mathrm{d}C_{\mathrm{A}}}{a\mathrm{d}t} = \frac{\mathrm{d}C_{\mathrm{Y}}}{y\mathrm{d}t}$, was just only one value in the same system. In order to clarify the reaction characteristics and efficiency of different substances, the system's reaction rate was presented by the formation rate of product or the consumption rate of reactant, such as:

$$\frac{\mathrm{d}C_{\mathrm{Y}}}{\mathrm{d}t} = K_{\mathrm{Y}} \cdot (C_{\mathrm{A}})^{a} \ \text{ or } \ \frac{\mathrm{d}C_{\mathrm{Y}}}{\mathrm{d}t} = K_{\mathrm{Y}} \cdot (C_{\mathrm{A}})^{n} \qquad (20)$$

$$-\frac{\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}t} = K_{\mathrm{A}} \cdot (C_{\mathrm{A}})^{a} \ \text{ or } -\frac{\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}t} = K_{\mathrm{A}} \cdot (C_{\mathrm{A}})^{m} \qquad (21)$$

(n, m is the experimental value, respectively)

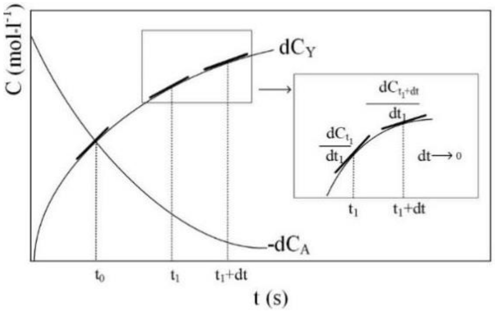

Figure 2. *The relation curve of the reactant/product concentration and time in the reaction process*

Figure 2 shows the relation between the reactant/product concentration and time, and the reaction rate constant can be obtained by the slope of the curve at a time. In fact, the reaction rate (ν) was equal to the reaction rate constant (K) at per unit concentration: $K_{\mathrm{Y}} = \frac{dC_{\mathrm{Y}}}{dt}$ or $K_{\mathrm{A}} = -\frac{dC_{\mathrm{A}}}{dt}$, thus, two formulas divide each other (equations (20) and (21)) as below:

$$\frac{K_{\mathrm{Y}}}{K_{\mathrm{A}}} = \frac{dC_{\mathrm{Y}}}{-dC_{\mathrm{A}}} \tag{22}$$

This formula means that the ratio of the reaction rate constant (K_{Y}) expressed by the product to the reaction rate constant (K_{A}) expressed by the reactant is equal to the ratio of the changed amount of concentration at this time. The slope (K_{Y}) at each point (time) can be denoted as a reaction rate at this time, such as $K_{\mathrm{Y}_1} = \frac{dC_{\mathrm{t}_1}}{dt_1}$ at t_1 time. Although dt trends to be equal to zero, the slope faced a definitely trivial change at (t_1+dt) time, that is to say, the slope of curve was gradual, therefore, the slope at the end state was a positively and gradually varied result in the whole time range, as shown in mosaic image in Figure 2.

Similarly, when the time changes from 0 to ∞, each point in the curve of concentration and time has the same relation. Obviously, the total change amount of concentration at the end state is also the accumulation of the concentration change during the time process (Jin, Xie, et al., 2019; Jin, Yin, et al., 2019; Jin, Zhang, et al., 2020; Simonson et al., 2019; Villanueva-Cab et al., 2010).

Thus, at the end state, $\frac{K_{\mathrm{Y}}}{K_{\mathrm{A}}}$ can be expressed as below

$$\frac{K_{\mathrm{Y}}}{K_{\mathrm{A}}} = \frac{\lim\limits_{\infty} K_{\mathrm{Y}}}{\lim\limits_{\infty} K_{\mathrm{A}}} = \frac{\sum_0^y \int_0^{\mathrm{C}_{\mathrm{Y}}} dC_{\mathrm{Y}}}{\sum_0^a \int_{C_{\mathrm{A}}}^0 -dC_A} = \frac{\sum_0^y (C_{\mathrm{Y}}-0)}{\sum_0^a (C_A-0)} = \frac{(C_{\mathrm{Y}})^y}{(C_{\mathrm{A}})^a} = K^{\theta}(T) \tag{23}$$

Although the rate constant has kinetic property, the ratio of the formation rate constant of product to the consumption rate constant of the reactant at the end state represents the extent of equilibrium movement in agreement with that of thermodynamic equilibrium constant $K^{\theta}(T)$. $K^{\theta}(T)$ is a macroscopic physical quantity containing static property, by contrast, the reaction rate constant (K_{Y} *or* K_{A}) is a microscopic quantity containing dynamic property, but the ratio of two reaction rate constants is always changing towards the final state with the time. In spite of macro or micro point of view, it can also be seen that the ratio of both shows a comprehensive effect of unidirectional development. In addition, $K^{\theta}(T)$ embodies an equilibrium nature, and the rate constant (K_{Y} *or* K_{A}) reflects a change nature and a process quantity. In summary, thermodynamic equilibrium constant and the ratio of $K_{\mathrm{Y}}/K_{\mathrm{A}}$ are consistent in essence which indicates the orientation of the equilibrium movement.

- *Dialectical Relation between Thermodynamic Equilibrium Constant and Reaction Rate Constant*

It can also be seen from the reaction mechanism that thermodynamic equilibrium constant has dynamical characteristics too. The reaction mechanism of the same system is shown as $aA \xleftrightarrow[K_{-1}, E_{\mathrm{a}}^{-1}]{K_1, E_{\mathrm{a}}^1} yY$ (Where, K_1 is equivalent to the above-mentioned K_{A}, representing the forward reaction rate constant; K_{-1} is the reverse reaction rate constant; K_{Y} shows the comprehensive effect of $K_1$and K_{-1} due to $\frac{\mathrm{d}C_{\mathrm{Y}}}{\mathrm{dt}} = K_{\mathrm{Y}} \cdot (C_{\mathrm{A}})^a$, E_a^1, E_a^{-1} is activation energy in the forward and reverse reaction, respectively), therefore, the formation rate of this product (Y) can also be expressed using equation (24) based on the reaction mechanism.

$$\frac{\mathrm{d}C_{\mathrm{Y}}}{\mathrm{dt}} = K_1 (C_{\mathrm{A}})^a - K_{-1} (C_{\mathrm{Y}})^y \tag{24}$$

When the reaction reaches equilibrium:

$$\frac{\mathrm{d}C_{\mathrm{Y}}}{\mathrm{dt}} = K_1(C_{\mathrm{A}})^a - K_{-1}(C_{\mathrm{Y}})^y = 0 \qquad (25)$$

$$K_1(C_{\mathrm{A}})^a = K_{-1}(C_{\mathrm{Y}})^y$$

The introduction of K_c:

$$K_{\mathrm{c}} = \frac{K_1}{\mathrm{K}_{-1}} = \frac{(C_{\mathrm{Y}})^y}{(C_{\mathrm{A}})^a} \qquad (26)$$

In addition, the new equation can be obtained by combining the formula (23) with (26), moreover, $K_1=K_A$.

$$\text{So, } K^{\theta}(T) = \frac{K_{\mathrm{Y}}}{K_{\mathrm{A}}} = \frac{K_{\mathrm{Y}}}{K_{\mathrm{C}}K_{-1}} \qquad (27)$$

$K^{\theta}(T)$ contains the characteristics of microscopic dynamics due to the effect of K_c or K_{-1}, at the same time, showing the degree of equilibrium state movement. The essential unity of both is also reflected in the consistency of the energy properties of E_a and ΔH. Figure 3 indicates the relation of activation energy and reaction enthalpy in the forward and reverse reaction, and it is obvious that the reaction enthalpy can be obtained from activation energy: $\Delta H = E_a^1 - E_a^{-1}$.

Although reaction enthalpy and activation energy are different forms of energy, both are the same in essence because they can affect the reaction of a system as an important factor. As mentioned before, both reaction enthalpy and activation energy are the important factors affecting the reaction rate, and this is that because the essential cause is attributed to the transition of electrons at different energy levels (Jin, Easton, Yin, et al., 2018; Jin et al., 2015; Yoon, 2014). When an electron transits from an energy level of a ground state to an energy level of an excited state, this molecule becomes an activated molecule. Activation energy is the energy absorbed by ordinary molecules when a large number of ordinary molecules transfer into activated molecules, therefore, the reaction enthalpy is exactly the sum of the activation energy difference of the forward and reverse reactions of a large number of molecules, as shown in the Fig. 3.

According to Arrhenius equation: $k_1 = A_1 \cdot e^{-\frac{E_a^1}{RT}}$; $k_{-1} = A_{-1} \cdot e^{-\frac{E_a^{-1}}{RT}}$

So, the above equation (26) can be changed to $K_{\mathrm{c}} = \frac{K_1}{\mathrm{K}_{-1}} = \frac{A_1 \cdot e^{-\frac{E_a^1}{RT}}}{A_{-1} \cdot e^{-\frac{E_a^{-1}}{RT}}} = A_0 e^{\frac{-(E_a^1 - E_a^{-1})}{RT}} = A_0 e^{\frac{-\Delta_r H_m^{\theta}}{RT}}$, ($A_0$, A_1, and A_{-1} is pre-exponential factor, respectively), which precisely corresponds to that of the isobaric Van't Hoff equation (13) due to the same form. Obviously, there are the same equilibrium properties for K_c and $K^{\theta}(T)$ at standard pressure condition. However, K_c is microscopic kinetic quantity and $K^{\theta}(T)$ is macroscopic thermodynamic quantity with dynamic characteristics, which is the main difference.

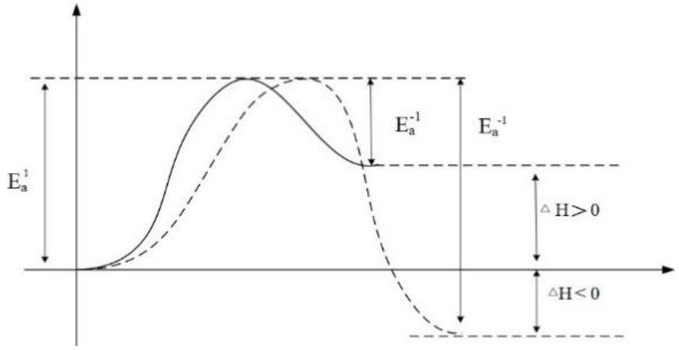

Figure 3. *The relation of activation energy and reaction enthalpy in the forward and reverse reaction*

In short, there exists an organic connection of Arrhenius equation to the isobaric Van't Hoff equation, and this organic connection presents a dialectical relationship through the thermodynamic equilibrium constant and reaction rate constant (Jinhong Fu et al., 2005; Gilbert & Treagust, 2009; Simonson et al., 2019). On the one hand, the dialectical relationship indicates some unity characteristics: both constant reflect the change of reaction extent (rate) with the change of temperature from different perspectives, on the other hand, the dialectical relationship indicates some contradiction characteristics: one constant is chemical thermodynamics, independent of time and macroscopic limit, the other is chemical kinetics, dependent of time and microscopic course. The activation energy and reaction enthalpy are also a pair of dialectically unified physical quantities, and they have a common origin which all reflect the inherent properties of the reacted substance in the closed system.

Our findings are consistent with the discussion of literatures (Kim et al., 2014; Mack & Towns, 2016; Sözbilir, 2004), showing that the learning difficulties can be improved through the analysis of problems and the adoption of an appropriate learning method.

Conclusion

The dialectical relation between thermodynamic equilibrium constant and reaction rate constant was presented through contrast method, firstly, both physical quantities have the same forms in the isobaric Van't Hoff equation and Arrhenius equation, showing the similar trend with the increase of temperature. Moreover, the connotation of thermodynamic equilibrium constant and the ratio of two reaction rate constants was consistent. On one hand, they all represented the reaction extent forward the end state; on the other hand, the thermodynamic equilibrium constant contained the characteristics of microscopic dynamics. Moreover, it can be seen as the gradually accumulated effect of both reaction rate constants in a long range of time. However, they still showed obvious differences, for example, thermodynamic equilibrium constant was static and macroscopic quantity, and reaction rate constant was dynamic and microscopic quantity. The reaction enthalpy and activation energy were closely related to each other and the essential nature of energy.

Finally, it is hoped that the findings of this research would provide the support for better grasp of theoretical knowledge and also provide reference for learning similar knowledge such as equilibrium state and reversible processes, partial molar quantity and chemical potential, etc. The application of the method is an interesting subject for future research and implications for research and practice, which would help students to analyze and solve problems in practical work.

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Conflict of Interest

The authors state that no conflict of interest is present in this paper.

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