



What Principle Governs the Chemical Dynamic/Kinetic Process (3)?

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Author's contribution

The sole author designed, analysed, interpreted and prepared the manuscript.

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ABSTRACT

In this work we discussed the description of the chemical dynamic/kinetic process. It is noticed that the conventional one way description about the chemical dynamic/kinetic process is a mathematically correct but physically incorrect description, because the chemical reaction doesn't follow the one way mechanism as scientist' will. Instead, the forward chemical dynamic/kinetic processes are always accompanied by the backward chemical dynamic/kinetic processes. Based on this physical picture for the chemical reaction dynamic/kinetic process, it is concluded: 1.the forward and backward chemical reactions follow the same route, just the time direction is reversed and 2.the exponential factor of the rate constant of the chemical reaction is the same for forward and backward chemical reaction dynamic/kinetic processes.

Keywords: *Forward chemical reaction; backward chemical reaction; "yin and yang" philosophy; microscopic reversibility; chemical dynamic/kinetic processes; chemical equilibrium.*

1. INTRODUCTION

The variation is a constant process going on in the Nature. Even the human beings themselves are the result of this kind of variation. The

curiosity of the human beings leads themselves continuously to pay their attention onto this variation. The researchers try their best to understand and elucidate why and how these variations around us happened [1,2]. Till now, the

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human beings already made great progress in understanding from the phenomenon to the mechanism of these variations in Nature. A lot of important dynamic/kinetic processes have been revealed, such as Big Bang theory regarding the birth of our universe [3], the bio-evolution theory regarding the human beings themselves [4]. Some of dynamic/kinetic processes have been made very clear and utilized to help the human beings. A typical example recently is the designing anti-virus drug for Covid-19 [5].

Here we would focus on the chemical dynamic/kinetic processes. In this field, scientist also made great achievement, such as the Arrhenius theory [6] and Boltzmann theory [7, 8]. Especially, since the quantum theory is founded [9], the chemical dynamic/kinetic processes are elucidated at microscopic level. Based on these progresses, the related technology is developed and controlling the chemical dynamic/kinetic process becomes more precision and much easier than before [10].

Now the most efforts in scientific field are paid to how to utilize those discoveries mentioned above to benefit the human beings. As a result, a lot of modern chemical factories are setup and new chemical material appears on the market almost every day [11].

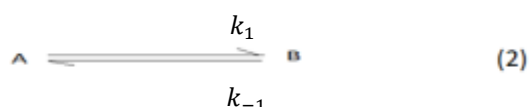
Just as we pointed out in our previous work [12, 13], due to the finite knowledge we obtained before, some characters about the chemical dynamic/kinetic processes are ignored or still uncovered. Therefore, in this work, we will continue exploring what is missing knowledge about the chemical dynamic/kinetic processes.

2. THEORY AND DISCUSSION

Here we would start our discussion from the following chemical reaction process.



Conventionally, we describe this chemical reaction process in following way,



$$\frac{d(C_0 - C)}{dt} = k_1 C - k_{-1}(C_0 - C) \quad (3)$$

$$-\frac{dC}{dt} = k_1 C - k_{-1}(C_0 - C) \quad (4)$$

$$\frac{dC}{dt} = k_{-1}C_0 - (k_1 + k_{-1})C \quad (5)$$

$$C = \frac{k_{-1}C_0}{k_1 + k_{-1}}(1 - e^{-(k_1 + k_{-1})t}) \quad (6)$$

Where

C_0 is the starting concentration of reactant; t is the reaction time; k_1 and k_{-1} are the forward and backward chemical reaction rate constants, respectively.

Above is the knowledge we understood and accepted about the chemical dynamic/kinetic processes. The right arrow (k_1) is the forward reaction, and the left arrow represents the backward reaction. This means k_1 describe the one way chemical dynamic/kinetic process (from left to right) and k_{-1} represents another one way chemical dynamic/kinetic process (from right to left). From these description and definition, it seems every step is correct. Indeed, in textbook, we do teach student with this kind of concept in analysis of chemical reaction.

However, from the conclusion in our previous work [12, 13], the chemical reaction process above can be described as

$$\frac{d(C_0 - C)}{dt} = k' C \quad (7)$$

$$\frac{dC}{C} = -k' dt \quad (8)$$

$$\int_{C_0}^C \frac{dC}{C} = \int_0^t -k' dt \quad (9)$$

$$C = C_0 e^{-k' t} \quad (10)$$

Where

k' is the chemical reaction rate constant.

Compare the eq.(6) with eq.(10), for the same chemical dynamic/kinetic process, the eq. (6) and eq.(10) are different. The question here is which equation correctly describes the chemical dynamic/kinetic process?

In the conventional case, eq. (6), we define the route (solid line in Fig.1 a) of chemical reaction

as one way for forward reaction (from left to right) and the route (dashed line in Fig.1 a) as another one way for backward chemical reaction, that means we treat the forward and backward chemical reactions separately. Equivalently to say, the forward and backward chemical reactions follow different routes which are one way routes. And conventionally we do analyze

the chemical dynamic/kinetic process in this way in the past [14].

In order for us to accept this analysis as correct description of the chemical dynamic/kinetic process, we have to ask one basic question, that is, the chemical reaction really proceeds in one way route?

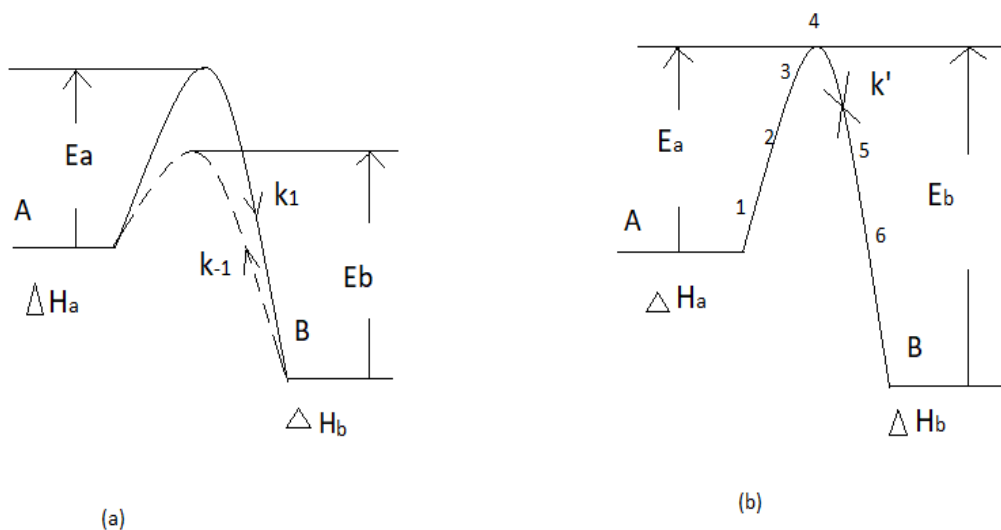


Fig.1. The Illustration of the Chemical Reaction Routes (Energy Diagram)

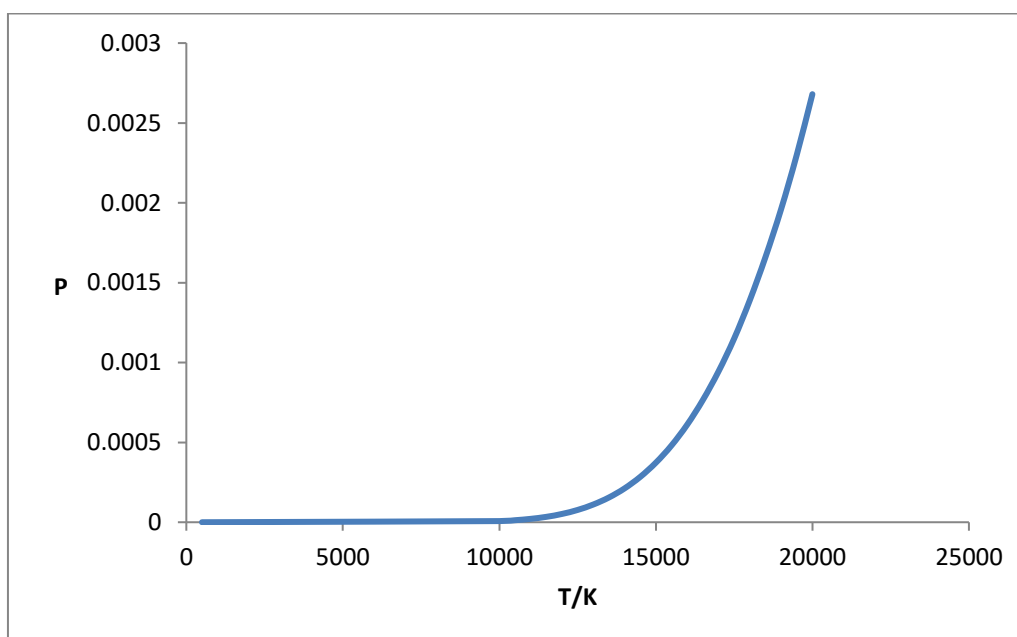


Fig. 2 The temperature dependence of probability for the excitation from E_{1s} to E_{2p} of hydrogen atom

(In Fig.1, E_a and E_b are the activation energies for forward and backward chemical reaction, ΔH_a and ΔH_b are the enthalpies of the reactant and product, respectively.)

It is obvious that the chemical reaction does not follow the one way route mechanism. For the process of chemical reaction, it can be illustrated in Fig.1 b. At any stage of the process of chemical reaction as shown in Fig.1 b (marked 1,2,3,4...), there always exists the possibility for chemical reaction going forward process (called forward chemical reaction) and backward process (called backward chemical reaction). The only difference among the different stage is in that the ratio of forward to backward chemical reaction process is different; From the left side of the energy barrier to stage 4, the forward chemical reaction rate (uphill) is slower than the backward chemical reaction rate (downhill); From the stage 4 to the right side of the energy barrier, the forward chemical reaction rate (downhill) is faster than the backward chemical reaction rate (uphill). If the analysis about the chemical reaction process here is correct, then, the forward and backward chemical reactions should follow the same route. That means the real chemical reaction does not happen in one way route as the scientist's will.

For the process of eq.(10), it seems we lost some information about the chemical reaction process, such as the forward or backward chemical reaction processes. However, as we pointed out in our previous work, the eq.(10) already includes the forward and backward chemical reaction information. That means the forward and backward chemical reaction follow the same route, the whole process just like we see the film in cinema, first see the film in forward way, then see the film in reverse way, but it is the same film. Our description about the process of chemical reaction is consistent with the principle of microscopic reversibility in physics and chemistry, and also matches the "Yin and Yang" Philosophy (for the detail discussion, see our previous work [12, 13, 15].

Now it is clear that the situation described in eq.(6) is not real process for chemical reaction experienced, instead the situation described in eq.(10) represents the process for the chemical reaction experienced in practice. Therefore, the description of eq.(10) should be adopted when we analyze the dynamic/kinetic process of chemical reaction.

In our previous work [12, 13], we proposed a way to determine the chemical activation energy as long as we can know one of them, that is, the activation energy of the forward or backward chemical reaction. And we got the eq.(11),

$$E_b = E_a + RT \ln \left[\frac{(2+e^{-x}-e^x) \pm \sqrt{(2+e^{-x}-e^x)^2 - 4}}{2e^x} \right] \quad (11)$$

Where

$x = \frac{E_a}{RT}$, E_a and E_b are the forward and backward chemical reaction energy called activation energy, respectively. From Fig.1 b, we know that

$$E_b - E_a = \Delta H_a - \Delta H_b \quad (12)$$

Where

ΔH_a , and ΔH_b are the enthalpies of the reactant and product [16], respectively.

Compare the eq.(11) with eq.(12), we know

$$\Delta H_a - \Delta H_b = RT \ln \left[\frac{(2+e^{-x}-e^x) \pm \sqrt{(2+e^{-x}-e^x)^2 - 4}}{2e^x} \right] \quad (13)$$

Furthermore, in equilibrium (corresponding the stage 4 in Fig.1 b, and as definition in our previous work [12, 13], following r_+ represents the rate constant of forward chemical reaction; the r_- represents the rate constant of backward chemical reaction),

$$r_+ = r_- \quad (14)$$

$$r_+ = \frac{e^{-x}-e^x}{2} \quad (15)$$

$$r_- = \frac{e^{-(x+\Delta x)} + e^{(x+\Delta x)}}{2} - 1 \quad (16)$$

At constant temperature, r_+ and r_- are constant also. Therefore, if we follow the definition about the equilibrium constant $\frac{r_+}{r_-}$ or $\frac{r_-}{r_+}$, the equilibrium constant should be always 1. More interesting point is, this equilibrium constant is generally valid and irrespective to whether the chemical reaction is 1 or 2,... order or not. We notice that this conclusion is totally different from the concept of the equilibrium constant of chemical reaction developed from the conventional definition.

The equilibrium position we talked is for the chemical reaction complex or transition state located at the top of the reaction route (Fig.1 b,

stage 4), which is the dynamic equilibrium position or transition position. At this position, the chemical reaction complex or transition state has 50% going forward and 50% coming backward. The component distribution at equilibrium can be determined by $\frac{e^{-\Delta H_a}}{e^{-\Delta H_a} + e^{-\Delta H_b}} C_0$ for product or by $\frac{e^{-\Delta H_b}}{e^{-\Delta H_a} + e^{-\Delta H_b}} C_0$ for reactant, which can be called the thermal equilibrium distribution. The $e^{-\frac{E_a}{RT}}$ and $e^{-\frac{E_b}{RT}}$ determine the time for system to reach the equilibrium position, not the concentration distribution. Only $E_a - E_b$ has indirect effect on the concentration distribution of the reactant and product. Now we see the method developed here is totally different from the conventional method for determining the concentration distribution at the equilibrium condition.

Another point we should notice is that the exponential factor conventionally is explained as collision frequency, and for the forward and the backward chemical reaction, this collision frequency is generally different. But based on our analysis above, the exponential factor must be the same for the forward and backward chemical reaction, not as we believed before from the literatures because the forward and backward chemical reactions follow the same route, just the direction of time is reversed.

From the discussion and comparing two different descriptions about the dynamic/kinetic chemical reaction processes above, it is clear that the conventional description about the dynamic/kinetic chemical process is mathematically correct but physically incorrect.

Here we would like to take the interaction between photon and hydrogen atom as an example [17],



For this process, the reaction activation energy for forward and backward process are the same ($E_a = E_{2p} - E_{1s}$) but just the signs are reversed, that is, the activation energy is positive for forward reaction (from left to right) and negative for backward reaction (from right to left). Due to the forward and backward reaction following the same route and the times for the forward and backward reaction processes are inversely proportional to the $e^{-\frac{E_a}{RT}}$ and $e^{\frac{E_a}{RT}}$, therefore, we can conclude the backward reaction is much faster than the forward reaction, corresponding to

the short lifetime of the excited state of hydrogen atom at H_{2p} .

Based on the discussion above, we can know the component distribution for the dynamic/kinetic process for the interaction between the photon and the hydrogen atom.

For H_{1s} , it is, $\frac{e^{-\frac{(E_{2p}-E_{1s})}{RT}}}{1+e^{-\frac{(E_{2p}-E_{1s})}{RT}}}$, for H_{2p} , it is, $\frac{1}{1+e^{-\frac{(E_{2p}-E_{1s})}{RT}}}$. That means when the photon meets the hydrogen atom, the probability to be excited to H_{2p} is, $\frac{1}{1+e^{-\frac{(E_{2p}-E_{1s})}{RT}}}$, which is pretty low probability for hydrogen atom to be excited from H_{1s} to H_{2p} at room temperature. This temperature dependence of the probability for hydrogen atom to be excited from H_{1s} to H_{2p} can be illustrated in Fig. 2.

3. CONCLUSION

We discussed the chemical reaction dynamic/kinetic process in this work. We can conclude that the forward chemical reaction process is always accompanied by the backward chemical reaction process. This description regarding the dynamic/kinetic chemical reaction process is consistent with the principle of microscopic reversibility in physics and chemistry, and also matches the "Yin and Yang" philosophy. The conventional description about the dynamic/kinetic chemical reaction process doesn't represent the real dynamic/kinetic chemical reaction process, which is a typical example of mathematically correct but physically incorrect description. The concentration distribution is determined by ΔH_s from the reactant and product, the chemical reaction energies, E_a and E_b (conventionally called activation energy), determine the time for system reaching the equilibrium, only $E_a - E_b$ is indirectly related with the concentration distribution at the equilibrium because $(E_a - E_b)$ is equivalent to $(\Delta H_a - \Delta H_b)$. And the last point we made clear in this work is that for the forward and backward chemical reactions, the exponential factors of the rate constants of the chemical reactions are the same, because the forward and backward chemical reactions follow the same route, just the direction of time is reversed.

COMPETING INTERESTS

Author has declared that they have no known competing financial interests or non-financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

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