

That the forward reaction rate equals the reverse reaction rate is a necessary but not sufficient condition for that chemical reaction to be at equilibrium

Que la velocidad de reacción directa es igual a la velocidad de la reacción inversa es una condición necesaria pero no suficiente para que la reacción química esté en equilibrio

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Abstract

We point out, the statement in general chemistry teaching and some textbooks of chemistry, that the rate of forward reaction equals to the rate of reverse reaction is sufficient-necessary condition for that the chemical reaction reaches equilibrium is not consistent with chemical thermodynamics and propose a new diagram for understanding chemical equilibrium.

Key words chemical equilibrium, sufficient condition, necessary condition

Resumen

Se señala, la declaración en la enseñanza de la química general y algunos libros de texto de química, que la velocidad de reacción directa es igual a la velocidad de la reacción inversa, es condición suficiente. Esta condición para que la reacción química alcance el equilibrio no es consistente con la termodinámica química, proponemos un nuevo diagrama para la comprensión de equilibrio químico.

Palabras clave: equilibrio químico, condición suficiente, condición necesaria

INTRODUCTION

In general chemistry teaching, the students are taught that in a reversible reaction system, there exist forward reaction and reverse reaction; if the rate of forward reaction equals to the rate of reverse reaction (proposition p), then the reversible reaction has reached chemical equilibrium (proposition q) (Pardue, Bodner, 1995), (Figure 1). In logic (Hurley, 2006), the above complex proposition may be expressed with $p \rightarrow q$, here, \rightarrow means "imply". On the other hand, the students also are taught that, meanwhile, if the rate of forward reaction does not equal to the rate of reverse reaction ($\neg p$, here \neg means negation), then the reversible reaction has not reached equilibrium ($\neg q$), the above compound proposition may be indicated with $\neg p \rightarrow \neg q$, or with $p \leftarrow q$. That means, in the general chemistry, people consider that forward reaction rate equals to reverse reaction rate is sufficient-necessary condition for that chemical reaction to have reached equilibrium, indicated with $p \leftrightarrow q$ (biconditional logical connective). In the other statement, the chemical reaction reaches equilibrium **if and only if** that forward reaction rate equals to reverse reaction rate.

CURRENT UNDERSTANDING OF CHEMICAL EQUILIBRIUM

If this is true, we can infer that any reversible reaction system with constant concentrations or partial pressures is a chemical equilibrium system, which may be inferred from that reaction system keeps constant concentrations or partial pressures (proposition r) **if and only if** that forward reaction rate equals to reverse reaction rate (proposition p), i.e. $p \leftrightarrow r$. According

to this conclusion, we must judge that the system shown in inset figure in Figure 2 is a chemical equilibrium system. Obviously the system is not a chemical equilibrium system, therefore, that any reversible reaction system with constant concentrations or partial pressures is a chemical equilibrium system is false, in logical expression, $((r \rightarrow q) \wedge r \rightarrow q) \rightarrow (r \wedge \neg q \rightarrow \neg(r \rightarrow q))$.

The chemical reaction rate is measured physically by the changes of concentration or partial pressure of reactants or products in the period of reaction time (Hu Ying, 2013). For a reversible reaction, when the concentrations or partial pressures of reactants or products keep unchanged, that the forward reaction rate equals to the reverse reaction rate can be concluded, for example, in the room temperature, the partial pressures of hydrogen, oxygen and water vapour in their mixture system will keep constant with time, so that it can be concluded that the forward reaction rate equals to the reverse reaction rate, but that the reaction reaches equilibrium cannot be judged certainly. However, in fact, the system does not reach the chemical equilibrium.

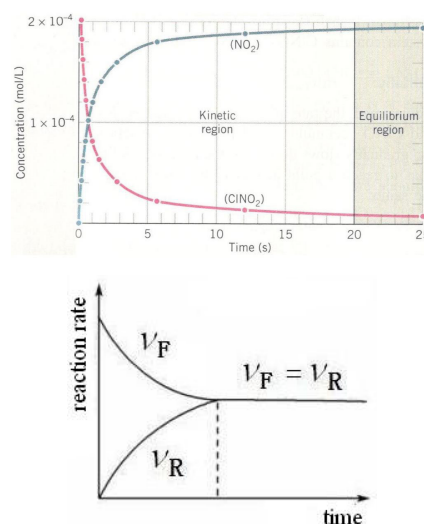


Figure 1. The chemical reaction reaches equilibrium **if and only if** that forward reaction rate equals to reverse reaction rate described in current textbook (Pardue, Bodner, 1995),..

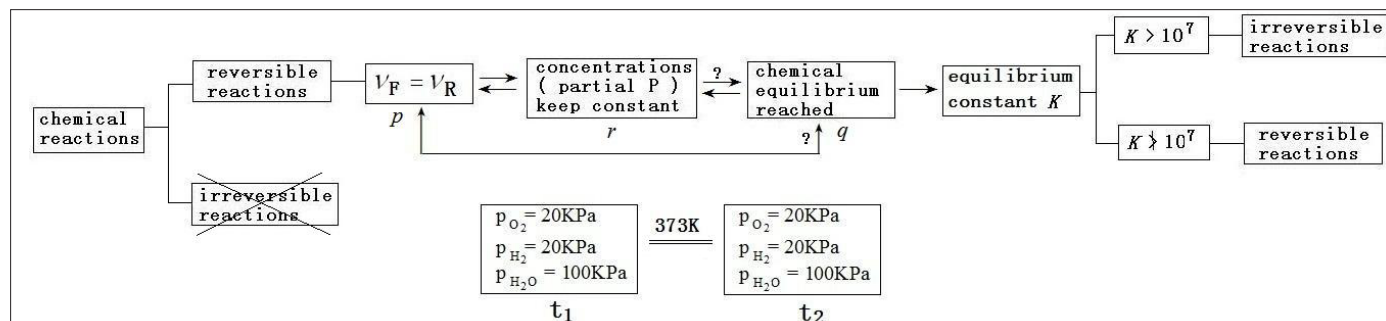


Figure 2: Current flow chart for instruction of chemical equilibrium. The question marks above the arrows indicate that we deny the implications. The figure inset shows a system with the constant concentrations (partial pressure) but not a chemical equilibrium system. We also consider that division of reaction into reversible and irreversible according to equilibrium constant is improper.

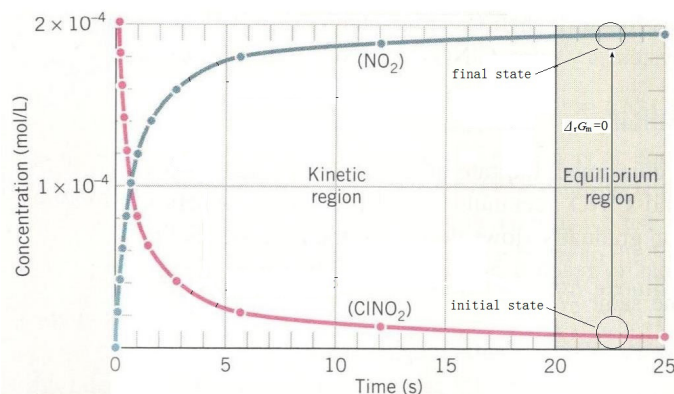


Figure 3: $\Delta_r G_m$ of the process at equilibrium region is 0 kJ/mol.

Chemical thermodynamics defines $\Delta_r G_m$ as the change of Gibbs free energy(G) of the process from reagents(initial state) to products(final state) per mole completely in certain reaction conditions. If $\Delta_r G_m < 0$ kJ/mol, then the process is naturally occurring (spontaneous), If $\Delta_r G_m > 0$ kJ/mol, then the process does not occur spontaneously. At the equilibrium region, as shown in Figure 3, the two circles in vertical line represent the initial state(reagents) and final state(products), respectively. The process is completely different from the process of changing between the states from starting time to equilibrium time of reaction. According to chemical thermodynamics, $\Delta_r G_m$ of the process at equilibrium region is 0 kJ/mol, and the process is the fictively reversible process (quasistatic process), neither spontaneous nor nonspontaneous.

A PROPOSED DIAGRAM FOR UNDERSTANDING CHEMICAL EQUILIBRIUM

Obviously if the rate of forward reaction does not equal to the rate of reverse reaction, then the reversible reaction does not reaches equilibrium. Therefore, that forward reaction rate equals to reverse reaction rate is not sufficient-necessary but necessary condition for that chemical reaction reaches equilibrium, in logical expression, $p \leftarrow q$ or $\neg p \rightarrow \neg q$.

On the other hand, that equilibrium constants are used to divide reversible and irreversible reactions is not proper. The study of chemical equilibrium locates in the domain of chemical thermodynamics in which there is not time variable (Atkins, 1988), but the reaction rate is determined with time variable. So that judgment of chemical equilibrium with reaction rate is inconsistent. In view of the chemical thermodynamics (Hu Ying, 2013), the chemical reactions are chemical equilibrium **if and only if** the Gibbs free energy change, $\Delta_r G_m(T, P) = 0$ kJ/mol(proposition s), in the logical expression, $q \leftrightarrow s$. A new flow chart for understanding chemical equilibrium is proposed in Figure 4.

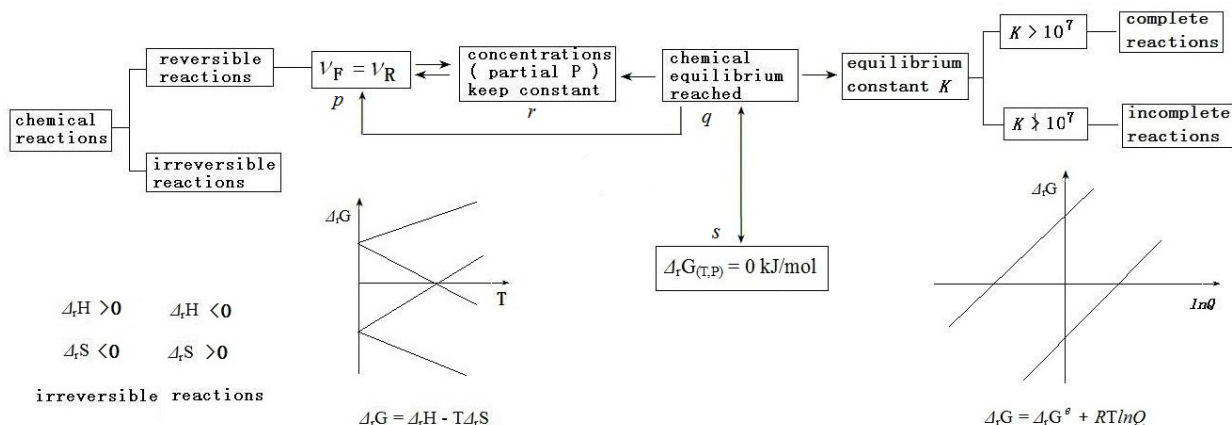


Figure 4: A proposed flow chart for understanding chemical equilibrium.

The figure inset left in Figure 4 shows the temperature dependence of $\Delta_r G_m$ for the pure solid or liquid reactions which may be used how to judge reversible reactions or irreversible reactions. The reactions with $\Delta_r G_m$ across the zero are reversible reactions, and the others are irreversible reactions.

The figure inset right in Figure 4 shows the dependence of $\Delta_r G_m$ for the reactions involving gases or solutions on $\ln Q$, here Q is the reaction quotient. All the reactions involving gases or solutions are reversible reactions, for $\Delta_r G_m$ may across zero. The standard Gibbs free energy change, $\Delta_r G_m^\ominus$ may be used as standard to divide complete reactions and incomplete reactions, the more negative $\Delta_r G_m^\ominus$, the more large $\ln Q$ when $\Delta_r G_m$ across zero, that is, the more large the equilibrium constant, and more complete the reaction may proceed.

CONCLUSIONS

In this paper, we point out, the statement in general chemistry teaching and some textbooks of chemistry, that the rate of forward reaction equals to the rate of reverse reaction is sufficient-necessary condition for that the chemical reaction reaches equilibrium is not consistent with chemical thermodynamics, and propose a new diagram for understanding chemical equilibrium. And how to separate the reversible reactions and irreversible reactions, as well as, how to divide complete reactions and incomplete reactions, is discussed.

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Received 17-01-2016 /Approved 30-11-2016

Editors' note: We found this short paper interesting although were not convinced by its argument. In our opinion the example of the constant composition mixture of hydrogen, oxygen and water vapour at room temperature is a situation where no appreciable reaction is occurring in either direction - hence this is not at equilibrium. A prerequisite condition for a chemical reaction to be at equilibrium is that reactions are taking place! We agree that the 0 value for the Gibbs' Free Energy function at equilibrium is also a necessary criterion for chemical equilibrium, but would suggest that this is not nearly such an accessible, or useful, concept for students or for chemists. However, the paper raises issues that are very significant for chemical education and we would hope the engage readers in this discussion.

What is the reader's opinion about chemical equilibrium? Are all chemical reactions reversible? If not, how do we distinguish between reversible and irreversible? There are important stable systems such as fuels mixed with air/oxygen and also living things where concentrations of chemicals remain static for long periods - and these are not in chemical equilibrium. Do your students struggle with these ideas?