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Research Article

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Discussion on definition and understanding of the thermodynamic spontaneous process

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Abstract: The spontaneous process is one of the most important concepts in thermodynamics. However, there are widespread confusions about it because of markedly different definitions in many textbooks of physical chemistry as well as its daily and nonscientific usage. To clarify the confusions, definitions of the spontaneous process in a number of widely used textbooks are reviewed and analyzed. Then, key points to correctly understand the thermodynamic spontaneous process are examined, and two modified definitions based on definitions in textbooks of physical chemistry are proposed. The recommended definition is that any closed system that is in equilibrium with its surroundings but not at equilibrium internally has the tendency to change to an equilibrium state, and this tendency of change is called the spontaneous process or the spontaneous direction. It emphasizes that the foremost precondition to define the spontaneous process is the equilibrium between the closed system and its surroundings. Accordingly, the "external influence" in several common definitions of the spontaneous process is revealed to be the energy irreversibly exchanged between the system and its surroundings, rather than energy or work in many definitions. Besides, typical criteria of the spontaneous process are discussed to reveal their necessary conditions based on proposed definitions, and some unanswered questions in textbooks of physical chemistry are resolved. The whole discussion would be helpful for chemistry lecturers and students to precisely understand the spontaneous process.

Keywords: thermodynamics; spontaneous process; spontaneity

1 Definitions of the spontaneous process

Spontaneity is one of the most important concepts in thermodynamics, and criteria of the spontaneous process are the most fundamental knowledge of chemistry thermodynamics. However, definitions of spontaneous process in textbooks of physical chemistry or thermodynamics are markedly different, as listed in Table 1. Consequently, confusions arise from words like "work", "external input", etc. in these definitions. In addition, the word "spontaneous" is commonly used in daily life, so students are prone to understand it literally rather than scientifically.[1] For this reason, some textbooks of physical chemistry even don't define or explain what the spontaneous process is but seem logical.[2] These quite different definitions or descriptions along with daily usage make the concept of spontaneous process very ambiguous, making it difficult to understand for learners as well as instructors.[3,4] To eliminate confusions, R.S. Ochs even proposed to eradicate "spontaneous" from the chemical lexicon.[5] It is a radical idea and is disagreed by B.L. Earl.[6] Despite different definitions and confusions, spontaneity remains a key concept in thermodynamics. Its precise scientific meaning necessitates definition and clarification. For this purpose, this paper attempts to analyze a few misconceptions related to the spontaneous process and then tries to eliminate confusions by clarifying definitions based on several textbooks of physical chemistry.

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Table 1: Typical definitions or descriptions of the spontaneous process in literature.

Definition or description of the spontaneous process	**Reference**
Any system that is not at equilibrium will evolve with time. We refer to the direction of evolution as the spontaneous direction.	7
By spontaneous, it is meant naturally *without any energy input* to aid the process.	8
Spontaneous process – a process that occur on its own *without energy input* from the surroundings; defined by a negative change in free energy.	9
The preferred direction occurs spontaneously, that is, *without the input of energy* from the surroundings.	10
A reaction is spontaneous if it occurs *without any additional energy input*.	11
A spontaneous process is a process that occurs on its own, specifically *without the need for a continuous input of energy* from its surroundings.	12
The spontaneous direction of change, the direction of change that *does not require work* to bring it about.	13
A spontaneous change is a change that has a tendency to occur *without work* having to be done to bring it about.	14
A spontaneous process *does not require any network* to be done on the system.	15
A process occurring inside a system is spontaneous if *the surroundings are not required to perform work on the system*.	16
A thermodynamically spontaneous reaction at a given temperature is one that can move in a specified direction to produce a measurable change in the composition of the system *without the necessity to do work* on the system.	17
The spontaneous processes are those which take place *without external interference* of any kind.	18
The term "spontaneous reactions" is used to describe chemical reactions that take place *without an external driving factor*.	19
A process which proceeds on its own accord, *without any outside assistance* is called spontaneous.	20
A spontaneous process is one that occurs *without outside intervention* (i.e., without work or heat transfer).	21
A spontaneous process may be defined as a process which proceeds of its own accord, *without the help of any external agency*.	22
In thermodynamics, a spontaneous process is a process which occurs *without any external input* to the system.	23
The spontaneous process is an irreversible process. All uncontrolled (spontaneous) natural processes are dissipative in nature.	24
The processes which proceed by themselves and bring the system closer to the equilibrium are called spontaneous processes.	25
A spontaneous process is defined as a change in a system the cause of which cannot be traced to a phenomenon originating in the surroundings, that is, one acting on the system at the boundary.	26

Based on key words of the definitions in Table 1, definitions of the spontaneous process may be classified into three major categories according to their literal meanings. In other words, there are three typical understandings of the spontaneous process. The first one is that there should be no energy input to the system for the spontaneous process.[8–12] This understanding mostly stems from the literal meaning of spontaneous in the dictionary. As defined by the Oxford dictionary, one of the literal meanings of spontaneous is "happening naturally, without being made to happen". The Merriam-Webster dictionary defines spontaneous as "developing or occurring without apparent external influence, force, cause, or treatment". Therefore, some students are prone to think that only the change of the isolated system can be spontaneous, which exchanges no energy or mass with its surroundings. It's indeed right that any change of isolated systems is spontaneous since there is no external influence. However, thermodynamics primarily studies the spontaneity of the closed system that exchanges heat and work with its surroundings. One of the main purposes of thermodynamics is to find the spontaneity criteria for closed systems, namely, chemical reaction systems and phase change systems. There may be energy input to these systems during the spontaneous process, such as volume-reducing and endothermal processes. Thus, this kind of definition of the spontaneous process is not applicable for the closed systems.

The second major definition is that there should be no work input to the system for the spontaneous process.[13–17] This definition may be the most widely-spread one. Definitions of spontaneous process in most physical chemistry textbooks explicitly state this, as shown in Table 1. The probable reason for excluding work might be that the word "work" implies intentional influence or man-made force. Therefore, if there is work done to the system, the occurred process is due to work and thus isn't spontaneous. However, work is a strictly defined concept in thermodynamics, which represents all energy exchanged between the system and its surroundings except heat. Regardless of these definitions of spontaneous process, all textbooks of physical chemistry derive the criteria for spontaneous process for a closed system at constant temperature and pressure without non-PV work (non-expansion work), namely, $dG_{sys}<0$. It doesn't exclude PV work (expansion work), however. For some spontaneous processes, the system gets *PV* work. For example, the spontaneous reaction $3O_2(g) + 4Fe(s) = 2Fe_2O_3(s)$ at 25 °C and under standard pressure, *PV* work is done to the reaction system by its surroundings due to volume reduction. Despite exchanged *PV* work, this reaction is thermodynamically spontaneous. Hence, presence of *PV* work does not exclude spontaneity, which seems to contradict these definitions and thus would cause confusions.

The third major category is that there should be no external influence on the system for the spontaneous process.[18–23] Such definitions are rigorous because they highlight that the root cause of the spontaneous process is the system itself rather than its surroundings. However, the exact meaning of the external influence is never explained, as far as our literature review shows. This makes it difficult for students majoring in chemistry or chemical engineering to precisely understand the concept. After looking up definitions of the second category, students are inclined to think that the external influence is the work done to the system, causing the same aforementioned confusion.

Therefore, neither energy nor work exchanged between the system and its surroundings rules out the spontaneity of the system. The real external influence that negates the spontaneous process is still a question to answer.

It's worthy to point out that "spontaneous direction" rather than "spontaneous process" is used by the two most popular textbooks of physical chemistry in their latest editions, as shown in Table 1.[7,13] This nomenclature change is pivotal to understanding the concept. The word "direction" highlights that being spontaneous is just a tendency of a system to change, rather than a process which occurs in reality. However, the spontaneous process is still used in this paper for its general usage. Besides, as long as it is clearly defined, its meaning should be definite.

2 Difference between the spontaneous process and the irreversible process

One of the keys to correctly understand the spontaneous process is that the term is concerned with a thermodynamic closed system. This may seem obvious, but some definitions in Table 1 don't explicitly point this out. Otherwise, the term is an ordinary daily phrase rather than a thermodynamic concept. To illustrate that the concept is system-oriented, two heat exchange cases are compared in Figure 1. Both cases involve spontaneous heat transfer from the hot part to the cool part. Figure 1a is used by many textbooks as the most typical spontaneous process, and it's absolutely correct to say that this heat exchange is spontaneous. However, this "spontaneous" means literally rather than thermodynamically (or scientifically). In this case, no closed system is specified, and all parts are considered as an isolated system. However, if the cool part is defined to be the system and the hot part is its surroundings (Figure 1b), the system still tends to absorb heat and becomes 30 °C (assuming that the surroundings is enormous and its temperature maintains at 30 °C). Now, it's improper to say that the change of the system is thermodynamically spontaneous. Its change is due to the temperature difference between it and its surroundings, rather than the system itself. For thermodynamics, the key question is what kind of systems have the tendency to change entirely due to the state of the system instead of its surroundings, as stated in many definitions in Table 1. In short, the closed system in concern must be clearly defined to discuss spontaneity.

The other key to understanding spontaneous process is to differentiate it from the irreversible process. They are very similar but different. The reversible process is clearly defined in all textbooks of thermodynamics. For the reversible process, the system must be in internal thermal and/or mechanical equilibrium, and it must be in

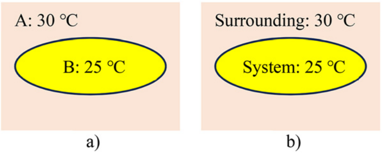

Figure 1: Illustration of typical cases in (a) daily usage and in (b) thermodynamics when the spontaneous process is discussed. The key difference is that a closed system must be clearly defined in thermodynamics.

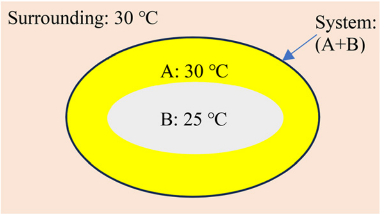

Figure 2: Illustration of a simplified spontaneous process of a system at thermal non-equilibrium internally but in equilibrium with its surroundings.

equilibrium with its surroundings during the change. Otherwise, the process is irreversible. For the case of Figure 1b, the system absorbs heat from its surroundings and the process is irreversible due to thermal difference. Therefore, discussing reversibility must consider both the system and the surroundings. The irreversibility might be due to the system at non-equilibrium state or due to the non-equilibrium between the system and its surroundings. In contrast, the spontaneity of a closed system focuses on the system and must exclude the influence of the surroundings. Hence, the closed system in concern must be in equilibrium to its surroundings to determine its spontaneity, including thermal equilibrium, mechanical equilibrium, electrical equilibrium, etc. That is, temperature, pressure and/or electrical potential of the system and its surroundings must be the same. Otherwise, non-equilibrium will lead to a change of the system, regardless of the state of the system.

Equilibrium between the system and its surroundings, however, doesn't exclude energy exchange between them if the system spontaneously changes due to internal non-equilibrium. Energy may be exchanged reversibly. To demonstrate the idea, a simplified spontaneous heat transfer process is illustrated in Figure 2. There are two parts in the closed system. The inner part is at 25 °C. The outer layer is adjacent to the surrounding and both are at 30 °C. The system is in equilibrium with the surrounding but the system is at non-equilibrium state, so the system is spontaneous to change. As heat transfers from the outer layer to the inner part infinitely slowly, the temperature of the outer layer tends to decrease and simultaneously heat will transfer from the surrounding to the outer layer reversibly. Despite heat transfer from the surrounding to the system, the state change of the system is entirely due to the state of the system rather than the surrounding. In other words, reversible heat transfer from the surrounding to the system is the result of the spontaneous system change, not the reason for the system change.

The above case takes reversible heat exchange as an example to illustrate the idea, and *PV* work and/or electrical work are the same. As long as energy is reversibly exchanged, either from or to the system, it is not the cause of the system change. Therefore, as long as the energy exchanged between the closed system and its surroundings is reversible, it has no influence on the spontaneity of the system. Accordingly, the irreversibly-exchanged energy, including both heat and work, is the external influence that changes the state of the system, making the spontaneity of the system unable to judge.

3 Modified definitions of the spontaneous process

Engel & Reid 2019[7] states that "Any system that is not at equilibrium will evolve with time. We refer to the direction of evolution as the spontaneous direction." This definition underlines that the root cause of the spontaneous process or direction is the non-equilibrium state of the system. It's much easier to understand because it avoids the phrase like "external influence" or other similar ambiguous expressions. However, based on the above discussion, it's necessary to introduce the key precondition that the system and the surroundings must be in equilibrium into the definition, to make the definition more accurate and clearer. Thus, a modified definition of the spontaneous process is proposed. That is, any closed system that is in equilibrium with its surroundings but not at equilibrium internally has the tendency to change to an equilibrium state, and this tendency of change is called the spontaneous process or the spontaneous direction. Equilibrium between the system and its surroundings guarantees that all exchanged energy between them is reversible. Under this condition, if the system has the tendency to change, it must be due to the non-equilibrium state of the system itself, thus the change is spontaneous. If this spontaneous process does take place, the process must be irreversible and the system may exchange heat or work with its surroundings. The modified definition emphasizes both the root cause and the essential precondition for judging the spontaneity. Hence, it should be more helpful for students to readily grasp its meaning.

Another modified definition is also proposed based on definitions that include “work” or “external influence”. That is, a thermodynamic spontaneous process of a closed system is a process that occurs without irreversibly-exchanged energy between the closed system and its surroundings. This definition explicitly points out that the “external influence” is the energy that is irreversibly exchanged between the system and the surroundings. It’s helpful to eliminate the ambiguity caused by the “external influence” or similar expressions in most definitions of the spontaneous process. Although two definitions are proposed, we recommend the first one because it is system-oriented rather than process-oriented. Being spontaneous is just the tendency of a system to change but not the process that actually occurs, because some thermodynamically spontaneous processes are not kinetically spontaneous. Therefore, the spontaneous direction used in Engel & Reid 2019[7] should be more appropriate than the spontaneous process. Nevertheless, it is worthwhile to present the second definition to help students understand the concept.

4 Understanding of common criteria of the spontaneous process

Based on the above discussion and modified definitions of the spontaneous process, it’s easier to understand common criteria of the spontaneous process and a few typical unanswered questions would be resolved, including 1) why $\Delta S_{\mathrm{tot}} \geq 0$ cannot be used to judge the spontaneity of the closed system? 2) why the Clausius inequality cannot be used to determine spontaneity? 3) why $\mathrm{d}G_{T,p} \leq \mathrm{d}W'$ cannot be used to determine spontaneity, but $\mathrm{d}G_{T,p,W'=0} \leq 0$ can be used as the spontaneity criterion?

As is adopted by most textbooks of physical chemistry, total entropy increase is introduced as the foundation for judging spontaneity and reversibility.

$$\Delta S_{\mathrm{tot}} \geq 0 \tag{1}$$

The typical understanding of this inequality is that the entropy of an isolated system always increases if the state of the isolated system changes. Since the system is isolated and there is no energy or material exchange between it and its surroundings, the occurring change must be spontaneous as well as irreversible. Thus, the inequality of total entropy increase may be used to determine spontaneity or reversibility of isolated systems. There is no confusion related to this fundamental inequality.

When a closed system and its surroundings are viewed together as an isolated system, the total entropy increase becomes the Clausius inequality.

$$\mathrm{d}S_{\mathrm{sys}} \geq \frac{\delta Q}{T_{\mathrm{sur}}},\ \mathit{or}\ \mathrm{d}S_{\mathrm{sys}} - \frac{\delta Q}{T_{\mathrm{sur}}} \geq 0 \tag{2}$$

When this inequality is applied to judge spontaneity, confusions start to arise if the system is not clearly defined. If the overall system formed by the closed system and its surroundings is concerned, it’s reasonable to say that the change of the overall system is spontaneous if $\mathrm{d}S_{\mathrm{sys}}$ is larger than $\delta Q/T_{\mathrm{sur}}$. However, if the closed system is discussed, it’s incorrect to say that the change of the closed system is spontaneous if $\mathrm{d}S_{sys}$ is larger than $\delta Q/T_{\mathrm{sur}}$. As illustrated by the case in Figure 1b, $\mathrm{d}S_{\mathrm{sys}}$ ($=\delta Q/T_{\mathrm{sys}}$) is definitely larger than $\delta Q/T_{\mathrm{sur}}$ because δQ is positive and T_{sys} is lower than T_{sur}, but the system change is due to the temperature between the system and its surroundings rather than the system itself, thus its state change isn’t spontaneous. In other words, the total entropy increase or the Clausius inequality cannot be used to judge the spontaneity of the closed system, as already pointed out by L. Guo et al.[27] The main reason is that the system and its surroundings may not be at equilibrium. In other words, there may be irreversible energy exchange between the system and its surroundings, leading to a state change of the system.

As the Clausius inequality is applied to the closed system that has the same temperature and pressure as its surroundings, its form becomes.

$$dG_{T,p} \leq dW^{'} \tag{3}$$

where $dW^{'}$ represents the non-*PV* work. *T* and *p* in subscript are always considered as constant temperature and pressure. It's worth noting that the differential form is used here because the integral form is inaccurate as discussed by L. Raff.[4,28] However, as the derivation procedure requires, *T* and *p* in the subscript also mean that *T* and *p* of the system and its surroundings must be equal. It's generally accepted that this inequality cannot be used to determine spontaneity of the system change, but the reason is seldom explained. The most common explanation is due to the presence of $W^{'}$, since the inequality becomes the most common spontaneity criterion when there is no non-*PV* work involved. The true reason, however, is not the presence of $W^{'}$. As discussed above, the key issue is the reversibility of the exchanged non-*PV* work $W^{'}$. Since the inequality doesn't require that the non-*PV* work exchanged between the system and its surroundings is reversible, the non-*PV* work might be irreversible, such as the irreversible electrical work exchanged due to finite electrical potential difference between the system and its surroundings. Therefore, if the non-*PV* work is reversibly exchanged, this inequality can be used to determine the spontaneity.[29]

Nevertheless, if there is no non-*PV* work involved, the inequality becomes the most widely used spontaneity criterion.

$$dG_{T,p,W^{'}=0} \leq 0 \tag{4}$$

No non-*PV* work and the same *T* and *p* of the system and its surroundings guarantee that all exchanged heat and work between the system and its surroundings is reversible. Therefore, it's suitable to judge spontaneity of the closed system. For example, most spontaneous chemical reaction systems or phase change systems exchange heat with its surroundings. No matter the process is endothermic or exothermic, as long as the system and its surroundings are maintained at thermal equilibrium and the heat exchange is reversible, the exchanged heat has no influence on the spontaneity of the process. The same is true for the work exchanged reversibly. In short, the energy reversibly exchanged between the system and its surroundings has no direct relation to the spontaneity of the process.

Similarly, when the system has fixed volume and the same *T* as its surroundings, and no non-*PV* work is exchanged, the Clausius inequality becomes the other well-known spontaneity criterion.

$$dA_{T,V,W^{'}=0} \leq 0 \tag{5}$$

Fixed volume means no *PV* work is exchanged between the system and its surroundings, and the same *T* assures that heat is reversibly exchanged. Therefore, these preconditions guarantee that all the energy exchanged between the system and its surroundings is also reversible, thus the inequality can be used as a criterion of the spontaneous process.

5 Conclusions

In summary, it is revealed that the “external influence” in many definitions of the spontaneous process is the energy that is irreversibly exchanged between the system and its surroundings, rather than energy or work in some definitions. In addition, two modified definitions of spontaneous process are proposed based on common definitions after analyzing the exact scientific meaning of the spontaneous process. The recommended definition is that any closed system that is in equilibrium with its surroundings but not at equilibrium internally has the tendency to change to an equilibrium state, and this tendency of change is called the spontaneous process or the spontaneous direction. It's highlighted that the key to define thermodynamic spontaneous process is to clearly define the system and the system must be in equilibrium with its surroundings, so that all heat and work exchanged between the system and its surroundings are reversible. That is, energy reversibly exchanged has no influence on the spontaneity of the system. The proposed definitions can clarify some common misconceptions related to the spontaneous process and answer a few unanswered questions related to criteria of spontaneity. The whole discussion and the proposed definitions will help learners and instructors of thermodynamics to properly understand the concept and criteria of spontaneity.

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