

# Discussion on the Derivation of Helmholtz and Gibbs Criteria in Chemical Education

Zhiqiang Zhou<sup>1\*</sup>, Jinsong Peng<sup>1\*</sup>, Chunxia Chen<sup>1</sup>, Li Guo<sup>1#</sup>, Qiang Liu<sup>2</sup>

<sup>1</sup>College of Chemistry, Chemical Engineering and Resource Utilization, Northeast Forestry University, Harbin, China

<sup>2</sup>Faculty of Science, University of Bristol, Bristol, UK

Email: #guoli\_nefu@nefu.edu.cn

**How to cite this paper:** Zhou, Z. Q., Peng, J. S., Chen, C. X., Guo, L., & Liu, Q. (2022). Discussion on the Derivation of Helmholtz and Gibbs Criteria in Chemical Education. *Creative Education*, 13, 1529-1535. <https://doi.org/10.4236/ce.2022.135094>

**Received:** March 9, 2022

**Accepted:** May 10, 2022

**Published:** May 13, 2022

Copyright © 2022 by author(s) and Scientific Research Publishing Inc. This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

## Abstract

Helmholtz and Gibbs functions are two very important criteria in chemical education. They must have solid origin, that is, their derivation must be rational and reliable. This paper discusses controversial issues concerning the derivation of Helmholtz and Gibbs criteria. The derivation of Helmholtz and Gibbs criteria based on Clausius inequality is claimed completely rational and reliable, while that starting from the total entropy criterion is analyzed and evaluated to be incompletely rational and reliable or at least controversial. Questions about the rationality and reliability of deriving Helmholtz and Gibbs criteria starting from total entropy criterion have been raised for wider discussion.

## Keywords

Critical Learning, Chemical Education, Helmholtz Criterion, Gibbs Criterion, Total Entropy Criterion, Second Law of Thermodynamics

## 1. Introduction

Helmholtz and Gibbs functions are two very important criteria in thermodynamics for predicting the spontaneity of a process at constant temperature ( $T$ ) and constant volume ( $V$ ) and a process at constant temperature ( $T$ ) and constant pressure ( $P$ ), respectively. The derivation of them must be rational and reliable. Generally, there are two versions of derivation of Helmholtz and Gibbs criteria. The first is based on Clausius inequality, and the second starts from the total entropy criterion. There is a controversy here that if the two versions are equivalent to each other or one is more solid than the other. It is necessary to

\*Jinsong Peng and Zhiqiang Zhou contributed equally to this work.

#Corresponding author.

discuss and clarify it.

## 2. Two Versions of Derivation of Helmholtz and Gibbs Criteria

### 2.1. Derivation Based on Clausius Inequality (Atkins & Paula, 2006; Engel, Reid, & Hehre, 2012b; Mortimer, 2000; Liu, Zhou, & Li, 2009; Yang, 2015b; Wang, Meng, & Ren, 2007; Hu, Lv, Liu, & Hei, 2007b; Sun, Song, Liu, He, & Zhang, 2016; Lin, Xu, Yin, Wu, & Shao, 2010; Chen & Tong, 2011b)

#### 2.1.1. Derivation of Helmholtz Criterion

The mathematical expression of the second law of thermodynamics, known as the Clausius inequality, is as follows:

$$dS \geq \frac{\delta Q}{T} \quad \begin{array}{l} \text{irreversible} \\ \text{reversible} \end{array}$$

For a process at constant  $T$  and  $V$  and with no non- $PV$  work ( $W' = 0$ ), we have

$$\delta Q_V = dU$$

Putting the above equation into Clausius inequality, we get

$$dS \geq \frac{dU}{T} \quad \begin{array}{l} \text{irreversible} \\ \text{reversible} \end{array}$$

Multiply both sides by  $T$ , and we get

$$dU - TdS \leq 0 \quad \begin{array}{l} \text{irreversible} \\ \text{reversible} \end{array}$$

$T$  is constant, so we have

$$d(U - TS) \leq 0 \quad \begin{array}{l} \text{irreversible} \\ \text{reversible} \end{array} \quad (1)$$

$$\text{Define } A = U - TS \quad (2)$$

as Helmholtz function.

Putting the definition Equation (2) into Inequality (1), we get

$$dA_{T,V} \leq 0 \quad (\delta W' = 0) \quad \begin{array}{l} \text{spontaneous} \\ \text{equilibrium} \end{array} \quad (3)$$

For a macroscopic process, Inequality (3) is written as

$$\Delta A_{T,V} \leq 0 \quad (W' = 0) \quad \begin{array}{l} \text{spontaneous} \\ \text{equilibrium} \end{array} \quad (4)$$

Inequalities (3) and (4) are the Helmholtz criterion giving that at constant  $T$  and  $V$  and with no non- $PV$  work ( $W' = 0$ ), a process is spontaneous if the Helmholtz function of the system decreases, and the system is in equilibrium when Helmholtz function reaches the minimum.

#### 2.1.2. Derivation of Gibbs Criterion

For a process at constant  $T$  and  $P$  and with no non- $PV$  work ( $W' = 0$ ), we have

$$\delta Q = dH$$

Putting the above equation into Clausius inequality, we get

$$dS \geq \frac{dH}{T} \quad \begin{array}{l} \text{irreversible} \\ \text{reversible} \end{array}$$

Multiply both sides by  $T$ , and we get

$$dH - TdS \leq 0 \quad \begin{array}{l} \text{irreversible} \\ \text{reversible} \end{array}$$

$T$  is constant, so we have

$$d(H - TS) \leq 0 \quad \begin{array}{l} \text{irreversible} \\ \text{reversible} \end{array} \quad (5)$$

$$\text{Define } G = H - TS \quad (6)$$

as Gibbs function.

Putting the definition Equation (6) into Inequality (5), we get

$$dG_{T,p} \leq 0 \quad (\delta W' = 0) \quad \begin{array}{l} \text{spontaneous} \\ \text{equilibrium} \end{array} \quad (7)$$

For a macroscopic process, Inequality (7) is written as

$$\Delta G_{T,p} \leq 0 \quad (W' = 0) \quad \begin{array}{l} \text{spontaneous} \\ \text{equilibrium} \end{array} \quad (8)$$

Inequalities (7) and (8) are the Gibbs criterion giving that at constant  $T$  and  $P$  and with no non- $PV$  work ( $W' = 0$ ), a process is spontaneous if the Gibbs function of the system decreases, and the system is in equilibrium when Gibbs function reaches the minimum.

## 2.2. Derivation Starting from Total Entropy Criterion (Liu, Zhou, Li, & Feng, 2017; Fan, Lu, Tang, Wang, Cao, Zhou, Xia, & Cai, 2005b; Qu, Li, Li, & Mo, 2009; Sun, Chen, Li, & Huang, 2012b; Peng, 2012; Ge, Yuan, & Peng, 2008)

For applying the principle of entropy increase in predicting whether a process is spontaneous or not, it is proposed in some textbooks (Engel, Reid, & Hehre, 2012a; Linder, 2011; Fu, Shen, Yao, & Hou, 2005; Sun, Chen, Li, & Huang, 2012a; Chen & Tong, 2011a; Yang, 2015a; Fan, Lu, Tang, Wang, Cao, Zhou, Xia, & Cai, 2005a; Hu, Lv, Liu, & Hei, 2007a) that the system (sys.) and its immediate surroundings (sur.) can be combined to form a composite isolated system (iso.), and the following inequalities are got

$$dS_{\text{iso}} = dS_{\text{sys}} + dS_{\text{sur}} \geq 0 \quad \begin{array}{l} \text{spontaneous} \\ \text{equilibrium} \end{array} \quad (9)$$

or

$$\Delta S_{\text{iso}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} \geq 0 \quad \begin{array}{l} \text{spontaneous} \\ \text{equilibrium} \end{array} \quad (10)$$

Inequality (9) can be written as

$$dS_{\text{sys}} + \frac{\delta Q_{\text{sur}}}{T_{\text{sur}}} \geq 0 \quad \begin{array}{l} \text{spontaneous} \\ \text{equilibrium} \end{array} \quad (11)$$

Inequalities (9), (10) and (11) are used to predict the spontaneity of a process, which is called total entropy criterion.

### 2.2.1. Derivation of Helmholtz Criterion

At constant  $T$  and  $V$  and with no non- $PV$  work ( $W' = 0$ ), putting  $T_{\text{sur}} = T_{\text{sys}}$  and  $\delta Q_{\text{sur}} = -\delta Q_{\text{sys}} = -dU_{\text{sys}}$  into Inequality (11) and omitting the subscript  $\text{sys}$  (since all the quantities are properties of the system), some people get

$$dS - \frac{dU}{T} \geq 0 \quad \begin{array}{l} \text{spontaneous} \\ \text{equilibrium} \end{array}$$

$T$  is constant, so they have

$$d(U - TS) \leq 0 \quad \begin{array}{l} \text{spontaneous} \\ \text{equilibrium} \end{array} \quad (12)$$

$$\text{Define } A = U - TS \quad (13)$$

as Helmholtz function.

Putting the definition Equation (13) into Inequality (12), they get

$$dA_{T,V} \leq 0 \quad (\delta W' = 0) \quad \begin{array}{l} \text{spontaneous} \\ \text{equilibrium} \end{array} \quad (14)$$

For a macroscopic process, Inequality (14) is written as

$$\Delta A_{T,V} \leq 0 \quad (W' = 0) \quad \begin{array}{l} \text{spontaneous} \\ \text{equilibrium} \end{array} \quad (15)$$

Inequalities (14) and (15) are the Helmholtz criterion giving that at constant  $T$  and  $V$  and with no non- $PV$  work ( $W' = 0$ ), a process is spontaneous if the Helmholtz function of the system decreases, and the system is in equilibrium when Helmholtz function reaches the minimum.

### 2.2.2. Derivation of Gibbs Criterion

At constant  $T$  and  $P$  and with no non- $PV$  work ( $W' = 0$ ), putting  $T_{\text{sur}} = T_{\text{sys}}$  and  $\delta Q_{\text{sur}} = -\delta Q_{\text{sys}} = -dU_{\text{sys}}$  into Inequality (11) and omitting the subscript  $\text{sys}$  (since all the quantities are properties of the system), and some people get

$$dS - \frac{dH}{T} \geq 0 \quad \begin{array}{l} \text{spontaneous} \\ \text{equilibrium} \end{array}$$

$T$  is constant, so they have

$$d(H - TS) \leq 0 \quad \begin{array}{l} \text{spontaneous} \\ \text{equilibrium} \end{array} \quad (16)$$

$$\text{Define } G = H - TS \quad (17)$$

as Gibbs function.

Putting the definition Equation (17) into Inequality (16), they get

$$dG_{T,p} \leq 0 \quad (\delta W' = 0) \quad \begin{array}{l} \text{spontaneous} \\ \text{equilibrium} \end{array} \quad (18)$$

For a macroscopic process, Inequality (18) is written as

$$\Delta G_{T,p} \leq 0 \quad (W' = 0) \quad \begin{array}{l} \text{spontaneous} \\ \text{equilibrium} \end{array} \quad (19)$$

Inequalities (18) and (19) are the Gibbs criterion giving that at constant  $T$  and  $P$  and with no non- $PV$  work ( $W' = 0$ ), a process is spontaneous if the Gibbs function of the system decreases, and the system is in equilibrium when Gibbs function reaches the minimum.

### 3. Analyzing and Evaluating the Two Versions

#### 3.1. The First Version

Clausius inequality is the mathematical expression of the second law of thermodynamics. Derivation of Helmholtz and Gibbs criteria based on Clausius inequality is just derivation based on the second law of thermodynamics. The derivation basis is solid, the derivation process is natural and reasonable, the conclusions of derivation are liable, and the derivation route is beneficial for beginners to understand.

#### 3.2. The Second Version

In a previous article by the same authors (Guo, Zhou, & Liu, 2020), the limitations of total entropy criterion was raised, and total entropy criterion was evaluated as “suspected of ‘changing the object of study’ and ‘giving an irrelevant answer’”, “a regression from the principle of entropy increase”, and “what the total entropy criterion tells is just that entropy of the universe increases as time goes by”. For any a process, the sum of the system’s entropy change and its surroundings’ entropy change  $\Delta S_{\text{sys}} + \Delta S_{\text{sur}}$  can only be greater than or equal to zero, but never less than zero. A decrease in the entropy of the universe will never be observed. It is bound that  $\Delta S_{\text{iso}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} \geq 0$  as time goes by. The English astrophysicist Eddington coined the phrase “entropy is time’s arrow” to emphasize this relationship between entropy and time. In fact, what the total entropy criterion predicts is the direction of the universe evolution and that of time, whose meaning is limited. Because the universe always keeps evolving forwards, the entropy of the universe always keeps increasing, and time always keeps going forwards. No violations of the second law of thermodynamics have ever been observed, and violations of it could be observed possibly only if the universe some day begins to contract instead of expanding. In view of the limitations or controversy of the total entropy criterion, derivation of Helmholtz and Gibbs criteria starting from total entropy criterion should not be recommended.

Let us take a step back and change a perspective. Putting the surroundings’ entropy change  $dS_{\text{sur}} = \delta Q_{\text{sur}}/T_{\text{sur}}$  into the total entropy criterion inequality (11), and considering  $\delta Q_{\text{sur}} = -\delta Q_{\text{sys}}$ , we get

$$dS_{\text{sys}} \geq \frac{\delta Q_{\text{sys}}}{T_{\text{sur}}} \quad (20)$$

Omitting the subscript, we can write Inequality (20) as

$$dS \geq \frac{\delta Q}{T} \quad (21)$$

We find here that the total entropy criterion can return back to the Clausius inequality. In this sense, one may argue that starting from total entropy criterion is just starting from Clausius inequality. Clausius inequality, as the mathematical expression of the second law of thermodynamics, is the most fundamental basis, while the total entropy criterion is something derived from Clausius inequality. And why should we “attend to trifles and neglect the essential”? And what is more, the rationality of total entropy criterion has been questioned and limitations of it have been raised.

To sum up, the stringency and rationality of deriving Helmholtz and Gibbs criteria starting from total entropy criterion is questionable and worth discussing.

#### 4. Conclusion

The derivation of Helmholtz and Gibbs criteria based on Clausius inequality is just derivation based on the second law of thermodynamics. The derivation basis is solid, the derivation process is natural and reasonable, the conclusions of derivation are reliable, and the derivation route is beneficial for beginners to understand. The stringency and rationality of deriving Helmholtz and Gibbs criteria starting from total entropy criterion are questionable and worth discussing, because the rationality of total entropy criterion is itself a controversy, or at least the total entropy criterion is just something derived from Clausius inequality other than Clausius inequality itself.

#### Acknowledgements

This work was financially supported by the Higher Education Teaching Reform Project in Heilongjiang Province (SJGY20200034), Northeast Forestry University Teaching Reform Project (DGY2021-35, DGYZD2021-02, DGY2020-04) and the Fundamental Research Funds for the Central Universities (2572018BC16, 2572015CB28).

#### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

#### References

- Atkins, P., & Paula, J. D. (2006). *Atkins' Physical Chemistry* (7th ed., pp. 108-110). Higher Education Press.
- Chen, L. P., & Tong, Y. X. (2011a). *Physical Chemistry* (pp. 59-60). Science Press. (In Chinese)
- Chen, L. P., & Tong, Y. X. (2011b). *Physical Chemistry* (pp. 64-66). Science Press. (In Chinese)

Chinese)

- Engel, T., Reid, P., & Hehre, W. (2012a). *Physical Chemistry* (3rd ed., pp. 98-101). Pearson Education, Inc.
- Engel, T., Reid, P., & Hehre, W. (2012b). *Physical Chemistry* (3rd ed., pp. 125-128). Pearson Education, Inc.
- Fan, K. N., Lu, J., Tang, Y., Wang, W. N., Cao, Y., Zhou, M. F., Xia, Y. Y., & Cai, W. B. (2005a). *Physical Chemistry* (2nd ed., pp. 459-461). Higher Education Press. (In Chinese)
- Fan, K. N., Lu, J., Tang, Y., Wang, W. N., Cao, Y., Zhou, M. F., Xia, Y. Y., & Cai, W. B. (2005b). *Physical Chemistry* (2nd ed., pp. 478-482). Higher Education Press. (In Chinese)
- Fu, X. C., Shen, W. X., Yao, T. Y., & Hou, W. H. (2005). *Physical Chemistry* (5th ed., pp. 144-146). Higher Education Press. (In Chinese)
- Ge, C. H., Yuan, G. Q., & Peng, C. (2008). *Physical Chemistry* (pp. 66-69). Higher Education Press. (In Chinese)
- Guo, L., Zhou, Z. Q., & Liu, Q. (2020). On the Limitations of Total Entropy Criterion, *Thermal Science and Engineering Progress*, 15, Article ID: 100380.  
<https://doi.org/10.1016/j.tsep.2019.100380>
- Hu, Y., Lv, R. D., Liu, G. J., & Hei, E. C. (2007a). *Physical Chemistry* (5th ed., p. 61). Higher Education Press. (In Chinese)
- Hu, Y., Lv, R. D., Liu, G. J., & Hei, E. C. (2007b). *Physical Chemistry* (5th ed., pp. 63-65). Higher Education Press. (In Chinese)
- Lin, X. J., Xu, H. Y., Yin, B. H., Wu, Y. F., & Shao, J. (2010). *Physical Chemistry* (pp. 53-57). Science Press. (In Chinese)
- Linder, B. (2011). *Elementary Physical Chemistry* (pp. 31-33). World Scientific Publishing Co. Pte. Ltd.
- Liu, J. J., Zhou, Y. P., & Li, S. L. (2009). *Physical Chemistry* (5th ed., pp. 122-125). Higher Education Press. (In Chinese)
- Liu, J. J., Zhou, Y. P., Li, S. L., & Feng, X. (2017). *Physical Chemistry* (6th ed., pp. 123-126). Higher Education Press. (In Chinese)
- Mortimer, R. G. (2000). *Physical Chemistry* (2nd ed., pp. 132-133). Elsevier Inc.
- Peng, X. G. (2012). *Handout on Physical Chemistry* (pp. 185-186, 190-192). Higher Education Press. (In Chinese)
- Qu, J. N., Li, Q. G., Li, J. H., & Mo, Y. C. (2009). *Physical Chemistry* (pp. 87-90). Renmin University of China Press. (In Chinese)
- Sun, S. G., Chen, L. T., Li, H. Y., & Huang, L. (2012a). *Physical Chemistry* (2nd ed., pp. 138-139). Xiamen University Press. (In Chinese)
- Sun, S. G., Chen, L. T., Li, H. Y., & Huang, L. (2012b). *Physical Chemistry* (2nd ed., pp. 163-167). Xiamen University Press. (In Chinese)
- Sun, Y. X., Song, R. J., Liu, Y., He, L. M., & Zhang, Y. J. (2016). *Physical Chemistry* (pp. 95-98, 107). Chemical Industry Press. (In Chinese)
- Wang, G. X., Meng, A. L., & Ren, Z. H. (2007). *Physical Chemistry* (3rd ed., pp. 61-63). Chemical Industry Press. (In Chinese)
- Yang, Y. H. (2015a). *Physical Chemistry* (pp. 59-61). Science Press. (In Chinese)
- Yang, Y. H. (2015b). *Physical Chemistry* (pp. 69-72). Science Press. (In Chinese)