

## Reply to “Comment on ‘An Alternative Presentation of the Second Law of Thermodynamics’”

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**ABSTRACT:** This letter is to respond to “Comment on ‘An Alternative Presentation of the Second Law of Thermodynamics’”, which discusses some shortcomings of our approach of teaching the second law of thermodynamics.

**KEYWORDS:** *Second-Year Undergraduate, Upper-Division Undergraduate, Physical Chemistry, Textbooks/Reference Books, Thermodynamics*

We much appreciate Dr. DeVoe’s attention to our communication, “An Alternative Presentation of the Second Law of Thermodynamics”.<sup>1</sup> In this letter, we would like to present some comments that augment our approach of teaching the second law, in response to Dr. DeVoe’s comments (“Comment on ‘An Alternative Presentation of the Second Law of Thermodynamics’”).<sup>2</sup>

Our approach to presenting the second law consists of three steps: (i) establishing the relation  $dS = \delta q_{\text{rev}}/T$  for an ideal gas,<sup>3</sup> (ii) generalizing the relation to arbitrary materials, and (iii) derivation of the Clausius inequality,  $dS \geq \delta q/T$ .<sup>4</sup>

Dr. DeVoe discussed the shortcomings in the last stage of the presentation, which actually adopted the approach given in ref 4. First, he mentioned “the derivation lacks generality, as it is limited to an irreversible process with  $P$ – $V$  work only and without phase transitions or chemical reactions.”

However, within the scope of equilibrium thermodynamics, the presentation in ref 1 holds also when phase transitions or chemical reactions are involved. In the usual situation, the outcomes of the phase transitions and/or chemical reactions occurring within the system are manifested as heat and/or work. Equations 7 through 10 in ref 1 can describe such cases without any modification. However, when the reactions are carried out in an electrochemical cell, electrical work, as well as heat and  $P$ – $V$  work, is involved. In this case eq 7 in ref 1 can be generalized to<sup>4,5</sup>

$$dU = \delta q + \delta w = \delta q - P_{\text{ex}} dV + \phi_{\text{ex}} dQ \quad (1)$$

The third term on the right-hand side represents the electrical work.  $\phi_{\text{ex}}$  and  $dQ$  denote the electrical potential applied externally to the system and the change in charge, respectively. The sign of  $dQ$  is positive if the charge flows in the direction as dictated by  $\phi_{\text{ex}}$ . Now if the same change in the state is carried out reversibly, eq 1 becomes

$$dU = \delta q_{\text{rev}} - P dV + \phi dQ \quad (2)$$

where  $\phi$  is the intrinsic cell voltage (the value at zero current). Now that  $U$  is a state function, its change calculated from eq 2 must be equal to that calculated from eq 1. We thus have

$$\delta q_{\text{rev}} - \delta q = (P - P_{\text{ex}}) dV + (\phi_{\text{ex}} - \phi) dQ \quad (3)$$

As shown in ref 1, the product  $(P - P_{\text{ex}})dV$  is always positive. Similarly, we have  $dQ > 0$  if  $\phi_{\text{ex}} > \phi$ , while  $dQ < 0$  if  $\phi_{\text{ex}} < \phi$ . That is, the product  $(\phi_{\text{ex}} - \phi) dQ$  is always positive. Therefore, it follows that  $\delta q_{\text{rev}} > \delta q$ . We can give the same type of arguments when other types of nonexpansion works<sup>3,6</sup> are involved.

Second, Dr. DeVoe argued that when the system changes from a state with internal energy  $U$  and volume  $V$  to a neighboring state with  $U + dU$  and  $V + dV$ , the change in entropy  $dS$  may not be determined by specifying only  $dU$  and  $dV$  because pressure and temperature become nonuniform within the system during an irreversible volume change so that more than two independent variables are needed to describe the state of the system.

This argument seems to follow from misunderstanding of our description in ref 1. The initial state with  $U$  and  $V$  and the final state with  $U + dU$  and  $V + dV$  are two neighboring equilibrium states. Therefore, the difference  $dS$  in the system entropy between the two states is the same whether the change is carried out reversibly or irreversibly.

Third, Dr. DeVoe mentioned that our derivation equates infinitesimal  $P$ – $V$  work to  $-P_{\text{ex}} dV$ , but the correct general expression for  $P$ – $V$  work is  $-P_{\text{b}} dV$  where  $P_{\text{b}}$  is the pressure exerted by the system at the moving boundary.<sup>6</sup>

To calculate the work involved in an irreversible process, one needs to be careful in defining the system and surroundings and specifying the process itself. It is true that when the system is defined solely by the gas, excluding the piston driving the change of its volume, the definition of the work given by  $\delta w = -P_{\text{b}} dV$  is more appropriate. However, the calculation of  $P_{\text{b}}$  requires a detailed hydrodynamic treatment in general. Only when the speed of the piston is much smaller than the sound speed, an approximate expression for  $P_{\text{b}}$  can be derived based on the kinetic molecular theory.<sup>7</sup> However, as shown by Kivelson and Oppenheim,<sup>8</sup> if the piston and the inner walls of the gas container are included as parts of the system, one has  $\delta w = -P_{\text{ext}} dV$ . This simpler expression is most used in the introductory textbooks of the thermodynamics.

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Now if one adopts the expression  $\delta w = -P_b dV$  for the work, the derivation of the Clausius inequality in ref 1 may be modified as follows. Equations 7 and 9 are modified as

$$dU = \delta q + \delta w = \delta q - P_b dV \quad (4)$$

$$\delta q_{\text{rev}} - \delta q = (P - P_b) dV \quad (5)$$

When the system expands with the piston speed slower than the sound speed, one has  $P > P_b$ .<sup>7</sup> On the other hand, when the system is compressed,  $P < P_b$ . In either case, one has  $\delta q_{\text{rev}} > \delta q$ .

Finally, Dr. DeVoe mentioned that the value of the denominator  $T$  in the derived inequality  $dS > \delta q_{\text{irrev}}/T$  is ambiguous when temperature is not uniform throughout the system, and that the correct expression is  $dS > \delta q_{\text{irrev}}/T_b$ , where  $T_b$  is the thermodynamic temperature at the portion of the system boundary across which the heat is transferred.<sup>6</sup>

It is true that in the case of irreversible processes, the operational relation  $dS > \delta q_{\text{irrev}}/T_b$  may be more appropriate if the system is defined solely by the gas, excluding the walls of the gas container. However, the calculation of  $T_b$  again requires a detailed hydrodynamic treatment in general. When the irreversible heat transfer occurs rather slowly, the local equilibrium approximation holds and the temperature gradient within the system may be calculated if the heat conductivity is known. Again, the difficulty of calculating  $T_b$  can be avoided by including the walls as parts of the system. Then, one has  $dS > \delta q_{\text{irrev}}/T_{\text{surroundings}}$  as stated in some textbooks of thermodynamics. In either case, eq 10 of ref 1 holds if one takes  $T$  to denote the mean temperature of the system. Since  $T < T_b < T_{\text{surroundings}}$  for  $\delta q_{\text{irrev}} > 0$  and  $T > T_b > T_{\text{surroundings}}$  for  $\delta q_{\text{irrev}} < 0$ , we can write

$$dS = \frac{\delta q_{\text{rev}}}{T} > \frac{\delta q_{\text{irrev}}}{T} > \frac{\delta q_{\text{irrev}}}{T_b} > \frac{\delta q_{\text{irrev}}}{T_{\text{surroundings}}} \quad (6)$$

In ref 1, there was some misprinting. In the sentence following eq 5 of ref 1,  $\delta q_{\text{rev,B}} = /T_B$  must be replaced by  $\delta q_{\text{rev,B}}/T_B$ .

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### Notes

The authors declare no competing financial interest.

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