Comment on “An Alternative Presentation of the Second Law of Thermodynamics”

Howard DeVoe*

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, United States


KEYWORDS: Upper-Division Undergraduate, Graduate Education/Research, Physical Chemistry, Textbooks/Reference Books, Thermodynamics

A recent article in this Journal describes a rigorous and pedagogically useful proof, not involving Carnot cycles, of the familiar relation $dS = \delta q_{rev}/T$ for an infinitesimal entropy change during a reversible process of a closed system. The article also describes a derivation, not based on the Clausius or Kelvin−Planck statements of impossible processes, of the inequality $dS > \delta q_{irrev}/T$ for an irreversible process. Unfortunately, the derivation of this inequality has several flaws that in my opinion make its presentation to students inadvisable.

First, the derivation lacks generality, as it is limited to an irreversible process with $P−V$ work only and without phase transitions or chemical reactions.

An essential part of the derivation is the assumption that when the system changes from a state of volume $V$ and internal energy $U$ to a neighboring state with $V + dV$ and $U + dU$ either reversibly or irreversibly, the entropy change $dS$ is the same in both cases. However, if pressure and temperature become nonuniform within the system during an irreversible volume change, more than two independent variables are needed to describe the state of the system, and $dV$ and $dU$ are therefore not sufficient to determine $dS$ as required by this assumption.

The derivation equates infinitesimal $P−V$ work to $−P_{ex} dV$, where $P_{ex}$ is an external pressure. However, the correct general expression for $P−V$ work has been shown to be $−P_{ex} dV$, where $P_{ex}$ is the pressure exerted by the system at the moving boundary. For instance, if the system is a gas confined in a cylinder by a piston, $P_{ex}$ is the pressure exerted on the outer face of the piston and $P_{ex}$ is the pressure exerted by the gas on the piston’s inner face. $P_{ex}$ and $P_{ex}$ are equal during a reversible volume change but have different values during an irreversible volume change. As a result, ref 1 uses an incorrect expression for $P−V$ work during an irreversible change.

Finally, the value of the denominator $T$ in the derived inequality $dS > \delta q_{irrev}/T$ is ambiguous when temperature is not uniform throughout the system.

The result of a rigorous and general treatment of entropy changes during an irreversible process is the inequality $dS > \delta q_{irrev}/T$, where $T_{th}$ is the thermodynamic temperature at the portion of the system boundary across which the heat $\delta q_{irrev}$ is transferred. This inequality differs from that derived in ref 1 by having $T_{th}$ instead of $T$ in the denominator.

AUTHOR INFORMATION

Corresponding Author

*E-mail: hdevoe@umd.edu.

Notes

The author declares no competing financial interest.

REFERENCES

(6) The subscript of $P_{ex}$ stands for the moving boundary. In place of $P_{ex}$, ref 2 uses $P_{surf}$/surf, and ref 3 uses $P_{surf}$ and ref 4 uses the symbol $P_{surf}$/surf.

Received: October 19, 2015
Revised: November 17, 2015