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Letter

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Comment on "An Alternative Presentation of the Second Law of Thermodynamics"

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ABSTRACT: This letter points out flaws in a derivation of the inequality $dS > \delta q_{irrev}/T$ as presented in a recent article in this *Journal* (Lee, S.; Lee, K.; Lee, J. *J. Chem. Educ.* **2015**, *92*, 771−773).

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

A recent article in this *Journal*[1] 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 $-P_b\,dV$, where P_b is the pressure exerted by the system at the moving boundary.[2−6] 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_b is the pressure exerted by the gas on the piston's inner face. P_{ex} and P_b 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 $dS > \delta q_{irrev}/T_b$, where T_b is the thermodynamic temperature at the portion of the system boundary across which the heat δq_{irrev} is transferred.[7,8] This inequality differs from that derived in ref 1 by having T_b instead of T in the denominator.

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Notes

The author declares no competing financial interest.

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