JOURNAL OF CHEMICAL EDUCATION

Article

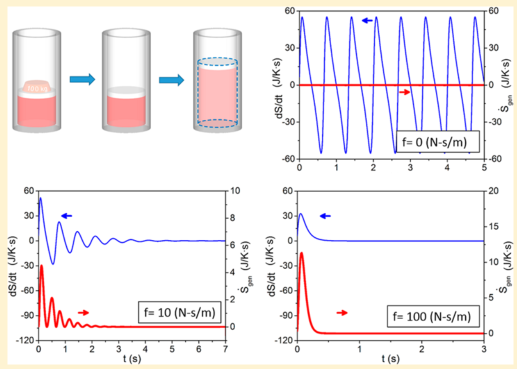
pubs.acs.org/jchemeduc

Investigating Friction as a Main Source of Entropy Generation in the Expansion of Confined Gas in a Piston-and-Cylinder Device

Dun-Yen Kang,* Kai-Hsin Liou, and Wei-Lun Chang

Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

Ⓢ *Supporting Information*



ABSTRACT: The expansion or compression of gas confined in a piston-and-cylinder device is a classic working example used for illustrating the First and Second Laws of Thermodynamics. The balance of energy and entropy enables the estimation of a number of thermodynamic properties. The entropy generation (also called entropy production) resulting from this process can also be used to determine the feasibility and reversibility of a process. In this work, we present an extended discussion involving quantitative analysis of the effects of friction between a piston and the interior wall of a cylinder. Our findings indicate that the friction force caused by the movement of the piston is a main source of entropy generation in this process. This explanation does not appear in most textbooks dealing with similar problems. We also discuss, from a quantitative perspective, the effects of friction on the dynamic physical and thermodynamic properties, including entropy generation. Our findings suggest that engaging students in a discussion related to piston-and-cylinder problems involving the effects of friction could provide valuable insight into entropy generation in practical applications.

KEYWORDS: *First-Year Undergraduate/General, Second-Year Undergraduate, Upper-Division Undergraduate, Physical Chemistry, Thermodynamics, Analogies/Transfer, Gases*

Gas subjected to expansion or compression while confined in a piston-and-cylinder device is a common topic in thermodynamics[1−3] and physical chemistry[4−6] textbooks to illustrate the First and Second Laws of Thermodynamics. Specifically, the conversion of energy between work, heat, and internal energy provides an excellent illustration of the First Law of Thermodynamics, which states that energy can be neither created nor destroyed but can change form. When performing an entropy balance for the same process, the value of entropy generation (also referred to as entropy production) can be used as a measure of process feasibility and reversibility. Specifically, the Second Law of Thermodynamics stipulates that processes with positive entropy generation are considered feasible and irreversible, those with zero entropy generation are considered reversible, and those with negative entropy generation are considered reversible. In cases of compression/expansion within a piston-and-cylinder device following a sudden change in conditions, such as the removal of weight on the piston in one step, entropy generation will be positive, and the process will be considered irreversible. By contrast, processes involving infinitesimal changes undergo entropy generation approaching zero such that the process will approach reversibility. Working examples appear in most textbooks on thermodynamics and physical chemistry; however, the role played by friction has not been discussed in a quantitative manner. The importance of friction produced between a piston and the interior wall of a cylinder with regard to the expansion/compression of confined gas is three-fold: (1) friction eventually causes the piston to stop moving; (2) friction determines the dynamic behavior of a piston before reaching a new equilibrium state; and (3) friction is a main source of the entropy generation. In this paper, we present several illustrations of gas confined within a piston-and-cylinder device subject to isothermal expansion. We present analysis of the energy and entropy without taking into account the effects of friction (conventional analysis) and compare this to analysis that considers the effects of friction. The effects of friction on the dynamics and the thermodynamic properties of the confined piston are discussed in a quantitative manner. We then discuss how this approach to analysis can help students to gain deeper insight into the issue of entropy generation and the Second Law of Thermodynamics.

■ ANALYSIS OF ISOTHERMAL EXPANSION WITHOUT CONSIDERING THE EFFECTS OF FRICTION

In this section, we present analysis of energy and entropy associated with a piston-and-cylinder device undergoing isothermal expansion initiated by the removal of weight from the piston. In this investigation, we disregard the effects of friction, as is the case in most existing textbooks on thermodynamics or physical chemistry. We investigate two cases: the removal of the weight in a single step and in an infinite number of steps. The examples presented in this section

Published: August 5, 2015

DOI: 10.1021/acs.jchemed.5b00361
J. Chem. Educ. 2015, 92, 1667−1671

serve as a control group for the subsequent investigation in which the effects of friction are discussed.

Removal of Weight in a Single Step

We initially consider one mole of ideal gas confined within a piston-and-cylinder device with a weight bearing down on it from above (Figure 1a).

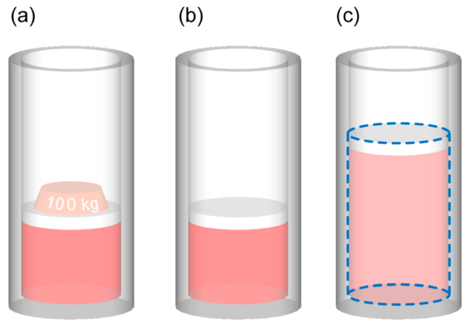


Figure 1. Illustration of expansion of confined gas initiated by the removal of the weight from the piston: (a) prior to the removal of the weight, (b) immediately after the removal of the weight, and (c) the point at which a new equilibrium state is reached. The dashed lines in panel c illustrate how the system is defined for analysis of energy and entropy.

The specifications in this example are identical to the illustrations found in the thermodynamics textbook written by Stanley Sander.[2] The temperature is fixed at 25 °C. The masses of the piston and weight are 5 kg and 100 kg, respectively. The pressure outside the device is fixed at 1.013×10^5 Pa. Expansion of the confined ideal gas is initiated by the removal of the weight in a single step (Figure 1b). The expansion process ends when a new equilibrium state is reached (i.e., the piston stops moving, Figure 1c). By using the ideal gas law, the initial and final volumes of the confined gas can be calculated as follows:

$$V_i = \frac{nRT}{P_i} = 0.01213\ (\text{m}^3) \tag{1}$$

$$V_f = \frac{nRT}{P_f} = 0.02334\ (\text{m}^3) \tag{2}$$

where V_i is the initial volume, n is the mole number, R is the gas constant, T is temperature, P_i is the initial pressure, V_f is the final volume, and P_f is the final pressure. The cross-sectional area of the cylinder is 0.01 m^2. Given the initial and final volumes of the confined gas, the work done on the gas during expansion can be calculated as follows:

$$w = -\int_{V_i}^{V_f} P_B\, dV \tag{3}$$

where w is the work done on the gas due to its volume change, V is the volume, and P_B is the pressure at the moving boundary of the system. The system is defined as illustrated in Figure 1, panel c, such that P_B is a constant (1.013×10^5 Pa). Thus, w can be calculated as equal to −1136 J. Estimating the heat transferred across the system boundary during expansion requires that an energy balance (the First Law of Thermodynamics) be employed:

$$\Delta U + \Delta\left[m\left(\frac{v^2}{2} + gh\right)\right] = q + w \tag{4}$$

where ΔU is the change in internal energy of the gas, m is the mass of the system, v is the velocity of the system, g is gravity, h is the height of the system, and q is the conductive heat transfer to the confined gas. The term in the bracket of eq 4 accounts for the kinetic and potential energy in the system. The system is static at the beginning and end of this process (assuming the presence of friction); therefore, the change in kinetic energy drops to zero. In addition, the change in internal energy during this process is also zero because the internal energy for an ideal gas is a function of temperature only, and expansion is assumed to be isothermal. Therefore, eq 4 can be simplified as follows:

$$\Delta(mgh) = q + w \tag{5}$$

As for the change in potential energy within the system (comprising confined gas and a piston), we take into account only that of the piston. The reason for this is the fact that the mass of the confined gas is relatively small compared to the mass of the piston. Using the calculated initial and final volumes of the gas and the cross-section area of the cylinder, we calculate the difference in elevation of the piston before and after expansion as 1.12 m. Thus, we can derive Δmgh as 55 J. After we acquired the values of w and Δmgh, q is calculated using eq 5, which results in 1191 J.

Entropy generation (also called entropy production) associated with this process can be obtained using the entropy balance equation:

$$\Delta S = \frac{q}{T} + S_{gen} \tag{6}$$

where ΔS is the change in entropy in the system, and S_{gen} is entropy generation in the system as a result of this process. Entropy is a state function, wherein changes in entropy for an ideal gas undergoing an isothermal process can be expressed as follows:

$$\Delta S = nR\ \ln\left(\frac{V_f}{V_i}\right) \tag{7}$$

By using eq 7, ΔS is calculated as 5.44 J/K. By using eq 6, we can then obtain the S_{gen} of the piston-and-cylinder device due to this process as 1.45 J/K. This positive value for S_{gen} indicates that this expansion is an irreversible process.

Removal of Weight in Infinite Steps

In this section, we examine the expansion of the confined gas in the same piston-and-cylinder device; however, the weight is removed from the piston in a different manner. Herein, we treat the weight as a pile of sand such that the grains are removed one at a time. In this manner, the process of expansion can be considered to occur in infinite steps with infinitesimal changes in weight on the piston. For each of these steps, the piston is assumed static, and the pressure at the system boundary (P_B) can be expressed by the pressure of the confined gas and the pressure caused by the weight of the piston. Thus, to calculate work performed by the system, we rewrite eq 3 as follows:

$$w = -\int_{V_i}^{V_f}\left(P - \frac{mg}{A}\right) dV \tag{8}$$

where P is the pressure exerted on the confined gas. According to the ideal gas law, P in eq 8 can be expressed in terms of V.

DOI: 10.1021/acs.jchemed.5b00361
J. Chem. Educ. 2015, 92, 1667−1671

Thereafter, w is calculated as −1568 J. By using eqs 4 and 5, q is calculated as 1623 J. Following the same analysis presented in the preceding section, ΔS and S_{gen} are calculated as 5.44 and 0 J/K, respectively. The zero value obtained for S_{gen} means that this process is reversible. The relevant physical properties of the confined gas during the expansion process caused by the two methods of removing the weight are listed in Table 1.

Table 1. Changes in Thermodynamic Properties of Confined Gas Undergoing Isothermal Expansion in a Piston-and-Cylinder Device

Properties	Removal of Weight in Single Step	Removal of Weight in Infinite Steps
ΔU (J)	0	0
$\Delta(mgh)$ (J)	55	55
w (J)	−1136	−1568
q (J)	1191	1623
ΔS (J/K)	5.44	5.44
S_{gen} (J/K)	1.45	0

The representation found in most textbooks on thermodynamics and physical chemistry indicates that the reversible process ($S_{gen} = 0$) caused by the removal of weight in infinite steps yields a larger amount of work performed by the system than is the case with an irreversible process ($S_{gen} > 0$) caused by the removal of weight in a single step.

■ ANALYSIS INCLUDING THE EFFECTS OF FRICTION

The previous analysis of energy and entropy is accurate; however, it is incomplete due to a failure to take into account

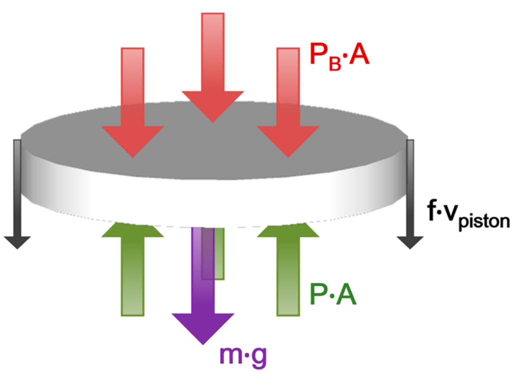


Figure 2. Illustration of force balance on piston.

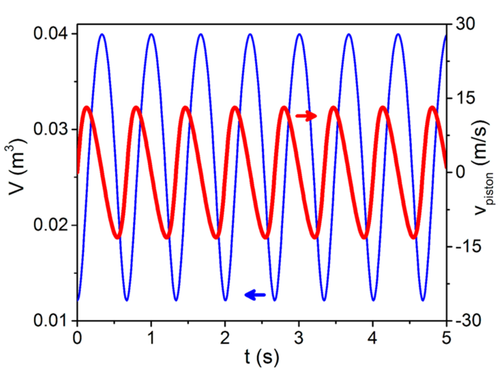


Figure 3. Volume of confined gas and piston velocity as functions of time following the removal of weight from the piston in a single step in the absence of friction ($f = 0$).

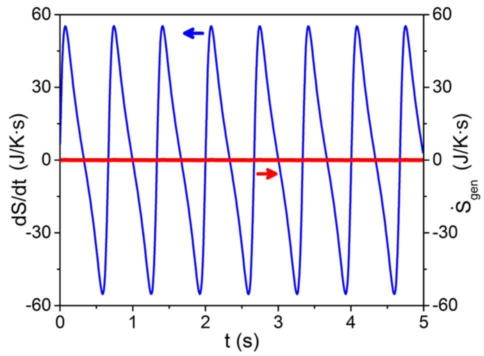


Figure 4. Rate of change of entropy in the system and entropy generation associated with expansion as functions of time in the absence of friction ($f = 0$).

the effects of friction. A failure to consider the effects of friction makes it impossible to gain an understanding of system dynamics prior to reaching equilibrium. In this section, we present a discussion of the effects of friction on the expansion of a confined gas, which is lacking in existing textbooks. The definition and specifications of the system are the same as those applied in the previous section. We begin analysis with the energy and entropy balance in differential form:

$$\frac{dU}{dt} + \frac{d\left(\frac{1}{2}mv^2\right)}{dt} + \frac{d(mgh)}{dt} = \dot{q} + \dot{w} \quad (9)$$

$$\frac{dS}{dt} = \frac{\dot{q}}{T} + \dot{S}_{gen} \quad (10)$$

where $\dot{q}$, $\dot{w}$, $\dot{S}_{gen}$ are the rates of heat transfer, work generated/consumed, and entropy generation, respectively. m in eq 9 represents the mass of the system, which includes 1 mol of ideal gas and a 5-kg piston. The mass of the 5-kg piston is much larger than that of the confined gas; therefore, the rate of change in kinetic and potential energy is dominated by the piston. The rate at which work is generated/consumed in eq 9 can be expressed as the product of the pressure at the moving boundary of the system and the rate of negative change in system volume. The internal energy of an isothermal system remains constant, and the rate at which entropy changes can be expressed using pressure, temperature, and the rate of change in the volume of the confined gas. Thus, eqs 9 and 10 can be rewritten as follows:

$$mv_{piston}\frac{dv_{piston}}{dt} + mg\frac{dh_{piston}}{dt} = \dot{q} - P_B\frac{dV}{dt} \quad (11)$$

$$\frac{P}{T}\frac{dV}{dt} = \frac{\dot{q}}{T} + \dot{S}_{gen} \quad (12)$$

where v_{piston} and h_{piston} are the velocity and height of the piston, respectively. The rates of change of the height of the piston and volume of confined gas in eqs 11 and 12 can be written as expressions of piston height and system volume in terms of piston velocity, as follows:

$$mv_{piston}\frac{dv_{piston}}{dt} + mgv_{piston} = \dot{q} - P_BAv_{piston} \quad (13)$$

$$\frac{P}{T}Av_{piston} = \frac{\dot{q}}{T} + \dot{S}_{gen} \quad (14)$$

DOI: 10.1021/acs.jchemed.5b00361
J. Chem. Educ. 2015, 92, 1667−1671

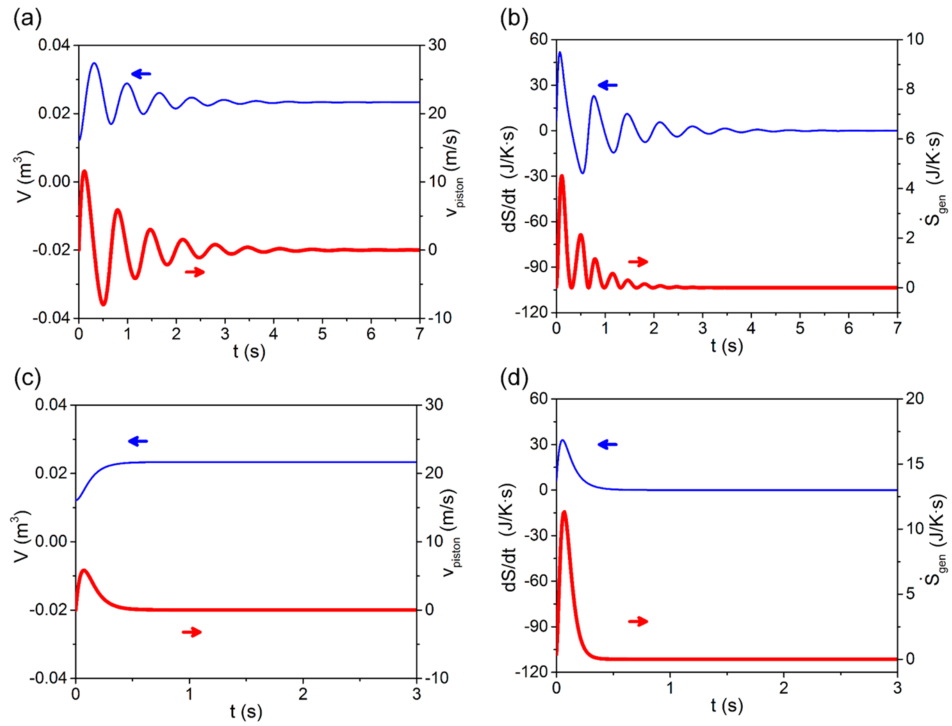


Figure 5. (a) Volume of confined gas (V) and the piston velocity (v_{piston}) as functions of time at $f = 10$ (N-s/m). (b) Rate of change of entropy in the system, and entropy generation during expansion as functions of time at $f = 10$ (N-s/m). (c) Volume of confined gas (V) and piston velocity (v) as functions of time at $f = 100$ (N-s/m). (d) Rate of change of entropy in the system and entropy generation during expansion as functions of time at $f = 100$ (N-s/m).

Table 2. Changes in Thermodynamic Properties of Confined Gas between the Initial and Final States of Isothermal Expansion Taking into Account the Effects of Friction

Properties	f = 10 (N-s/m)	f = 100 (N-s/m)
ΔU (J)	0	0
$\Delta(mgh)$ (J)	55	55
w (J)	−1136	−1136
q (J)	1191	1191
ΔS (J/K)	5.44	5.44
S_{gen} (J/K)	1.45	1.45

To understand the role of friction, we must consider the force balance of the piston. Four types of force are applied to the piston following the removal of the weight, as illustrated in Figure 2.

The force balance equation is expressed as follows:

$$m\frac{dv_{piston}}{dt} = (P - P_B)A - mg - fv_{piston} \quad (15)$$

where f is the coefficient of friction, which is always equal to or greater than zero. To correlate entropy generation and friction, eq 13 is subtracted from eq 14 multiplied by T plus eq 15 multiplied by v_{piston}. The resulting equation is presented in the following:

$$\dot{S}_{gen} = \frac{fv_{piston}^{2}}{T} \quad (16)$$

Eq 16 clearly indicates that friction is a main source of entropy generation associated with the expansion of confined gas in a piston-and-cylinder device. In the following two sections, we present quantitative analysis of the effects of friction on the physical and thermodynamic properties of the piston and the confined gas.

Piston-and-Cylinder Device in the Absence of Friction

Herein, we consider the expansion of the gas in the piston-and-cylinder device in the absence of friction ($f = 0$). Expansion is initiated by the removal of weight from the piston in a single step. Following the removal of weight, we tracked the velocity of the piston as well as the volume of the confined gas as a function of time. These two properties can be derived by solving eq 15, which is a first-order ordinary differential equation, with the initial condition of zero velocity. However, the dependent variable v_{piston} in eq 15 is a function of the V, so an additional equation is needed to describe the relationship between v_{piston} and V:

$$\frac{1}{A}\frac{dV}{dt} = v_{piston} \quad (17)$$

Eq 17 is also a first-order ordinary differential equation, with the initial condition of $V = 0.01213$ m^3. The resulting values of V and v_{piston} as functions of time are presented in Figure 3. MATLAB code for solving eqs 15 and 17 is available in the Supporting Information.

In this case, the piston continues oscillating with no apparent damping effects. Using the values obtained for V and v_{piston} in conjunction with eqs 13 and 14, we can derive the kinetic and potential energy, heat transfer rate, work production/consumption rate, rate of change of system entropy, as well as the rate of entropy generation (production) in this process. The results are presented in Figure 4.

As shown in Figure 4, all thermodynamic properties, except for the entropy generation rate, change periodically with the oscillation of the piston. An entropy generation rate of zero is observed in the absence of friction, which is in agreement with eq 16.

Piston-and-Cylinder Device in the Presence of Friction

In this section, we discuss the same process under the same conditions; however, analysis includes a consideration of friction. We can obtain the piston velocity and volume of confined gas as functions of time at $f = 10$ and 100 N-s/m by solving eq 15 using the initial conditions of zero velocity and a gas volume of 0.01213 m^3. After we obtain v_{piston} and V as functions of time, we can derive a number of thermodynamic properties, including the rate of change of work, heat flow, entropy, and entropy generation, using the same procedure described in the preceding section. The results are summarized in Figure 5.

The figures illustrating piston velocity (v_{piston}) and the volume of confined gas (V) as functions of time suggest that in the presence of friction, the piston will eventually undergo damping, wherein a larger coefficient of friction leads to more pronounced damping of the piston. Thus, systems with a larger coefficient of friction reach a new equilibrium state with fewer oscillations. More importantly, it was found that in the presence of friction, entropy generation rate is no longer zero, as was the case in the absence of friction in the previous section. With the available rate of change in the thermodynamic properties of the system, numerical integrations with respect to time can be performed for deriving the change in thermodynamic quantities during the expansion. The results for $f = 10$ and 100 N-s/m are listed in Table 2.

It should be noted that all of the values derived for $f = 10$ and 100 N-s/m are identical and match those obtained when the weight was removed in a single step, as shown in Table 1. This indicates that the value of friction, as long as it is greater than zero, affects only the process dynamics and has no effect on the final state of equilibrium. The illustration presented is for ideal gas confined in an isothermal piston-and-cylinder device. An extended discussion about nonideal gas and an adiabatic system is presented in the Supporting Information. The investigation of nonideal Carnot engine[7,8] and the friction effects on a piston-and-cylinder device[9,10] can also be found in the previous report.

■ CONCLUSIONS

This paper presents an investigation into the effects of friction on the expansion of a confined gas in a piston-and-cylinder device. Our aim was to elucidate the relationships among friction, the dynamics, the thermodynamic properties, and entropy generation. Our analysis results identify friction as a main source of entropy generation in the expansion of gas in a piston-and-cylinder device. Specifically, in the absence of friction, the piston will oscillate perpetually and thereby produce no entropy. By contrast, a non-negative rate of entropy generation is observed during the expansion of gas in the presence of friction. The path by which a new equilibrium state is achieved depends on the value of the coefficient of friction. Several excellent methods have been devised to illustrate the Second Law of Thermodynamics and the physical meaning of entropy from a molecular/statistical perspective.[11−13] Our macroscopic analysis could play a complementary role in helping undergraduate students to gain insight into the process of entropy generation and the Second Law of Thermodynamics.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00361.

Extended discussion (PDF)
MATLAB codes (ZIP)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dunyen@ntu.edu.tw

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was jointly supported by the Ministry of Science and Technology (MOST) of Taiwan (NSC102-2218-E-002-015-MY2, MOST 104-2218-E-002-006, and MOST 104-2628-E-002-009-MY3) and National Taiwan University (NTU-CDP-104R7814). The authors acknowledge Shiang-Tai Lin for the insightful discussion regarding the physical meaning of the Second Law of Thermodynamics.

■ REFERENCES

(1) Smith, J. M.; Abbott, M. M.; Van Ness, H. C.; Yang, Z. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; McGraw-Hill: New York, 2008.

(2) Sandler, S. I. *Chemical, Biochemical, and Engineering Thermodynamics*, 4th ed.; John Wiley: Hoboken, NJ, 2006.

(3) Sonntag, R. E.; Borgnakke, C.; Van Wylen, G. J. *Fundamentals of Thermodynamics*; Wiley: New York, 1998.

(4) Atkins, P. W.; de Paula, J. *Physical Chemistry*, 9th ed.; Oxford University Press: New York, 2010.

(5) Silbey, R. J.; Alberty, R. A.; Bawendi, M. G. *Physical Chemistry*, 4th ed.; Wiley & Sons: Hoboken, NJ, 2005.

(6) Mortimer, R. G. *Physical Chemistry*, 3rd ed.; Acadamic Press: Boston, MA, 2008.

(7) Makarieva, A. M.; Gorshkov, V. G.; Li, B.-L.; Nobre, A. D. A Critique of Some Modern Applications of the Carnot Heat Engine Concept: The Dissipative Heat Engine Cannot Exist. *Proc. R. Soc. London, Ser. A* **2010**, *466* (2119), 1893−1902.

(8) Rebhan, E. Efficiency of Nonideal Carnot Engines with Friction and Heat Losses. *Am. J. Phys.* **2002**, *70* (11), 1143−1149.

(9) Chernov, N.; Lebowitz, J. L. Dynamics of a Massive Piston in an Ideal Gas: Oscillatory Motion and Approach to Equilibrium. *J. Stat. Phys.* **2002**, *109* (3−4), 507−527.

(10) Kestemont, E.; Van den Broeck, C.; Mansour, M. M. The "Adiabatic" Piston: And Yet It Moves. *Europhys. Lett.* **2000**, *49* (2), 143−149.

(11) Ben-Naim, A. Entropy: Order or Information. *J. Chem. Educ.* **2011**, *88*, 594−596.

(12) Ben-Naim, A. An Informational−Theoretical Formulation of the Second Law of Thermodynamics. *J. Chem. Educ.* **2009**, *86*, 99.

(13) Novak, I. The Microscopic Statement of the Second Law of Thermodynamics. *J. Chem. Educ.* **2003**, *80*, 1428.

DOI: 10.1021/acs.jchemed.5b00361
J. Chem. Educ. 2015, 92, 1667−1671