

# Teaching Thermodynamics and Kinetics to Advanced General Chemistry Students and to Upper-Level Undergraduate Students Using PV Diagrams

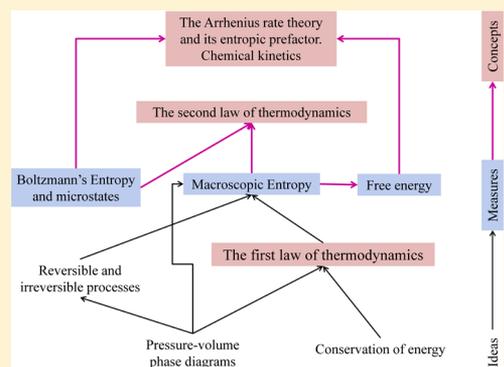
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## Supporting Information

**ABSTRACT:** We describe how complex concepts in macroscopic chemistry, namely, thermodynamics and kinetics, can be taught at considerable depth both at the first-year undergraduate as well as upper levels. We begin with a careful treatment of PV diagrams, and by pictorially integrating the appropriate area in a PV diagram, we introduce work. This starting point allows us to elucidate the concept of state functions and nonstate functions. The students readily appreciate that for a given transition, the area enclosed by the PV curve (work) depends on the path taken. It is then argued that heat, within this chosen framework, is a consequence of energy conservation and the fact that work is not a state function. This leads to a visual introduction of all the components involved in the first law of thermodynamics. The PV diagrams are then used to introduce entropy as being related to the maximum possible work to be done by the system. This macroscopic description of entropy is then related to the usual microscopic view of Boltzmann. This equivalence connects the area inside the PV diagram (work from a specific kind of pathway) and the number of microstates involved in the Boltzmann expression. The connection between the macroscopic and microscopic description of entropy also illuminates the exponential dependence of the number of microstates (or probability) on an energy, known as free energy. The Arrhenius picture of chemical kinetics then readily follows from the exponential dependence stated above, and finally, a reactive event is viewed as a statistically rare event, to further clarify the appearance of entropy in the rate expression.

**KEYWORDS:** First-Year Undergraduate/General, Upper-Division Undergraduate, Physical Chemistry, Interdisciplinary/Multidisciplinary, Curriculum, Kinetics, Mathematics/Symbolic Mathematics, Thermodynamics, Rate Law



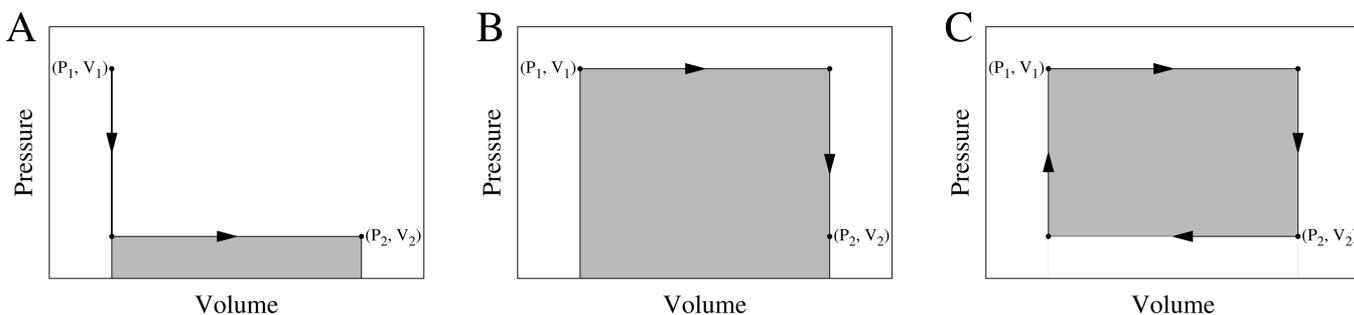
The flow of energy that often accompanies chemical transformations is a difficult concept to grasp for students, teachers, and researchers.<sup>1–5</sup> The difficulty arises from the abstract nature of many energy concepts such as work, heat, entropy, and free energy. The complexities involved in learning these topics may be gauged through the large number of innovative teaching tools proposed in the literature that are specific to thermodynamics. These teaching paradigms range from innovative mnemonic tools<sup>6,7</sup> that help visualize and internalize the relations between different thermodynamic variables, graphical ideas that illustrate these dependencies<sup>8–10</sup> and others that gauge the effective portrayal of entropy and free energy<sup>11,12</sup> through connections to Shannon's<sup>13,14</sup> information theory.<sup>15–17</sup>

Our approach is to simplify the discussion of work and state functions, through a pictorial introduction of these concepts using pressure–volume phase diagrams. These ideas are subsequently used as a conduit to introduce other thermodynamic quantities. For example, a discussion on reversible and irreversible processes helps connect entropy to pressure–volume phase diagrams, through work. When microscopic descriptions of entropy and free energy are invoked, this allows us to introduce chemical kinetics in a coherent manner.

This material dealing with macroscopic concepts comprises the second half of a one-semester course for select, high-achieving first-year undergraduate students. The composition of this honors course and its logistics have been previously presented,<sup>18</sup> but for convenience is also provided as part of Supporting Information (Appendix A).

It is important to juxtapose our efforts with the “organic-first”<sup>19</sup> and “bio-organic-first”<sup>20</sup> teaching efforts. The general philosophy of “explicitly linking what we know about chemistry with what we do in the classroom” is something we share with Ege and co-workers as they described in ref 19. However, there are critical differences. In Figure 2 of Ege’s work,<sup>19</sup> physical chemistry appears at the pinnacle of undergraduate education. Thus, grounding in the key physical topics of thermodynamics and kinetics is the last area students learn before they graduate. In contrast, in this publication and a previous publication,<sup>18</sup> we have attempted to place the physical concepts underlying all of chemistry and biochemistry upfront. These principles form the underpinnings of all chemistry and biochemistry and

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**Figure 1.** Plots in (A) and (B) show the use of PV diagrams to explain the path dependence of work. Plot (C), which is derived from (A) and (B) is used to explain the concept of state and nonstate functions.

if well understood, can lead to a more rigorous treatment of other aspects of chemistry in later years. For example, as part of the material presented here for honors general chemistry, we included a discussion on Michaelis–Menton kinetics following the introduction of chemical kinetics. It was found that once the students became familiar with the conceptual basis presented here, the Michaelis–Menton problem was accessible. A detailed discussion on this topic is however reserved for the upper-level biochemistry class, given the time frame restrictions; however, we believe that connecting the problems at this early stage would help the students when these ideas are revisited in upper level.

This paper is organized as follows: The pressure–volume (PV) phase diagrams are discussed in the next section with the goal of introducing work and heat; entropy and free energy follow through the concept of reversibility, also introduced using PV diagrams. We then connect these macroscopic ideas to the microscopic description of entropy given by Boltzmann to arrive at a microscopic view to spontaneity. Chemical kinetics is then introduced through this probabilistic microscopic picture arising from the discussion of entropy and free energy. The case is made that a reactive process is a rare event when viewed from a probabilistic or statistical angle. This course has a prescribed textbook;<sup>21</sup> however, there are substantial deviations as one would expect based on analysis of this paper and a previous publication.<sup>18</sup> A detailed syllabus is presented as part of Supporting Information. We believe that this presentation of the material, somewhat modified, may also be appropriate in part to upper-level physical chemistry classes. Hence, advanced material more applicable for upper-level undergraduates is also discussed in Supporting Information.

## ■ USING PV DIAGRAMS TO INTRODUCE WORK, HEAT, AND THE CONCEPT OF STATE FUNCTIONS

We begin our treatment of energy and thermodynamics using PV diagrams for an ideal gas. Although many students are intimately familiar with the numerical manipulation of ideal gas laws through their high school experience, they are typically not comfortable in relating the mathematical equations to curves in a PV diagram. Once they understand how all ideal gas laws, can be derived from PV diagrams, they are in a position to elucidate physical relationships from  $xy$  plots such as the dependence of the pressure of an ideal gas on its volume under constant temperature conditions. It is stressed in class that Boyle's law ( $P \propto 1/V$ ) and Avogadro's law ( $P \propto$  the amount of a gas) can be understood directly from a single PV diagram. Charles law ( $V \propto T$ ) can be rationalized through the relative placement of two isothermal PV curves at different temperatures on the same

PV plot. Deviations in real gas behavior are then introduced through modified PV diagrams.

Once PV diagrams are discussed, plots similar to those in Figure 1 are used to (i) convey the concept of work, (ii) note that work is not a state function, and (iii) emphasize work performed during a closed path in a phase diagram is related to the area enclosed within the path. Toward this goal, we first recall that work is force multiplied by displacement. Utilizing the standard textbook example of a cylinder with a moving piston that contains a gas, we are then able to express the PV work done *on* the system as

$$w = - \int P \, dV \quad (1)$$

From this launching point it is possible to compare different changes made in the PV diagram. For example, the plots in Figure 1A,B show two different pathways for the transition from  $(P_1, V_1)$  to  $(P_2, V_2)$ . In the path depicted in Figure 1A, the pressure is first *quickly* changed from  $P_1$  to  $P_2$ , holding the volume constant. Then, the volume is increased *suddenly* from  $V_1$  to  $V_2$  while holding the pressure fixed at  $P_2$ . Although the italicized words *quickly* and *suddenly* do not have much meaning to the student at this point, they become useful when we discuss reversible and irreversible processes later. Hence, the students are asked to note this terminology for later reference. In the second path shown in Figure 1B, the pressure is initially maintained at  $P_1$  and the volume is increased as before from  $V_1$  to  $V_2$ . Next, the pressure is decreased from  $P_1$  to  $P_2$  while holding the volume constant at  $V_2$ . Since PV work done *on* the system is given by eq 1, it is clear that no work is done in the vertical transitions when the volume is held constant. Moreover, it is graphically evident to the students that the work done in each of the two paths shown in Figure 1A,B is different. Due to the higher pressure in the second case, the magnitude of the work done on the system in this case is larger than that in the first case. This result is very significant as it implies that the work done is path dependent!

Students readily recognize that reversing the direction of the path in the first case (Figure 1A) reverses the sign of the work. One is now able to combine the two paths previously presented to create a closed loop, as depicted in Figure 1C. The system begins and ends at  $(P_1, V_1)$  and the work done in the process is the difference between the work done in the two half-cycles shown in Figure 1A,B. As a result, the work performed in traversing the loop is the area enclosed by the rectangle shown in Figure 1C.

The path dependence of work that has been demonstrated is a fundamental result. Because a state function depends only on the state of the system and not on the path taken to reach that

particular state, work done cannot be a state function. A sample examination problem is provided in Box 1. Note that the

**Box 1. An exam problem that reinforces the idea of work being path dependent: The performance analysis indicates that a large fraction of the students are able to assimilate these challenging concepts.**

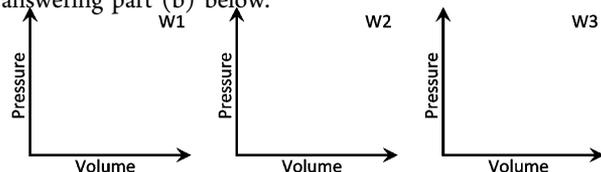
Consider the following changes for 1 mol of an ideal gas. Here  $W_1$ ,  $W_2$ , and  $W_3$  are the work done (with the usual sign convention).

$W_1$ : Expansion from 1 to 10 L against an external pressure of 2 atm.

$W_2$ : A two-step process: First, an expansion from 1 to 5 L against opposing pressure of 4 atm. Second, an isothermal expansion from 5 to 10 L.

$W_3$ : Isothermal expansion from 1 to 10 L, where the final pressure is 2 atm.

**Part (a):** Represent  $W_1$ ,  $W_2$ , and  $W_3$  in the figures below and explain the ideas that you have used to draw each figure. Show scale on axes and make sure these are consistent across plots. This would make it easier while answering part (b) below.



**Part (b):** Based on the figures you drew above which of the following statements is true? Explain your answer.

- I.  $W_1 > W_2 > W_3$ .
- II.  $W_3 > W_2 > W_1$ .
- III.  $W_1 > W_2 < W_3$ .
- IV.  $W_1 = W_2 = W_3$ .
- V. None of the above.

quantity  $W_3$  in Box 1 is an isothermal reversible work that has not yet been formally introduced to the students. (It is introduced in the next section.) However, the students are able to answer this question using their understanding of ideal gas laws (which has already been underlined using PV diagrams at the beginning of this section) and the fact that work is related to the enclosed area in PV diagrams for any chosen transition. It is the understanding of the latter aspect that is tested in this

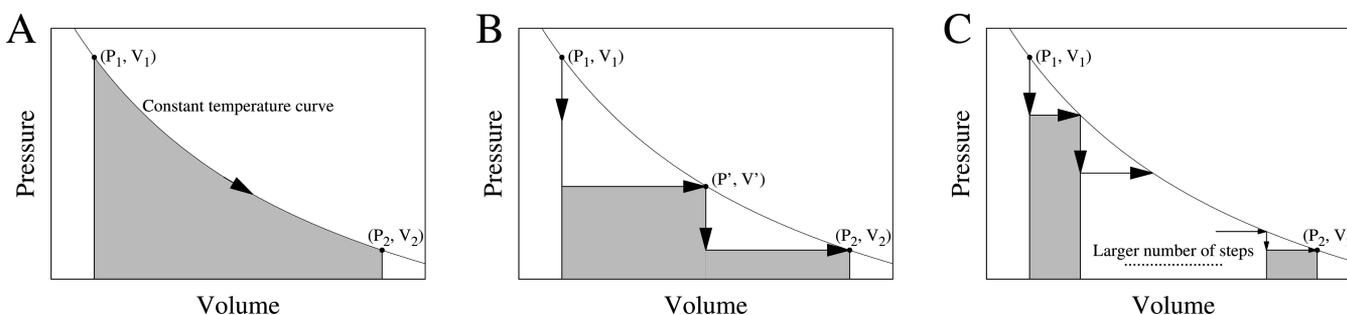
question. Based on the performance of the students on this and similar questions we infer that the concepts presented are internalized by a large fraction of the student population.

We next reflect on the significance of the direction in which the loop is traversed, either clockwise or counterclockwise. Mathematically, it is easy to see that the sign is positive when the loop is traversed in the counter-clockwise direction and negative when traversed clockwise. But what is the consequence of the sign? When work is done on the system, (a) the particles may come closer to each other, thus changing the potential energy of the system or (b) the particles may move faster, changing their kinetic energy, or (c) both (a) and (b). Because the internal energy of the system is defined as the sum of potential and kinetic energies of the particles, work done on the system is converted to internal energy. Generally, when work is done on the system, PV work is considered positive as per the definition in eq 1, and the internal energy of the system also increases.

However, internal energy, which contains both kinetic and potential energies, is a state function, although work is not.<sup>22</sup> Energy conservation mandates that work done on the system be fully converted to some form of energy. For example, both panels A and B in Figure 1 represent the transition from  $(P_1, V_1)$  to  $(P_2, V_2)$ . The work done on the system in the two cases is different and is represented by the respective shaded areas. This work is converted to internal energy. But the change in internal energy that results from the work done during the transitions is the same for the two pathways, because the beginning and end points of the transitions are the same. (This is a direct result of the fact that internal energy is a state function, but work is not.) But if work is path dependent and internal energy is path independent, there is clearly the need for another term that would help conserve the total energy in these transitions by suitably balancing the path dependence of work. This role is provided by the quantity known as heat. On the basis of the above discussion, heat may be interpreted as the consequence of the fact that (a) work is not a state function and (b) the total energy must be conserved. This discussion leads to the statement of the first law of thermodynamics, where the change in internal energy,  $\Delta E$ , equals the sum of heat,  $q$ , and work,  $w$ :

$$\Delta E = q + w \quad (2)$$

Indeed, in class, this dramatic entry of the important thermodynamic quantity known as heat, purely by invoking energy conservation and path dependence, has an effect on several students who have toiled their way through the concept of heat through traditional introductions. It is also interesting



**Figure 2.** The transition in (A) is reversible, whereas the ones in (B) and (C) are not reversible. The magnitude of the area for the reversible process is clearly greater and will always be greater even if the number of steps is increased in (B) and (C). Entropy for processes depicted in (A)–(C) is the shaded area in (A) plus any change in internal energy that accompanies the process (which for an ideal gas situation would be zero, as there is no change in temperature) divided by the temperature at which the process occurs. Hence, entropy is related to the maximum possible work done by the system, or the “work capacity” of the system for a given transition.

for the students to note that whereas everything on the right side of the above equation is path dependent, this path dependence cancels out when the individual components are added so that what remains on the left side is a path independent state function.<sup>4</sup>

Thus, all components that appear in the first law are physically motivated and rationalized using PV diagrams. Note that we have side-stepped the usual phenomenological introduction of heat and work<sup>3,4</sup> and replaced it with a description where heat follows from energy conservation, provided work is well established. We find that in this fashion, much of the difficulty in understanding heat and work is alleviated. Once heat is introduced in this manner, enthalpy follows as a specific manifestation of heat where the path of a transformation is to be constructed in a specific manner, that is, under constant pressure. The discussion on enthalpy leads to heat capacity and Hess's law. These topics are treated as in standard texts<sup>18</sup> and hence not discussed further in this manuscript.

## ■ REVERSIBILITY DERIVED FROM PV DIAGRAMS LEADS TO ENTROPY

### Isothermal Reversible Work in PV Diagrams

Having familiarized the students with the topic of work, we next broach the distinction between reversible and irreversible work using PV diagrams. The concept of reversible work and its companion reversible heat leads naturally to the concept of thermodynamic entropy.

Consider the transformation depicted in Figure 2A. This transformation from  $(P_1, V_1)$  to  $(P_2, V_2)$  is assumed to be conducted at constant temperature, that is, along an isotherm. Equation 1 indicates that the work done on the system is the negative of the area enclosed under the curve. However, this kind of a transformation could equally well have been attempted in steps, as depicted in Figure 2B. Although the intermediate point  $(P', V')$  in Figure 2B still remains on the same isotherm as the initial and final phase space points, the area under the curve for this "box-like-transformation" is not the same as that in Figure 2A. Now, what happens when the number of steps depicted in Figure 2B is increased, as shown in Figure 2C? Clearly, one gets closer to the result in Figure 2A; however, there exists no sequence of discrete box-like-transformations where the step size in pressure and volume are both finite, that will lead to a transformation that is identical to that in Figure 2A.<sup>23–25</sup> Only an infinite number of "box-like-transformations" such as those in Figure 2B,C, where each step is of infinitesimal size can be used to mimic the process in Figure 2A.<sup>26</sup>

What is the physical realization of the process in Figure 2A, when an infinite number of rectangular transformations such as those in Figure 2B,C are concatenated to achieve the process in Figure 2A? One can use the classic textbook example of a gas enclosed within a cylinder and confined with the help of a piston to illustrate this idea. It suffices to state that when the external force used to expand or contract the system volume is increased monotonically by infinitesimal amounts, the process in Figure 2A is realized. *But, what happens if the direction of the external force is suddenly reversed by an infinitesimal amount?* Because the change is only infinitesimal, the effect of the change may not be immediately apparent to an observer. However, there are nontrivial changes that occur at the microscopic level, and it can be seen that when the direction of the external force is changed by a small amount, the process in

Figure 2A is microscopically reversed! Thus, one arrives at a pictorial definition of reversible transformations from PV diagrams.

Hence, Figure 2A represents a "reversible" transition. This is clearly not the case for Figure 2B or Figure 2C, where a small change in the external pressure will not change the direction of the transition. Thus, Figure 2A represents a microscopically reversible process, whereas the processes in Figure 2B,C are not microscopically reversible and are hence irreversible. Despite the clarity of the above discussion, one may find that this discussion on reversibility is not accessible to even many bright undergraduate students. In that case, we have in place an additional discussion, with an additional figure to clarify this concept as part of Appendix B in Supporting Information.

The graphical changes described above also allow one to explore the meaning to the italicized terminology "quickly" and "suddenly" seen in the paragraph following eq 1. Indeed for the transformation in Figure 2B, the pressure reduction  $P_1 \rightarrow P'$  ought to be constructed *suddenly* and *quickly*. If this was not the case, and the pressure was changed gradually, then the system will remain on the isotherm as the volume is also allowed to relax slowly during the "gradual" pressure change.

It is also clear from the above discussion that the area under the curve in Figure 2A will always be larger in magnitude irrespective of the number of finite steps used in Figure 2B,C. It is thus illustrated that the magnitude of the reversible work will always remain a maximum. *In other words, the reversible work is the maximum work that the system can perform on the surroundings during the chosen process.*

At this juncture, it may also be useful to underscore that any other smooth transformation from  $(P_1, V_1)$  to  $(P_2, V_2)$  will contain a thermal contribution because it would not be along the isotherm. In this situation, when the direction of external force is suddenly reversed, that is, when a sequence of infinitesimal expansions is interjected by a sudden, infinitesimal, compression, the system has two degrees of freedom, pressure and temperature, which it can use to respond to such a sudden external change. Thus, the reverse trajectory of compression may not follow the exact same path as the expansion because both temperature and pressure can change in the reverse process. For the reversible process constructed earlier in this section, the additional degree of freedom that the system possesses for its response, temperature, is eliminated through the isothermal constraint. Hence, in such a case, the infinitesimal compression guarantees an identical change in pressure as in the case of expansion, thus assuring that the reverse pathway of compression is identical to the forward pathway of expansion. It may also be useful to note that a reversible process could equally well have been constructed as an isobaric transition depicted within a V–T phase diagram, or a constant volume transition represented in a P–T diagram. We have chosen to use a PV diagram here to convey our ideas as our goal was to pictorially explain work and all discussions funnel from that focal point.

### Entropy in Terms of Isothermal Reversible Work

Using the first law of thermodynamics, we note that there exists a reversible heat that is connected to reversible work. This reversible heat includes contributions from the internal (kinetic plus potential) energy in addition to contributions from work. That is, using eqs 1 and 2,

$$q_{\text{rev}} = \Delta E - w_{\text{rev}} = \Delta E + \int_{\text{rev}} P \, dV = \Delta E + \alpha_{\text{rev}} \quad (3)$$

where the quantity " $\alpha_{\text{rev}}$ " above is the area enclosed by the transition pathways depicted in the PV diagram when such transition is constructed in a reversible manner. This aspect is denoted in the above expression through the subscript "rev" under the integral sign.<sup>27</sup> The quantity reversible heat is special and is the basis for the thermodynamic quantity entropy. Specifically, when an infinitesimal (or small) quantity of heat is reversibly added ( $dq_{\text{rev}}$ ) to a system at temperature " $T$ " a corresponding change occurs to the entropy of the system as given by

$$dS = \frac{dq_{\text{rev}}}{T}$$

When this infinitesimal change in heat is extended over the entire reversible path, one obtains the change in entropy for the process as

$$\Delta S = \int_i^f dS = \int_i^f \frac{dq_{\text{rev}}}{T} = \frac{q_{\text{rev}}}{T} = \frac{\Delta E}{T} + \frac{\alpha_{\text{rev}}}{T} \quad (4)$$

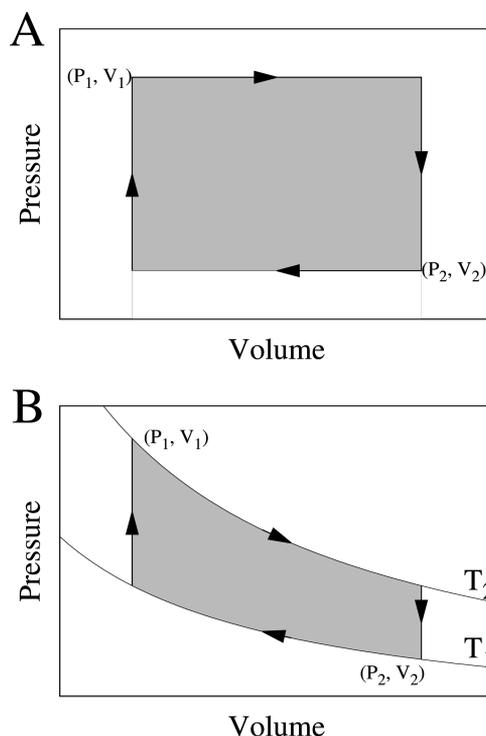
where we have assumed that the reversible heat, " $q_{\text{rev}}$ ", for the process depicted as " $i$ "  $\rightarrow$  " $f$ " in the definite integral is independent of temperature.<sup>29</sup> In addition, we have used eq 3 to express the change in entropy in terms of the change in internal energy and the work that is depicted within PV diagrams.

On the basis of the expressions above, it is also noted that the entropy for all three processes depicted in Figure 2 is defined as the area highlighted in Figure 2A plus the change in internal energy divided by the temperature at which the process occurs. Note that the areas in Figure 2B,C do not arise in the determination of entropy because those processes are not reversible. For an ideal gas, the change in internal energy would be zero, as there is no change in temperature, and the entropy change is simply the quotient of the shaded area in Figure 2A divided by the temperature. Thus, the entropy change is related to the maximum possible work, or "work capacity" for a given transition through its connection to  $\alpha_{\text{rev}}$ . (This idea is revisited when free energy is introduced, as discussed below.)

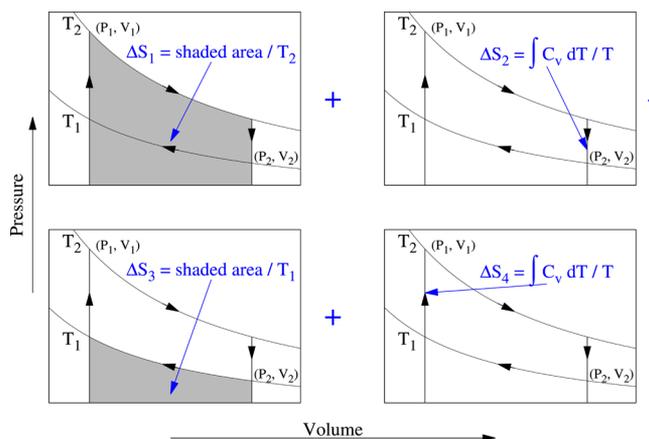
At this point, entropy is simply another way of writing work or, more specifically, reversible work. The physical implications of this new variable are made clear in the next section.

It is useful to further emphasize the challenging concepts introduced in the previous paragraphs. We do so by noting that Figures 1A,B and 2, all represent different paths for the transition from  $(P_1, V_1)$  to  $(P_2, V_2)$ . However, it is only the process represented in Figure 2A that is reversible. Hence it is the area under the curve in Figure 2A that defines the entropy and not the areas in Figures 1A,B and 2B,C. Similarly, panels A and B in Figure 3 represent two different pathways for the cyclic transformation  $(P_1, V_1) \rightarrow (P_2, V_2) \rightarrow (P_1, V_1)$ . The individual component pathways of Figure 3B are reversible, and hence, it is the area enclosed within Figure 3B that is associated with entropy.<sup>28</sup>

Each segment within Figure 3B contributes a specific amount to the total entropy. These contributions are illustrated in Figure 4. Specifically, contributions toward the entropy for this process can be divided into four parts and these are shown diagrammatically as the sum of the four subplots in Figure 4. Note that the terms  $\Delta S_2$  and  $\Delta S_4$  do not contain contributions from PV work because the volume is constant in these cases. However, these segments do contribute entropy through the change in internal energy,  $\Delta E$ , as dictated by eq 4, and this may



**Figure 3.** The plots represent different pathways for the cyclic transition  $(P_1, V_1) \rightarrow (P_2, V_2) \rightarrow (P_1, V_1)$ . The components of plot B are constructed using two isotherms and the different components of plot B are reversible. Hence, it is the area enclosed within plot B that contributes to entropy.<sup>28</sup> This specificity of the path involved further underscores the path independence of entropy, although entropy has been derived using the concept of work. The various components of the entropy for this particular change are depicted in Figure 4.



**Figure 4.** A graphical representation of the total entropy for the cyclic transformation  $(P_1, V_1) \rightarrow (P_2, V_2) \rightarrow (P_1, V_1)$  represented in Figure 3: the total entropy in this case is  $\Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4$ . The quantity,  $\Delta S_1$ , is the area of the shaded region on the top left panel divided by the temperature  $T_2$ . This is similarly the case for  $\Delta S_3$ ; however, the contribution is negative because the system contracts. The quantity  $\Delta S_2$  does not have any contributions from PV work (see eq 4) and the change in internal energy is obtained from the constant volume heat capacity. This is also the case for  $\Delta S_4$ . The figure is further analyzed in Supporting Information, Appendix C, where a final expression is also provided.

be computed using the (temperature dependent) constant volume heat capacities.<sup>30</sup> The entropies corresponding to  $\Delta S_1$

and  $\Delta S_3$  are, of course, constructed using the areas under the curve as shown in Figure 4 and may contain additional contributions if the potential energy also changes, as would be true for real gases and other states of matter. Such contributions from the PV diagram, when entered into eq 4, yield the value of the total entropy change for the  $(P_1, V_1) \rightarrow (P_2, V_2) \rightarrow (P_1, V_1)$  transition. As a result of the fact that entropy is a state function, the final answer for the above closed path transition may be expected to be zero. An analysis to this effect, along with a derivation of  $\Delta S_1$ ,  $\Delta S_2$ ,  $\Delta S_3$ , and  $\Delta S_4$ , is provided as part of Supporting Information, Appendix C. A discussion toward this final goal could definitely be a part of upper-level education and can be included at the introductory level with some care. Irrespective of this detail, the above discussion provides rationale connecting entropy to the other thermodynamic quantities encountered as part of the first law, along with a pictorial depiction.

We have found that students generally know how to solve problems involving entropy, free energy, and other state functions using Hess's law and other similar definitions, but they have difficulty accomplishing a conceptual grasp on these challenging ideas. The above discussion appears to us as one cogent development that clarifies the physical basis for these concepts without becoming mathematically embroiled.

## ■ MACROSCOPIC TO MICROSCOPIC CONNECTIONS THAT ENHANCE THE TREATMENT OF ENTROPY AND FREE ENERGY

### Microscopic Definition of Entropy (Boltzmann Entropy)

The above discussion connects entropy to the macroscopic thermodynamic properties and specifically to the area enclosed inside a PV diagram. However, at this point, entropy is just another variable that signifies a specific kind of work (see eq 4). To delve further into the physical basis behind the concept of entropy and make connections to the microscopic world, we introduce Boltzmann's definition of entropy:

$$S = k \ln \Omega \quad (5)$$

where we now introduce the number of microstates,  $\Omega$ , namely, the number of realizations of the system in a given configuration and the Boltzmann constant,  $k$ . The latter is simply the ratio of the ideal gas constant and the Avogadro number. The quantity  $\Omega$  is abstract, and to make this transparent, we utilize standard textbook examples,<sup>18</sup> such as counting the number of ways in which a set of gas molecules can be spread in a closed container if (a) the molecules are constrained to remain in one-half of the container, or (b) the molecules are free to expand and occupy the entire volume of the container. Once the students see that the answer obtained from basic combinatorics is also the chemically relevant solution, they have one more physical picture of entropy that is based on the number of microstates, or the number of ways in which a system can manifest itself under a given set of conditions. Furthermore, using eq 4, along with the analysis of Figure 4 presented in Appendix C in Supporting Information, one obtains a rationalization for the logarithmic dependence in eq 5.

Equations 4 and 5 yield a connection back to the macroscopic description as

$$\begin{aligned} \Delta S &= S_f - S_i = k \ln \Omega_f - k \ln \Omega_i = k \ln \frac{\Omega_f}{\Omega_i} \\ &= \frac{\Delta E}{T} + \frac{\alpha_{\text{rev}}}{T} \end{aligned}$$

where we have used  $\Omega_i$  and  $\Omega_f$  to represent the number of microstates available to the system at the initial ("i") and final ("f") points of a certain transition. The accompanying changes in internal energy and work are those stated on the right side of the above equation. This equation can also be written as

$$\frac{\Omega_f}{\Omega_i} = e^{(\Delta E + \alpha_{\text{rev}}/kT)} = e^{(\overline{\Delta E} + \overline{\alpha_{\text{rev}}}/RT)} = e^{(\overline{\Delta S}/R)} = e^{(\Delta S/k)} \quad (6)$$

where overbars represent molar quantities. Thus, as the number of microstates increases from the initial to the final configuration (that is,  $\Omega_f > \Omega_i$ ), the entropy increases, which in turn is microscopically facilitated by (a) the change in kinetic and potential energy of the molecules, that is, internal energy, during the transformation and (b) the magnitude of the graphical interpretation of work, " $\alpha_{\text{rev}}$ ", that we have discussed in some detail.

Equation 6, in some sense is a culmination of our efforts in elucidating the connections between work (from the pictorial, PV diagrams perspective), entropy, and number of microscopic states available to the system. This, in our experience, is a departure from most curricula where, at the very least, Boltzmann's interpretation of entropy is presented as a disconnected side-bar, leaving the inquisitive student with two separate notions about entropy and thus not realizing the connections between these two approaches.<sup>3,17</sup> The connection is one of the major goals that are achieved in the current layout.<sup>31</sup> In addition, eq 6 turns out to be a fundamental step that is later used in the description of free energy and in chemical kinetics.

### Microscopic Connections for the Second Law of Thermodynamics

On the basis of heuristic discussions involving the number of possible ways in which four marbles can be placed inside four containers,<sup>18</sup> the students already understand the meaning of the term "most probable event". To extend this to thermodynamics, we further analyze eq 6. If the final state, "f", is more probable as a result of an increased number of microstates (that is,  $\Omega_f > \Omega_i$  in eq 6), then the left-hand side of eq 6 is greater than one. This is, however, only possible if  $\Delta S$  on the right side of eq 6 is concurrently greater than zero.

The discussion in the above paragraph only involves the system and this discussion on probabilities needs to be generalized to include the universe. This universe contains a system where a chemical change is taking place and its surroundings. The role of the surroundings (or reservoir) is critical because arguably the surroundings in the immediate vicinity of the system may also exhibit significant change during a transformation. Consequently, we note that for a transformation to occur *spontaneously*, the number of microstates available to the universe in the final configuration should be greater than those available to the initial state. This statement is an extension of eq 6, where the analysis is now reflected on the universe. This leads to the statement of the second law of thermodynamics in terms of microscopic states:

$$\begin{aligned} \Omega_f^{\text{univ}} &> \Omega_i^{\text{univ}} \text{ and} \\ \Omega_f^{\text{univ}} &= e^{(\Delta S_{\text{univ}}/k)} > 1 \end{aligned} \quad (7)$$

In other words,

$$\Delta S_{\text{univ}} = (\Delta S_{\text{sys}} + \Delta S_{\text{surr}}) > 0$$

Notice that in the above discussion our starting point is the fact that the increase in microstates implies spontaneity. The corresponding increase in entropy is only a consequence. We find that this provides further rationalization to the second law, making it easier to understand for students.

Because the change in Gibb's free energy is defined using the entropy change for the universe, that is,  $\Delta G = -T\Delta S_{\text{univ}}$ , it follows that  $\Delta G < 0$  for a spontaneous process.

One can also connect it to the graphical interpretation of work described above. That is,

$$\begin{aligned}\Delta G &= -T\Delta S_{\text{univ}} \\ &= -(\Delta S_{\text{sys}} + \Delta S_{\text{surr}}) \\ &= -(\Delta E_{\text{sys}} + \alpha_{\text{rev}}^{\text{sys}}) - (\Delta E_{\text{surr}} - \alpha_{\text{rev}}^{\text{surr}})\end{aligned}\quad (9)$$

where we have assumed that the work done on the system and surrounding are of opposite signs. Thus, the sign in front of  $\alpha_{\text{rev}}^{\text{surr}}$  has been switched to allow the area,  $\alpha_{\text{rev}}^{\text{surr}}$ , to always have a positive numerical value. This is because when work is done on (by) the system, it is done by (on) the surrounding. (See Supporting Information, Appendix D, for a discussion on the physical meaning of free energy.)

The connection between free energy and microstates can also be made by combining eqs 7 and 9 to obtain

$$\Delta G = -T\Delta S_{\text{univ}} = -kT \left( \ln \left[ \frac{\Omega_{\text{f}}^{\text{univ}}}{\Omega_{\text{i}}^{\text{univ}}} \right] \right) \quad (10)$$

The ratio on the right side includes all microstates in the universe as part of the final and initial configurations, and hence is essentially the number of the possibilities in which the universe can exist when the system is in the final or initial states. Thus, one may be inclined to interpret this, as a ratio of probabilities. As upper classmen, and later as graduate students, the students will see that this ratio of probabilities is essentially the isothermal–isobaric partition function, but this connection is not made in class.

If we further decompose the number of microstates in the universe using those from the system and surrounding, that is,  $[\Omega_{\text{f}}^{\text{univ}}/\Omega_{\text{i}}^{\text{univ}}] = [\Omega_{\text{sys}}^{\text{f}}\Omega_{\text{surr}}^{\text{f}}/\Omega_{\text{sys}}^{\text{i}}\Omega_{\text{surr}}^{\text{i}}]$ , we obtain

$$\begin{aligned}\Delta G &= -kT \left( \ln \left[ \frac{\Omega_{\text{f}}^{\text{univ}}}{\Omega_{\text{i}}^{\text{univ}}} \right] \right) = -kT \left( \ln \left[ \frac{\Omega_{\text{sys}}^{\text{f}}\Omega_{\text{surr}}^{\text{f}}}{\Omega_{\text{sys}}^{\text{i}}\Omega_{\text{surr}}^{\text{i}}} \right] \right) \\ &= -kT \left( \ln \frac{\Omega_{\text{sys}}^{\text{f}}}{\Omega_{\text{sys}}^{\text{i}}} + \ln \frac{\Omega_{\text{surr}}^{\text{f}}}{\Omega_{\text{surr}}^{\text{i}}} \right) = -T(\Delta S_{\text{sys}} + \Delta S_{\text{surr}})\end{aligned}\quad (11)$$

This last expression will be used in the next section, when chemical kinetics is introduced.

## CHEMICAL KINETICS: THE MICROSCOPIC PICTURE AND CONNECTIONS TO THERMODYNAMICS

### The Arrhenius Formula

Let us reconsider eq 11. If we were to assume that the reactive component is buried within the definition of “system”, we may obtain a free energy for activation, “reactant”  $\rightarrow$  “transition state” where the latter configuration is represented by “TS”, as

$$\Delta G_{\text{activation}} = -kT \left( \ln \frac{\Omega_{\text{sys}}^{\text{TS}}}{\Omega_{\text{react}}^{\text{sys}}} + \ln \frac{\Omega_{\text{surr}}^{\text{TS}}}{\Omega_{\text{react}}^{\text{surr}}} \right) \quad (12)$$

Notice that in the above expression we have used eq 11, and substituted “TS” for “f” and “react” for “i”. If we further assume that the surrounding contributions are virtually the same for reactant and transition states, since all reactive components (and hence modifications from reactant to transition state, TS) are represented within the system, then the free energy difference between reactant and transition state may be written (to very good approximation) as

$$\Delta G_{\text{activation}} = -kT \left( \ln \frac{\Omega_{\text{sys}}^{\text{TS}}}{\Omega_{\text{react}}^{\text{sys}}} \right) \quad (13)$$

or

$$\left( \frac{\Omega_{\text{react}}^{\text{TS}}}{\Omega_{\text{react}}^{\text{sys}}} \right) = e^{-[(\Delta G_{\text{TS}} - \Delta G_{\text{react}})/kT]} = e^{-(\Delta G_{\text{activation}}/kT)} \quad (14)$$

Equation 14 is, of course, the celebrated Arrhenius rate equation when the left-hand side,  $\Omega_{\text{react}}^{\text{TS}}/\Omega_{\text{react}}^{\text{sys}}$ , is interpreted as the rate constant for the reaction. Since the idea of probabilities has been introduced, the statement in eq 14 lends further credence to the physical interpretation that the rate constant within the classical regime is nothing but ratio of the probability of finding the system at the transition state configuration and at the reactant configuration. In addition, the form eq 14 includes the Arrhenius pre-exponential factor, and hence when one uses the fact that

$$\Delta G_{\text{activation}} = \Delta H_{\text{activation}} - T\Delta S_{\text{activation}}$$

one obtains the textbook form of the Arrhenius formula as

$$\left( \frac{\Omega_{\text{react}}^{\text{TS}}}{\Omega_{\text{react}}^{\text{sys}}} \right) = [e^{(\Delta S_{\text{activation}}/k)}] e^{-(\Delta H_{\text{activation}}/kT)} = A e^{-(\Delta H_{\text{activation}}/kT)} \quad (15)$$

and the term inside square brackets, is the Arrhenius pre-exponential term,

$$A = e^{(\Delta S_{\text{activation}}/k)} \quad (16)$$

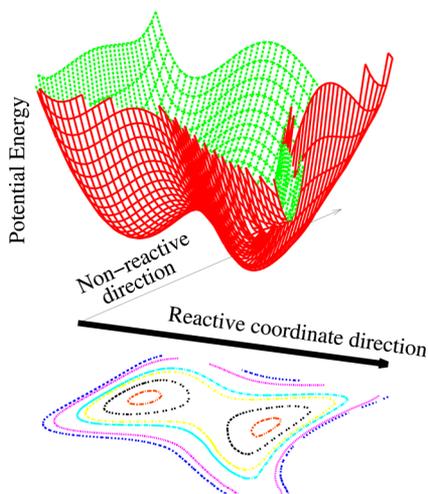
No wonder, this term is purported to be the “entropic factor”.<sup>3</sup> The connection between the pre-exponential term and PV diagrams can be further understood using eq 4. Furthermore, we can readily relate the exponent in eq 14 to the area enclosed within the PV diagrams using eq 10. In this fashion, the (empirical) Arrhenius equation is introduced in a physically meaningful fashion. Thus, a connection between kinetics and thermodynamics is achieved. Now that we are equipped with eq 14, we may go back to thermodynamics and revisit the meaning behind spontaneity and the second law of thermodynamics. Also note that eq 15 is closely related to the celebrated Eyring equation. These subtle issues are considered in the Appendix E (see Supporting Information). It may further be noted that the roots for the exponential dependence of rate in eq 15 may be directly traced to the logarithmic dependence of entropy on the number microstates in introduced in eq 5.

It must also be understood that the concepts presented here are among the most challenging ideas to be encountered during the class. Hence, these ideas require reiteration across semesters, perhaps through a reintroduction as part of upper-level physical chemistry. However, the students' retention of concepts across semesters may be a concern. To alleviate such factors, we have suggested to several honors general chemistry students that they pursue the physical chemistry sequence soon

after completion of general chemistry (during second year). This mentoring has been easier to implement for students joining research programs immediately following general chemistry (and there are generally a good fraction of students from the honors class that do join research programs within the department following the honors freshman class) and this experiment has thus far proven to be successful. However, the long-term effectiveness of this change in the traditional curricula sequence remains unexplored.

### The Chemical Reaction Is Statistically a Rare Event

Finally, we touch upon an important message that is either omitted or simply mentioned in passing at the undergraduate level. The reactive process is, statistically speaking, a rare event. This idea is illustrated using Figure 5. We spend some time to make sure the students understand that a chemical system has  $3N$  degrees of freedom. However, the reaction profile noted in most textbooks is represented as a transition in just one-dimension. Of course, the situation presented in textbooks is an idealized situation and in general more than one degree of freedom can be involved. However, there are still a large number of degrees of freedom that do not lead to a reactive event. In Figure 5, the set of all degrees of freedom that lead to a reactive



**Figure 5.** A reactive process is in general a rare event. The illustrated scenario shows one dimension that leads a facile process. This direction is implied here to be a composite direction that contains a subset of all dimensions involved in the reaction process. The remaining  $3N - X$  directions (that are for clarity combined into a single degree of freedom orthogonal to the reactive process) are nonfacile. As energy is randomly distributed within a molecular system, the probability of having sufficient energy along the reactive direction is generally small. Thus, a reactive process is a rare event. (While this figure serves as a generic example here to convey the concept of rare events in chemical kinetics, the particular example shown is that pertaining to a hydrogen transfer event within the catalytic cycle for the enzyme soybean lipoxygenase-1 studied in ref 34).

event are represented in one axis, whereas the remaining, nonreactive, dimensions are represented in an orthogonal axis. When a reactant is placed in its stable configuration, that is, its potential well, there are  $3N$  orthogonal directions for these reactant molecules to sample. Of these  $3N$  directions, there is generally only a very small subset (one if you look at a chemistry textbook and in reality, perhaps only a few more) of the degrees of freedom that can lead to a reactive event. Because energy is generally distributed in a random fashion, the probability of the

reaction is related to the probability of the system being present in one of the reactive pathways. Quantum mechanically speaking, when multiple pathways are available all of these paths will simultaneously contribute to the process. This, along with the previous paragraph, exposes the students to a statistical description of reaction rates.

We find that the subject matter of the paragraph above is generally quite challenging for most students. Hence, we construct a real-life analogy to help the students better assimilate the concept of rare events in reactive systems. (The pictorial representation of such analogies is known as concept-maps<sup>32,33</sup> in the learning community.) Let us consider the entire class of students and let us also assume that each student has exactly \$50 in their respective wallets. Now, one student in the front row, labeled as student A for further discussion, feels that he or she needs to buy a television for the dorm room. The student is aware that all the students in his favorite class, S117, have enough resources when combined such that if a large portion of this money (for example, \$1000) were *redistributed* to student A, he or she would be able to achieve the goal of buying a television. However, such a redistribution process is highly unlikely and hence is deemed as a rare event.

Now, if we allow for exchange of capital through collisions, perhaps during an episode of flag football, then the likelihood of student A achieving the goal improves. However, this may not be a significant improvement if the games were drab and boring due to player lethargy. However, as the energy involved in each player (and at this juncture the word “player” is replaced by “degrees of freedom” in our discussion) increases, perhaps they collide more often during the football game, which further facilitates exchange of capital and improves the chance that student A might be able to achieve their goal.

The analogy above was presented in our Honors general chemistry class, and it was found that the students were quite comfortable in assimilating the concept of rare events when it was pointed out to them that each student in the classroom, in this example, is a metaphor for a degree of freedom in a molecular system and exchange (or *redistribution*) of energy in molecular systems occurs through collisions. Furthermore, since energy is randomly arranged in a molecular system (for example, \$50 per degree of freedom!), the likelihood that a large quantity of energy (or capital in the above example) appears in one of the molecular modes is less. The number of different ways in which energy can be arranged in a system is, of course, related to the number of microstates defined in eqs 5 and 6, and hence, the connection between entropic factor in chemical reactions and redistribution of energy between molecular degrees of freedom is made. Certainly, the jovial nature of the discussion above helps the cause to an extent and we find that abstract notions can be easily conveyed once the activation barrier is lowered through the use of such analogies.

## CONCLUSIONS

We have presented a novel approach to introducing the underpinnings of macroscopic chemistry, namely, fundamental thermodynamic and kinetics concepts. Specifically, the entire realm of thermodynamics is introduced beginning from PV phase diagrams that were originally used to conceptualize the ideal gas laws. The discussion, while having a strong mathematical basis, is presented in a rational, diagrammatic fashion. Ideas related to state functions and reversibility are directly obtained from transitions constructed on PV diagrams. These developments, in turn, allow for a pictorial description of work, heat, entropy, and free-energy based on the PV diagrams. Connecting the macroscopic definition

of entropy with the microscopic definition of Boltzmann entropy, one obtains a relation between the number of microstates, or the probabilistic interpretation of entropy, and the area enclosed within the PV diagram.

We then proceed to introduce chemical kinetics using the connections gathered between entropy, free energy, and the number of available microstates. The second law is first introduced as a byproduct of simple statistics. Following this, the fundamental basis behind classical transition state theory is realized allowing for a conceptually elegant description of the Arrhenius formula. Furthermore, the connection between the rate constant and the number of microstates responsible for entropy is established. It is further stressed that a reactive process is a rare event, when viewed within a statistical framework. Analogies are presented to drive home the concept of rare events. This presentation allows the students to fundamentally understand the connection between the concept of probabilities of events and reaction rates.

## ■ ASSOCIATED CONTENT

### Supporting Information

The major portion of the supporting information includes an advanced discussion on the topics covered here. These include, additional discussions on reversibility, further analysis of Figure 4 and a statement on how the entropy is to be computed from such a figure, the physical correspondence between free energy and the maximum possible work, an examination of ideas related to spontaneity, treatments on chemical kinetics that connect to the quantum mechanical description in ref 18, barrier recrossing, and the Eyring equation. In addition to these we also discuss course logistics issues such as student population and course syllabus. This material is available via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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- (22) The students may wonder as to why is internal energy a state function? It may be stated that internal energy is directly related to the configuration of the system, independent of the pathway utilized to get to that configuration. For example, temperature is determined from the molecular kinetic energies. (Kinetic theory of gases is also studied in class as seen in the Supporting Information.) Pressure and volume determine the average intermolecular spacing thus affecting the potential energy. Thus, the internal energy is unique at a given PV phase space point.
- (23) Reference 24 includes a symbolic mathematics template based on Mathcad, to demonstrate the monotonic decrease in work done *on* the system (or increase in work done *by* the system) when the number of steps in Figure 2C is gradually increased. The asymptote, where the number of such steps goes to infinity and step-size becomes small, of course, converges to the integral of the curve in Figure 2A.
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- (26) This last result allows one to make a parenthetical remark as to how the area under any curve (and hence the corresponding definite integral) could equally well be constructed using rectangular slices with small widths. There is of course a terminology already present in mathematics for such small widths, for the case where the area enclosed within these rectangular pathways is in fact identical to that obtained from Figure 2A. Such steps-sizes have to be infinitesimal in magnitude. Such connections allow the students to realize the physical implications of the mathematical ideas that they might be learning in the first year of calculus at the undergraduate level.
- (27) Note that while the PV charts were originally introduced to teach ideal gas laws, this restriction is now abandoned and we find that the students are able to make the transition to general systems. This adjustment is further facilitated by showing PV diagrams for real gases, prior to the discussion of work.
- (28) In reality, it turns out that the plot in Figure 3A is also reversible and one gets the exact same result for the total entropy from Figure 3A and 3B. However, this is a detail that is important to emphasize only at the advanced level. At the freshman level, these figures are used to heuristically explain the consequence of path dependence.
- (29) The lack of dependence of  $q_{rev}$  on the temperature is, of course, not a requirement, and when this is not the case, the integral would need to be evaluated appropriately. Discussions pertaining to such dependence may be mentioned in passing.
- (30) The question of whether these two constant volume transformations are reversible or not, does not arise, because  $\Delta E$  is

a state function. However, this is an extremely subtle point that could use a reiteration.

(31) Moreover, this interrelationship of the macroscopic with the microscopic has been achieved without explicitly introducing statistical thermodynamics, which is more appropriate for the upper class students. The left-hand side of eq 6 can of course be related to probabilities, but this aspect is only briefly mentioned in class.

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