

Geometry and Thermodynamics: Exploring the Internal Energy Landscape

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It is well known that fundamental functions in thermodynamics portray variable relationships that yield complete sets of thermodynamic information for a system. These relationships concern several combinations of U - S - V , H - S - P , A - V - T , and others, which are coupled mathematically through the Legendre transform. Fundamental functions contain at least one non-measurable thermodynamic property and therefore cannot be constructed directly from experimental data. They are developed from integrations of real measurements, often cast in the form of equations of state that mostly relate the pressure with the volume and temperature of a state of a system, preserving in that way all useful thermodynamic data.

Gibbs was the first to suggest that fundamental functions could be interpreted quantitatively from their geometric analogies (1, 2), and this idea has helped the development of thermodynamics tremendously. It has enriched our understanding and has emerged into what is called today "scientific visualization" (3). A characteristic example of the above is the case of general relativity theory, where the presence of mass changes the space-time coordinate system. However, it is a fact that little work has been done in integrating the geometric method into the teaching practice. If we look through the literature, we see, for example, Weinreich in his book *Fundamental Thermodynamics* (4) formulating the theorem of practical thermodynamics, as well as treating thermodynamics using surfaces with analytical tools (e.g., derivatives). Callen also in his book *Thermodynamics and an Introduction to Thermostatistics* (5) uses the concept of the fundamental function to describe thermodynamics and confirms that, if the fundamental equation of a system is known, every thermodynamic attribute is completely and precisely determined.

Looking in the literature one cannot find specific references to the percentage of the students who prefer geometrical to analytical thinking, though it is clear enough that the students from their first years at school become more familiar with mathematical equations and analytical thinking than the geometrical constructs. Today, despite the fact that many science and mathematics educators believe that computers can be used to expose the underlying principles of their disciplines more convincingly than exercises found in standard texts (6), with few exceptions, even in chemistry and physics, the use of computers in science education remains relatively unsophisticated compared to what it could be if the capabilities of symbolic computing systems were to be fully exploited (7). As research indicates, the use of graphical representations during science instruction enables the introduction of multiple forms of knowledge representation and problem-solving procedures (8). The development of multiple cognitive representations of complex scientific relationships contributes to the enhancement of a student's conceptual understanding and problem-solving strategies (9). Moreover the graphical representations that are used to teach fundamental principles of science pro-

mote visualization of complex structures and contribute to a deeper understanding of the subject (10).

In the present article we propose a simple way to teach thermodynamics through the use of the computer along with geometric objects, like surfaces, which both can enhance inventive thinking abilities and practical skills of the undergraduates. The method was applied to second-year students of thermodynamics who had already attended first-year introductory courses that included thermodynamics. Our aim was to help students comprehend the relation between thermodynamics and geometry and to show them how geometry can help scientists explain and estimate thermodynamic data by using simple tools. The effort is part of a project running in all Greek Universities,¹ intended to promote the experimental character of the courses, computer utilization in the class, and innovation.

Method

Thermodynamic Potential

One of the most important results of classical thermodynamics is that a function called thermodynamic potential, which in the following we will call "potential" for short, suffices to describe the thermodynamic behavior of a system (4). There are many implications of such a finding, two of which are of great importance. Firstly the potential U , like any multivariable function, can be presented geometrically, and secondly it consists of a field to be determined for a given system from experimental measurements or statistical mechanics. Each geometric feature of the potential has a relation to a physical property, and each experimental result provides a relation between geometrical properties of the potential. Therefore, if we know the potential we can calculate the thermodynamic properties of the system and its behavior in general. Conversely, experimental results allow us to determine in part or fully the potential. In the following we will write down the specific relations and geometric features for the

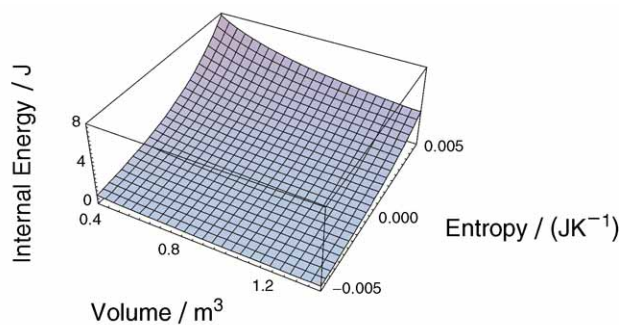


Figure 1. Three-dimensional computer-visualized thermodynamic surface of the internal energy function, for the ideal gas case.

potential internal energy. One must not fail to recognize that the potential is not the physical quantity “internal energy” expressed in any set of variables but in a given set of variables. For the internal energy potential and a pressure–volume system the natural variables are entropy S and volume V , that is,

$$U = U(V, S)$$

The geometric representation of such function is a surface in the coordinate system U , S , and V . In Figure 1 we present a three-dimensional computer-visualized thermodynamic surface of the internal energy potential for the ideal gas case. All the thermodynamic properties and behavior of the ideal gas are contained in this surface. A slope along a V axis, that is, at constant entropy, is numerically equal to the negative of pressure:

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \quad (1)$$

A slope along an S axis, that is, at constant volume, is numerically equal to the temperature:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad (2)$$

Therefore, the slope along each variable is equal to the conjugate variable. The steeper the surface along the entropy axis is, the higher the temperature is, and the steeper the slope along the volume axis, the higher the pressure is. In Figure 2 we present the thermodynamic surface of the internal energy of the ideal gas projected onto the S – V plane.

If we have numerical data, then an approximation of the slope can be obtained by finite differences $(\Delta U/\Delta S)_V$ and $(\Delta U/\Delta V)_S$. If we record the values of V_i as intersections of a slice of constant entropy with the equal potential curves, then it is possible to obtain $\Delta V_i = V_{i+1} - V_i$ as seen in Figure 3A and calculate thus $P_i = -(\Delta U/\Delta V)_S$. Similarly if we record the values of $S_i - S_0$ as intersections of a slice of constant volume with the equal potential curves then it is possible to obtain $\Delta S_i = S_{i+1} - S_i$ (Figure 3B) and calculate the temperature $T_i =$

$(\Delta U/\Delta S)_V$. For $\Delta U = 0.1$ J the approximate derivatives give working results as we will see below. A way to compute the pressure and temperature of the gas at constant entropy and different values of volume is presented in Figure 4.

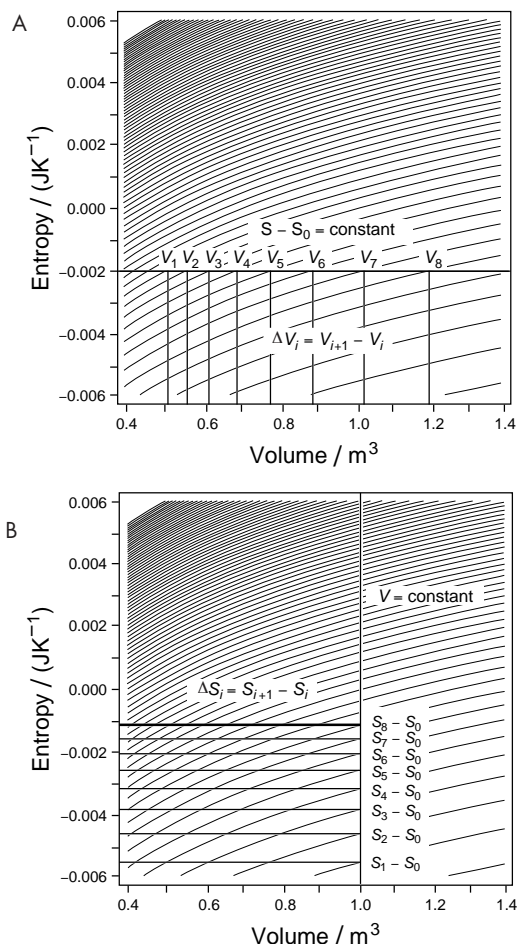


Figure 3. Obtaining ΔV_i (A) and ΔS_i (B) on the internal energy potential of the ideal gas projected onto the S – V plane.

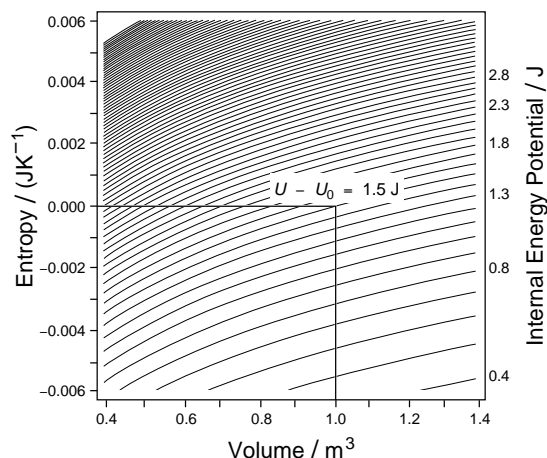


Figure 2. Internal energy potential $U - U_0$ of the ideal gas projected onto the S – V plane. A change of 0.1 J occurs between curves.

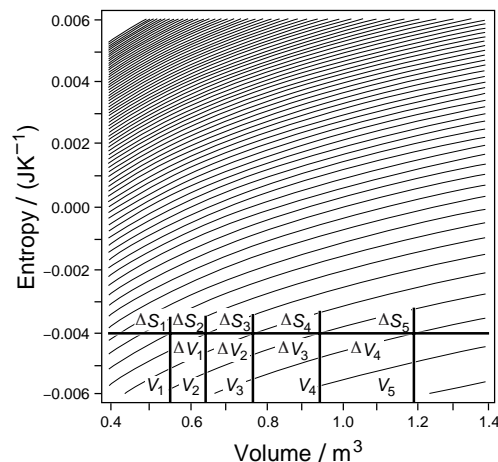


Figure 4. Obtaining ΔV_i and ΔS_i on the internal energy potential of the ideal gas projected onto the S – V plane, in order to compute the pressure and temperature of the gas at constant entropy.

Calculating Nonstate Quantities for the Ideal Gas Case in Reversible Processes

Since all the variables we use are state variables, the question is how to calculate nonstate quantities such as heat Q and work W . We will describe how to do so for the present case of an ideal gas. It is known that for a closed system the change in internal energy, dU , is defined in differential form by the first law of thermodynamics, as the difference between the heat added to the system Q and the work done on the system W , that is,

$$dU = dQ + dW \quad (3)$$

On the $U - U_0$ diagram of the ideal gas (Figure 2) we can draw the isothermal curves. If we define ΔS as the difference in entropy between two states with the same volume, which belong to two subsequent contours of the internal energy, we will notice that ΔS is the same for all states that belong to the same contour, that is, they have constant U . Since ΔU is also constant that implies that the temperature $T = (\Delta U / \Delta S)_V$ is constant for all states belonging to the same contour, that is, they have the same temperature.

It is known that in an isothermal process, heat is transferred between the system and its surroundings and work is performed. To evaluate the work done on the system, we recognize for the ideal gas $dT = 0$ implies $dU = 0$. Thus, the heat transferred to the system Q is equal to the negative of the work done on the system W , that is,

$$Q = -W \quad (4)$$

and also

$$Q_{\text{rev}} = T\Delta S \quad (5)$$

where Q_{rev} is defined as the isothermal reversible heat transfer from a reservoir at temperature T .

In addition, we can define the isentropic lines of the system. What we actually use is a projection of the energy surface on the $S-V$ plane, where the values of internal energy are represented through the contours, as seen in Figure 2, and as a result the isentropic lines are straight lines. During an adiabatic reversible process, no heat is transferred between the system and its surroundings $dS = 0$, thus $dQ = 0$. As a consequence, the first law of thermodynamics gives:

$$dU = dW_{\text{rev}} \quad (6)$$

and the change in internal energy gives the work performed.

Curvatures

The next geometric feature of the potential surface that is related to thermodynamic quantities is the curvature. The inverse of the curvature along the entropy axis is related to the heat capacity at constant volume:

$$C_V = \frac{T}{\left(\frac{\partial^2 U}{\partial S^2}\right)_V} \quad (7)$$

and along the volume axis to the isentropic compressibility:

$$k_S = -\frac{1}{V} \left(\frac{\partial^2 U}{\partial V^2}\right)_S \quad (8)$$

The volume expansion coefficient β can also be calculated:

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad (9)$$

We consider that the initial state of the gas may not be uniform. Normally changes in the gas take place because constraints imposed by the surroundings change. Thus, instability in a gas is normally dependent on the surroundings as well as the contents of the system. Details about the stability of the system can be found in standard texts (5, pp 203–210) and it is not the purpose of the present work to analyze further the subject. Here what we want to show is that by inspection we can readily infer whether the system that we study is in a thermal and mechanical stable state or not.

The heat capacity at constant volume can help us determine whether the system that we study is in a stable thermal state. All we have to do is to find the sign of the curvature $(\partial^2 U / \partial S^2)_V$. By inspection of Figure 3B and drawing a line with constant volume, we notice that as we move across this line, ΔS_i is getting smaller as the values of the entropy increase. Since ΔU is the same that implies that $\Delta U / \Delta S_i$ is getting bigger and thus $\Delta^2 U / \Delta S_i^2$ is positive. As a result C_V is also positive. In a similar way we can conclude that the isentropic compressibility k_S is positive too and as a result we understand that the system that we study will move to mechanical equilibrium if a constraint is released or the external conditions change.

Realizing the variety of information one could extract by representing a thermodynamic function geometrically in the form of a surface, we decided to study the thermodynamic behavior of the ideal gas by performing simple tasks.

Realization

To practice the new methodology, we need the standard theoretical background concerning thermodynamics. Then by using the fundamental functions in thermodynamics and treating them as geometric objects like surfaces and with analytical tools like derivatives, we can obtain the thermodynamic properties of the system that we study. To create the diagram of the internal energy potential $U(V, S)$ of the ideal gas, we derive the exact potential function as follows:

$$U = n c_V T + U_0 \quad (10)$$

where c_V is the specific heat capacity at constant volume and

$$PV = nRT \quad (11)$$

Thus

$$\begin{aligned} dS &= \frac{1}{T} dU + \frac{P}{T} dV \\ \Rightarrow S - S_0 &= n c_V \ln \frac{T}{T_0} + nR \ln \frac{V}{V_0} \\ \left(\frac{T}{T_0}\right) \left(\frac{V}{V_0}\right)^{\frac{R}{c_V}} &= e^{\frac{S-S_0}{n c_V}} \Rightarrow T = T_0 \left(\frac{V}{V_0}\right)^{-\frac{R}{c_V}} e^{\frac{S-S_0}{n c_V}} \quad (12) \end{aligned}$$

So, eq 10 in combination with eq 12 becomes:

$$U - U_0 = n c_V T_0 \left(\frac{V}{V_0} \right)^{-\frac{R}{c_V}} e^{\frac{S - S_0}{n c_V}} \quad (13)$$

For plotting the contours of $U - U_0$ to prepare the exercises proposed in the article, we have the freedom to choose the pressure, volume, and temperature of the state (P_0 , V_0 , T_0) at the middle of the graph. Different choices lead to different sets of exercises and the instructor will know before hand the expected results. From the state equation we can obtain n_0 . The contour plots are of $U - U_0$ as a function of V and $S - S_0$. We chose $P_0 = 1(\text{N/m}^2)$, $V_0 = 1 \text{ m}^3$ and $T_0 = 300 \text{ K}$. From eq 11 we calculated $n_0 = 4.1 \times 10^{-4} \text{ mol}$. So, eq 13 became:

$$U - U_0 = 1.5V^{-\frac{2}{3}} e^{200(S - S_0)} \quad (14)$$

One can produce a bitmap file of a contour plot of $U - U_0$ using any suitable software (Mathematica 5.0 in the present case; ref 11) to be handed to the students. We chose the change in internal energy between the equal potential curves to be constant and equal to $\Delta U = 0.1 \text{ J}$. The students can extract numerical data from the bitmap graphic, as is shown below, using, for example, MSPaint (12), which is commonly available. All that is needed is the utility to draw straight lines and find the position of a point in the pixel coordination system. Subsequently these points are transformed to values of volume and entropy needed for estimating through numerical calculation of the quantities $(\Delta U/\Delta V)_S$ and $(\Delta U/\Delta S)_V$ to obtain the pressure and temperature. MS Excel (13) is suitable for this last step and also for graphing and for curve fitting.

Cases and Respective Diagrams

In Search of Relations between the Intensive and Extensive State Variables of the System

As a first task we want to study the connection between the intensive and extensive state variables of the system. We create some diagrams from which we can extract useful information. First of all by calculating the slope along each axis on the potential surface we compute the pressure and the temperature of the system.

Constant entropy: Initially we assume that the entropy of the system remains constant at a certain value and draw a horizontal straight line on the bitmap file of the internal energy potential diagram, parallel to the V axis, at that point. Afterwards we compute the pressure and the temperature of the ideal gas at constant entropy. Having done so, we create the diagrams of the pressure, temperature, and internal energy as a function of the volume of the gas at constant entropy, as seen in Figures 5, 6, and 7, respectively.

The equation of the trendline in Figure 5 is $P = 0.9497V^{-1.7057}$, that is, $PV^{1.7057} = \text{constant}$. Actually what we draw in Figure 5 is a reversible adiabatic curve for the ideal monatomic gas case. From standard thermodynamics we expect the form of the equation between the two magnitudes to be $PV^\gamma = \text{constant}$, where γ is the ratio of the heat capacities at constant pressure and volume and equals to $5/3$ for

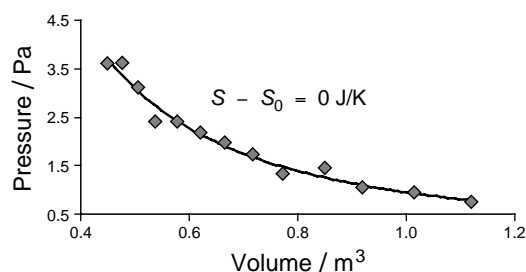


Figure 5. The pressure as a function of the volume of the ideal gas at constant entropy.

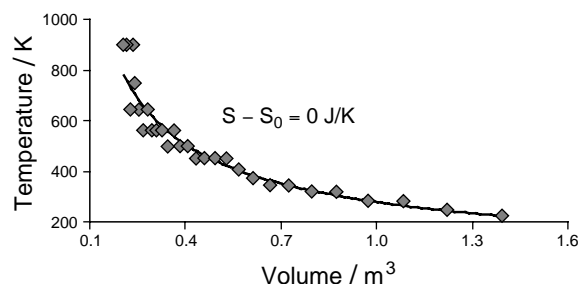


Figure 6. The temperature as a function of the volume of the ideal gas at constant entropy.

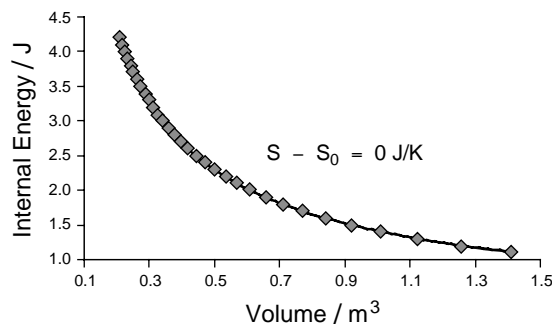


Figure 7. The internal energy of the ideal gas as a function of its volume at constant entropy.

the ideal gas case. The estimated value of γ is 1.7057, which is off by 2.14% of the expected one. This declination is due to the digitization and the calculation of derivatives using finite differences and shows that the approximations give working results.

Additionally it is known from standard thermodynamics that the relation between the temperature and the volume of the ideal gas, calculated at constant entropy, is $TV^{\gamma-1} = \text{constant}$. The term $\gamma - 1$ is equal to $2/3$ for the ideal monatomic gas, and what we find from the plot in Figure 6 is $TV^{0.6562}$, which is in accordance to theory. The estimated error between the theoretically expected exponent and the experimentally calculated one comes up to 2.06%.

We also expected from eq 14 the relation between the internal energy and the volume of the ideal gas to be $U - U_0 \propto V^{-2/3}$. What we got from the fit of the curve in Figure 7 is $U - U_0 \propto V^{-0.6662}$. The error between the two exponents is approximately equal to 0.075%.

Constant internal energy and constant volume: We assume next that the internal energy or the volume of the system remains constant and by using a methodology similar to what is mentioned above, we create some diagrams of the pressure, temperature, internal energy, and entropy of the system at constant internal energy or constant volume. (For details see the Supplemental Material.^W) In summary we drew the following conclusions:

- The relation between the pressure and the volume of the gas at constant internal energy is in the form of $PV^k = \text{constant}$. More specifically we computed $PV^{0.9756} = \text{constant}$. Since it is known that the relation between the pressure and the volume of an isothermal process of an ideal gas is $PV^1 = \text{constant}$, we estimated the error between the theoretical value and the value of the k exponent we computed.
- The temperature of the gas is constant for all states with constant internal energy, which was expected from the properties of the ideal gas, since it is known that for the ideal gas case the isothermal curves coincide with the internal energy potential curves.
- The entropy of the ideal gas is proportional to the logarithm of its volume and is also proportional to the negative logarithm of its pressure at constant internal energy.
- The internal energy of the gas is proportional to its temperature at constant volume.
- Finally, there is an exponential relation between the internal energy and the entropy of the gas at constant volume, which is in accordance to expectations.

Illustrating a Carnot Cycle for the Ideal Gas

We want to study the energy relationships of an ideal gas by drawing a Carnot cycle on the potential surface, as seen in Figure 8. In this presentation the reversible adiabatic curves are straight lines, and the reversible isothermal curves have equal energy. As is known, the closed system that we study in Figure 8 undergoes an isothermal reversible expansion from point A to point B, an adiabatic reversible expansion from point B to point C, an isothermal reversible compression from point C to point D and finally an adiabatic reversible compression from point D to point A.

The internal energy at the points A and B, in Figure 8, is $U_2 - U_0 = 1.3$ J, while at the points C and D is $U_1 - U_0 = 1.2$ J. Also the points A and B have the same computed temperature, which is $T_2 = 271.43$ K, while the computed temperature at the points C and D is $T_1 = 245.16$ K. For calculating the thermal efficiency of a Carnot cycle η , we use the well-known equation:

$$\eta = \frac{W}{Q_a} = \frac{Q_a - Q_c}{Q_a} = 1 - \frac{T_1}{T_2} \quad (15)$$

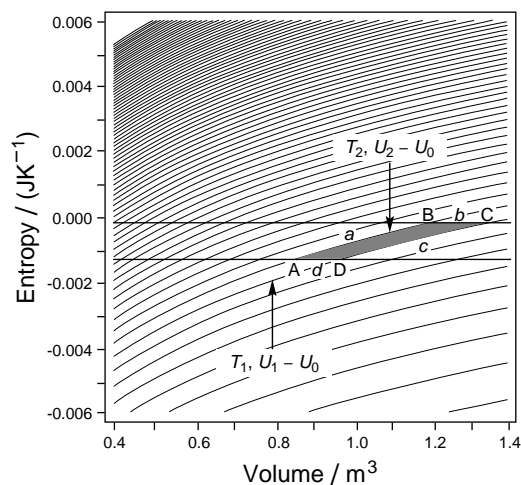


Figure 8. Illustrating a Carnot cycle on the potential surface.

According to eqs 4, 5, and 6 we can calculate the whole work W done during the cycle and also $Q_a = T_2\Delta S$ and $Q_c = T_1\Delta S$. The thermal efficiency for the chosen cycle has been computed and found $\eta \approx 0.1$.

Proposal for a Lab Session

After we had successfully treated the thermodynamic potential surface the way we described earlier, we decided to prepare a set of exercises aiming to help students with core knowledge of thermodynamics to recognize and appreciate the relation between geometry and the physical properties of a thermodynamic surface. As it is well known, learning with understanding is facilitated when new knowledge is structured around the major principles and core concepts of the discipline (14). So, we want students to extract the physical quantities of the ideal gas from the geometrical features of the potential surface by performing simple tasks. The basic element of these exercises is the presentation of the surface by a set of equal potential curves, projected onto a two-dimensional graph with axes the variables V and $S - S_0$, as seen in Figure 2. The change in the internal energy between the equal potential curves is constant, and its value is $\Delta U = 0.1$ J.

In order for the students to elaborate the diagram of $U - U_0$ in many different ways and create several charts, we propose to use a familiar drawing program such as MSPaint, CorelDraw (15), Adobe Photoshop (16), Macromedia Fireworks (17), and so forth. Such a program allows students to read the position of each point on the $U - U_0$ diagram expressed in the pixel coordinate system, while they move the mouse of their computer over the diagram.

The data analysis can take place in a workbook of Microsoft Excel, which gives the students the opportunity to organize various kinds of related information in a single file. First of all they can use a sheet to list the recorded values of the position of points in terms of the pixel coordinate system. At the same time they can make the appropriate transformations of these data to measurements of the physical quantities entropy and volume.

Calculations Keeping the Entropy Constant

As a first task we asked the students to create a chart of the pressure P of the system as a function of its volume V at constant entropy. The values of entropy ranged from -0.006 to 0.006 J/K. It was their decision which value of entropy to choose in order to calculate the pressure. The P - V curves that were derived corresponded to adiabatic curves of the system. We wrote down on a table the equations of the several trendlines that were derived from the diagrams by using Excel software and had a discussion in class.

Comparing results, the students concluded that the product PV^γ remains constant for different values of constant entropy and calculated the value of the ratio of constant heat capacity pressure and constant heat capacity volume. Student values for γ ranged from 1.6235 to 1.7217. They expected the value of the γ exponent to be equal to $5/3$ because they examined the monatomic ideal gas. They estimated the error between their observed γ and the expected value.

As a second task, we asked students to derive the relationship between the temperature and the volume of the system at constant entropy. The students came up to the conclusion that the temperature-volume product is constant and that the relation between the two magnitudes is $TV^k = \text{constant}$. Students values for k ranged from 0.614 to 0.7193. They expected from the fit of the curve the value of the k exponent to be equal to $2/3$. From their results they estimated the error in the k exponent.

Finally by dividing the relation $PV^\gamma = \text{constant}$ by $TV^k = \text{constant}$, both of which were computed earlier, they found the ideal gas equation of state in the general form of $PV/T = \text{constant}$, as expected.

Calculations Keeping the Internal Energy Constant

Another thing we asked students to do was to write down the position of several points along an isopotential curve, in terms of the pixel coordinate system. Then we asked them to calculate the temperature of each point and create a diagram of the temperature T of the system as a function of its volume V at constant internal energy. What they obtained as a result was a horizontal straight line on the chart, parallel to the volume axis, from which they concluded that the temperature of the system remains constant and independent of the volume of the gas at constant internal energy, which is the result of the Joule experiment.

Calculations Keeping the Volume Constant

Finally, we asked the students to consider the volume of the system constant at a value of their preference, as they had already done for the entropy. Then we asked them to calculate the temperature of each point that came up as intersection of the constant volume slice with the equal potential curves and derive the relation between the internal energy $U - U_0$ of the system and the temperature T .

From the form of the equations that were derived with Excel, the students concluded that there is a linear dependence between the internal energy and the temperature of the gas, that is, $U - U_0 \propto aT$. Comparing their results to eq 13 they concluded that the coefficient a is equal to the product nC_V . The coefficient a was expected to be equal to 0.005

according to eq 14. Since student values for a ranged from 0.0042 to 0.0054 , they also estimated the uncertainties of the method.

Defining a Carnot Cycle on the Potential Surface

After we had chosen the $U - U_0 = 1.1$ J curve as the reference isothermal curve for defining a Carnot cycle on the potential surface, we asked the students to draw a second isothermal curve as well as the two isentropic ones and define a Carnot cycle. A first group of students chose the second isothermal curve to be the nearest one to the 1.1 J curve, which is the $U - U_0 = 1.2$ J, while a second group of students chose the second isothermal curve to be the $U_2 - U_0 = 1.3$ J one, and so on until the last group of students. Since the temperatures of the two reversible isothermal heat-transfer processes had already been calculated by them, they were asked to compute the heat that is supplied to the cycle and the heat that is rejected from the system during the isothermal processes and calculate the net work done on the cycle. They were also asked to compute the thermal efficiency of the cycle η . The students concluded that the value of the thermal efficiency of the Carnot cycle increases as the temperature of the second isothermal curve they choose increases from one cycle to another. This was expected from the theory, since the thermal efficiency of a Carnot cycle depends on the low and high temperature of the isothermal curves we choose.

Calculating the Curvatures on the Potential Surface

Lastly, we asked the students to find the sign of the curvatures $(\partial^2 U / \partial S^2)_V$ and $(\partial^2 U / \partial V^2)_S$ on the potential surface and draw conclusions in relation to the state of the system. From their computations, they concluded that the heat capacity at constant volume is positive all over the potential surface, which means that the ideal gas that they study is in thermal equilibrium. They also concluded that the isentropic compressibility of the system is positive and as a result the system is in mechanical equilibrium as well.

Discussion

In thermodynamics, the knowledge of the fundamental functions of a system can help us study its thermodynamic behavior, despite how complex the system might be, as was indicated for the first time many years ago. There are two ways of treating the fundamental functions to obtain the thermodynamic properties of a system. One way is to use the mathematical analysis and its tools, like derivatives and integrals, to gain the results that are expected. The procedure just described can also be realized in reverse order, beginning from the experimental information about the system and going through the solution of differential equations to obtain the fundamental functions of the system. A second way is to represent a fundamental function of the system geometrically in the form of projection of a surface onto two-dimensions or as a three-dimensional geometric object, extract data from this surface and finally gain results for other variable by digitization.

If we try to compare the two methods, we see that the first method requires a good knowledge of mathematics. Because of the fact that the whole procedure reminds us of what

is usually done at school, where we have to solve a problem in the typical way we have been taught, a low level of intuition is demanded. In addition to that, this procedure discourages constructivism. As for its scientific value, it is restricted to obtaining numerical results from the mathematical elaboration of the equations. On the other hand, in the second way of treating a thermodynamic system, basic computer skills, which involve the knowledge of common programs, are required. In this case a higher level of intuition is demanded. This approach reinforces constructivism, especially through the visual representation of data processing, and is a scientific method that leads to results that can be easily manipulated. Also the uncertainties that are observed in results, as well as the possible differences from the expected values, can be understood.

The question that arises next is whether it is possible to embed this approach of studying the thermodynamic behavior of a system into the teaching practice and what kind of difficulties we might face. Applying this pilot project with second-year students of thermodynamics, the results indicated that all students understood the way geometry is connected to thermodynamics. It is a fact that the knowledge of all the equations of state of a system is equivalent to the knowledge of a fundamental function, and as a consequence a fundamental function suffices to describe completely the thermodynamic behavior of a system. As a result, the use of geometry in thermodynamics convinced the students that the graphical method of elaborating a thermodynamic surface, which represents a fundamental function, is a dynamic way of not only making a qualitative interpretation but also a quantitative assessment of the system.

In addition, this method helped the students make effective use of the computer. It encouraged active learning and constructivism, as well as students' participation in the class. It also increased students' intuition and interest in thermodynamics in general and led to a better understanding of thermodynamics and interpretation of their results in a more scientific way. Moreover, it helped the students to gain metacognitive abilities and motivated them to use the computer as an efficient educational tool that contributes to the betterment of the instruction. Research demonstrates that providing students with opportunities to articulate their ideas to peers and to hear and discuss others' ideas in the context of the classroom is particularly effective in enhancing conceptual learning and metacognition skills (18). As a result, the interaction and collaboration between the students on the instructional tasks we proposed enhanced learning as well.

From the above analysis we can see how useful it is to embed the method into the course of thermodynamics. We can do so without spending a lot of time illustrating it to the students, since no such need arises. Also only common means are required for this purpose. All this work is realizable if one has the core knowledge of thermodynamics and treats it with the use of a computer with standard equipment and common software. For this reason it is possible to apply the method at the first-year introductory level as a thermodynamics laboratory.

After we have assimilated the new methodology and practiced it successfully on simple tasks by using software fa-

miliar to everybody, we proceed to performing more complicated tasks. The method provides a wide range of applications. In addition to the ideal gas case that we studied, which represents a closed system where the initial and final thermodynamic states are in equilibrium, one can also study the behavior of other pure materials, binary or ternary systems, which are more complicated and which may exhibit phase transitions, as well as states that are out of equilibrium (19). Those systems are fully described not only by the internal energy function U but also by many other thermodynamic functions of great interest, such as enthalpy H , Helmholtz free energy A , and Gibbs energy G , as well as others without common names, that can be interpreted quantitatively from their geometric analogies and qualitatively from their representation as two-dimensional projection or three-dimensional surfaces.

The geometric method can be applied to any thermodynamic potential. One should use the potential that is suitable each time. For instance for the van der Waals gas, Helmholtz free energy is more suitable. One can obtain a closed form of the Helmholtz free energy by integrating the van der Waals equation of state for constant temperature, as has been recently done by Ascoli and Malvestuto (20). If we assume in addition that C_V is constant, then we can obtain a full expression of Helmholtz free energy as a function of V and T . This case is very interesting as one can find places of mechanical instability, that is, overheated liquid or undercooled gas, since the thermal stability is ensured by the choice of positive C_V . A work along these lines is in preparation. Finally, approximate but analytical expressions of thermodynamic potentials exist for interesting physical systems that exhibit phase transitions like ferromagnets.

Conclusion

The connection between geometry and thermodynamics has been a matter of study for a long time. Looking at the past, we see that Faraday first tried to introduce geometry into physics by calculating the force as the negative gradient of the potential energy. Then, there was Gibbs, who used geometry mentally to interpret quantitatively physical magnitudes in thermodynamics but made no effort to display what he had in his mind. A little bit later Maxwell with his natural artistic approach and his great interest in the science displayed Gibbs's data relating to thermodynamics by using a plaster model.

Nowadays technological advances allow us to create rapidly three-dimensional surfaces on the computer. Nevertheless the original idea and the image that we conceive and visualize on the computer are exactly the same as what Gibbs conceived and Maxwell displayed in clay and plaster. The connection between geometry and thermodynamics, along with the variety of possibilities and applications in this connection, should be sought. Additionally the way of introducing this relation into teaching should be made widely known and explored for the different areas of the science of chemistry and physics. We must not forget after all that technology today gives us the ability to use the various means needed for this purpose without any hardship.

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^wSupplemental Material

Diagrams of the pressure, temperature, internal energy, and entropy of the system at constant internal energy or constant volume are available in this issue of *JCE Online*.

Note

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