Improving our thermodynamic perspective

Kent W. Mayhew[a)]
68 Pineglen Cres., Ottawa, Ontario K2G 0G8, Canada

(Received 5 June 2007; accepted 14 May 2011; published online 14 July 2011)

Abstract: We will discuss the fact that our traditional thermodynamic perspective may be skewed and present some alternatives. © *2011 Physics Essays Publication*. [DOI: 10.4006/1.3597597]

Résumé: Nous discuterons le fait que notre perspective thermodynamique traditionnelle pourrait être déformée et présentons quelques alternatives.

Key words: Joule's Experiment; Internal Energy; Entropy; Work; Ideal Gas; Second Law; First Law; Temperature; Efficiency; Global Warming.

I. INTRODUCTION

We shall discuss the traditional thermodynamic perspective and some of its consequences. Moreover, we shall demonstrate that another perspective exists, which is not only simpler but equally explains our thermodynamic reality. According to Occam's razor, this dictates that our new perspective be given favorable consideration.

The first law of thermodynamics is written[1–4] as

$$dQ = d\varepsilon - W, \tag{1}$$

where dQ, $d\varepsilon$, and W, respectively, represent the heat entering/exiting the system, the change to its internal energy, and the work done by/onto the system. With P and V, respectively, representing a system's pressure and volume, work (W) is traditionally defined by[1–4]

$$W = PdV. \tag{2}$$

Work is traditionally considered as being performed onto a system's walls,[1,3] which can be real or imaginary, i.e., steam engine vapors displacing our atmosphere. Imagine that there are no walls, nor surroundings, then, when contemplating work, the dilemma of onto what is the work done arises. This was the problem facing Enrico Fermi who stated, for an expanding universe, the work "goes into the hands of god."[5]

Mayhew[6] has discussed that Eq. (2) is based upon our perspective on the isobaric Earth. Moreover, Eq. (2) can be thought, in terms of the work that is required, to displace a system of gas to the location where the pressure at a given height [$P(h)$] equates to the system's final pressure (P_f), i.e., $Pf = P(h)$. In which case the work required is

$$W = (NkT)In[P_0/P(h)], \tag{3}$$

where N is the number of molecules, $P(h)$ is the function of how the pressure changes with elevation, P_0 is a constant, and k is the Boltzmann's constant (1.38×10^{-23} J/K). Admittedly, this analogy is awkward. Even so, it remains an analogy designed to make one ponder the validity of the traditional interpretation of work, thus a secondary goal, herein, is to provide some clarity to Eq. (3).

Letting σ be the surface tension and A be the surface area, Mayhew[7] has used the empirical data from other researchers to show the work required for nucleation is

$$W = \sigma dA + d(PV). \tag{4}$$

To this author, the root of the problem being addressed, herein, resides in how we traditionally derive all of our thermodynamic relations, as was previously discussed.[7] For the purpose of clarity, consider Reif,[1] who starts with the isothermal isobaric relation,

$$TdS = d\varepsilon + PdV, \tag{5}$$

where S and T, respectively, represent entropy and temperature. Traditionally, the following relations: $PdV = d(PV) - VdP$ and $TdS = d(TS) - SdT$, are used to transform Eq. (5) into a host of other equations. Obviously, such transformations are based upon the differentiation of the parameter relation: $TS = \varepsilon + PV$. That being

$$d(TS) = d\varepsilon + d(PV). \tag{6}$$

Strangely, thermodynamics remains a rarity, wherein one starts with a part and then subtracts the whole in order to calculate the other parts. Partially, we do so because our experimentation often begins, and ends, at 1 atm and room temperature, i.e., we reside on the isothermal isobaric Earth. Unfortunately, few have contemplated the ramifications of such traditional logic.

Consequences known to thermodynamics are the two following relations:[1]

$$dS = dQ/T, \tag{7}$$

$$dS \geq 0. \tag{8}$$

Obviously, Eq. (7) states that entropy increases when heat (dQ) is isothermally added to a system. While Eq. (8) states, for any process, entropy (S) is always constant, or increasing, forming the basis of the second law.[1,4] Interestingly, Nikulov and Sheehan[8] give a good summation of the challenges to the second law.

Entropy has witnessed numerous definitions. Rudolf Clausius (1822–1888) realized its mathematical significance. In the mid-20th century, entropy's definition was the

[a)]kent.mayhew@gmail.com

"randomness of matter in incessant motion,"[2] while more recently Lambert[9] altered it to "The dispersal of a system's molecular energy." Although, conceived over 150 yr ago, entropy remains contentious.

Herein, we shall show that another perspective exists and discuss some problems with traditional interpretations. Interestingly, the perspective given herein is not only simpler but can also explain some conundrums that tradition cannot. Due to the costs of publication, the discussion will remain short, leaving a more thorough dialog to this author's book, if it ever becomes published.

II. WORK: SEVEN SCENARIOS

Based upon Eqs. (4) and/or (6), an interpretation for an ideal system is

$$W = d(PV). \tag{9}$$

Certainly, Eq. (9) goes against the traditional Eq. (2). In order to demonstrate how Eq. (9) can be applied, we will contemplate several simple scenarios. Consider some expanding ideal gas as system 1, which is separated by a frictionless piston from system 2, as is illustrated in Fig. 1. Let the subscripts "1," "2," "i," and "f," respectively, represent system 1, system 2, and the initial and final states.

Scenario 1, expansion into a vacuum, wherein the piston is massless, and system 2 is a vacuum. This first scenario is not particularly realistic, at least for us on the Earth. However, it is often used as teaching tool, and it might apply to work done in outer space.

Using Eq. (9), we could argue in terms of system 1: $d(P1V1) = 0$, $d\varepsilon 1 = 0$, thus, $dQ = 0$ and $W = 0$. However, this would not be the correct approach, because no work can be done onto a vacuum, i.e., work must involve the movement of mass against gravity!

Scenario 2, steam engine: System 1 is a steam engine with a massless piston, and system 2 is the surrounding Earth's atmosphere. Both systems start out at: T and P. As dQ enters system 1, water vaporizes, increasing its molecular volume, thus moving the piston hence performing work on system 2: $W(1 \rightarrow 2) = P1dV1 = P1Ady$, where A is the piston's surface area and dy is the piston's displacement. In order to push the piston, $P1 > P2$, however, the incremental pressure difference remains small, hence: $W(1 \rightarrow 2) = d(P1V1) \approx P1dV1$. Although empirically correct, it is not logically correct, because the work is done onto system 2!

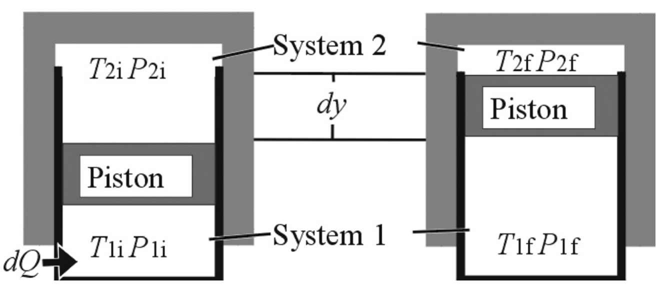

FIG. 1. It shows the initial (i) and final (f) states of system 1 displacing system 2.

Realizing that the result is the displacement of the Earth's atmosphere against gravity, a better way to write this is, $W(1 \rightarrow 2) = P2dV2$. Of course, writing it this way assumes that the atmosphere's volume is increasing, i.e., the newly created steam is part of the atmosphere. If we want to consider that the newly created steam is still part of system 1, then we would write $W(1 \rightarrow 2) = P2dV1$.

It is very important to realize that the Earth's atmosphere has mass, hence work is required to displace it against gravity ($\vec{g}$). And, since it takes work to displace the atmosphere, then energy (dQ) is required. Instead of being massless, now consider that the piston has mass (M) and the same initial conditions exist. The work required becomes $W = M\vec{g}dy + P2dV1$, hence a greater amount of energy would be required for the same volume increase.

Scenario 3, compressed gas: Piston is massless, system 1 is a tank of compressed ideal gas, and system 2 is the surrounding atmosphere. The reason that the compressed gas expands is that the mean molecular volume of gas is lower than in the surrounding atmosphere. Therefore, the flux of gas molecules hitting the piston in system 1 is higher than the flux hitting the piston in the opposite direction in system 2. Understandably, the piston moves because of the net effect of gas molecules passing their kinetic energy onto it.

Consider that the only work being done is the displacement of the atmosphere. As the compressed gas in system 1 expands, it performs work and cools. If the walls are not insulated, then the thermal radiation will pass from system 2, through the walls, back into system 1. Eventually, system 1 and system 2 will be at the same temperature and mean molecular volume. The only changes are being the upward displacement of the Earth's atmosphere and the transfer of heat into system 1. Since system 1 is so much smaller than the Earth's atmosphere, the heat transfer can go unnoticed causing some to conclude that the whole process was isothermal, when it really is not.

An analogy in terms of Eq. (3): When in its high-pressure state, it is as if system 1 was displaced in a gravitational field. That is, it is similar to the potential energy that one stores when they raise a mass, except reversed. Although fictitious, this analogy drives home the point that we are dealing with displacements against gravity.

A less awkward analogy: The compressed air acts like a compressed spring, retaining potential energy until that time when it can do work against the Earth's gravity. Moreover, this potential to do work is $W_{\text{pot}} = V1(P1 - P2)$. No matter how one views it, the act of compressing an ideal gas required work, resulting in a potential to do work.

Scenario 4, a lower pressure gas: Consider system 1 as an ideal gas whose pressure is lower than the surrounding atmosphere (system 2). Certainly, this low-pressure gas cannot perform work onto the atmosphere. Rather, if the massless piston was allowed to move, it would be the atmosphere that drives the piston into system 1. Even so, this too can move man and/or machine.

In order to form the low-pressure system 1, then work must have been done, resulting in the upward displacement of the Earth's atmosphere. That is, in order to lower the pressure within a hermetically sealed piston-cylinder, a force must be applied onto the piston, pulling the piston away from the cylinder's bottom. The work required to displace the atmosphere is $W_{done} = W_{pot} = P_{atm} dV1$. And this is then stored as a potential work in the atmosphere. If the expanding force is removed, then the atmosphere's pressure drives the piston back into the cylinder.

We can try to envision the work done in terms of system 1; however, one would need to circumnavigate $P1dV1 = -V1dP1$. Certainly, after the pressure reduction, in terms of system 1 $W_{done} = W_{pot} = V1(P2 - P1)$.

Scenario 5, heating of a gas: Consider system 1 as an ideal gas being heated. Since $T1\uparrow$ and $P1\uparrow$, the piston moves displacing the Earth's atmosphere (system 2). Lets consider the total kinetic energy (EkT) of a monatomic ideal gas,[1,3]

$$EkT = (3/2)NkT1 = (3/2)P1V1. \tag{10}$$

As dQ enters system 1, $EkT\uparrow$ and we write

$$dEkT = (3/2)NkdT1. \tag{11}$$

The work done is $W(1 \rightarrow 2) = P2dV1$, but this does not equate to Eq. (11). Seemingly, there is an inherent difference between an energy change of the gas and the work done by that gas. We will discuss this later on in Section X.

Scenario 6, steam engine inflating a massive balloon: Consider system 1 as a steam engine with a massless piston, and imagine that system 2 is the Earth's atmosphere surrounded by a rubber impermeable membrane.

Understandably, due to the tension of the rubber, the Earth's atmosphere experiences both pressure and volume increases, as the steam engine works. Therefore, $W(1 \rightarrow 2) = d(P2V2) \approx P2dV2 + V2dP2$. We can consider the actual work done as $P2dV2$, while $V2dP2$ is an increase of the potential to do work.

Scenario 7, heating a closed balloon: Consider system 1 as closed balloon being inflated by heat, which is surrounded by the Earth's atmosphere (system 2). In terms of the work required to inflate the balloon, $W = d(P1V1)$. How much of this work goes into the displacement of the Earth's atmosphere? The answer is $P2dV1$. We could also consider the work in terms of actual work done, plus, the potential to do work, and write $W \approx P2dV1 + V1dP1$.

We have just discussed seven scenarios, based upon Eq. (9). In scenario 1, we concluded that work involves the movement of mass against gravity ($M_{against\,\vec{g}}$). In scenario 2: We concluded that work often involves the upward displacement of the Earth's atmosphere and that it can be written in a couple of different ways. In scenario 3: We concluded that a pressure increase could be considered as an increase to the potential to do work. In scenario 4: We concluded that a pressure decrease could also be considered as a potential to work, albeit often an impractical way of storing work. In scenario 5: We concluded that there might be issues in comparing the energy required to heat a gas, to the ability of the gas to do work. In scenarios 6 and 7: We concluded that we should use Eq. (9).

The perspective presented herein considers that work involves the movement of mass against gravity ($M_{against\,\vec{g}}$), which differs from the traditional interpretation of work being done onto a system's walls.[1,3] We enhanced this by concluding that the displacement of the Earth's atmosphere requires work. This should not be revolutionary, since our atmosphere has weight! We shall certainly show throughout this paper that the concept of work required for atmosphere displacement can explain so much. Traditionalists might argue that we have proven nothing, and this author agrees. It will come down to the reader to decide which is simpler and can explain more.

This author believes that the traditional interpretation for unrealistic scenario 1 is as follows: Since $dQ = 0$, and $W = 0$, then by Eq. (1) $d\varepsilon 1 = 0$. In order to show that $W = 0$, the tradition rewrites Eq. (5) as $d\varepsilon 1 = T1dS1 - P1dV1$ and then considers $T1dS1 > 0$, thus, $P1dV1 > 0$. The point becomes that tradition uses a convoluted path of logic, which includes infinitesimal free expansion with a multitude of boundaries and a vacuum in between. Is it necessary? Certainly, if one wanted to simply explain it in terms of system 1, they could write $P1dV1 = -V1dP1$, but this defies Eq. (2). The simple answer is work involves: $M_{against\,\vec{g}}$.

How about the concept of isometric pressure increase being an increase in the potential to do work? Certainly, no physics text would even entertain such thought. It is interesting that Engineering thermodynamic texts[4] do consider isometric pressure increases, as part of the work in inflating balloons, but they do avoid stating Eq. (9).

III. WHERE TRADITION IS $W = d(PV)$

Example 1,"Throttling (or Joule–Thomson) process": Reif[1(pp. 178–179)] considers the work by an ideal gas flowing through a porous plug, in a pipe. He defines a mass of gas on the left hand side of the plug in terms of $p1V1$ and that same mass after passing through the porous plug in terms of $p2V2$. The work done is $W = p2V2 - p1V1$. Unwittingly, traditional thermodynamics is thinking in terms of Eq. (9), rather than Eq. (2).

Example 2, latent heat: In order to go from a liquid to a gaseous state, the latent heats of vaporization for an ideal gas is $W = PdV$. Interestingly, steam tables[7] give changes to the latent heat of vaporization for water, as a function of pressure. In accepting this, traditionalists remain oblivious to the reality that they are thinking,

$$W = d(PV) \approx PdV + VdP. \tag{12}$$

Of course tradition does not consider that the Earth's atmosphere is displaced by the vapors. Instead of a pot of water, consider that we boiled an ocean. Adding so many water vapor molecules into our atmosphere will increase its mass hence will increase both P_{atm} and V_{atm}. If both the volume and pressure increase, then we should apply Eq. (12). Traditionalist may enlist a cumbersome infinitesimal based argument of PdV, and then integrate, taking into account the fact that the pressure is increasing, as the ocean boils. Again we have two different perspectives giving the similar answers, so ask: Which is simpler? We can take this a step further and say that boiling a pot of water increases the mass of the atmosphere; therefore, an infinitesimally small pressure increase, thus $W = PdV$, is just an approximation for boiling processes.

For real substances, we need to have consider any changes to the bonding potential (dU),

$$W = dU + d(PV) \approx dU + PdV + VdP. \tag{13}$$

Traditionalists may not like Eq. (13). Mayhew,[7(p. 481)] using steam tables, showed that the changes in latent heat of vaporization of water with pressure can be explained in terms of changes to the bonding potential associated with a cloud of charged particles.

Embracing Eq. (13) allows us to deal with processes wherein both P and V change, i.e., nucleation. This author believes part of the proof lay in his paper on nucleation,[7(p. 488)] wherein it was shown using other's empirical data that Eq. (4) applies to bubble nucleation. Note: This data are illustrated in Fig. 14 of said paper[7] and is based upon laser-induced bubbles nucleated at various pressures, as performed by Wolfrum *et al.*[10]

IV. PERSPECTIVES

Traditionalists may say no way! Even so, perhaps they can accept that $W = PdV$ is based upon an isobaric perspective, i.e., 1 atm. Furthermore, when experiments and/or our machinery perform work at other pressures, we correlate it to work at 1 atm pressure. Think about it. Actual work done at some pressure other than 1 atm is still $W = PdV$. Now ask: Is this really not the same as writing $W = d(PV)$, and then taking the isobaric case at the other pressure?

Standing on the Earth, it is hard to realize that the work that we witness often involves in the displacement of our atmosphere. Interestingly, the man on the Moon, with all his precision, would see that the Earth's atmosphere's volume increased, yet, he would not realize the exact reason. Understandably, a person on the Earth, and the man on the Moon, may consider the same process in completely different terms, all due to their perspectives.

V. A DISCUSSION ABOUT: *W*, *T*, AND OUR UNIVERSE

Our traditional perspective is, in part, based upon what happens to a system's temperature, when work is done. That is, when an ideal system performs work, as defined by Eq. (2), then the temperature of that system decreases. The fact that mechanical work results in a temperature decrease seemingly solidifies the traditional stance.

However, if we define ideal work by Eq. (9) and consider the isobaric case, then nothing changes. Except for our new understanding that a system, which displaces our atmosphere, either experiences a temperature decrease or requires an input of energy.

What happens if we are dealing with an increase to the potential work? Isometric work is defined as $W = VdP$. When the pressure changes, systems tend to experience a temperature change. It is traditionally accepted that the temperature increases as a system's pressure increases, and this is often explained in terms of viscous dissipation, implying molecular friction.

In a truly natural system, when the pressure increases, the temperature follows suit. Is such a P–T relation also due to molecular friction? Or, should we simply associate it with the overlying weight? Why not consider the two explanations interrelated! Certainly, the deep interior of our Earth resembles a natural P–T system. What about our atmosphere?

Our atmosphere is not a simple P–T system, because the Sun's blackbody radiation maintains our atmosphere at an elevated temperature. The reason that this is not fully appreciated is that a system's temperature increase generally results in a net heat flow into the surrounding atmosphere, i.e., process being considered isothermal, when it really is not. Again, we have the issue of perspective, but this time in terms of temperature.

All this then raises question: Can we apply the gambit of thermodynamic relations empirically proven on the isobaric isothermal Earth, to our universe? We can, so long as we understand the relation's limitations. That is:

(1) Consider, our expanding universe. Certainly, the necessity of Fermi's assertion dissipates if we think in terms of either Eq. (9) or work involves: $M_{\text{against}}\,\vec{g}$.
(2) Consider the first and second laws, traditionally written in terms of PdV. Should they just apply to isobaric systems? Yes! Perhaps, this author was right in stating that a blackhole is nothing but an isometric horizon[7] into which matter and energy seemingly stream, in which case the elusive blackhole paradox[11] fades away.

Again nothing was proven! However, would not our universe simplify if we envisioned work in terms of Eq. (9)?

VI. JOULE'S EXPERIMENT AND INTERNAL ENERGY

A system's equation of state[1,4] is written as

$$TS = \varepsilon + PV. \tag{14}$$

Joule's experiment (1843) is illustrated in Fig. 2, wherein tanks A and B were submerged in a water bath and separated by a valve. Tank A was filled with high-pressure air (say 300 psi), while tank B was a vacuum.[4]

The temperature was measured, and then the valve was opened. While the pressure in the tanks equalized, the process was found to be isothermal. Joule rightfully concluded that neither the heat was transferred from the heat bath into the tanks nor was any work done. Although right, he was so for the wrong reasons. Joule was thinking in terms of

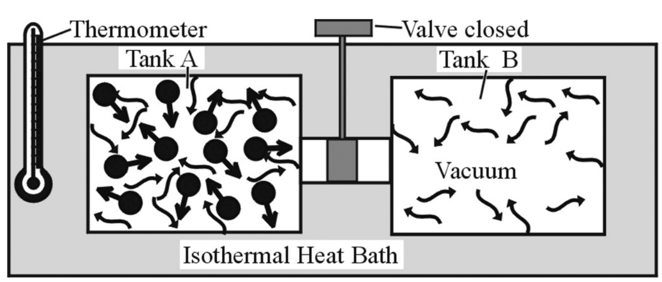

FIG. 2. It shows the Joule's experiment wherein tank A is separated from a vacuum, that being tank B by a valve, which is closed. The valve is then opened and the temperature is monitored.

Eqs. (1) and (2): $dQ = 0$ and $W = PdV = 0$, therefore $d\varepsilon = 0$. Joule then concluded that ε was neither a function of pressure nor volume, therefore it can only be a function of temperature[4] $\varepsilon = f(T)$. It seems so convoluted, when simplicity is $PdV = -VdP$. Furthermore, do Eqs. (1) and (2) not then imply that VdP is part of ε?

Again, if we realize that work involves: $M_{\text{against}}\,\vec{g}$, therefore, $W = 0$. Even if we wanted to think in terms of Eq. (9), then $W = 0$. Now what is ε in Eq. (14)? It becomes the bonding potential between the molecules. If that is the case, then what happens to the way we write the first law? Things will simplify if we drop Eq. (1) and state that the first law is simply about energy conservation.

VII. FREELY GIVEN ENERGY, *W*, AND THE SECOND LAW

Lambert[9] uses a version of Joule's experiment without the heat bath. After opening the valve, he claims, "there has been no change in the number of particles (or the temperature, or q)." Like others, he has casually forgotten that blackbody radiation resides in the tank B, both before, and after, the valve was opened. Moreover, this blackbody radiation represents an input of energy (dQ), albeit small! This is not Lambert's fault rather it illustrates a problem with the traditional interpretation!

Now consider an adiabatic variation of Joule's experiment, wherein the vacuum is also void of thermal radiation, i.e., at absolute zero. The heat bath is removed and two tanks are 100% insulated. If we could eliminate any energy contained within the walls then, when opening the valve, the temperature in tank A decreases, as the temperature in tank B increases! Since, the energy associated with blackbody radiation would be extremely small, the temperature change may be immeasurable. The point remains that a gas cannot isothermally attain an entropy/volume increase, without the addition of blackbody radiation. To this author, it remains strange that the second law is based upon calculating all the various infinitesimal energy states,[1] and yet we omit the addition of blackbody radiation, which is energy at that very level.

Since blackbody radiation is often freely given into an isothermally expanding system through that system's walls, it generally goes unnoticed in one's analysis. Our traditional preference is to say: given sufficient time the system will attain thermal equilibrium, i.e., a quasistatic process. In doing so, we are conveniently ignoring any flux of blackbody radiation, into/out of, that system.

The point becomes, in a laboratory we study thermodynamics in systems with walls, which enables thermal equilibrium to exist. Thermal equilibrium means more than mean molecular kinetic energy of the gas is related to the mean kinetic energy of the wall's molecules. It also means that the blackbody radiation surrounding those molecules is related to the wall's temperature. Questions arise as follows: Can we simply apply the second law, as witnessed here on the Earth onto our universe? Unless our universe expands isothermally, we cannot! Does thermal equilibrium always apply, without walls? Not necessarily!

There remains a bigger issue, that being the issue of work. What is seemingly lost in both Joule's and Lambert's, analyses is the fact that it took work to form the vacuum in the first place. If one accepts that vacuums do not occur spontaneously here on the Earth, then such second law arguments are inherently weak. The proper argument should be, potential to do work was stored in the atmosphere, as the vacuum was created. We then opened the valve between the gas and vacuum at which point the gas molecules disperse, while no actual work is done. If we end the process by opening a valve between the tank and the Earth's atmosphere, then gas molecules will stream into the low-pressure tank raising its pressure to 1 atm. Interestingly, now the tank has started and ended at 1 atm, with the same number of gas molecules occupying the same volume, all at the same temperature, therefore there was no entropy change!

Beyond querying our traditional logic, we have not resolved the issue of the applicability of the second law. We did show that our isothermal isobaric perspective might be problematic.

VIII. THE IDEAL GAS LAW

The ideal gas law is written[1,3,4] as

$$PV = NkT. \tag{15}$$

Consider the isothermal expansion of an ideal gas and any changes to the parameter relation (14). If an isothermally expanding gas experiences a molecular entropy increase, then, $dS > 0$ and $dT = 0$. Therefore, TS is increasing, which suits the second law. However, $PV = NkT =$ constant. Therefore, the implication is ε is increasing, but how? The point becomes that once more, a convoluted argument based upon infinitesimal change: $d\varepsilon = TdS - PdV$, will be required.

A simpler argument: $PdV = -VdP$ and $dT = 0$; therefore, the total kinetic energy of the gas remains constant, even though the gas has witnessed an increased volume. This confounds the accepted notions of entropy. However, it all makes sense when you realize that it takes work to expand the gas, simply because the gas must displace our atmosphere. Accordingly, there must be an influx of heat to keep the expanding system isothermal.

So what is the ideal gas law? If you are willing to think in terms of Eq. (9), then it signifies the ability of a gaseous system to do work, in relation to the system's temperature. Or, if you prefer it tells us much work was involved in forming a gas, whose temperature is T.

IX. ENERGY LOSS

Traditional thermodynamics emphasizes the isobaric, isothermal relation Eq. (5). This in turn has empowered entropy into a special status, as given by Eqs. (7) and (8), allowing the second law to even explain energy loss.[1,3,4]

Visualize an experiment wherein an isobaric gaseous system receives an influx of energy: dQ, thus allowing it to approximately expand isothermally. To the one performing the experiment, the volume increase means a system entropy increase. To the man on the Moon, the Earth's atmosphere has just experienced a volume increase. Again, ones version is perspective dependant!

Since the displacement of the Earth's atmosphere requires work, then the displaced atmospheric gases must experience a potential energy increase. Obviously, there is very little that the above expanding system can do to regain that work. This is no different than the work that you exert when lifting a rock. That energy is lost by you, and is passed onto the rock, as potential energy.

Is the above process reversible? Certainly not! Moreover, in this case, we do not have to employ a traditional argument based upon the system's constraints and accessible states,[1(p. 91)] to understand why this is so. Our explanation is as follows: The expanding system increases the Earth's atmosphere's potential energy. Accepting this explanation means entropy, and its accompanying second law, may become results, rather than reasons.

There is no denying that statistical arguments based upon Ludwig Boltzmann's brilliance, does enhance our understanding of thermodynamics. However, basing so much upon the second law, even when the definition of entropy remains so debatable, should have left room for doubt. Strangely it has not.

The above irreversible energy loss while displacing the Earth's atmosphere also helps explain the difference between isobaric and isometric specific heat,[1,3] that being $W_{atm} = P_{atm} dV_{atm}$, which also equates to the ideal gas constant (R) for a mol of gas molecules and seemingly confirms our new understanding of Eq. (15).

X. EFFICIENCY AND GLOBAL WARMING

Back in scenario 5 of Section II, we discussed that there are issues concerning work, and the change in kinetic energy of a gas, namely: Can all of kinetic energy change of a gas be transformed into work? Consider that we add dQ into a system of gas. The change in kinetic energy of gas is obtained by differentiating Eq. (10) with respect to T, giving Eq. (11). Similarly, the work done can be obtained by differentiating Eq. (15) with respect to T. In terms of efficiency (η),

$$\eta = W_{out}/dQ_{in} = NkdT/(3/2)NkdT = 2/3. \tag{16}$$

Based upon Eq. (16), the maximum efficiency that we can expect from certain gaseous powered systems/engines becomes 66.67%. This should not come as that much of a surprise. Specifically, if we start off with Eq. (10) and then reversed all those calculations used in the kinetic theory of gases,[1(pp. 262–282)] we would arrive at the work done in forming a gas that being PV. Similarly, if we asked how much energy is associated with an ideal monatomic gas defined by PV, our answer would be Eq. (10) and not Eq. (15).

In real life, friction, heat loss, etc. will reduce η. What about the cyclic nature of engines? Consider an engine that functions as a closed system, during the power and compression stroke, and as an open system in the other strokes. Since, the power stroke involves the expansion of a gas, it also represents the displacement of the Earth's atmosphere. Then logic dictates that for certain cyclic engines, another large loss in efficiency must occur.

Understandably, the inefficiency of cyclic engines contributes to global warming. Something not so apparent: During the compression stroke, the atmosphere will behave as if its volume decreases, thus, the potential energy of certain atmospheric molecules should be converted into kinetic energy. Accordingly, the temperature associated with those molecules should increase. Obviously, to what degree the cyclic nature of engines contributes to global warming may require consideration.

XI. A COMMENT ON TEMPERATURE

Traditionally, we omit the energy of the blackbody radiation that resides in the freespace between gas molecules and only consider temperature (T), in terms of the kinetic energy of matter.[1,3] Although the energy of radiation is generally infinitesimally small, we have seen that its omission can lead to misinterpretation. If we consider radiation, as part of the energy within a system, then we will have to reconsider whether a vacuum has a T. This author's preference would be as follows: If a thermometer measures a T, then that system has a T, irrelevant as to whether, or not, the system contains matter.

XII. CONCLUSIONS

Thermodynamics is a mature science. Even so, one cannot simply accept its postulates without continually questioning them. We discussed how our traditional interpretations of work, Joule's experiment, the ideal gas law, as well as both the first and second laws, may all be skewed due to our isobaric isothermal perspective.

The plausibility of work being $W = d(PV)$ was clearly demonstrated. We then emphasized that work involves the movement of mass against gravity. For us located on the isobaric Earth, this transforms the ideal case into $W_{atm} = P_{atm} dV_{atm}$, that being the work required to displace our atmosphere's weight. We also recognized that a gaseous system's potential to do work increases, with increasing pressure.

Indirect proof resides in the traditional treatment of latent heat of vaporization and Joule–Thomson throttling. Two direct empirical proofs reside in this author's paper on nucleation,[7] which sadly has not been embraced. Furthermore, the blackhole paradox and the issue of work in an expanding universe, both become explainable in simple terms.

It is accepted that here on the Earth, expanding systems tend to cool down, which can be explained in terms of work. The corollary is that the natural tendency of a system's temperature is to increase, with increasing pressure. Although not fully discussed herein, both the P–T and V–T, relationship can be correlated to the weight of the overlying atmosphere.

When systems expand, our displaced atmosphere experiences a potential energy increase; hence, energy becomes irretrievably lost by the expanding system. Herein, lay the foundation for a simple explanation for such energy loss, which does not necessitate the consideration of the second law. Furthermore, this improves our lucidity as to why engines have such poor efficiencies. We also realized that only 2/3 of the kinetic energy change of a gas can be used for work, which sets a baseline for most engine efficiencies.

We also discussed that cyclic engines may contribute to global warming in ways not previously envisioned.

This new perspective would be equally capable of explaining the same empirical data that traditional thermodynamics does. If nothing else, we enhanced the notion that empirical data can disprove a theory but does not necessarily prove any one theory.

Somebody told me that if I want to shake the foundations of thermodynamics, then I must find something simple and unquestionable that does so. Sadly, all we accomplished was to show that another perspective exists, albeit, one that is both simpler and readily dissipates certain conundrums.

ACKNOWLEDGMENTS

I want to thank the referee for his comments. I also want to extend a belated thanks to Bonnie Bonaventura, who helped me with my first paper.[7] Also thanks go to Frank Lambert and Alex Driega, who were participants in certain correspondence.

[1]F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965).
[2]D. E. Tilley, *Contemporary College Physics* (Benjamin/Cummings Publishing, Don Mills, Ontario, 1979).
[3]F. Reif, *Statistical Physics* (McGraw-Hill, New York, 1967).
[4]K. C. Rolle, *Thermodynamics and Heat Power*, 4th ed. (Maxwell Macmillan, Toronto, Canada, 1994).
[5]R. A. Alpher and R. C. Herman, *Genesis of the Big Bang* (Oxford University Press, United Kingdom, 2001).
[6]K. Mayhew, Phys. Essays **19**, 577 (2006).
[7]K. Mayhew, Phys. Essays **17**, 476 (2004).
[8]V. Nikulov and D. P. Sheehan, Entropy **6**, 1 (2004).
[9]F. L. Lambert, J. Chem. Educ. **79**, 187 (2002).
[10]B. Wolfrum, T. Kurz, O. Lindau, and W. Lauterborn, Phys. Rev. E **64**, 046306 (2001).
[11]D. Sheehan, J. Sci. Explor. **12**, 303 (1998).