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A New Thermodynamics

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Abstract

Accepting that expanding systems must upwardly displace Earth's atmosphere's weight, and that this signifies lost work, renders most useful processes irreversible. This simple realization has not been properly addressed in thermodynamics, allowing ill-conceived second law based explanations to prevail. We will discuss how this mistake originates with Clausius' theorem, and continues with Boltzmann's entropy. We will discuss why we can never extract systems as much work from a system as the thermal energy that we put in. Then we will discuss why the traditional treatment of partial differentials remains so troublesome, and then provide a simpler understanding of free energies, which will lend itself to a better possible interpretation of entropy, one that removes our reliance on the second law. Ultimately, thermodynamics could be a simple constructive science. Our new interpretations may also have ramifications to our consideration of global warming.

A: Introduction

Have you ever asked, why is thermodynamics so complicated? How about visualizing free energy, whether it be Helmholtz or Gibbs, the shuffling of all those differentials sure do not make it simple. In this paper we shall examine why this is, seeking out the possibility of simplifying the science. As an accepted mature science, few dare question thermodynamics' underlying fundamental principles, as we shall do.

Before we do consider. If you were analyzing expanding systems at the bottom of the ocean, you would have to consider any work that is required to displace the water's weight. So why is it that the Earth's atmosphere's weight is not taken into proper consideration in thermodynamics, when considering expanding systems here on Earth?

Terms like entropy (S) remain unchallenged although its true interpretation lacks clarity. In the 19th century, Rudolf Clausius realized that entropy multiplied by temperature (T) equated to energy, although the exact correlation remained vague. Throughout the 20th century, Boltzmann's entropy's (S) was considered to represent a system's disorder all based upon the total number of system microstates (!) and Boltzmann's constant (k), i.e.[1,2]:

$$S = k\ln! \qquad (1)$$

That led to the simple accepted relationship for entropy increase (!S) in terms of a volume increase i.e. if V_f is the final volume while V_i is the initial volume then [3,4,5]: !

$$S = k\ln(V_f/V_i) \qquad (2)$$

Ben Naim [4,5] rightfully questions our understanding of randomness, pointing out that its interpretation rests in the eyes of the beholder, hence has little actual scientific merit. Mayhew[3] has taken this a step further claiming that entropy may be nothing more than a mathematical contrivance. Although this explains entropy's befuddling lack of clarity, such degradation is not to be taken lightly.

Mayhew's realized that lost work (W_{lost}) by useful expanding systems can be explained in terms of the upward displacement of our atmosphere's weight during a system's isobaric expansion[3,6,7]. By weight we mean the atmosphere's mass in a gravitational field. Let subscript "atm" signify our atmosphere, then the work lost through an expanding system's walls, into Earth's atmosphere is:

$$W_{lost} = P_{atm}dV \qquad (3)$$

The above requires the acceptance that the Earth and its surrounding atmosphere is an open system constrained by gravity. Certainly a subsystem's expansion within such an open system may initially result in localized pressure increase, but mechanical equilibrium between the atmosphere's gaseous molecules will only allow for one result that being the isobaric displacement/expansion of the Earth's atmosphere, as defined by equation (3). In this notation "dV " is the expanding system's volume increase[3,6,7].

The reason the work is lost is because it is impossible to harness the potential energy increase associated with any elevation increase of Earth's atmosphere's molecules[3,6,7]. This certainly differs from the elevation of condensed matter, i.e. a rock, wherein the work results in a potential energy increase, which can be harnessed. Accepting that useful processes power man and/or machine, and that such processes tend to experience system expansion, we now understand why useful processes tend to be irreversible[6,7]. This in part explains the low efficiencies experienced by a long list of devices e.g. steam engines. This overlooked fundamental understanding puts sense into what is often referred to as non-sensible energy loses.

Clearly 3) does not explain all lost energies by systems, as defined in Clausius' theorem:

$$\oint (dQ/T) \ ! \ 0 \qquad (4)$$

Other factors like friction, shock waves in fluids, electrical resistance, inelastic deformation, internal damping, etc all can led to inefficiencies, hence energy losses in

processes, hence irreversibility[7,8]. To further complicate matters, Mayhew[7,8] points out that based on kinetic theory, the kinetic energy of an N molecule gas is $3NkT/2$, while the ability of that gas to do work is based upon the ideal gas law ($PV = NkT$) thus is only

NkT. Seemingly, only 2/3 of the energy that we put into an expanding system, such as a piston-cylinder apparatus, can actually be used for work. In this paper we will further examine this inherent inefficiency along with our new understanding of lost work.

This basic, inarguable, correlation between gravity, mass, and potential energy rattles the foundations of thermodynamics. Even so, there remains steadfast individuals who cannot see how equation (3) renders logarithmic functionality as witnessed by equations (1) and/or (2). Accordingly, a goal of this paper is to show how lost work renders logarithmic functionality. More importantly this paper will examine fundamental thermodynamic principles, demonstrating other traditional erroneous logic.

B: Fundamental principles

The first law states that when thermal energy (Q) is provided to a system, then this must equal the total energy change of that system ($!E_{tot}$) plus any work done (W) by that system [1,2]:

$$Q = !E_{tot} + W \tag{5}$$

In terms of an infinitesimal process, equation (5) can be written as:

$$dQ = dE_{tot} + dW \tag{6}$$

For the traditional case of isobaric work wherein volume is the only parameter of relevance then equation (6) becomes:

$$dQ = dE_{tot} + PdV \qquad \text{`} \tag{7}$$
$$dQ = dE_{tot} + P_{atm}dV \qquad \text{`} \tag{7a}$$

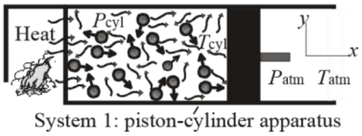
Traditionally equation (7) is used, which fails to give clarity. Certainly in order for isobaric expansion the pressure in the system must be taken to be greater than that of the atmosphere, but for such an isobaric process it is taken to be infinitesimally greater i.e.

P ! P_{atm} hence equations (7) and (7a) are equal. Accordingly, we are concerned with the work lost onto the surrounding atmosphere ($p_{atm}dV$).

If the thermal energy also moves man/machine ($W_{machine}$), as well as overcomes friction ($W_{friction}$) then:

$$dQ = dE_{tot} + P_{atm}dV + W_{machine} + W_{friction} \qquad (8)$$

C: Heating a piston-cylinder



System 1: piston-cylinder apparatus

Fig. I Shows a locked piston-cylinder filled with N gaseous molecules being heated, i.e.: $T_{cyl} > T_{atm}$, $P_{cyl} > P_{atm}$.

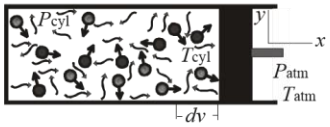


Fig. II Shows the unlocked piston -cylinder expanding, hence doing work, hence cooling, i.e.: $T_{cyl} > T_{atm}$, $P_{cyl} = P_{atm}$.

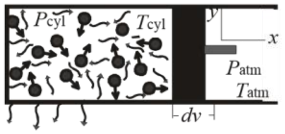


Fig. III Shows the unlocked piston-cylinder returning to its original volume as it continues to cool down, i.e.: $T_{cyl} = T_{atm}$, $P_{cyl} = P_{atm}$.

Consider the heating of a closed piston-cylinder apparatus filled with N gaseous molecules, as illustrated in Fig. I. If the piston is locked in position and thermal energy

(dQ) is added, then based upon kinetic theory:

$$dQ = 3NkdT/2 \qquad (9)$$

As the gas' temperature increases, its the kinetic energy increases, hence its pressure increases i.e. $P_{cly} > P_{atm}$. Similarly this increases the gas' ability to do work ($dW_{ability}$):

$$dW_{ability} = NkdT \qquad (10)$$

Equation (10) will be new to most indoctrinated in traditional thermodynamics, however our recent realization concerning lost work means that we have to rethink, and herein we have begun that process. We will reconsider equation (10) in the next section

Why is the increase in the ability to do work, not equal to the gas' kinetic energy increase? This is synonymous to asking why, when a gas' temperature changes its kinetic energy change does not equate to changes of the ideal gas law. This analysis can be deduced by reverse engineering of kinetic theory[7]. It is actually a result of the fact that not all gaseous molecule's momentum in a system can contribute to work by that system.

For the piston-cylinder, gas molecules with no components of motion along the *x*-axis, cannot contribute momentum onto the piston's motion along that axis. Accordingly, the total ability to do work is considered as a maximum ability of a gaseous system to do work. Similarly, change to the ability to do work is considered as the maximum change to that ability.

Assume, $W_{machine} = W_{friction} = 0$. When the piston is unlocked, it can fully expand (Fig. II). Since only some molecule's momentum can actually contribute to the piston's motion, the upper limit for work done in displacing our atmosphere will be 66.667% of dQ, i.e.:

$$W_{done} = P_{atm}dV = NkdT \qquad (11)$$

As the gas within the piston-cylinder does work, it cools down until the gas' pressure within the piston cylinder equals the surrounding atmospheric pressure ($P_{cly} = P_{atm}$). At this point the minimal increase of thermal energy within the system should be:

$$dE_{tot} = NkdT/2 \qquad (12)$$

If the heat source is removed and the piston's walls are not insulated, then heat will escape. Eventually the pressure inside the piston-cylinder will be less than the atmospheric ($P_{cly} < P_{atm}$) causing the piston to return to its initial position ($P_{cly} = P_{atm}$), as illustrated in Fig. III. At which point the energy increase as defined by equation (12) will have radiated out through the piston-cylinder's walls.

Next consider, the heat source remains and the piston's walls are fully insulated. Herein the system is isobaric as the piston moves quasi-statically outward. Now the total change in thermal energy is the energy required to heat the gas as defined by equation (9) plus the work done, as defined by equation (11). That being:

$$dQ = dE_{tot} = 3NkdT/2 + NkdT = 5NkdT/2 \qquad (13)$$

Equation (13) is the isobaric case for a temperature increase of dT. Comparing the work done in the isometric case that being equation (9), to the work done in equation (13) for the same temperature increase, we see that:

$$(5NkdT/2)/(3NkdT/2) = 1.667 \qquad (14)$$

This is exactly the value one obtains for the ratio of isobaric (C_p) to isometric (C_v) heat capacities of ideal gases. Examples: $C_p/C_v = 1.667$ for helium, neon, argon etc. Obviously, for ideal monatomic gases the explanation given herein is an exact fit to empirical data. However, for polyatomic gases there will be energies associated with the intermolecular vibrations, hence the work out will be significantly less. Or if one prefers, the efficiency of the system will decline.

D: Deriving equation (10) and ability to do work

Equation (10) can be obtained by differentiating the ideal gas law ($PV = NkT$):

$$d(PV) = NkdT \qquad (15)$$

Herein equation (15) becomes the change to a system's ability to do work[3,6,7]. Now taking the isobaric ($dP = 0$) result and equating it to the work that is done:

$$W_{atm} = PdV = NkdT \qquad (16)$$

The following isometric ($dV = 0$) result is taken to be an increase in work potential (W_{pot})3,6,7.

$$W_{pot} = VdP = NkdT \qquad (17)$$

Pressure increases are not limited to temperature increases. Mass transfer of a gas into an isometric system will also result in a potential to do work increase, i.e:

$$W_{pot} = VdP \qquad (18)$$

Mayhew[7] considers equations (17) and (18) to be the potential to do work. Although, deemed novel, this should be a fundamental building block because it puts the internal parameters pressure (P) and volume (V) on an equal footing. If a closed high-pressure system of gas expands, then the Earth's atmosphere would be upwardly displaced and any previously gained potential to do work would become lost work. Equations (3) and

(18) are respectively ideal isobaric and ideal isometric solutions.

E: High pressure expansion

Consider a closed high-pressure gaseous system that is at the same temperature as its surroundings, whose pressure drops as its volume increases. Based upon the ideal gas law, pressure multiplied by volume equals a constant (*C*), i.e.

$$PV = C = NkT \qquad (19)$$

Therefore we can write:

$$P = C/V \qquad (20)$$

Let the subscripts "*f*" and "*i*" respectively represent the system's final, and initial, states. If we let the system expand quasi-statically then the total work lost is defined by the integration of infinitesimal work (dw), i.e.:

$$W_{lost} = \int dw = \int_{V_i}^{V_f} Pdv \qquad (21)$$

Work now takes the more general form that being the summation of all the work associated with each infinitesimal volume change. Substituting equation (20) into equation (21), gives:

$$W_{lost} = \int dw = C\int_{V_i}^{V_f} dv/V \qquad (22)$$

Performing the integration we obtain:

$$W_{lost} = C\ln(V_f/V_i) \qquad (23)$$

Substituting for C:

$$W_{lost} = (NkT)In(V_f/V_i) \qquad (24)$$

Equation (24) clearly shows how the natural logarithmic function comes into play when a high-pressure gaseous system is doing work wherein its pressure decreases as its volume increases, in an isothermal process. Certainly this has numerous applications. More importantly this bodes the question; is entropy as defined by equation (1), and/or entropy change as defined by equation (2), absolutely necessary for us to understand thermodynamic relations? At this point the answer is now no!

Furthermore, equation (24) is not the only solution. We could have equally written:

$$W = !dw = {}_{P}{}^{P}!{}_{1}{}^{1}V_{i_f}{}_{1}dp_1 \qquad (25)$$

Performing similar substitutions and calculations, we obtain:

$$W = (NkT)\ln(P_i / P_f) \qquad (26)$$

Such that:

$$(NkT)In(P_i / P_f) = (NkT)In(V_f / V_i) \qquad (27)$$

For ideal gases equations (24) and (26) are interchangeable, which also bodes the question; was the choice simply arbitrary? No matter which solution one prefers, the above applies to many high-pressure applications including explosions and reactions in physical chemistry.

F: Freely given energy and quasi-static expansion

In the previous example, the system expanded quasi-statically, thus allowing the system to remain isothermal, as it performed work onto its surrounding atmosphere. Did it experience a significant energy change during its expansion? Since both the number of molecules, and temperature remained constant throughout expansion, then based upon kinetic theory the gas' total energy (E_{tot}) remained constant, i.e.:

$$E_{tot} = 3NkT/2 = \text{constant} \quad (28)$$

How can this be? If the above expanding closed system is doing work, then logic dictates that its temperature should decrease. Quasi-static expansion allowed for thermal energy to pass through the system's walls, thus maintaining temperature equilibrium between the expanding system, and its surrounding Earth's atmosphere. Herein, the thermal energy actually must equal the atmosphere's potential energy increase, i.e. work done.

Often energy exchanges between systems and surroundings goes unnoticed, hence we shall refer to this as "freely given energy". This most often happens when its surrounding is a heat bath, or a system that acts as one i.e. Earth's atmosphere, oceans and or planet.

Consider a rapidly expanding high-pressure system wherein its temperature decreases, as it expands. Now, we cannot simply use equation (22) to calculate the lost work during the expansion, because equation (22) is limited to isothermal processes. However, if the expanding system is not 100% insulated, and one waits long enough for temperature equilibrium to be re-attained, then (equation 22) would again define the work done.

Again isothermal entropy based arguments were not needed. Depending upon their distribution, at any given instant one could argue that the molecules randomness has increased during the system's expansion. But this is nothing more than a result of the system's mean molecular volume increase.

Herein an entropy change as defined by equation (2) was simply a result, and not the reason for lost work. Something traditional thermodynamics wrongly implies.

We now see how freely given energy often influences our understanding. By limiting to quasi-static processes[1,2], systems can remain in thermal equilibrium. Although this helps traditionally accepted relations correspond to what we witness in isothermal processes, it also has reinforced traditional misconceptions.

G: An example of the traditional mistake

The traditional consideration of equations 6) and 7) has put us into a falsified theoretical corner, wherein work is limited to isobaric volume increases. Certainly the vast majority of work, as witnessed on isobaric Earth's surface, can be classified as such, but this is not always the case, so why allow the theoretical corner?

This has been previously discussed but is given herein demonstrating how traditional thermodynamics has missed the mark. Consider that the work required for nucleation (W_n), as traditionally defined by Gibb's nucleation equation[9,10,11]:

$$W_n = A! + VdP \qquad (29)$$

Equation (29) wrongly defines work for all nucleation processes in terms of isometric pressure change, surface area (*A*) and surface tension (!). It is interesting that work is even herein considered in terms of isometric pressure change (*VdP*). Based upon equation (29) the work/energy required for nucleation could not be explained[9]. Only the energy required for globule nucleation[9] is actually defined by equation (29), e.g. an isometric process where an immiscible liquid globule nucleates within a surrounding liquid[9] For example Wolfrum et al[12] admitted that traditional theory could not explain their experimental findings for laser induced bubble nucleation.

Bubble nucleation is a process wherein both the pressure and volume increase plus there is an internal energy change (*d*!) i.e. the energy required to form the tensile layer (*A*!).

As pointed out by Mayhew the work must be defined by[3,9,11]:

$$W = d! + d(PV) \text{ " } A\# + PdV + VdP \qquad (30)$$

Using equation (30) Mayhew was able to match theory with data[9,11].

Part of the problem was a poor translation from Gibbs 350 page paper into his 50 page treatise[9], which is published in the same book[12]. But the issue goes deeper than this. It has to do with our indoctrination of equation (7) and the false limitations we traditionally put upon work.

H: Traditional analysis revisited

Before we can fully apply our new simpler consideration of thermodynamics, we must take a step back and reconsider traditional analysis, wherein one generally starts with the following isothermal ($dT = 0$), and isobaric ($dP = 0$) relation:

$$TdS = d! + PdV \tag{31}$$

where ! the system's internal energy.

Equation (31), can be rewritten as[1,2,7]:

$$d! = TdS \text{ " } PdV \tag{32}$$

Realizing that for infinitesimal changes:

$$PdV \text{ ! } d(PV) \text{ " } VdP \tag{33}$$

Traditionally equations (32) and (33) are combined, to obtain[1,2,7]:

$$d! = TdS \text{ " } d(PV) + VdP \tag{34}$$

Collecting the terms one obtains[1,2,7]:

$$d(! + PV) = TdS + VdP \tag{35}$$

Traditionally "enthalpy (H)" is defined as'[1,2,7]:

$$H = ! + PV \tag{36}$$

Differentiating equation (36), gives the "enthalpy relation" [1,2,7]:

Combine equations (35) and (36):

$$dH = TdS + VdP \tag{37}$$

Traditional analysis started with a part PdV , from which the whole $d(PV)$ was then subtracted, thus obtaining the other part VdP.

Some issues. Firstly, everywhere else in the world of differential equations, logical dictates that one starts with the whole $d(PV)$, and then deduce the various parts i.e.

PdV & VdP.

Secondly, the only reason equation (31) holds such relevance is that 19th century science wrongly limited work to isobaric processes due to lost work ($P_{atm}dV$) by idealized heat engines.

Thirdly, every time you shuffle these differentials we are simply either moving an ability to do work [$d(PV)$], or a potential to do work (VdP), or work that is done (PdV), without any defined reasoning, except to obtain a desired result.

Fourthly, we now have entropy multiplied by temperature (ST) related the ability to do work, when previously (Clausius theorem) entropy multiplied by temperature (ST) was related to a system's energy. This would be fine if the ability to do work always equated to a system's energy, but due to inherent inefficiencies it does not, all because a gaseous system can never turn 100% of the gas' momentum into work!

Clausius' acceptance that ST defines energy, all combined with the fact that a heat engine could not return to its original state without an influx of energy lead to Clausius' theorem

followed by Lord Kelvin's interpretation, which became the second law of thermodynamics. Seemingly, our 19th century greats had put the cart before the horse, so to speak.

Instead of equation (31), consider that we start with the whole, i.e.:

$$ST = ! + PV \qquad (38)$$

Certainly equation (38) can be simply obtained by the integration of equation (31). For change we differentiate equation (38), thus obtaining:

$$d(ST) = d! + d(PV) \qquad (39)$$

Infinitesimally small changes can be approximated by:

$$SdT + TdS = d! + PdV + VdP \qquad (40)$$

For isothermal ($dT = 0$), isobaric ($dP = 0$) processes we again obtain equation (31).

More issues. Firstly, equation (31) wrongly gives volume a preferential status over the parameter pressure. Secondly, along with the second law, it wrongly allowed Boltzmann's entropy to take hold, enshrining the misconstrued relationship between randomness and energy, thus giving entropy an unwarranted elevated status throughout the 20th and well into the 21st century. Obviously, the science just snowballed unfettered from here being applied to all realms[3,6,7,9].

Problems with equation (31) extend beyond nucleation. Consider an expanding system that does work by upwardly displacing its surrounding's mass against gravity. Unless an external source of energy enters the expanding system, then it must cool, which confounds the concept of isothermal work. Such arguments are not meant to expunge equations (31) through (37), rather they provide an enlightened context, as to their validity, and how freely given energy during quasi-statistic expansion may have blinded us of certain realities.

Certainly anyone indoctrinated in the science is going have reservations concerning the simplification discussed herein. So let us examine free energy.

I. Free energy

Free energy is the energy that is available from a system, to do work. We begin with a pragmatic approach for free energy.

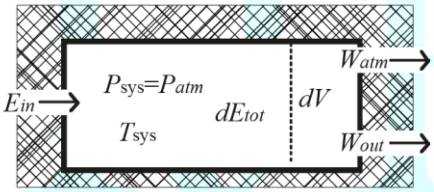
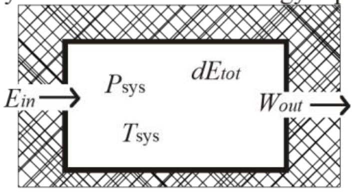


Fig. V Shows an insulated isobaric system with a thermal energy input (E_{in})



I

Fig. IV Shows an insulated isomet

T_{atm}

system with a thermal energy
input (E_{in}) and work output
(W_{out})
and a work output (W_{out})

Fig. IV shows an input of thermal energy (E_{in}) into an insulated isometric system.

Consider that no work goes out, i.e.$W_{out} = 0$. The increase in the system's total energy (dE_{tot}) can be defined in terms of its isometric heat capacity (C_v) multiplied by the temperature change (dT) for n moles, i.e.:

$$E_{in} = dE_{tot} = nC_v dT \qquad (41)$$

Imagine that the system, now experiences isobaric expansion as shown in Fig. V. Work done to the Earth's atmosphere is $W_{atm} = P_{atm}dV$. Consider that no other work is done, i.e. $W_{out} = 0$. Now the energy input (E_{in}) must equal the increase to the system's thermal energy plus any work done onto Earth's atmosphere. Therefore:

$$E_{in} = dE_{tot} + P_{atm}dV \qquad (42)$$

Which can be rewritten in terms of heat capacity and internal temperature change as:

$$E_{in} = nC_v dT + P_{atm}dV \qquad (43)$$

If the energy input is the same, then temperature increase in the isometric system (equation 41) must be greater than it is for the isobaric system (equation 43).

Consider that we are extracting work out (W_{out}) of the isometric system shown in Fig. IV. Assuming 100% efficiency, then the maximum amount of work that can be extracted from such an isometric system is:

$$W_{out} = E_{in} - nC_v dT \qquad (44)$$

Next consider, that we are extracting work out (W_{out}) of an isobaric system, as shown in Fig.V. Assuming 100% efficiency, then the maximum amount of work that can be extracted from such an isometric system is:

$$W_{out} = E_{in} - nC_v dT - P_{atm} dV \qquad (45)$$

Obviously, the isobaric free energy involves the displacement of our atmosphere, while the isometric free energy does not.

J: Isobaric versus isometric heat capacity

Let us investigate. The molar isobaric heat capacity (C_p) and isometric heat capacities (C_v) are related by the ideal gas constant (R)[1,2].

$$C_p - C_v = R \qquad (46)$$

Accepting this author's assertion[7] that the ability to do work is defined by the ideal gas law, $W_{ability} = PV = NkT = nRT$. We can now consider the ideal gas constant (R) as the molar ability of a gas to do work per degree Kelvin. Differentiating the ideal gas law for an isobaric process doing work, we obtain:

$$PdV = nRdT \qquad (47)$$

Realizing that the work is done onto Earth's atmosphere and substituting equation (46) into (47), we obtain:

$$n(C_p - C_v)dT = P_{atm}dV \qquad (48)$$

Therefore we can write:

$$C_p - C_v = P_{atm}dV / ndT \qquad (49)$$

Equation (49) is another way of envisioning the differences between isobaric and isometric heat capacities. In terms of lost work done in a process we could write:

$$n(C_p - C_v)dT = W_{lost} \qquad (50)$$

In the previous section, when dealing with the work that we can extract out of an isobaric expanding system, we can now rewrite equation (45) as:

$$W_{out} = E_{in} - nC_pdT \qquad (51)$$

K: Helmholtz free energy

The equation for changes to Helmholtz free energy (dF) for chemical reactions is written in terms of chemical potential change (dU), entropy change (dS) and work (PdV). It is traditionally derived through a prolonged cumbersome shuffling of differentials, making the logic rather hard follow. This shuffling can be found in many texts[1,2] arriving at:

$$dF = d(U - TS) = dU - SdT - pdV \qquad (52)$$

Assume that a chemical reaction releases thermal energy. Compare equations (45) and (52). Realizing that for a chemical reaction giving energy into a system, we can write:$dF = W_{out}$, $dU = E_{in}$, $P_{atm}dV = pdV$. We are left with the question. Is entropy (S) simply equated to the isometric heat capacity (C_v)? As likely as this may seem the reality is this. Only monatomic gases have their heat capacity constant throughout all temperature regimes. Combine this with the previously discussed upper limit for work out efficiency of a monatomic gas is 66.67%. For the case of polyatomic gases the system's energy is not entirely kinetic, hence the system's work efficiency diminishes. This is mainly due to vibrational energies within polyatomic gases. So is the answer limited to monatomic gases?

Before we try to answer, let us compare the measurement of entropy to specific heat. The fundamental equations for measurement are[1,2,13]:

$$dS = dQ/T \qquad (53)$$

$$C_y = (dQ/dT) \quad (54)$$

"The absolute entropy of any substance can be calculated using equation" (53) "in the following way. Imagine cooling the substance to absolute zero and forming a perfect crystal (no holes, all the atoms in their exact place in the crystal lattice). Since there is no disorder in this state, the entropy can be defined as zero. Now start introducing small amounts of heat and measuring the temperature change. Even though equation” (53) “only works when the temperature is constant, it is approximately correct when the temperature change is small. Then you can use equation” (53) “to calculate the entropy changes. Continue this process until you reach the temperature for which you want to know the entropy of a substance (25 ºC is a common temperature for reporting the entropy of a substance).” [13]

Certainly the logic of adding thermal energy and having the process remain isothermal is questionable at best. Even so, entropy as defined in equation (53) is really not all that different than specific heat capacity, as defined in (54). However, the isometric molar specific heat of a monatomic gas is accepted as being: C_v=12.5 (J/K), while the published values for entropy of helium and neon are respectively[14], 126.04 and 146.23 [J/(mol.K)].

So even for our high efficiency monatomic gas, equate entropy to specific heat.

Perhaps the issue lay in the fact that entropy of monatomic gases is based upon the Sackur-Tetrode equation, that being[15]:

$$S = kN(\ln[(V/N)(4!mU/3h^2N)^{3/2}] + 5/2 \qquad (55)$$

The fact that there is a lack of correlation between molar heat capacity and accepted entropy does leave us with a conundrum. Yet it should not deter us from our simple analysis. Understandably the most efficient gases for performing work are monatomic. Polyatomic gases cannot perform work with the same efficiency due vibrational energies lowering their efficiency.

If entropy was measured in Helmholtz free energy type experiments, then one might give entropy the definition heat capacity in process that is not a 100% efficient i.e. entropy becomes some sort of heat capacity for inefficiency! The reality is that this may just complicate the issue, as entropy already has too many variations of interpretation as it is.

L: Enthalpy

The enthalpy of a chemical reaction is defined as:

$$H = U + PV \qquad (56)$$

Consider the enthalpy of vaporization, A.K.A. latent heat of vaporization. For open systems, work is done onto Earth’s atmosphere as defined by the isobaric differential for equation (56):

$$dH = dU + P_{atm}dV \qquad (57)$$

It should be stated that lost work ($P_{atm}dV$) is often called non-sensible energy that is lost during vaporization. Although our understanding of work being done onto the atmosphere brings clarity to latent heat of vaporization, it does not alter our expected empirical findings. However, the fact that during vaporization the lost work is into the surrounding atmosphere means that this work cannot magically return during condensation. Accordingly, the magnitude of the latent heat of vaporization ($L_{(l\,!\,g)}$),

cannot equal to magnitude of the latent of condensation ($L_{(g\,!\,l)}$).[7]

$$L_{(l\,!\,g)} = N(u_g \,\text{"}\, u_l + P_{atm}dv) \qquad (58)$$

$$L_{(g\,!\,l)} = \text{"}N(u_g \,\text{"}\, u_l) = \mathrm{N}(u_l \,\text{"}\, u_g) \qquad (59)$$

Where: u_l = bonding energy per molecule in a liquid state, u_g = bonding energy per molecule in the gaseous state, N = number of molecules changing states

M: Gibbs free energy

Consider Gibbs free energy. Like Helmholtz free energy, it was derived through a cumbersome shuffling of differentials as can be found in numerous texts[1,2]. Changes to Gibbs free energy (dG) is traditionally written[1,2].

$$dG = dU + VdP \;!\; SdT \qquad (60)$$

If I were to say that equation (60) is basically the isometric case depicted in Fig. IV, it would come as a shock to most. Consider that $dU + VdP$ is the isometric differential of enthalpy [equation (56)]. Herein VdP is the increase in potential to do work, which occurs when we increase the pressure within an isometric system [equation (18)].

Again we are left with the question of is entropy in equation (60) related to heat capacity. Seemingly, entropy in isometric Gibbs free energy relates heat capacity in a similar manner as it did in isobaric Helmholtz free energy. Thermodynamics would become simpler if entropy equated to heat capacity but strangely it does not. And of course the fact that entropy lacks clarity, does not remedy the situation in the least.

N: Discussion

Obviously, the 19th century greats were not thinking in terms of heat capacity and simple efficiency. Perhaps they convinced themselves that the entropy change was somehow responsible for the differences between Helmholtz and Gibbs free energies. And this allowed the thermodynamics to become the complication that it is. Of course

Boltzmann’s assertions just solidified the complication.

The fact that statistical mechanics, is accepted as an inarguable proof behind traditional thermodynamics, may speak more of the power of statistics than of anything else. Boltzmann’s entropy is now in question as his consideration of randomness explaining lost work lacks merit. Even so his brilliant probability based mathematics remains great at giving results, just not so much reasons. Consider the dealing of cards, the reason remains the dealing, the results are given by probabilities.

This all makes one ponder, “have we been asking the right questions concerning thermodynamics?” This author’s book[7] is far from perfect and will be rewritten shortly based upon the contents herein and hopefully the help of others. It does serve as a possible start for a future pandect for simplifying thermodynamics, which can only become complete once other like thinking individuals' input is obtained. It certainly does prove that more than one theory can explain empirical results, as is witnessed herein.

You might be wondering why I wrote dE_{tot} in equation (6) and $d!$ in equation (31). The reason being is in my writings things became more understandable if I let ! be all the energy's in a system other than the mechanical energy e.g. pressure-volume (PV). In equation (31), ! is written in its more traditional context. I apologize but sometimes we must take numerous steps backwards, before we can actually move forwards.

O: Reconsidering entropy

Whatever its definition becomes, we now see that entropy is not a reason for lost work. Obviously, Clausius' theorem and all that followed are misconceptions based upon the

need to explain the fundamentals of lost work[5,6,7]. This bodes well with entropy being an ill conceived mathematical contrivance[6,7], which certainly does explain Von Newmann's assertion that "no one knows what entropy really is "[5].

Consider, Arthur Eddington's words[16]: "*The law that entropy always increases, holds, I think, the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations — then so much the worse for Maxwell's equations. If it is found to be contradicted by observation — well, these experimentalists do bungle* *things sometimes. But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation*."

Eddington shows how dangerous it is to make a bold statement concerning a concept that lacks clarity. Moreover, our new understanding of lost work[3,6,7] has rendered the basis of second law into possibly one of the biggest misunderstanding in the history of science. As this author previously explained the second law is limited to closed isolated systems[6,7]. Although an expanding system here on Earth may be closed, it cannot be isolated because it must do work onto its surrounding atmosphere[6,7] e.g. lost work.

Yet, entropy is fully indoctrinated into most realms of the sciences. It must be said that its 19th and early 20th century interpretations were not beholden to all. Max Planck wrote: "However, the error committed by an overly narrow interpretation of Clausius' theorem, and which I have fought against tirelessly for my entire life, is, it seems, not to be eradicated. For, up to the present day, instead of the above definition of irreversibility, I have encountered the following: "An irreversible process is one that cannot run in the reverse direction". That is not adequate. For, at the outset, it is well conceivable that a process, which cannot proceed in the reverse direction, by some means or another can be

made fully reversible"[17,18]

We now understand the validity of Planck's concerns. Entropy is no longer required to explain reversibility, as reversible processes simply are those wherein no work/energy is lost, while irreversible processes remain those wherein work/energy is lost, e.g. lost work by expanding systems, and/or friction[3,6,7] etc.

What about Boltzmann's entropy, as defined by (1)? Boltzmann's entropy ties perceived randomness to lost work/energy, an association which is not particularly scientific[3,4,5,7]. A concept that Planck[17] and others did not endear. Just because an expanding system has a perceived randomness increase becomes irrelevant! Accordingly, entropy's supreme position, as heralded by Eddington is now suspect.

There are inherent dangers in taking empirically verified concepts here on Earth, and then boldly claiming they have universal status. Ultimately, both entropy, and the second law are limited concepts that should not even apply to fields like cosmology! Entropy's fundamentals are to be questioned. Should it even apply to radiation? Should entropy be restricted to condensed matter? Does entropy go the way of phlogiston?

Before we can answer entropy requires clarity. Reconsider entropy's initial conception by Rudolf Clausius: Entropy multiplied by temperature represents energy. This implies that entropy is a generic form of heat capacity for any system, with heat capacity being limited to homogeneous matter specific systems. Herein, entropy change remains defined by[1,2,7] equation (53).

We discovered when considering free energy that entropy, as defined by equation (53) is not simply a form of heat capacity. Heat capacity gives temperature increase for a given input of thermal energy, but entropy may be better understood as the heat capacity for inherent system inefficiencies. Which is to say that since we can never extract as much work out of a system in comparison to the energy that we put in, then entropy is part of the measurement of the heat left behind. Of course do we now need isobaric versus isometric entropy?

Things have come full circle. I can now consol why some of the great minds i.e. Clausius, Maxwell, Kelvin, Boltzmann, seemingly believed in entropy's relationship to reversibility, when the reality is that it concerns simple system inefficiency. Entropy no longer signifies randomness, hence it's definition by equation (1), may require reconsideration. Furthermore, entropy may not be the best term to associate with the ability to do work i.e. equation (38).

Another choice is to embrace equation (1), and reconsider entropy's relevance to equations (53), and (38). Perhaps we leave it in equation (38) and reconsider entropy's significance to equations (1) and (53).

Whatever the ultimate outcome is, giving entropy clarity is a real step towards rewriting thermodynamics so that it becomes a simple eloquent science. If not for the sake of current scientists, let us do it for future generations. Moreover, scientists should embrace this as an opportunity rather than treat the inarguably obvious with disdain.

P: Discussion & global warming

Equation (7) has been empirically proven and is well accepted by all[1,2,7]. However the traditional explanation for lost work is poor at best i.e. work into the system's walls[1,2] irrelevant of whether the walls are real or imaginary. Mayhew's realization that work is through a system's walls onto its surroundings[7,8] has profound implications to subjects like cosmology, wherein our expanding universe may not have walls, hence the question of "where does the work of our expanding universe go?", becomes non-sensible[7,8]. This can be further rectified by Mayhew's understanding that lost work as defined by equation (3), cannot be done unless the surroundings have mass, which is upwardly displaced in a gravitational field i.e. work cannot be done onto a vacuum[3,7,8].

Acceptance that expanding systems increase Earth's atmosphere's potential energy may also alter our understanding of global warming. Firstly, when expanded systems shrink then the increased potential energy of the atmosphere's molecules must convert into kinetic energy, which ultimately transforms into heat. Secondly, there is the previously discussed inefficiencies. When considering continuous running cyclic engines, the ramifications of these facts may become significant, and warrant reconsideration.

Q: Conclusions

Ultimately, this paper demonstrates that thermodynamics can be simplified, if the will to do so exists. Simplifying will not be easy, it will take the cooperation of others, but it should be done for future generations. Understandably, the vast majority of those fully indoctrinated in thermodynamics may not appreciate what is discussed herein. In many ways this paper is for everyone else.

The Earth and its surrounding atmosphere compose an open system constrained by gravity. We must accept that most useful systems/processes experience expansion at some point hence they must upwardly displace Earth's atmosphere's mass against

gravity. We elaborated on the previous disclosure[3,6,7] that this signifies lost work ($W_{lost} = P_{atm}dV$). We also discussed that generally work is definable as an isobaric process but unlike traditional thermodynamics, we realize that work cannot be limited to being isobaric, giving the previously discussed bubble nucleation[3,7,9] as proof. This raises questions about accepted thermodynamics.

The misunderstanding concerning lost work, along with a macabre application of differentials, then allowed Boltzmann's entropy to wrongly associate randomness with lost work/energy. An association that is not particularly scientific! Yet it endured throughout the 20th and into the 21st century, and became fundamental to most realms of the sciences. Our ignoring the fact that probabilities give results and not reasons only compounded the issue! This is not to say that it is not beneficial to learn statistical thermodynamics i.e. the dependence of density of states on external parameters[1]. Rather it is to say we need to unleash the claim that thermodynamics is a mature science by accepting the indignity that randomness is a result rather than a reason! Ultimately attaining new limitations/understanding for the various thermodynamic relations from entropy through to latent heats.

The fact that only a portion of a gas' momentum can actually do work means that the upper limit of efficiency for an expanding monatomic gaseous system doing work seems to be 66.667%, or if one prefers 2/3 of the energy input. This theoretical limit is based

upon the ideal gas law and kinetic energy of gases, as previously discussed[7,8]. The 19th century science greats missed this fact, seemingly thinking work (or the ability thereof) always equated to energy change, hence the ill constructed foundation for the second law was laid.

Interestingly, this also gave us foresight into a new interpretation for entropy based upon the free energy relations, i.e. entropy may be better understood as the heat capacity for inefficiencies. Perhaps there is a preference for another interpretation of entropy. It can remain as Clausius first envisioned, that being something which when multiplied by temperature defines energy, e.g. a heat capacity for inhomogeneous systems. Or it can be as Boltzmann envisioned. Or it can be any of its other guises. But it can no longer remain

everything to everyone. Clarity[3,7] remains required! This means some hard choices must be made.

Inefficiency and the consequences of lost work may have significant ramifications to our understanding of global warming. We also discussed the principle of quasi-static expanding systems and how freely given energy is often attained from their surroundings

e.g. heat baths. We pointed out, that this does lend to misconceptions.

The reason that energy relations are directly proportional to temperature is because the thermal energy density from our Sun can be approximated by the Rayleigh-Jeans equation. Since our Sun's radiation controls the thermal energy within Earth's heat baths,

e.g. our atmosphere, ocean and planet Earth itself, we now begin to understand why thermal energy relations tend to be proportional to temperature.

This paper also shows the dangers of believing that a set of empirical data indisputably proves a given theory. Accepting that more than one theory can explain any given set of empirical data, one has to accept that empirical data can only disprove a theory just as bubble nucleation disproves traditional thermodynamics. Of course you can avoid the logic given herein by arguing that the upward displacement of the Earth's atmosphere's weight does not require work. I remain unsure how one does that but stranger things have happened.

References

1. F. Reif, *Fundamentals of Statistical and Thermal Physics*, (McGraw-Hill, New York, 1965)
2. F. Reif, *Statistical Physics*, (McGraw-Hill, New York, 1967
3. K. Mayhew Phys. Essays, **28**, 352 (2015)
4. A. Ben-Naim, *A Farewell to Entropy: Statistical Thermodynamics Based on Information* (World Scientific Publishing Co., London, New York 2011)
5. A. Ben-Naim, *Entropy and the Second Law* (World Scientific Publishing Co., Singapore, London, 2012)

6. K. Mayhew, Phys. Essays, **28**, 152 (2015)

7. K. Mayhew, *Changing our Perspective: Part 1: A New Thermodynamics* (Self-published 2015) Available at www.new-thermodynamics.com, www.newthermodynamics.com and https://createspace.com/5277845

8. K. Mayhew, Phys. Essays, **24**, 338 (2011)

9. K. Mayhew, Phys. Essays, **17,** 476 (2004)

10. J.W. Gibbs *The scientific papers Vol 1* Dover Publishing Inc, New York,1961

11.K. Mayhew, Phys.Essays, **27**, 4 (2014)

12. B. Wolfrum, T. Kurz, O. Lindau, and W. Lauterborn. Phys.Rev. E **64**, 046306 (2001)

13.https://www.chem.wisc.edu/deptfiles/genchem/netorial/modules/thermodynamics/entropy/entropy04.htm

14. D.R. Lide, *CRC Handbook 84th ed.* (CRC Press, Boca Raton, Florida 2003)

15. https://en.wikipedia.org/wiki/Sackur%E2%80%93Tetrode_equation
16. http://en.wikiquote.org/wiki/Arthur_Eddington

17. C. Hartmann, 21st Century Science, “On the 150th Birthday of Max Plank: On Honesty Towards Nature” (2014)

18. From the lecture ”New Paths in Physical Knowledge” delivered by Planck on Oct., 15, 1913