

NEW THERMODYNAMICS: REVERSIBILITY AND FREE ENERGY

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Abstract

Most accept that thermodynamics is a mature science. It will be discussed that reversibility can be an illusion. Furthermore, new explanations that do not require the parameter entropy will be given for free energies. Moreover, it will be shown that entropy's removal clearly lends itself to the science's simplification, at least in so far as free energies are concerned.

Keywords:

Entropy, Gibbs free energy, Helmholtz free energy, Reversibility

Introduction:

This paper is a continuation of this author's previous paper "Resolving Problematic Thermodynamics" [1], which described an alternative thermodynamic narrative. In that paper, I stated that free energies are to be left to future discussions, hence this paper.

Interestingly, Norman and Dunning-Davis [1] point out that "probabilistic ideas are usually, if not always, used in physics when some vital pieces of information needed for a truly exact solution are missing". Yet such probabilistic arguments form thermodynamics' accepted basis. This has lent itself to the emboldened assertion that probabilities give reasons in different scientific realms. Have we lost sight of probabilities original structure that being a mathematical expression providing plausible results? If so, then certain accepted statistical arguments may be self-serving for those believing that thermodynamics is a mature science.

What if probability based statistical thermo-dynamics is based more upon mathematical conjecture than constructive logic? How would one show that to be the case? Probabilistic arguments would not provide the necessary yet missing vital information! Perhaps showing that simpler alternative explanations based upon constructive logic is the best answer.

Three fundamental enshrined thermodynamic principles are reversibility, Gibbs free energy, and Helmholtz free energy. So herein we shall investigate the illusion of reversibility and then show that alternatives explanations for both free energies can be obtained. Note; free energies describe the energy that can be extracted from systems.

The accepted writing of energy change and work associated with an expanding system, in terms of isothermal entropy change is:

$$TdS = dE + PdV \quad (1)$$

Where T is temperature, S is entropy, E is internal energy, P is pressure and V is volume.

An inherent problem with eqn (1) being that PdV lacks clarity [1]. This author realized that the work as defined by PdV , is "lost work" done onto the surrounding atmosphere [1,3,4] by an expanding system i.e. an energy transfer from the expanding system into the massive surrounding atmosphere, which remains both isobaric and isothermal [1,3]. "Since, after expansion the system is at the same pressure and temperature as the atmosphere, then the atmosphere cannot return either work or energy back into the expanded system. Thus PdV is lost work i.e. irreversible work" [1,3,4].

Giving eqn (1) clarity and rewriting it in terms of the first law by considering the energy input (dq) into an expanding system, gives:

$$dq = dE + (PdV)_{atm} \quad (2)$$

At this point we must emphasize that as was previously discussed intermolecular collisions are not necessarily elastic, as is traditionally professed [1,4,5]. This provided clarity as to why pressure temperature (P - T) relationships exist [1] i.e. increase P and T tends to increase.

Hence $(PdV)_{atm}$ represents some combination of an atmospheric potential energy and/or heating of the atmosphere through viscous dissipation [4,5]. The fact that $(PdV)_{atm}$ signifies lost work alters our perceptions of entropy and the second law [3]!

Concerning My Previous Paper:

Equation (10) in my previous paper [1] concerning the relationship between iso- baric (C_p) and isometric/isochoric (C_v) heat capacities, the temperature change on the L.H.S. of the equality was unfortunately not included. Hence the eqn (10) should have been written as¹:

$$(C_p dT)_{sys} = (C_v dT)_{sys} + (PdV)_{atm}$$

I.e. the isobaric heat capacity includes the work done onto the atmosphere $(PdV)_{atm}$ plus the energy required for the system's temperature increase $(nC_v dT)$.

Illusionary Thermal Reversibility in Boiling

Consider a boiling liquid below a piston-cylinder, as shown in Fig 1. The expanding gas in the piston-cylinder does irreversible lost work onto its surrounding atmosphere i.e. $(PdV)_{atm}$. The energy in (dq_{in}) is defined by the following first law based equation:

$$dq_{in} = dE_{sys} + (PdV)_{atm} \quad (3)$$

The mass transfer from the liquid to vaporous state drives the expansion by being infinitesimal- ly hotter with an infinitesimally higher pressure than the surrounding atmosphere. Note: In order for the approximation of $dP=dT=0$, to hold then Eqn (3) assumes that the expanding system is fully insulated hence and that its expansion is quasi static.

In normal boiling the change to the system's internal energy (dE_{sys}) equals its change in bonding energy (dU) i.e. the change in inter-molecular bonding energy when going from the liquid to the vaporous state. Accordingly, eqn (3) can be rewritten as:

$$dq_{in} = dU + (PdV)_{atm} \quad (4)$$

Consider that the heat is turned off ($dq_{in}=0$) and that the insulation is now removed, as shown in Fig 2. As vaporous molecules condense, energy (heat from the molecule' bonding energy) slowly vacates outwards through the condensing system's walls. Understand that the work done onto the atmosphere [$(PdV)_{atm}$] during boiling was lost [1,3], hence it cannot magically return during condensation!

We know that no actual work is done onto System 1 during condensation because its pressure, temperature and mean molecular volume all remain relatively constant. Herein, System'1 total volume decreases as vaporous molecules condense back into the liquid state.

Of interest: As System 1's total volume decreases then some of the atmosphere's potential energy will be transformed into kinetic energy (A.K.A. infinitesimal heat)¹. Mathematic-ally it is as if a VON (volume of nothingness) [1] was removed from the base of the atmosphere.

During condensation, the heat leaving the system dissipates into the surrounding atmosphere as defined by:

$$dq_{out} = -dU = -dE_{sys} \quad (5)$$

Since the magnitude of eqn (5) is less than eqn (4) by lost work $[(PdV)_{atm}]$, then boiling is an irreversible process, although it can possess the visual illusion of being reversible!

If one could somehow collect and then measure the dispersing thermal energy leaving the system during condensation, one would determine that in terms of magnitudes:

$$|(dq_{in})_{Fig1}| = |(dq_{out})_{Fig2}| + |[(PdV)_{atm}]_{Fig1}| \quad (6)$$

It must be emphasized that the casual observer has never actually measured the heat out (dq_{out}), i.e. in other words he/she traditionally (wrongly) assumed that: $dq_{out} = -dq_{in}$. Ultimately, the casual observer simply visually witnesses the system continually maintaining mechanical pressure equilibrium as heat (dq_{out}) slowly disperses out from the condensing system.

The above has also left most with the misconception that the atmosphere can do work onto a system whose pressure is also atmospheric.

To emphasize; one can readily measure the latent heat/enthalpy of vaporization in an isobaric calorimeter, i.e. herein eqn (4) defines the heat of vaporization, which equals dq_{in} . However, based upon the illusion of reversibility, we have assumed (wrongly?) that the magnitude for heat of condensation equals that for vaporization. If one could actually measure the heat of condensation it would be determined to equal eqn (5)!

The above clearly challenges the accepted considerations of reversibility, which often involves (wrongly?) statistical arguments. This alone changes the way thermodynamics is contemplated.

Gibbs free energy:

In deriving his free energy, Gibbs started off with eqn (1), and then subtracts the following total differential [6]:

$$d(TS) = dE + d(PV) \quad (7)$$

Logic dictates that one should start off with a total differential, from which its partials are determined. A reason that this absurdity of subtracting a total differential from a partial differential to obtain the other parts was acceptable is it gave isothermal entropy change relations [i.e. eqn (1)] a sense of supremacy, something that this author challenges.

Eqn (7) wrongly treats both dE and $d(PV)$ as if they are part of the same system. Logic dictates that if PdV in eqn (5) is work done external to the expanding system then $d(PV)$ is also external¹ i.e. it renders eqn (7) into an absurdity.

Consider that the energy required for an endothermic reaction comes from the thermal energy contained within a system: $dU > 0$, and: $dT < 0$. If these are the only system changes then one could use the isometric molar heat capacity and write for n moles of molecules.

$$dU = -nC_vdT \quad (8)$$

Eq. (8) assumes that there is no change to the mechanical parameters i.e. neither a volume nor pressure change.

Next consider that the system experiences an isometric pressure change as is illustrated in Figures 3 and 4.

There is no actual work done onto/into the rigid closed & insulated system! But there is a pressure decrease and based upon the P - T relation; there should be an associated temperature change. Can we now write?

$$dU = -nC_vdT + VdP \quad (9)$$

Considering eqn (9); in a 100% insulated isometric system part of the witnessed temperature change would be caused by the pressure change! I.e. if there were no other changes to the system, and its pressure increased, then so too would the system's temperature! Conversely, if the pressure decreased so to would its temperature.

Can we say that VdP in eqn (9) is the energy associated responsible with the above system's temperature changes? I.e. is the energy associated with the natural P - T relation. Then for closed insulated experimental systems, it also relates to the ideal gas law i.e. $VdP = NkdT$. Note; the ideal gas law, Avogadro's hypothesis etc. are now considered as being limited to sufficiently dilute gases in closed systems, i.e. most gaseous experimental systems [4,5].

It must be emphasized that we have not discussed any reaction in particular rather we seek an understanding of how the parameters relate to one and another.

Based upon eqn (9), the energy that could now be theoretically extracted (G_{ex}) from the system becomes:

$$G_{ex} = dU - VdP + nC_vdT \quad (10)$$

The change in chemical potential can also be written in terms of the number of molecules (N) and the molecular chemical potential i.e. $dU = d(N\mu)$. Compare eqn (10) to the following Gibbs-Duhem relation:

$$G = Nd\mu - VdP + SdT \quad (11)$$

If $S=nC_v$, then eqn (10) is eqn (11).

Our new realizations are certainly plausible however before they can be accepted one must similarly reinvestigate Helmholtz free energy.

Helmholtz free energy

Consider an endothermic reaction that requires energy from an external source i.e. $dU>0$. Fig 5 shows System 1 in State 1 being heated, thus providing energy ($dq_1=dE_1$).

Note; we start with $dF_{ex}=0$.

The result: System 1 is transformed into expanded State 2. Since an isobaric volume increase occurred then work is done onto the surrounding atmosphere [$W=(PdV)_{atm}$] as shown in Fig. 6.

Next consider that the temperature of State 2 is higher than that of State 1, hence the thermal energy required for the temperature increase is $nC_p dT$.

If dU equals the change to the system's chemical bonding energy, then the energy change in going from State 1 to State 2 is defined by:

$$dq_1 = nC_p dT + dU \quad (12)$$

The isometric heat capacity (C_v) does not include the work done/lost [$(PdV)_{atm}$]. Therefore, in terms of isometric heat capacity eqn (12) becomes:

$$dq_1 = nC_v dT + (PdV)_{atm} + dU \quad (13)$$

Consider that energy is now extracted from State 2: $dF_{ex}>0$, then eqn (12) becomes:

$$dq_1 = nC_p dT + dU + dF_{ex} \quad (14)$$

The energy (dF_{ex}) that can be extracted from State 2 becomes:

$$dF_{ex} = dq_1 - nC_p dT - dU \quad (15)$$

Ultimately, dF_{ex} is a generality for the maximum amount of energy that can be extracted from a system in order to perform work, i.e. move a car.

Consider the case of no heat/energy input ($dq_1=0$) hence eqn (15) becomes:

$$dF_{ex} = -nC_p dT - dU \quad (16)$$

Eqn (16) implies the extraction of negative energy, which is not realistic. However, if the chemical reaction is now exothermic then: $dU < 0$. The maximum amount of energy that can be extracted from this exothermic reaction becomes:

$$dF_{ex} = |dU| - nC_p dT \quad (17)$$

Rewriting in terms of molar isometric heat capacity (C_v) and work done onto the atmosphere [$W=P_{atm}dV_{sys}=(PdV)_{atm}$]:

$$dF_{ex} = |dU| - nC_v dT - (PdV)_{atm} \quad (18)$$

Eqn (18) is a traditionally accepted change to Helmholtz free energy (dF) for an exothermic chemical reaction i.e.:

$$dF = |dU| - SdT - PdV \quad (19)$$

Comparing eqn (18) to eqn (19); they are one and the same if: $S=nC_v$. If there were no chemical reaction ($dU=0$) then the maximum amount of energy/work that could be extracted becomes:

$$dF_{ex} = -nC_v dT - (PdV)_{atm} \quad (20)$$

Compare eqn (20) to an accepted equation for changes to Helmholtz free energy (dF):

$$dF = -SdT - PdV \quad (21)$$

Again, entropy (S) seemingly equals the number of moles times the isometric molar heat capacity (nC_v). Certainly, the traditional writing of PdV i.e. eqn (21), lacks the clarity¹ that eqn (20) possesses.

Discussion:

We can now argue that traditional considerations for both Gibbs free energy and Helmholtz free energy were sort of right but for the wrong reasons.

Is entropy based thermodynamics really necessary, or is it a mathematical contrivance [7] resulting in the science's over-complication. Certainly, unlike entropy based equations, eqn 10 and eqn 20 are readily envisioned.

This author's further asserts that other accepted equations such as the Clausius-Clapeyron equation can also be explained without entropy. Ditto applies to chemical equilibrium. These all may be discussed in future papers.

Conclusions:

In boiling one can readily measure the energy required to break the liquid's intermolecular bonds (dU) plus the work done onto the surrounding atmosphere due to isobaric expansion [$W=(PdV)_{atm}$] i.e. latent heat/enthalpy of vaporization.

Conversely, the heat of condensation is not so readily measured! Rather we simply have assumed that its magnitude equates to that for vaporization. This erroneous assumption was accepted, in part, because of the illusion of reversibility in closed system boiling.

Based upon heat capacity, temperature change, bonding energy, lost work and natural P - T relations, simple logic based constructive formalizations for both Gibbs free energy and Helmholtz's free energy were obtained. Note: VdP in Gibbs free energy attained clarity by realizing that intermolecular collisions are inelastic [1,4,5].

Abiding by Occam's razor, one soon realizes that thermodynamics without entropy is clearly a logical choice. This does not necessitate the removal of complex statistical based arguments rather it demonstrates the power of clear logic over the traditional mathematical driven science. Certainly, an acceptance of what is stated will alter how we structure thermodynamics.

Figures

Fig. 1: Shows isobaric isothermal boiling i.e. the mass transfer from a liquid to va-porous state resulting in expansion.

Fig. 2: Shows condensation i.e. removing both the heat and insulation from Fig. 1. This allows the system to return to its original state thus providing the illusion of being reversible.

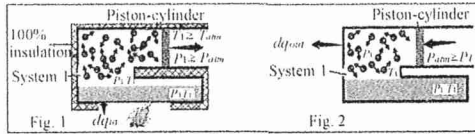


Fig. 3: Shows a system of n moles of gas as reactants for an endothermic reaction.

Fig. 4: Shows a gaseous system as the products of the reaction shown in Fig. 3.

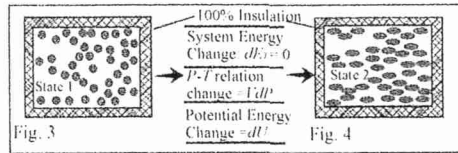
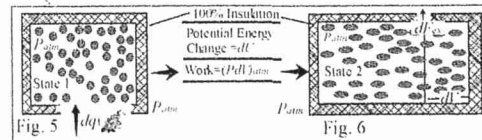


Fig. 5: Shows the heating of a system of n moles of gas as reactants in an endothermic reaction.

Fig. 6: Shows that the gaseous system shown in Fig. 5 has expanded hence performs isothermal and isobaric work onto the surrounding atmosphere.



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