Classical Thermodynamics: A Web of Convoluted Myths. The Carnot Cycle and the Joule-Thomson Effect Unravelled

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ABSTRACT – It is argued that several key ideas upon which thermodynamics was founded are likely dubious and may well need to be abandoned altogether. This particularly applies to certain concepts based on the ideal gas laws, *e.g.* isothermal and adiabatic expansion and compression. Indeed, this is apparently the reason for the invalidity of the Carnot cycle, a cornerstone of thermodynamics that has widely influenced the evolution of scientific thought and technological innovation over nearly two centuries. (It has been previously argued that the Carnot cycle is self-evidently invalid, as a closed system operating in a cycle cannot yield net work.) Likewise, a re-evaluation of the Joule-Thomson effect indicates that the actual operations performed relate neither to the model employed nor to the derived theoretical construct. In fact, the proof of constant enthalpy during the adiabatic expansion is debatable, the calculated volume changes being invalidated by the accompanying transfer of mass. Thus, the imputed conversion of kinetic to potential energy is unlikely to be valid (the latter, in fact, being associated with higher – rather than lower – pressures). The Joule-Thomson effect is likely the result of simple pressure changes (including a possible Bernoulli Effect at the nozzle), along with mass changes which affect the energy density, akin to those found at high altitudes ('hill-station effect').

INTRODUCTION

Thermodynamics apparently originated during the interim between the eras of Newtonian and quantum mechanics. Thus, Newtonian ideas of energy ultimately led to the kinetic theory of gases, which offered a cogent theoretical basis for the observed gas laws. The consequent ideal gas law, considered formally valid, served as an enabling medium for the evolution of key ideas relating to energy and work in their various manifestations (Eqn. 1, the symbols have the usual meaning, *vide infra*):

$$PV = nRT \tag{1}$$

The first quarter of the nineteenth century witnessed both the culmination of the classical period and the efflorescence of modern ideas. Thus, Dalton's atomistic view enhanced the basis of the kinetic theories, leading up to the founding of statistical mechanics in the latter half of the century. However, it was the Carnot cycle (1824) that first attempted to explore the relationship between energy and work, apparently leading not only to a theory of heat engines, but also to a fundamental view of energy. Thus, the Carnot theorem apparently offered the first glimpse of entropy, the related quantitative relation between energy, work and temperature believed to this day to represent one of the fundamental standards in science.

Intriguingly, however, and as argued elsewhere,[1] the Carnot theorem is self-evidently invalid. This is essentially because – even superficially – no net work can be obtained in the closed cycle of operations that the Carnot cycle represents. In fact, closer scrutiny reveals more fundamental flaws in the Carnot hypothesis that can be traced to key ideas involving the operations themselves, as argued further below.

Another fascinating phenomenon of far-reaching practical significance, and that was also discovered during the era of classical thermodynamics, is the Joule-Thomson effect. The now familiar lowering of temperature accompanying the irreversible expansion of certain gases is,

however, theoretically intriguing. Again, current explanations are apparently based on dubious assumptions involving the operations performed on the gases.

Both the above cases thus raise serious questions about the theoretical underpinning of thermodynamics, itself a cornerstone of current scientific theory with critically important technological implications.

DISCUSSION

Carnot cycle

Statement of the problem[1]

The Carnot cycle is constituted of the cyclic sequence of operations: isothermal expansion, adiabatic expansion, isothermal compression and adiabatic compression. The operations are performed reversibly on a sample of ideal gas contained in a cylinder with a movable piston. The cylinder is initially placed in a heat source at temperature T_1 during the isothermal expansion stage. The cylinder is removed from the heat sink and jacketed to prevent heat transfer, for the adiabatic expansion stage. The jacket is removed and the cylinder placed in a heat sink at temperature T_2 ($< T_1$) for the isothermal compression stage. The cylinder is removed from the sink and again jacketed for the adiabatic compression stage, which – importantly – raises its temperature back to T_1. The cycle is repeated.

It is believed that heat is absorbed by the system at the source (at T_1), and is partly converted to work that is performed on the surroundings during the two expansion stages. The remainder of the purported heat is consigned to the sink (T_2) as a part of the compression stages, when work is performed on the system by the surroundings. Ostensibly, the work performed upon the system during the compression stages is less than the work obtained from the system during the expansion stages.

Furthermore, it is believed that the work involved in the two adiabatic stages cancel each other out, so the overall net work (w) purportedly obtained from the system depends on the two isothermal stages only, given by:

$$w = RT_1\ln(V_2/V_1) - RT_2\ln(V_3/V_4) \tag{2}$$

In Eqn. 2, V_1 and V_2 are the volumes of the gas at the beginning and end of the expansion stage, and V_3 and V_4 the volumes at the beginning and end of the compression stage (R being the gas constant). Also, it can be shown that, for the adiabatic stages:

$$(V_2/V_1) = (V_3/V_4) \tag{3}$$

Therefore, from Eqns. 2 and 3:

$$w = R(T_1 - T_2)\ln(V_2/V_1) \tag{4}$$

Eqn. 4, apparently, indicates that net work is obtained from the system, as all terms on the right hand side are positive ($T_1 > T_2$ and $V_2 > V_1$).

As argued previously,[1] this curious result is manifestly invalid in a sealed system which is returned to its initial state. Thus, even if it be assumed (although erroneously, *vide infra*) that work is obtained from the system during the expansion stage, an equal amount of work needs to be performed on it to return it to the original state at T_1. Clearly, no net work can be obtained from the system by the surroundings (*i.e.* $w = 0$), which is self-evident and does not need further proof. It only now remains to examine the above protocols and identify the flaws in the arguments. These, in fact, reveal even more fundamental problems with the Carnot cycle.

Solutions

A singular flaw with the Carnot cycle is the assumption that heat is absorbed by the system from the source at T_1. This is impossible because the system is in thermal equilibrium with

the source. Thus, in principle, no work can be obtained from a system at thermal equilibrium with its surroundings.

The gas in the cylinder constituting the system may indeed be expanded isothermally but only if the external pressure is reduced. However, this does not qualify as work performed by the system, as it is then merely reacting to a change in the surroundings. These arguments can be supported by the following mathematical approach.

In fact, the definition of work purportedly obtained in the isothermal stages is itself incorrect (Eqn. 2), as can be seen from the corresponding enthalpy changes. Thus, the changes in enthalpy (H), internal energy (E), pressure (P) and volume (V) are related as:

$$dH = dE + d(PV) = dE + PdV + VdP \tag{5}$$

(Note that $H = E + PV$; also, H is conventionally defined at constant P, but this is inapplicable here as P varies.)

Furthermore, at constant temperature (isothermal conditions) $dE = 0$, so:

$$dH = d(PV) = PdV + VdP \tag{6}$$

The work obtained (dw) indicates a corresponding change in the enthalpy (dH):

$$dw = dH = d(PV) = PdV + VdP \tag{7}$$

Eqn. 7 can be recast into Eqn. 8 with the help of Eqn. 1 (n refers to number of moles):

$$dw = dH = d(PV) = PdV + VdP = nRT_1[(dV/V) + (dP/P)] \tag{8}$$

Integrating Eqn. 8 leads to Eqn. 9 (P_1 and P_2 are the pressures corresponding to the volumes V_1 and V_2 respectively):

$$w = \Delta H = nRT_1[\ln(V_2/V_1) + \ln(P_2/P_1)] = nRT_1[\ln(P_2V_2/P_1V_1)] \tag{9}$$

Interestingly, by the ideal gas law (Eqn. 1):

$$P_1V_1 = P_2V_2 = nRT_1 \qquad (10)$$

Therefore, Eqn. 9 reduces to:

$$w = \Delta H = nRT_1[\ln(P_2V_2/P_1V_1)] = 0 \qquad (11)$$

Thus, the isothermal expansion stage yields no net work, *i.e.* the stage itself is implausible! Clearly, neglect of the VdP term in Eqn. 7 in the original treatment leads to the illusion of net positive work (Eqn. 4)! [The same result can be obtained by integrating $d(PV)$ in Eqn. 8.] In other words, under isothermal conditions, not only is the internal energy unchanged ($\Delta E = 0$), but also no expansion work is possible.

It is particularly noteworthy that the above isothermal expansion is only possible if the pressure of the surroundings is reduced (in the above case from P_1 to P_2). Importantly, there is no uptake of energy from the heat source: again, the uptake is impossible as both the source and the system are initially at the same temperature T_1!

Identical arguments apply to the purported isothermal compression stage, when the volume changes from V_3 to V_4. This can only occur if the pressure of the surroundings changes correspondingly from P_3 to P_4 ($P_3 < P_4$). Thus, $P_3V_3 = P_4V_4 = nRT_2$, which again implies that the systemic enthalpy is unchanged (Eqn. 11). Again, the system is merely responding to a change in the surroundings, with no heat given off to the sink as the system is also at the same temperature T_2.

Clearly, the operations constituting the Carnot cycle can only be executed by independently changing the state of the surroundings, particularly its pressure. This requires that the surroundings perform work in both the isothermal stages. Thus, far from obtaining net work from the system in the Carnot cycle, an input of energy would be required to keep it going!

In fact, closely similar arguments apply to the two adiabatic stages of the Carnot cycle. Again, neither expansion nor compression is possible if the external pressure remains

constant. However, and rather amusingly, as no energy exchange occurs with the surroundings during these operations anyway (*vide supra*), the jacketing of the system is unnecessary! Thus again, $P_2V_2 = P_3V_3$ and $P_4V_4 = P_1V_1$, which also implies that the temperature would remain constant during these purported operations (Eqn. 1).

Therefore, since the Carnot cycle is fundamentally invalid, the question of obtaining work from its operation does not arise at all. Its key flaw is the assumption that expansion work (whether positive or negative) can be obtained at constant temperature (isothermal stages) or without input of energy (adiabatic stages), both of which are ruled out for an ideal gas by Eqn. 1.

In fact, positive expansion work is only possible if there is an increase in the temperature of the system due to uptake of energy. This would require the temperature of the heat source to be raised, with a consequent expansion of the gas in the system but at a higher temperature. However, these conditions represent a radical departure from the Carnot cycle, and in any case are not conducive to a cyclical process.

Thus, purely mechanical work *via* expansion or compression of an ideal gas is ruled out, essentially because both the size and the mutual interactions of the constituent atoms are neglected.

Consequences

The collapse of the Carnot theorem apparently strikes at the conceptual roots of thermodynamics, as the heat (dq_{rev}) purportedly transferred between the system and the surroundings in the two reversible isothermal stages was believed to give rise to a corresponding entropy change (dS):

$$dS = dq_{rev}/T \qquad (12)$$

In fact, Eqn. 12 represents the first stirrings of the idea of entropy itself, which was later related to molecular disorder or randomness. These ideas were incorporated into the Gibbs free energy (G) concept, leading to the definition of a spontaneous change as one that occurs with a lowering of G:

$$\Delta G = \Delta H - T\Delta S \tag{13}$$

It is believed that ΔH represents the heat given off by the system to the surroundings, so that ΔG represents this plus the part of the heat change retained by the system to increase its own randomness ($-q_{sys}$, corresponding to $\Delta S > 0$). The enthalpy change ($-\Delta H$ relative to the surroundings) then relates to the change in the entropy of the surroundings (ΔS_{surr}, q_{surr} being the heat received by the surroundings):

$$-\Delta H = q_{surr} = T\Delta S_{surr} \tag{14}$$

Thus, ΔG is believed to represent the overall entropy change (system + surroundings), $-\Delta G$ being then associated with an increase in the overall entropy. Eqn. 13 may thus be recast:

$$\Delta G = -(q_{surr} + q_{sys}) \tag{15}$$

Eqn. 15 implies that the Gibbs free energy change is equal to the overall heat change accompanying the process in question. (Note: $-q_{surr}$ and $-q_{sys}$ imply evolution of heat during the transformation in question.)

Seen in this way, the collapse of the Carnot theorem and the derived entropy concept is less cataclysmal than it appears, as the purported entropy changes are derived from heat changes. This is the likely reason for the general success of the Gibbs free energy formulation despite the collapse of the Carnot theorem.

Joule-Thomson effect

Statement of the problem[2]

The Joule-Thomson effect (JTE) refers to the observed cooling of many real gases when they undergo a rapid and irreversible expansion, a process usually performed *via* a nozzle or a porous plug, under adiabatic conditions. The phenomenon has found widespread technological application since its discovery in the mid-nineteenth century, particularly in the liquefaction of gases (the Linde process) and in the ubiquitous household refrigerator. Interestingly, however, its scientific basis remains intriguing (some gases even undergoing warming upon expansion). Thus, although the current theory views the JTE as a manifestation of the non-ideal behaviour of a gas, this appears only partly true as argued below.

The JTE, in fact, was presaged by the Joule expansion. In this, an ideal gas is allowed to expand into a vacuum, no change in temperature being observed. This is readily explained by recourse to Eqns. 1 and 10 above, relating to isothermal changes in *P* and *V* of an ideal gas. In light of this, the initial discovery of the JTE was apparently intriguing, essentially because the expanding gas was clearly not performing work. Thus, the enthalpy was apparently constant, indicating an isothermal process. (As no work is thus performed in the process, explanations for the apparent 'spontaneous cooling' need to avoid conflicts with both the first and second laws of thermodynamics.)

The proposed explanation for the observed cooling by the JTE, in fact, invokes the idea that the expansion process is accompanied by a conversion of kinetic energy to potential energy. However, this appears unlikely as an increase in potential energy is to be associated with an increase, rather than a decrease, in pressure. (Indeed, then work would be done on the system!) Also, it is unclear as to how non-ideal behaviour fits into this explanation, as weak

intermolecular interactions would be enhanced by an increase of pressure and thus be associated with an increase in potential energy.

In fact, the formation of a 'van der Waals complex' (B_n) by the association of n gas molecules (A) would be endergonic, thus being favoured by an increase of both temperature and pressure:

$$nA \rightarrow B_n \tag{16}$$

Conversely, the decomposition of the complex B_n would be favoured at lower pressures, being accompanied by a release of energy, thus leading to an increase in temperature. Clearly, the formation of B_n involves an increase of potential energy, which would be released as kinetic energy upon its decomposition. (The idea that the associated complexes are 'ripped apart' during the expansion is unwarranted, as this requires that work be performed on the system, which is untenable in a free expansion!)

Thus, the observed cooling of many gases upon irreversible expansion must have a basis other than the accepted isenthalpic explanation. In fact, a serious problem with the current explanation is that the model employed differs rather drastically from the actual experiment. Thus, the experimental set-up employs – essentially – a source of compressed gas, which is let out through a nozzle or plug, to diffuse freely to the outside. A temperature measuring device, of course, is included, but it appears the gas essentially exits the set up at relatively high velocity.

However, the model employed to explain the JTE involves a two-compartment cylinder interconnected by a nozzle or plug (a sealed system). One of the compartments possesses a piston which can compress the gas inside and thus force it through the nozzle or plug into the other compartment (of equal volume as the first). As the gas does no work upon expansion, and the process is adiabatic, it is also isenthalpic ($\Delta H = 0$).

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Also, this is apparently bolstered by a mathematical treatment involving, however, rather dubious pressure-volume changes. Thus, it is argued that the volume decreases from an initial value V_i to 0 at the higher pressure (P_i), but increases from an initial value of 0 to a final value V_f at the lower pressure (P_f). Thus, the corresponding volume changes are V_i and V_f:

$$\Delta H = \Delta E + (P_i\Delta V_i + P_f\Delta V_f) = \Delta E + (P_iV_i - P_fV_f) = 0 \qquad (17)$$

A problem with the above approach is that the ΔV terms involve not just volume changes but also concurrent mass transfer across the nozzle. Thus, the approach is invalid and cannot lead to the work performed during the process.

In fact, the mass transfer implies that $V_i = V_f$ and $P_i = P_f$, ignoring any friction at the nozzle, noting that cooling is implausible in the described set-up! The isenthalpic criterion – ostensibly – leads to the idea that the kinetic energy is converted to potential energy during the process. However, as argued above, the approach is apparently bedevilled by inconsistencies at every stage.

Solutions

As mentioned above, in the actual experiment involving the JTE, the gas exits the nozzle or porous barrier into a region of greatly reduced pressure. Now, in a fixed volume of space (say around the temperature sensor), this implies a corresponding reduction in temperature by Eqn. 1: intriguingly, even in the case of an ideal gas!

In fact, in the case of a nozzle, the gas would exit into the low pressure region at relatively high velocity. This indicates the possibility of a further reduction in pressure by the well-known Bernoulli Effect[2] in the vicinity of the nozzle. This would also contribute to a lowering of the temperature (Eqn. 1).

Furthermore, the temperature sensor (be it a traditional thermometer or a thermocouple based device), essentially responds to the energy density around it. In an open system wherein the

gas flows freely out into the open, the energy density would be relatively low on the low pressure side, hence the observed cooling. Thus, there is no conflict with first law of thermodynamics as the total energy of the overall sample of gas would be conserved.

In the case of cooling devices (*e.g.* refrigerators) a fixed amount of a compressed refrigerant is allowed to expand into a low pressure region of fixed volume. Apparently, these conditions are rather different from those employed in the classical JTE (described above). However, the refrigerant is recycled *via* a compressor, and thus removed continually from the low pressure chamber. This ensures that the expansion chamber is almost continuously maintained at very low pressure, with a corresponding lowering of temperature.

In fact, it is well known that low temperatures may be obtained by evaporation of liquids under reduced pressure. Thus, low material density is associated with low energy density, and hence lower temperatures. This is apparently the basis of the lower temperatures observed at higher altitudes ('hill-station effect'). It would appear that this phenomenon plays a role in the operation of cooling devices such as refrigerators, *via* the continual evaporation of the refrigerant and its subsequent recompression, as described above.

Therefore, the operation of refrigerators appear to involve a combination of effects, perhaps including 'Bernoulli cooling' at the throttle and the 'hill-station effect' as discussed above. (The former leads to the condensation of the refrigerant at the throttle, and the latter the transfer of heat *via* mass transfer.) These alternative explanations are necessitated by the fact that the conventional explanation based on isenthalpic conversion of kinetic to potential energy appears unviable, as discussed at length above.

The Joule-Thomson inversion temperature. An intriguing aspect of the JTE is that, above a certain temperature termed the 'inversion temperature', the above described expansion leads to a warming, rather than a cooling of the gas. The inversion temperature is characteristic of

each gas, with most gases undergoing cooling at normal temperatures. (The exceptions are hydrogen, helium and neon, which thus have abnormally low inversion temperatures.)

In light of the above discussion, it would appear that above the inversion temperature, adiabatic expansion leads to a release of potential energy as kinetic energy. This is entirely plausible as higher pressures and temperatures are associated with an increase in potential energy (*vide supra*). Thus, by Eqn. 16, there is an increase in the association of gas molecules at higher temperatures and pressures, leading to an increase of potential energy.

Therefore, above the inversion temperature the cooling effects of the expansion are apparently overwhelmed by the warming effects. Presumably, different gases would store potential energy *via* different mechanisms. In fact, the low inversion temperature of hydrogen may be due to the equilibrium between the *ortho* and *para* hydrogen spin isomers, the equilibrium favouring the higher energy *ortho* form at high pressure even at relatively moderate temperatures.

Interestingly, the other two gases with low inversion temperatures (He and Ne) are of low atomic weight and electronegativity, and inert. These would apparently favour association of the atoms because of the absence of repulsive effects. Thus, these are high potential energy systems even at normal temperatures.

Conclusions

The JTE has been studied and well-established by ingenious experimental approaches, and is the basis of important technological processes related to cooling and refrigeration. However, its scientific basis appears almost mysteriously unclear, with current explanations based on the non-ideal behaviour of gases being unsatisfactory. In particular, the conversion of kinetic to potential energy at lower pressures seems unlikely. (The inversion temperature, on the

other hand, likely indicates an increase in the potential energy at higher temperatures and pressures.)

It appears that the classical JTE derives from a lower pressure – hence a lower energy density – in the immediate region beyond the throttle. The operation of cooling devices (refrigerators, etc.), however, may be complex and only obliquely related to the JTE. In particular, the Bernoulli Effect may well operate at the throttle, leading to a lower temperature due to lower pressures. Also, the re-evaporation of the condensed refrigerant may well be the major contributor to the cooling effect, as it allows heat to be removed *via* mass transfer.

CONCLUSIONS

Classical thermodynamics deals with the interaction of matter with heat energy (as opposed to radiant energy, the purview of quantum theory). The three laws of thermodynamics that grew out of this endeavour are now considered sacrosanct in an almost theological sense, constituting a scientific standard to which all rational experience must conform. Practically, thermodynamics – with the relation between work and energy as its central preoccupation – also provided the framework for understanding the functioning of all manner of engines, whether steam or internal combustion.

Theoretically, however, thermodynamics founders, major flaws apparently lurking in its conceptual labyrinths. The choice of the mythical ideal gas – a useful relic of the early gas laws – as the preferred material medium towards understanding the flow of heat, has led to a framework apparently far removed from normal experience. In particular, the fact that an ideal gas is in principle infinitely compressible at constant temperature turns the idea of expansion work into a conundrum! Also, practical engines are open systems, and the closed piston-cylinder models employed classically are over-idealized and grossly inaccurate.

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The most intriguing challenge, however, relates to the concept of entropy, which now appears inescapably dubious. A cornerstone of classical thermodynamics, the entropy idea also represented a philosophic denouement of nineteenth century science. Yet, closer scrutiny of the operations of the Carnot cycle confirms earlier suspicions about the nature of entropy, thus equally demanding that we re-examine its molecular-statistical offshoot, the notion of randomness.

It is noteworthy that thermodynamics, always eminently practical, dealt with the palpable universe. However, thermodynamics apparently rests on a foundation of Newtonian intangible, such as energy, work, heat, etc. All the same, its outcomes are perceivable to the human senses, in contrast to the inferential reality of the quantum-molecular world. It is indeed intriguing that the foundations of thermodynamics now appear no less mystifying, perhaps even dubious, a conclusion that strikes at the heart of the scientific method itself.

REFERENCES

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