THERMODYNAMIC QUANDARIES: SAVING THE FIRST LAW FROM THE GIBBS ENERGY; AND REVISITING NUCLEAR FUSION

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Abstract – It is argued that the conventional view of the Gibbs free energy apparently contravenes the first law of thermodynamics because of the temperature dependence of the entropy term therein. Thus, the yield of the Gibbs free energy in a system undergoing change is not constant, hence implying that energy is being created or destroyed in the process. The ambiguity can be traced to the entropy concept of the original Carnot theorem, which is manifestly dubious and illusory, as argued previously. Unrelatedly, the nuclear fusion controversy is explored in terms of chemical potential changes, arguing that fusion would be viable—if at all—in a closed equilibrium reactor: in the absence of this constraint, fusion runs afoul of mass-energy equivalence. (This also has devastating implications for the stability of the material universe.) It is also most intriguing that nuclear fusion was initially proposed as the origin of solar energy, and appears to have predated the theory of nuclear structure.

INTRODUCTION

Gibbs Energy and the First Law of Thermodynamics

Heat, Work and Free Energy

Modern thermodynamics apparently evolved out of concerns about the nature of energy and work, particularly in heat engines, during the course of the nineteenth century. The theoretical basis of the conversion of heat into work, in terms of a practical and quantitative measure of the efficiency of the process, was a prime consideration of these studies.

The Carnot cycle and the entropy idea. A particular concern was the efficiency of heat engines operating in cycles, which apparently led to a theoretical model in the form of the Carnot cycle. However not only was this based on an analysis which is manifestly dubious [1], but it also led to the concept of entropy, dealing with heat changes during isothermal expansion and compression. Since internal energy is constant in an isothermal process, it was implied that heat exchange led to changes in entropy, identified with disorder in later statistical models as applied to molecular ensembles.

External work and free energy. The concept of entropy was followed by the concept of 'free energy', defined as the part of the energy change accompanying a process that was available for external work. The 'unavailable energy' is often identified with the energy change that typically occurs in an isothermal process, *i.e.* the entropy change, this being unrelated to the work obtained. The Gibbs free energy (G) was thus defined as in Eq. 1, and changes in G as in Eq. 2 (H is the enthalpy, S the entropy and T the absolute temperature):

$$G = H - TS \qquad (1)$$

$$\Delta G = \Delta H - T\Delta S \qquad (2)$$

As argued previously [1], however, the entropy concept is problematical but may be accommodated in terms of the mass/energy ratio, an increase in this being identified with increasing entropy (hence stability).

Critique

Eq. 2 is indeed employed widely in chemistry, and its validity as such is examined herein. (G is also termed the Gibbs energy henceforth, as per current usage.) A particular problem with Eq. 2 is that it is apparently in conflict with the first law of thermodynamics. This is because ΔG now changes with T, so energy would be created or destroyed (depending on the signs and magnitudes of ΔH and ΔS) with varying temperature. Such violation, however, can be traced to the dubious assumptions inherent in the illusory Carnot cycle, thus raising serious concerns about the validity of Eqs 1 and 2 also.

The Nuclear Fusion Problem

Mass-energy equivalence and the mass defect

The nuclear binding energy curve. The idea that nuclear fusion yields energy is based on the presumed validity of the nuclear binding energy curve. However, as argued previously [2], there are serious problems concerning these assumptions, arising from the inherent inaccuracies of early mass spectrographic studies, which thus cast doubt on the mass-defect idea. Furthermore, the nuclear fusion idea apparently runs into conflict with the mass-energy equivalence idea, by which heavier nuclei would possess more energy than lighter nuclei, on an atom-per-atom basis. (This is ironical as the mass defect is itself based in mass-energy equivalence!)

Nuclear fusion and equilibrium. However, nuclear fusion can be justified on the grounds that the overall mass would be conserved in an equilibrium process, but this is predicated on the validity of the mass defect idea. All the same, once the equilibrium criterion is removed, heavier atoms should gradually disintegrate to more stable lighter atoms, by mass-energy equivalence.

Historical intrigues. The historical development of the nuclear fusion idea is also intriguing, as it apparently preceded the evolution of the basic concepts of nuclear and atomic structure. Thus, nuclear fusion was originally proposed to explain the origins of solar energy, based on spectral evidence for the presence of hydrogen and helium in the sun's radiation. However, this raises the question whether the assumption of nuclear fusion influenced the development of the theories of nuclear and atomic structure, particularly the mass defect idea!

DISCUSSION

Gibbs Energy and the First Law of Thermodynamics

Defining the Problem

Restatement. The problem with Eq. 2, again, is that it is apparently in conflict with the first law of thermodynamics, which states that energy cannot be created or destroyed. By Eq. 2 ΔG changes with T, implying that the energy output from the system (say a chemical reaction) that can be employed for external work, is not constant. This is clearly unacceptable, as the first law of thermodynamics is a cornerstone of modern scientific theory.

Clear conflict with the First Law. Thus, for instance, in the case of a process with $\Delta H < 0$ and $\Delta S > 0$, ΔG would become increasingly negative (*i.e.* the reaction increasingly exergonic) with increasing temperature T (*cf.* Eq. 2). This implies that with increasing temperature the system yields more energy for external work. The higher temperature at which the system is maintained would, of course, be the same as that of the surroundings, which implies the input of extra energy. Thus, the system would only be returning part of the extra energy to the surroundings (at higher T), although Eq. 2 does not make this clear!

Source of the Problem

The Carnot cycle conundrum. These anomalies apparently have their origins in the Carnot cycle, particularly the concept of isothermal pressure-volume work. As argued previously [1], the validity of the Carnot cycle including the original idea of entropy, and indeed the viability of pressure-volume changes in an isothermal process, are dubious and at best complex.

Thus, although isothermal pressure-volume changes may occur for an ideal gas, this does not qualify as work by the system. And neither is heat exchange possible at constant temperature. These arguments may be examined via the definition of enthalpy (Eq. 3), where E is the internal energy, P the pressure, V the volume, n the number of moles and R the gas constant. (Also, for an ideal gas: $PV = nRT$.)

$$H = E + PV = E + nRT \qquad (3)$$

Eq. 3 makes it abundantly clear that the enthalpy H remains constant for an isothermal process, as the internal energy E is constant at constant temperature T. This also implies that no work is performed by the system under these conditions (by the first law of thermodynamics).

<u>The entropy problem</u>. The constancy of PV at constant T implies that $P_1V_1 = P_2V_2$, greater volume being then the result of a correspondingly lower (external) pressure but not of an intake of energy, as invoked in the idea of entropy (Eq. 4):

$$\mathrm{d}S = \mathrm{d}Q_{\mathrm{rev}}/T \qquad (4)$$

In Eq. 4, $\mathrm{d}Q_{\mathrm{rev}}$ refers to the heat absorbed (reversibly) at constant temperature T. Thus, $\mathrm{d}Q_{\mathrm{rev}}$ can be identified with the change in the enthalpy ($\mathrm{d}H$) which should be 0 by Eq. 3.

In fact, and most importantly, although $\mathrm{d}Q_{\mathrm{rev}}$ is considered to be distinct from the enthalpy change, *i.e.* relating only to the entropy change, this appears sophistic and presumptive in light of the above arguments.

In a more general sense, the invalidation of the entropy idea also invalidates the idea of heat change at constant temperature. Thus, the $T\Delta S$ term in Eq. 3 is highly dubious, and this indeed is the reason for its conflict with the first law of thermodynamics.

<u>Entropy and Gibbs energy</u>. Intriguingly, another source of ambiguity is that, in the original Carnot theorem, an increase in entropy S is believed to result from the absorption of heat by the system (also *cf.* Eq. 4); however, by Eq. 2, a positive ΔS results in a release of heat to the surroundings! In fact, confusion apparently surrounds the Gibbs energy concept, with treatments differing with the source, although all converge on the idea that a lowering of the Gibbs energy characterizes a spontaneous process.

The Nuclear Fusion Problem

Defining the Problem

The mass-defect ambiguity. The possibility that nuclear fusion would be a source of clean and bountiful energy is clearly alluring. However, as has been previously argued at length [2], there are serious problems with the very concept of nuclear fusion, essentially because of the likely invalidity of the nuclear binding (‘mass defect’) energy concept. This is because of the inaccuracies of the early mass spectrographic studies on which the theory of nuclear structure and stability is based.

The mass-energy equivalence conundrum. A second source of ambiguity concerning nuclear fusion is the idea of mass-energy equivalence, by which heavier atoms should be less stable than lighter ones [2]. This can be a serious theoretical stumbling block to realizing fusion, quite apart from the ambiguity of the binding energy concept. However, the mass-energy equivalence argument would apply only on an atom-to-atom basis, hence fusion can possibly be justified under certain experimental conditions, as discussed further below.

The Equilibrium Reactor for Nuclear Fusion: Circumventing Mass-Energy Equivalence

Chemical potentials and a hypothetical reactor. It is possible to envisage a nuclear fusion reactor, the thermodynamic basis for which is shown in Fig. 1. This displays the changes in chemical potential for the fusion of two nuclei of atom A form a product atomic nucleus B. This approach assumes—for argument—the validity of the mass defect idea, hence the formation of nucleus B is accompanied by the release of fusion energy ($\Delta\mu$). The case for fusion rests on the enormous value of $\Delta\mu$ expected by mass-energy equivalence (the basis of the mass-defect idea) [2].

Note, however, that the chemical potential of nucleus B is still higher than that of a single nucleus A, by mass-energy equivalence. The problem now is that fusion will occur as long as the reactant nuclei (A) are present, particularly in excess. However, in the absence of them, the equilibrium would tend to revert to the reactants with the decomposition of nucleus B. (This indeed would happen once the equilibrium reactor is removed.) And the mass-energy equivalence effect would be orders of magnitude greater than the mass-defect value, as this time whole nuclei are involved!

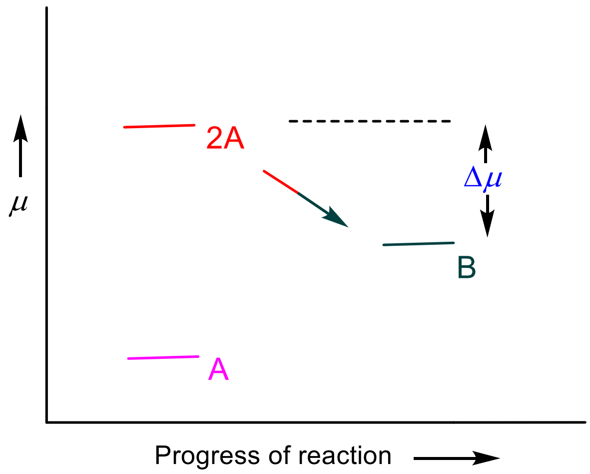

Fig. 1. Nuclear Fusion Thermodynamics.

Changes in the chemical potential (μ) during the fusion of two nuclei of atom A to form the new product nucleus of atom B: $2A \rightarrow B$. $\Delta\mu$ represents the stabilisation energy corresponding to the mass defect in the nucleus of B, deriving from mass-energy equivalence. Based on these assumptions, fusion can be justified in an enclosed equilibrium reactor. However, on an atom-by-atom basis A is more stable than B, although the chemical potentials add up in 2A. Thus, if the reactor enclosure is removed, B should revert to A, mass-energy equivalence now working in reverse. (Other radiative and non-radiative by-products are not shown and energy changes are not to scale.)

Fusion as manifestly unviable! Thus, there may be serious practical problems to realizing nuclear fusion—even assuming the validity of the mass-defect idea—as the thermodynamic basis for fusion is subtle. Furthermore, in a more general sense, the above thermodynamic analysis of nuclear fusion requires that the relatively heavier nuclei decompose—however slowly—to lighter nuclei.

The implications of this conclusion for the stability of the material universe are, of course, both intriguing and ominous! And conversely, however, the observed stability of the material universe implies that the case for nuclear fusion remains dubious! (It is also intriguing that the idea of fusion in an open system, *e.g.* a thermonuclear device, seems unviable.)

Historical Background to Nuclear Fusion

An intriguing precedent. It is noteworthy that the idea of nuclear fusion had been the subject of speculation even before the development of the modern theory of nuclear structure. Thus, the origins of solar energy had intrigued the imagination of astronomers and related practitioners, even as early as the late nineteenth century. Ingenious spectral studies of solar radiation had led to the discovery of both hydrogen and helium, from their emission lines, in the sun. This had led to speculation that the conversion of hydrogen to helium could be the source of at least a part of solar energy. It is intriguing, again, that the theory of nuclear structure was to follow in the wake of these speculations!

CONCLUSIONS

Gibbs Energy and the First Law of Thermodynamics

The concept of free energy is derived from key ideas behind the Carnot theorem. The invalidation of the Carnot theorem thus raises serious concerns about the validity of the Gibbs energy itself. In particular the entropy term therein seems unviable as it is apparently based on a fallacy, *i.e.* the idea of exchange of heat between a system and its surroundings in an isothermal process. This apparently raises an unresolvable conflict with the first law of thermodynamics, which being fundamentally valid, must prevail.

The Nuclear Fusion Problem

The thermodynamic basis of nuclear fusion—even assuming the validity of the mass-defect idea—is subtle. Apparently, nuclear fusion can possibly occur in a reactor designed to sustain the equilibrium between the reactant and product nuclei. Generally, however, both the ambiguous mass-defect idea and mass-energy equivalence apparently conspire against nuclear fusion. In fact, mass-energy equivalence implies that heavier nuclei should disintegrate into lighter ones, if the theory of nuclear fusion is valid! The historical background to nuclear fusion apparently indicates that its speculative origins may have shaped the further development of atomic and nuclear theory. Thus, the real potential of nuclear fusion as a source of energy in these troubled times is indeed unclear.

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