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Historical Observations on Laws of Thermodynamics[†]

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Most textbooks quote four anonymous laws of thermodynamics (zeroth, first, second, and third), but it seems that every author has their own idiosyncratic statements. Why are there so many versions? Why are the laws of thermodynamics not credited with names of their discoverers? We revisit the history of the laws of thermodynamics and consider whether it would be less confusing, to both students and practitioners, if we define separate laws for reversible and irreversible thermodynamics and simply assign names to them. Central to our understanding of chemical thermodynamics are the concepts of "equilibrium" and "state functions"; these require definition before the various laws can be properly formulated. The idea of a state function is implicit in Black's caloric theory of heat and also suggested by Priestley in phlogiston theory, but it was Gibbs who first represented thermodynamic properties as two-dimensional "surfaces" in 1878; that is, 30 years after the various principles that became the laws of thermodynamics had been discovered. It was even later that Duhem rigorously specified equilibrium states in general, and hence state functions. Here we conjecture that confusion has arisen because there should be two different sets of laws: one for equilibrium thermodynamic processes, and another set for irreversible processes. Then we can identify the laws of equilibrium thermodynamics for changes in enthalpy, energy, and entropy, which can be credited to Hess, Rankine, and Carnot, and corresponding laws of irreversible thermodynamics assigned to Joule, Mayer, and Clausius, respectively.

Introduction

It seems to be now generally accepted in the pages of popular science that there exist four laws of chemical thermodynamics which are of such fundamental importance as to drive all change in the universe.[1] To whom do these laws belong? Almost all of the fundamental laws of nature have been credited to their discoverers: Newton's laws of motion, Faraday's laws of electrolysis, Ohm's, Fick's, Fourier's, and Darcy's, laws of transport, and so forth. Why, we ask, have the laws of thermodynamics not been credited? One reason can be clearly found in Professor Rowlinson's book,[2] which asks the question "Why do gases condense to liquids, and why do liquids freeze to solids". The subject of thermodynamics answers all of these questions; indeed, simple laws relating energies of materials to heat and work we now know explain all physical and chemical processes at the phenomenological level of interpretation (as distinct from molecular and electronic levels).

On the page of Rowlinson's book that deals with the history of the thermodynamic laws, one finds the names Joule, Kronig, Herapath, Clausius, Maxwell, Carnot, Mayer, Thompson, Rankine, Helmholtz, and Laplace! Is it possible to allocate credit and would this be helpful toward a better understanding of thermodynamics? Does a chemical engineering student need to know that Rudolf von Clausius said "the entropy of the universe is increasing towards a maximum"?

Various textbooks throughout the 20th century have indexed, formulated, and quoted the laws quite differently. In mechanical engineering, the second law was considered to deal with the efficiency of heat engines only, whereas what was called the third law dealt with entropy increases. Directly defining zero points for entropy calculations was not considered by some to be a law at all. Gradually, the older second and third laws have been combined into the second law, and the more modern third law has become widely adopted. A "zeroth law" was added 100 years after the first and second, but it is difficult to see why.

The present situation can only be described, at best, as "confusing". McGlashan, student of renowned thermodynamicist Guggenheim, and author of student textbook "Chemical Thermodynamics" famously stated "thermodynamics is difficult enough without troubling the students with its history".

Not all scientists recognize that there are four laws of thermodynamics, but everyone acknowledges that there are at least two. From a teaching point of view that may be all that is necessary (see the choice of chapter titles of the book by Rowlinson and his colleagues;[3] they make no reference to zero or third laws). Teachers of engineering can be more pragmatic; from an engineering perspective, it does not matter who got the laws. Indeed, in the spirit of McGlashan's quip, we can present the subject without even "troubling the students" with the concept of laws at all. We can simply start with the conservation equations of mass and momentum and proceed to treat energy and entropy likewise, without mention of any laws of heat and work.[4] In a pure treatment of equilibrium thermodynamics there is no "heat" or "work", just the functions of state such as heat capacity, thermal expansion, and compressibility.

Principles of Thermodynamic Equilibrium

Newton's Principle: Mechanical Equilibrium. The fundamental laws governing the mechanical equilibrium of solid and fluid systems were formulated by Isaac Newton in 1687 in

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Principia first in Latin and later in English.[5] Simply stated, for a single component system, in the thermodynamic limit in which the system is essentially of infinite extent compared to its containing surface, the system is in mechanical equilibrium if there are no pressure gradients within the system, excepting the gravitational force on a static fluid.

Pressure is the constant of proportionality between a force vector and an area upon which the force acts and as such is in general a tensor; at equilibrium all forces are balanced. The off-diagonal elements are shear stresses, which must equal zero. It further follows that all of the gradients of all of the normal elements of the pressure tensor, of a system at mechanical equilibrium, are equal to zero in accord with Newton's laws.

For heterogeneous thermodynamic systems the criteria for mechanical equilibrium become more complicated as we have to consider the forces at the interface. Around 1805, using Newton's formalism for force balances, Young[6] and also Laplace[7] described the pressure drop across an interface. At that time, these laws were justified on purely mechanical grounds. After the various laws of thermodynamics had been discovered, it was not until 1878 that Gibbs[8] used thermodynamic potentials to show that force balance laws of Newton, Young and Laplace were necessary conditions for mechanical equilibrium of heterogeneous systems, that is, systems of more than one phase defined by interfacial boundaries.

Newton's principle can be simply restated: "*If there exists in any fluid body gradients of potential energy, i.e. forces, there will be bodily movement in the direction of the forces until all forces are balanced and the system is at rest in mechanical equilibrium*". The bodily movement referred to in the thermodynamic systems defines the concept work (W), with the dimensions of energy.

Black's Principle: Thermal Equilibrium. It could be argued that the discovery of the "principle of thermal equibrium" should be credited to the inventor of the thermometer. The development of thermometry, however, cannot be accredited to a single person. Thermometers evolved over hundreds years from thermoscopes (heat detectors). The first clear diagram of a thermoscope showing a scale and thus constituting a thermometer was published by English physician Robert Fludd in 1638, but the history of thermoscopes and thermometry is rather longer than that (see Wikipedia: thermometry). We may even have to go back 2000 years to Philo, ancient philosopher who died in 50 AD, and who conducted an early experiment on the expansion of air with heat. He created a device which has been called the first thermometer, meaning "heat meter" in Greek.

The first person to state the principle underlying thermometry and use the word "equilibrium" was Joseph Black, in his lectures delivered in 1787 at the University of Edinburgh.[9,10] He said, "*even without the help of thermometers, we can perceive a tendency of heat to diffuse itself from any hotter body to the cooler around, until it be distributed among them, in such a manner that none of them are disposed to take any more heat from the rest. The heat is thus brought into a state of equilibrium*". Black then states, the principle of thermal equilibrium, that "*... all bodies communicating freely with each other, and exposed to no inequality of external action, acquire the same temperature, as indicated by a thermometer. All acquire the temperature of the surrounding medium*." This appears to have been the first statement of the principle of thermal equilibrium that was later to become the "zeroth law".

Maxwell's "law of equal temperatures", published[11] almost 100 years after Black, also stated "*if when two bodies are placed in thermal communication neither of them loses or gains heat, the two bodies are said to have equal temperatures and are then said to be in thermal equilibrium*".

The term "zeroth law" first appears in the literature in 1939 in the book by Fowler and Guggenheim.[12] The say: "*This postulate of the 'existence of temperature' could with advantage be known as the zeroth law of thermodynamics*." There seems to be no more rationale, however, for a "zeroth law" of thermodynamics for Black's principle of thermal equilibrium than there is for Newton's principle of mechanical equilibrium. We see from Duhem's theorem[13] below that both these two principles are equally important criteria for specifying the thermodynamic state of a system at equilibrium as one that does no work, that is, has no unbalanced forces, and that also exchanges no heat, that is, has no gradients of temperature.

Duhem's Theorem: Equilibrium State. Duhem at the age of 24 wrote a thesis in 1884 which he submitted at the Sorbonne in Paris. This thesis was refused through the influence of Berthelot, who was still trying to support his erroneous maximum work principle. The thesis was published two years later:[13] Duhem was among the first to recognize the great work of J.W. Gibbs which, ten years after it was published, indeed in Gibbs lifetime, was not understood by others in the field, Duhem being the exception.

In a system of fixed composition, there are only two ways of changing the energy, doing work or exchanging heat, so two variables define the state of the system. This statement is a prerequisite to the laws of thermodynamics. The description of the equilibrium position includes complete knowledge of the extensive and intensive properties of the system. This is applicable to all closed systems. For example, a fixed amount, or mass, of a gas is a simple case of a two-dimensional system. In this example, the system state is uniquely specified by two parameters, such as pressure and temperature, or perhaps density and temperature.

Duhem's theorem[13] formally states the relation between the variance, that is, number of degrees of freedom, of a closed system and its equilibrium position. The theorem states: "*for a closed system of known composition of individual masses of all its components, only two other independent variables are required to define the equilibrium state of the system*".

Whatever the number of phases, the number of components, or the number of chemical reactions, the equilibrium state of a closed system, for which we know the initial masses of all components, is completely defined by two independent state variables. For any system in mechanical equilibrium with no unbalanced forces, and in thermal equilibrium with no temperature gradients, the state variables are temperature (T) and pressure (P). According to Duhem's theorem, then volume (V), for example, is a unique function of state $V(T,P)$.

Gibbs's Principle: Equilibrium State Function. The principles of mechanical and thermal equilibrium apply to all fluids or solids: well-defined systems of pure components, or homogeneous composites of more than one component are amenable to evaluation of properties. It is these two principles that lead directly to the very simple laws of thermodynamics from which the principle of chemical equilibrium was deduced by Gibbs. Simply stated, if a thermodynamic system is composed of more than one component, then it is in a state of chemical equilibrium when there are no gradients of chemical potential of any component within the system.[14,15]

Central to an understanding of chemical thermodynamics is the concept of a "state function" that requires a definition before the various laws can be properly formulated. The idea of a state function is implicit in Black's caloric theory of heat. Black and his contemporaries did not know the difference between internal energy (U) and heat (Q), which is transferred energy.

The earliest suggestion that the driving force for chemical change was also a property that the amount of which varied from one substance to another and depended on state is the phlogiston theory of chemical reactions.[16] Phlogiston was never clearly defined; some philosophers regarded phlogiston and fire as being synonymous, when a solid burned, it simply transferred its phlogiston to the air.

We now know that the understanding of chemical reactions is inextricably dependent upon an understanding of the concept of "heat". A big step forward in the XVIII century was the introduction of the concept of a state function caloric by Joseph Black. Unfortunately, at that time, scientists did not know the difference between energy the state function and heat, which is not internal energy within a material but energy on the move. Prior to the advent of thermodynamics around 1850, all scholars of science believed in the caloric theory that heat was a conserved fluid with no mass. It was present in various amounts in all materials and flowed from high to low concentrations. The caloric content depended on temperature and the physical state; gases had a high caloric content and solids a low caloric content. The basic misconception was that caloric was a conserved substance, that it could be "neither created nor destroyed". We now know that what was thought to be the "caloric" content is more akin to internal energy, or perhaps more appropriately, enthalpy, as most measurements were made at constant (atmospheric) pressure, not constant volume.

Priestley was the principle and eventually the only phlogiston protagonist. In 1792, after Lavoisier had discovered the law of conservation of mass in chemical reactions, and thereby "proven that phlogiston could not exist", Priestley addressed his paper on the composition of water to all of the "antiphlogistonists", quote[16] "*...The phlogiston theory is not without its difficulties. The chief of them is that we are not able to ascertain the weight of phlogiston, or indeed that of the oxygenous principle. But neither do any of us pretend to have weighed light, or the element of heat, though we do not doubt but that they are properly substances, capable by their addition, or abstraction, of making great changes in the properties of bodies, and of being transmitted from one substance to another*".

In 1873 Gibbs in his paper[14] "Graphical Methods in the Thermodynamics of Fluids", states: "The quantities V, P, T, U, and S are determined when the state of the body is given, and it may be permitted to call them functions of the state of the body". Let us add H (enthalpy) to Gibbs's list ($H = U + PV$). Now, the first observation that we can make, with hindsight, is that "H is a state function" is one form of the first law of thermodynamics. For all state functions, the functional value remains unchanged in a cyclic process, and the value H can only be changed by adding or subtracting heat (Q). The statement "energy ($U = H - PV$) is a state function", is also an alternative form of the conventional first law since PV is, by definition, a state function equal to work (W).

It follows that, since Q/T is also a conserved quantity in reversible processes, a sufficient statement of the second law for equilibrium thermodynamics is simply "entropy S (defined by $\Delta S = Q/T$) is a state function". "Gibbs free energy ($H - TS$) is a state function" and "Helmholtz free energy ($U - TS$) is a state function" are equivalent statements of the second law.

Laws of Thermodynamic Equilibrium

Hess's Law (1840): Enthalpy Is a State Function. Hess is noted today for two fundamental principles of thermochemistry:[17] the law of constant summation of heat, best known simply as Hess's law, and the law of thermoneutrality. These discoveries, published in 1840, were postulated from simple experimental measurements without any supporting theoretical framework; Hess worked independently in isolation and total ignorance of his contemporaries involved in the early developments of thermodynamics. He investigated chemical affinity in condensed phases which led to thermometric investigations of the amounts of heat generated by chemical reactions. His experiments, carried out on systems such as the various hydrates of sulfuric acid, showed that the heat evolved in their formation was always the same, whether the reactions proceeded directly or stepwise through intermediates. Hess's law is still used to calculate enthalpy changes when direct measurements are difficult or impossible.

All Hess's experiments were on condensed phases, so there was no work involved. He could not distinguish energy from enthalpy; there was just the "caloric". With hindsight Hess's discovery of "constant heat summation" can be seen as a specific example of the law of the conservation of energy for changes in states of systems not involving work.

The law states: "*the energy change for any chemical or physical process is independent of the pathway or number of steps required to complete the process provided that the final and initial reaction conditions are the same*". Hess's law is based on the principle of the path independence of energy changes. In other words, an energy change is path-independent, only the initial and final states being of importance. This path independence is true only for state functions, so we can simplify Hess's law to the statement "*Enthalpy is a state function*".

Rankine's Law (1855): Internal Energy Is a State Function. Rankine[18] was the first to define thermodynamics: "*It is a matter of ordinary observation, that heat, by expanding bodies, is a source of mechanical energy; and conversely, that mechanical energy, being expended either in compressing bodies, or in friction, is a source of heat. The reduction of the laws according to which such phenomena take place, to a physical theory, or connected system of principles, constitutes what is called the science of thermodynamics*".

Rankine's book was the culmination of 10 years of study in which he wrote a series of papers on "The Mechanical Action of Heat", with supplements, published in the Royal Society of Edinburgh, which related chiefly to the "mutual conversion of heat and mechanical power, by means of the expansion and contraction of gases and vapours."[19] In this paper, Rankine set out to mathematically describe the variations of heat in a system, deriving from variations in volume and temperature, during an expansion−contraction cycle, after which the body returned to its original state.

Rankine correctly reasoned[20,21] that variation of heat in the body would be due to volume changes ($P-V$ work) or heat conversion to work transformations, each arising from "molecular distribution" changes that remained unspecified. These changes in energy, which he first described as "internal energy" changes, were represented by Rankine with the symbol U.

Specifically, Rankine stated: "*if, on the whole, any mechanical power has appeared, and been given out from the body, in the form of expansion, an equal amount must have been communicated to the body, and must have disappeared in the form of heat; and if any mechanical power has appeared and been given out from the body in the form of heat, an equal amount must have been communicated to the body, and must have disappeared in the form of compression*." He states this principle using the following formula: "$\Delta\Pi + \Delta Q' = U$, *Where* Π, *when* *positive, represents "expansive power" mechanical energy given out, when negative, compression power absorbed; and Q′ represents, when positive, heat given out, when negative, heat absorbed*". Rankine's law appears to be the earliest formulation of what is commonly known as "the 1st law of thermodynamics".

In relation to Carnot's caloric particle heat supposition, that the "quantity of heat remains unchanged" in its passage through the working substance, from a hot body to a cold body, Rankine was able to conclude "that no mechanical power can be given out in the shape of expansion, unless the quantity of heat emitted by the body in returning to its primitive temperature and volume is *less* than the quantity of heat originally received".

This, however, was not new but is consistent with what had already been deduced and published by Carnot in 1824 and later by Clapeyron in 1834. Rankine reviewed the second laws some years later and gave due credit to Carnot, Clapeyron, and Clausius for their various "entropy principles".[22]

Carnot's Law (1824): Entropy Is a State Function. It is often said, "thermodynamics owes more to the heat engine than the heat engine owes to thermodynamics". Early engines were designed empirically without the knowledge of thermodynamics, but their performance encouraged leading engineers to become scientists. The first such engineer was Sadi Carnot, who in 1824 published[23] (in French) *Reflections on the Motive Power of Fire*, a discourse on heat, power, and engine efficiency. Carnot's publication marked the start of thermodynamics as a modern science. Although work is 100 % converted into heat content, or enthalpy of its recipient body fluid, heat cannot be wholly reconverted to work when it flows from hot to cold. Sadi Carnot was the first to establish what fraction of thermal energy can be converted to work (mechanical energy) in any cyclic process using a working substance (steam) at equilibrium.

Carnot said[23] "*The production of motive power is then due in steam engines not on actual consumption of the caloric (sic heat) but to its transportation from a hot body to a cold body*". On the study of the efficiency, Carnot said "*The motive power of a waterfall depends on its height and on the quantity of the liquid; the motive power of heat depends also on the quantity of caloric used and on what may be termed the height of its fall, i.e. the difference of temperature of bodies between which the exchange of caloric is made...in the fall of the caloric, the motive power increases with difference in temperature*".

Carnot effectively had the second law, before anything resembling a "first law" had been stated by either Joule or Mayer, or formulated by Rankine; the term "entropy" was yet to be coined. Not all of the heat was converted into work, so the working substance had "unavailable" heat that depended on its temperature.

In 1834, Emil Clapeyron[24] made his first of many contributions to chemical thermodynamics by publishing a report entitled the *Driving Force of the Heat*, in which he further developed the work of Carnot, deceased two years before. Though Carnot had developed a compelling analysis of a generalized heat engine, he had employed the caloric theory, however, that believed heat, or equivalently caloric, to be the conserved quantity.

Clapeyron, in his memoir, presented Carnot's work in a more accessible and analytic graphical form, showing the Carnot cycle as a closed curve on an indicator diagram, a chart of pressure against volume (named Clapeyron's graph in his honor). In 1843, Clapeyron[25] further developed the idea of a reversible process already suggested by Carnot and made a definitive statement of *Carnot's principle*, which is the first version of the second law of thermodynamics.

It was Clausius who later defined entropy, but the essential concept of the unavailable energy being the relative of state function entropy is contained in the modern-day temperature versus entropy plot of the reversible Carnot cycle. On this basis, we feel credit for the law of entropy balance in reversible processes should be Carnot's law.

Laws of Irreversible Thermodynamics

Joule's Law (1843): Enthalpy Change Equals Work Done. The two names that are normally associated with the conventional first law of thermodynamics are Joule and Mayer. While it was Mayer who was the first person to state the principle of "*conservation of energy*", it was Joule who should be credited with all of the painstaking experimental research that led to the principle and accurate experimental determination of the "mechanical equivalent of heat". These two principles are not quite the same.

Prior to Joule there were two forms of energy: work (W) measured in ergs, and heat (Q) measured in calories. Joules experiments showed that doing an amount of work W on a thermodynamic system, in any process however irreversible, the enthalpy will increase by an amount W, which has the same effect as increasing the temperature ΔT by adding an equivalent amount Q of heat. That is obtainable from the heat capacity (C_p) for an adiabatic system, hence $W = Q = C_p\Delta T$.

Joule invented a very accurate gas thermometer. He measured heat from electrical work[26] produced by battery generator and deduced "Joule's law" (power equals resistance times current squared). He measured heat from friction between moving cast iron plate surfaces.[27] He measured heat caused by shear flow from rotating paddles in various liquids[28] that resulted in Einstein's law (power per unit volume equals viscosity times shear rate squared). Joule also measured heat from elongational flow, liquid forced through small tubes by mechanical pressure. Eventually, after 10 years of very careful experimentation he deduced the "mechanical equivalent of heat" and measured its value.[29] The modern SI unit for energy, heat, or work, is named in his honor: 1 thermochemical calorie = 4.184 J.

Since all Joule's experiments and conclusions relate to irreversible processes, his "mechanical equivalent of heat" principle relates to a more general law for changes in enthalpy than that of Hess who considered only heat changes. All work is 100 % converted to its equivalent heat energy, that is, it increases the enthalpy of the recipient system in all processes reversible or irreversible by the amount W or equivalently Q.

Joule's law was summarized more eloquently by Thompson[30] in 1850 "*when equal quantities of mechanical effect are produced by any means whatever out of thermal sources, or lost in purely thermal effects, equal quantities of heat are put out of existence or are generated*".

Mayer's Law (1843): Energy Change Is Zero. Mayer was the first person to state the law of the conservation of energy,[31,32] that is, "*the total energy of a system remains constant in any isolated system of objects that interact with each other only by way of forces that are conservative*". It applies to all thermodynamic processes, reversible or irreversible, and is far more general than Hess's and Rankine's law that enthalpy and/or internal energy are state functions.

Mayer predicted and showed, for example, that if kinetic energy transforms into heat energy, water should be warmed by vibration. He not only performed this demonstration but predicted also a quantitative factor of the transformation, calculating the mechanical equivalent of heat about the same time as Joule.[33] In a later treatise[34] Mayer independently predicted a more accurate numerical value of the mechanical equivalent of heat: in confirmation of the earlier work of Joule. He theorized that in all chemical and physical processes, reversible or irreversible, heat transfer or work, energy is the conserved quantity, not heat.

This relation $W = Q$ implies that, although work and heat are different forms of energy, work is entirely transformed in increasing the enthalpy of its recipient fluid (Joule's law) Mayer's law gave rise to an alternative, more general principle of conservation of energy in all universal processes, including radiation and electromagnetic. Indeed, the general laws of conservation of energy were definitively stated and formulated by Helmholtz in 1847.[35] Neither Joule, who was a brewer, nor Meyer the physician were particularly scholarly. Their discoveries, it could be argued, needed to be "tidied up" by Helmholtz the academic. In 1847, however, Helmholtz[35] was apparently unaware of the discoveries of Mayer, but he references Joule's 1845 paper.[28] On page 52 of "*selected writings*"[35] Helmholtz wrote "*Concerning the law of the conservation of force, let me supply an omission here by noting that Robert Mayer published his essays...in 1842 and...in 1845. The conviction that there is an equivalence between heat and work was expressed in the first essay; the second essay is in reality the same as mine. I only came to know of them later*". In 1847, Helmholtz published his far more scientifically accomplished paper on laws of energy conservation independently of Mayer and the later work of Joule. To his credit, however, in all subsequent writings and lectures, he later always places Mayer's name first and gives due recognition to Joule.

Clausius's Law: Entropy Always Increases. In his classic paper of 1850, Clausius[36] confirmed the already existing theories of Mayer[33] on the conservation of energy and Joule[28] on the mechanical equivalent of heat, and then he went on to investigate the observation that heat always flows naturally from hot to cold. This observation had not previously been quantified. Clausius knew that some heat had to be rejected from a Carnot cyclic heat engine (Q_L) just as Carnot had proposed 20 years earlier, so he knew that $Q_L = W_{net} - Q_H$, but there was no principle to fix the absolute amount of rejected heat. Clausius, however, made the simple observation that the ratio of the heat input to the rejected heat was consistently equal to the ratio of the temperature of the heat source to the heat sink; but if, and only if, the temperature of the high (T_H) and low (T_L) temperature reservoirs are always expressed on an absolute temperature scale. He deduced $Q_H/Q_L = T_H/T_L$. Rearranging for a reversible heat engine, he obtained $Q_H/T_H = Q_L/T_L$. Clausius had discovered Carnot's extensive thermodynamic property that he later called "entropy".

Clausius then examined irreversible processes[37] and found that the relationship did not hold. That is, for irreversible processes, the ratio of heat lost over absolute temperature increases in the direction of natural heat flow. The ratio of heat to temperature has characteristics of a property, since it does not change in a cycle, but it is also associated with heat transfer a path function.

In 1865 Clausius named the heat−temperature ratio (Q/T) entropy,[38] from the Greek word for "transformation". Clausius's 1865 paper ends with now famous statement that is the broadest possible application of the laws of thermodynamics: "The energy of the universe is constant", 1st law, and "The entropy of the universe tends toward a maximum", 2nd law.

Clausius's statement of the second law of thermodynamics was for all processes, but it was his definition of entropy as the ratio of two macroscopic components, heat and absolute temperature, the state function, that was the breakthrough. The concept of entropy enabled Gibbs to derive his universal principles for all physical, chemical, and electrochemical processes in the universe in terms of these simple laws of heat and work.

Conclusions

If we can include the thermodynamic property enthalpy ($H = U + PV$) in Gibbs' list, we see below that Gibbs' statement[14] that thermodynamic potentials are state functions is actually a very concise restatement of the laws of equilibrium thermodynamics. For idealized reversible processes we have:

Hess's law: enthalpy is a state function. $\Delta H = \int dQ$.

Rankine's law: energy is a state function. $\Delta U = \int dQ + \int dW$.

Carnot's law: entropy is a state function. $\Delta S = \int (dQ/T)$.

For all real processes then the laws of irreversible thermodynamics are:

Joule's law: enthalpy change equals work. $\Delta H = W$.

Mayer's law: energy is conserved. $\Delta U = Q + W$.

Clausius's law: entropy increases. $\Delta S > Q/T$.

Finally, we might ask, what about the "3rd law"? This is not a law of thermodynamics in the sense above, in that it does not deal with effects of heat or work on the state functions and indeed is not always valid as it is generally formulated. We can however, formulate simple mathematical statements about what happens to the thermodynamic state functions in the limit of approach to Kelvin's absolute zero (0 K) with assignments. We suggest, in the limit $T(\mathrm{K}) \rightarrow 0$.

Nernst:[39] enthalpy change tends to free energy. $\Delta H \rightarrow \Delta G$.

Einstein:[40] energy tends to a ground state. $U \rightarrow U_0$.

Planck:[41] entropy tends to zero. $S \rightarrow 0$.

These statements could be classed as "theorems"; indeed the "3rd law" is often referred to as Nernst "heat theorem". The main reason is that the temperature scale is logarithmic and Kelvin's extrapolation of the ideal gas law is arbitrary. Nevertheless, Planck's concept of absolute entropy has many practical applications in the determination of entropies and free energies of chemical compounds, but one hesitates to refer to these theorems as "laws of thermodynamics". Planck, moreover, could only introduce the concept of absolute entropy after Boltzmann had given his explanation of entropy at the molecular level;[42] the implication being that "the 3rd law" would not be a law of classical or irreversible thermodynamics anyhow, but of statistical thermodynamics.

Note Added after ASAP Publication: This paper was published on the Web on August 6, 2010. In the abstract, the order of the names Mayer and Joule was reversed. The corrected version was reposted on August 11, 2010.

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