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PAPER

On determining absolute entropy without quantum theory or the third law of thermodynamics

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E-mail: a.steane@physics.ox.ac.uk**Keywords:** entropy, third law of thermodynamics, Saha equation, Gibbs–Duhem equation, Sackur–Tetrode equation

Abstract

We employ classical thermodynamics to gain information about absolute entropy, without recourse to statistical methods, quantum mechanics or the third law of thermodynamics. The Gibbs–Duhem equation yields various simple methods to determine the absolute entropy of a fluid. We also study the entropy of an ideal gas and the ionization of a plasma in thermal equilibrium. A single measurement of the degree of ionization can be used to determine an unknown constant in the entropy equation, and thus determine the absolute entropy of a gas. It follows from all these examples that the value of entropy at absolute zero temperature does not need to be assigned by postulate, but can be deduced empirically.

The aim of this paper is to clarify some issues in classical thermodynamics, concerning absolute entropy and the third law of Thermodynamics. Absolute entropy is simply the total entropy of a given system, usually indicated by the symbol S . In many situations, one does not need to know the total entropy, only the entropy change ΔS in some given process. A similar statement applies to other extensive properties such as mass and volume. However, whereas it is relatively straightforward to measure total mass or total volume, and to understand the case of zero mass or volume, it is less straightforward to measure total entropy and to understand the case of zero entropy. For this reason, the term ‘absolute entropy’ is introduced to draw attention to those cases where we are interested in the entropy itself, not just the change. The fact that conditions of zero entropy are not self-evident is also the reason why the third law of thermodynamics is introduced. However, this does not mean that we cannot determine absolute entropy without the third law. It is simply that the third law is a useful summary: like any law of physics, it is at once a generalization from empirical observation, and also part of a self-consistent and elegant theoretical framework.

The third law has been useful to physicists in understanding heat capacities and other response functions at low temperature, and it proved to be very useful and influential in the foundations of chemistry. It underpins several techniques to evaluate reaction constants and affinities.

The third law, in its modern formulation, asserts that the absolute entropy tends to zero, in the limit as temperature tends to absolute zero, for each aspect of a system that remains in thermal equilibrium. The conditions are impossible to realize exactly, in a finite amount of time, but the statement is very useful nonetheless because in practice many aspects of many systems approach sufficiently closely to thermal equilibrium at low temperature that their entropy is negligible, at the lowest achievable temperatures, compared to the entropy at some other temperature of interest.

There are systems, such as a glass, which do not strictly attain a thermal equilibrium state, so the third law as stated above does not apply to them. One may still associate a temperature with a glass, and make statements about the behaviour of entropy in the low temperature limit, but the present paper is concerned purely with thermal equilibrium so we do not need to consider such systems. Similarly, we may for present purposes ignore the case of a degenerate ground state, by the argument that such a degeneracy would always be lifted in practice by some tiny interaction or loss of symmetry, so that the true ground state is not degenerate. It is an open

question whether that argument always applies, but in any case, we shall consider systems for which it does apply, and then comment briefly on the impact of ground state degeneracy at the end.

The introduction of the third law into the foundations of classical thermodynamics may leave one with the impression that, without it, the absolute entropy of a physical system could not be determined by classical thermodynamic methods, without an appeal to quantum theory. The main purpose of this paper is to show that this is wrong. But first let us examine the usual account.

The standard way to determine the absolute entropy at a given temperature T_f is to employ an integral such as

$$S(T_f) - S(0) = \int_0^{T_f} \frac{dQ_{\text{rev}}}{T}, \quad (1)$$

where dQ_{rev} is the heat entering the system by a reversible process at each temperature T . It is often convenient to use the equivalent expression

$$S(T_f) - S(0) = \int_0^{T_f} \frac{C}{T} dT + \sum_i \frac{L_i}{T_i}, \quad (2)$$

where $C(T)$ is the heat capacity under the conditions of the change, and L_i are latent heats. If one asserts that $S(0) = 0$ on the basis of the third law, then $S(T_f)$ can be determined by evaluating the integral and sum on the right-hand side. In practice this is done by a combination of empirical observation and mathematical modelling. The latter is required, for example, in order to carry out an extrapolation to $T = 0$.

It is widely believed and asserted that, without the third law, classical thermodynamics only makes statements about entropy changes, and cannot give values of absolute entropy, because it is based on equations such as

$$dU = TdS - pdV. \quad (3)$$

We will show that this is not true, in the following sense. Only volume change dV , not absolute volume, V , is involved in the expression for work done on a simple compressible fluid, but it does not follow from this that there is no ready definition of absolute volume, or empirical method to determine absolute volume, without appealing to a postulate concerning, for example, the value of V in the limit of infinite pressure. Similarly, only entropy change dS , not absolute entropy, S , is involved in the expression for heat exchange, but it does not follow from this that there is no ready definition of absolute entropy, or empirical method to measure it, without appealing to the third law.

We will present several simple empirical methods that allow the absolute entropy of a fluid to be deduced without any use of quantum theory, and without calorimetry or cooling to near absolute zero. This will clarify what classical thermodynamics can and cannot tell us about entropy. In particular, it is not true to say that classical thermodynamics can predict entropy changes but not the absolute entropy of an ideal gas, as if entropy were a special case, unlike internal energy, pressure, temperature and so on. In fact in each of these cases a combination of a modest amount of empirical observation is combined with thermodynamic reasoning in order to yield general information about the system properties, and this is just as true of absolute entropy as it is of other properties.

Of course quantum theory correctly describes the structure of any system, within the limits of our current understanding of physics, and classical theory does not. An attempt to model a gas in terms of classical particles obeying Newton's laws of motion, for example, completely fails to describe the low-temperature behaviour correctly. So in this sense quantum theory is needed and cannot be avoided. However, the argument of the present paper, like many thermodynamic arguments, is playing a different role. It is showing how thermodynamic reasoning can be invoked to connect one physical property to another, so that an empirical measurement of one property allows us to infer the other, without the need for a theoretical model of the structure of the system. That is the sense in which we shall present methods to determine absolute entropy without the use of quantum theory.

The methods to be discussed do not invoke the third law. Therefore, by also determining the values of the integrals and sum on the right-hand side of (1) or (2), one can infer the value of $S(0)$ without appealing to the third law. The third law remains a useful observation about the results of such studies.

It follows from this that the value of the entropy at absolute zero cannot be assigned arbitrarily. It is *not* the case that a universal offset in the entropy would have no observable consequences in classical thermodynamics. The situation is different from that of potential energy, for example, and gauge freedom more generally. Some textbooks do not address this issue, but most, such as Callen (1985), Carrington (1994) or Blundell and Blundell (2006) imply that the absolute entropy is undetermined without a postulate such as the third law, and some, such as Wilks (1961) and Adkins (1983), include an explicit statement that there is such a freedom, akin to gauge freedom. Carrington, p 190 states: '... it (the third law) means that we may consistently fix the constant of integration in the definition of the entropy of a simple system. ... In particular, we can establish an absolute value

for the entropy of each of the chemical species' This is not wrong, but it implies that such fixing and establishing could not be done without the third law. Blundell and Blundell p 193 states: 'thus it seems that we are only able to learn about *changes* in entropy, ... and we are not able to obtain an absolute measurement of the entropy itself.' The line of argument is the same as the one followed by Wilks, p 54, where it is more explicit: 'to obtain absolute values of entropy it is necessary to make use of the third law.' Adkins, p 242 states: 'the essential point of the third law is that the constant is the same for all systems, and it is strictly a matter of convenience to set it equal to zero.' Callen p 279 states: 'in the thermodynamic context there is no *a priori* meaning to the absolute value of the entropy.' The arguments of the present paper imply that such claims are false.

Section 1 considers the entropy of thermal radiation; section 2 the entropy of an ideal gas, and section 3 that of a more general simple compressible system. All the arguments are related to the Gibbs–Duhem equation, but for the middle section of the paper that connection is indirect. Section 2.1 uses thermodynamic reasoning to obtain an expression for the total entropy of an ideal gas whose heat capacity is independent of temperature and has been given; the expression contains a single unknown additive constant. Section 2.2 presents a derivation of an equation equivalent to the Saha equation (Saha 1920, Kingdon and Langmuir 1923, Fridman 2008), which enables the unknown constant to be determined by the measurement of the degree of ionization of a hydrogen plasma. Section 2.3 discusses the validity of the method and the connection to statistical methods. The main conclusion of all the examples is that absolute entropy can be determined without appealing to either a microscopic model or the third law. The paper concludes in section 4 by presenting the implications for, and uses of, the third law of thermodynamics, in view of this.

1. Thermal radiation

First, consider thermal radiation. Note, we have no need of a particle model (or a wave model for that matter) of the radiation inside a cavity in thermal equilibrium. We require only the knowledge that the energy flux and the pressure are both directly related to the energy density. Then, the first shows, following the thermodynamic reasoning of Kirchhoff (Adkins 1983), that the energy density u is a function of temperature alone, $u = u(T)$ and the second then implies that the pressure also is a function of temperature alone. In fact one finds $p = u/3$; this can be regarded either as an empirical observation or as following from classical electromagnetism for isotropic radiation.

The entropy S of a volume V of thermal radiation in a cavity at a temperature T can be considered as a function of V and T , so that we have

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV = \left(\frac{\partial S}{\partial T}\right)_V dT + \frac{dp}{dT} dV,$$

where we used a Maxwell relation and the fact that $p = p(T)$. Therefore

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{dp}{dT}. \quad (4)$$

But, since S and V are extensive and T is intensive, we have $(\partial S/\partial V)_T = S/V$. Using this in (4) gives

$$S = V \frac{dp}{dT}. \quad (5)$$

Hence, in order to obtain S for a given V , it suffices to measure p as a function of T .

One can also, of course, adopt a less direct approach, for example by obtaining $p = aT^4$ by a standard thermodynamic argument, where a is a constant related to the Stefan–Boltzmann constant. By measuring the latter, one obtains a and thus $p(T)$ and hence S . This method makes use of the fact that the relationship $a = (4/3)\sigma/c$ between a and the Stefan–Boltzmann constant σ depends only on energy, not entropy, so does not involve Planck's constant.

We conclude that by measuring either the pressure or the energy flux at some known temperature, we can find the absolute entropy of a quantity of thermal radiation without recourse to the third law or quantum theory or any other model of the microscopic structure of the radiation.

2. The entropy of an ideal gas

We now turn to the case of an ideal gas. We will describe an experimental method to determine S which involves general thermodynamic reasoning and a single measurement of a neutral hydrogen plasma. The method is quite different to the one invoked for thermal radiation in the previous section. It relies on a connection between entropy and chemical potential, and requires a greater amount of theoretical development. First, in section 2.1,

we develop an equation for the entropy of an ideal gas, which gives the dependence on internal energy, volume and particle number, up to an unknown additive constant. Then, in section 2.2, we show how measurement of a plasma, combined with the Saha equation, yields the constant.

2.1. Entropy as a function of its natural variables

Much of the argument of the present section is in standard thermodynamics texts, but some texts stop short of the full result. We begin by considering a closed simple compressible system, and then generalize to open systems.

For a closed simple compressible system we have that the entropy may be considered a function of two variables, and we pick temperature and volume for convenience, so that we may write

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV = \frac{C_V}{T} dT + \left(\frac{\partial p}{\partial T} \right)_V dV \quad (6)$$

using the definition of constant-volume heat capacity C_V , and a Maxwell relation. For a system such as an ideal gas, where the equation of state is $pV = Nk_B T$, this gives

$$S = \int \frac{C_V}{T} dT + Nk_B \ln V. \quad (7)$$

If we now further assume that the heat capacity is independent of temperature then we have

$$S = S_0 + C_V \ln T + Nk_B \ln V, \quad (8)$$

where S_0 is an unknown constant. This is a standard ‘textbook’ result¹.

When the heat capacity is independent of temperature for an ideal gas, one can show that it is given by

$$C_V = Nk_B(\gamma - 1)^{-1}, \quad (9)$$

where γ is the adiabatic index.

The less widely known part of the argument generalizes (8) to open systems by obtaining the dependence of S_0 on N . The method is to use the extensive nature of entropy. If one begins the argument afresh, but treating $S = S(T, V, N)$, then one obtains (8) again but now S_0 is a function of N , not a constant. To find the dependence, one may use the fact that $S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)$ for any λ , and therefore $S(U, V, N) = (N/N_0)S(N_0 U/N, N_0 V/N, N_0)$ by choosing $\lambda = N_0/N$. To make use of this, one needs also the relationship between internal energy and temperature, which is

$$U = U_0 + C_V T, \quad (10)$$

where U_0 is a constant of integration. Empirically, this U_0 is the intercept with the U axis of a line tangential to $U(T)$, but note, we do not require that (10) is valid all the way to absolute zero, and in fact it is not, because the gas will liquify and/or solidify and enter the quantum degenerate regime at low temperatures. We have included U_0 here (often it is set equal to zero) in order to be clear about what assumptions we do and do not need to make in the argument. Since U and C_V are extensive, and T is not, it is clear that this U_0 must also be extensive, which we use in the following.

After expressing the temperature in terms of energy, and using the extensive nature of entropy, the result is

$$S(U, V, N) = Nk_B \ln \left[\zeta \frac{V}{N} \left(\frac{U - U_0}{N} \right)^{\frac{1}{\gamma-1}} \right], \quad (11)$$

where ζ is a constant that does not depend on U , V or N . This is the equation giving the entropy of an ideal gas of constant heat capacity, in terms of the natural variables of S . The complete thermodynamic behaviour can be derived from it. When the value of the constant ζ is also given in terms of fundamental quantities, this is the Sackur–Tetrode equation. Our interest here is in obtaining ζ from empirical measurements.

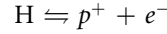
2.2. Saha equation

We now turn to the consideration of the thermal equilibrium of a hydrogen gas. Such a gas is ordinarily considered to consist of a set of molecules, or, when dissociated, neutral atoms, in thermal motion, and this is a very good approximation for a wide range of densities and temperatures. However, in fact there is always some non-zero degree of ionization, and this becomes especially important in the context of astrophysics and plasma physics, where it is a major source of information about the photospheres of stars and other plasmas. In the

¹ A general ideal gas (i.e., a system that obeys Boyle’s law and Joule’s law) need not necessarily have a heat capacity that is independent of temperature, and in fact many gases that are ideal to good approximation over some range of temperature have a heat capacity that changes significantly within that range (e.g. nitrogen in the range 300–3000 K at one atmosphere). However the restriction to constant heat capacity applies to any gas over a sufficiently small range of temperature, and describes monatomic gases very well at temperatures not near the boiling point.

following we consider an atomic hydrogen gas, allowing for its non-zero state of ionization in thermal equilibrium, but in conditions where the degree of ionization is small.

We recall the standard derivation of the Saha equation (Saha 1920, Kingdon and Langmuir 1923, Fridman 2008) which gives the degree of ionization in terms of temperature and atomic properties. The ionization/recombination process is



and at equilibrium one has

$$\mu_{\text{H}} = \mu_{\text{p}} + \mu_{\text{e}}, \quad (12)$$

where the subscripts refer to hydrogen atoms, protons and electrons, respectively. This condition can be expressed in terms of other quantities by treating the protons, electrons and hydrogen atoms as a mixture of ideal gases, but we must account correctly for the binding energy E_{R} . The effect of the latter can be understood as follows. Each gas in the mixture obeys equation (10), so we have

$$U_i = U_{0,i} + C_{V,i}T. \quad (13)$$

Where the subscript i runs over the proton, electron and neutral hydrogen gas. If one were studying any one gas in isolation, then the value of $U_{0,i}$ for that gas could be set arbitrarily, but when the three interact, the values of $U_{0,i}$ are not independent. Since each U_i is extensive, we have

$$U_{0,i} = N_i u_i, \quad (14)$$

where u_i is that part of the energy per particle that does not depend on temperature. By conservation of energy, we have

$$u_{\text{H}} + E_{\text{R}} = u_{\text{p}} + u_{\text{e}}. \quad (15)$$

Where E_{R} is the energy required to ionize a hydrogen atom. In the following we will take it that this binding energy is given, to good approximation, by the ground state ionization energy, also called Rydberg energy. This approximation ignores the internal thermal excitation of the hydrogen atoms; it assumes that in order to ionize an atom the full Rydberg energy must be provided. This is a good approximation for $k_{\text{B}}T \ll E_{\text{R}}$; we assume this limit for the rest of the argument. Since $E_{\text{R}}/k_{\text{B}} \simeq 1.5 \times 10^5$ K, the approximation will hold very well in typical laboratory conditions (as well as in the photospheres of stars). Note, also, that the entrance of E_{R} into the argument does not imply that we have assumed any particular model of hydrogen atoms, such as the one provided by quantum physics. We require only the empirical observation that a fixed amount of energy is required to ionize each atom.

In a standard approach, one might now introduce a formula such as $\mu = k_{\text{B}}T \ln(n\lambda_{\text{T}}^3)$ where λ_{T} is the thermal de Broglie wavelength. This formula can be obtained, for example, by a statistical mechanical argument. Here we will not need that argument, because we can instead obtain an expression for chemical potential from the entropy.

Consider the Gibbs function of a single-component ideal gas:

$$G = \mu N = U - TS + pV. \quad (16)$$

For a gas having constant heat capacity we may use (10) and therefore

$$\mu = \left(k_{\text{B}} + \frac{C_V}{N}\right)T - T\frac{S}{N} + \frac{U_0}{N}. \quad (17)$$

We now apply this equation separately to the electrons, protons and hydrogen atoms in the plasma. This is justified by the usual argument that, at low density, different gases in a mix of ideal gases contribute their entropies independently, and here it also involves an assumption of overall neutrality of the plasma, in order to justify ignoring the contribution of the electromagnetic field. Under the approximation that the latter can be neglected, we may substitute (17) three times into (12) and thus obtain

$$T(s_{\text{e}} + s_{\text{p}} - s_{\text{H}}) = \frac{5}{2}k_{\text{B}}T + \alpha, \quad (18)$$

where we used $C_V/N = (3/2)k_{\text{B}}$ for each species, s_i is the entropy per particle in each case, and

$$\alpha = u_{\text{p}} + u_{\text{e}} - u_{\text{H}} = E_{\text{R}} \quad (19)$$

Using now the entropy equation, (11), to express s_{H} and s_{p} in terms of the constants ζ_{H} , ζ_{p} and other quantities, we find

$$s_{\text{e}} = k_{\text{B}} \left[\frac{5}{2} + \frac{E_{\text{R}}}{k_{\text{B}}T} + \ln \left(\frac{\zeta_{\text{H}} n_{\text{p}}}{\zeta_{\text{p}} n_{\text{H}}} \right) \right], \quad (20)$$

where n_i is number density.

An alternative derivation of equation (20) is given in the appendix.

Next, we argue that $\zeta_H \simeq 2\zeta_p$, to an accuracy of order one part per thousand, because when the effect of electrical charge is neutralized by the presence of the electrons, the gas of hydrogen atoms and the gas of protons are alike, except one has four energetically available internal states per particle, the other two. This neglects the slight difference between the mass of a neutral hydrogen atom and the mass of a proton. The factor 2 can be argued as a thermodynamic statement, not an appeal to Boltzmann's formula $S = k_B \ln W$, because when all the spin states are equally occupied one can always model each gas as an equal mixture of distinguishable gases, one in each spin state, and apply the entropy formula to each part in the mixture. This point is presented more fully in the appendix. Hence we find that, under the stated approximations, the entropy of a gas of electrons forming a component of a neutral hydrogen plasma in thermal equilibrium is given by

$$S_e = N_e k_B \left[\frac{5}{2} + \frac{E_R}{k_B T} + \ln \left(\frac{2n_p}{n_H} \right) \right], \quad (21)$$

where N_e is the number of electrons, E_R is the Rydberg energy and n_p, n_H are the number densities of protons and hydrogen atoms, respectively, in the plasma. Equation (21) may be regarded as a way of writing the Saha equation that is convenient to our purposes. The significance of our analysis is that it shows how the properties of the plasma may be related directly to entropy using only classical thermodynamic reasoning, without the use of statistical mechanics or quantum theory.

The experimental determination of S_e now proceeds by measuring the density and the degree of ionization at a known temperature, and deducing the entropy of the electron gas from (21). This is the total entropy, without unknown additive constants, sometimes called the absolute entropy. By using this result to supply the value of the otherwise unknown constant ζ in equation (11), one obtains the entropy under all conditions for an ideal gas of electrons in a neutral plasma. Equations (21) and (11) can be combined to give an explicit formula for ζ_e in terms of the measured quantities:

$$\zeta_e = 2e^{5/2} \frac{n_p n_e}{n_H} \left(\frac{3}{2} k_B T \right)^{-3/2} e^{E_R/k_B T}. \quad (22)$$

(In a neutral plasma, $n_e = n_p$ and $n_H + n_p = \text{constant}$.)

2.3. Discussion

Equations (22) and (11) give our second example of the main point asserted in this paper. They show that, in order to find out how much entropy a monatomic gas has got, under ordinary conditions where it behaves to good approximation like an ideal gas, one does not need quantum theory and one does not need to carefully track the heat supplied as the system is warmed reversibly from absolute zero. This is because the law of mass action (of which the Saha equation is an example) can be converted into a statement about entropy, instead of the usual form in terms of chemical potential. This observation may not be completely new, since similar reasoning applies to a large number of chemical reactions and chemists are familiar with this type of strategy for avoiding calorimetry when studying chemical potential. However, we have brought out some implications for the third law that appear to have been overlooked.

The thermodynamic point here is that the calculation of the absolute entropy does require empirical input, of course it does—because one cannot say anything about a system which has not been measured or specified in some way—but the amount of empirical input is small compared to the amount of physical prediction that can then be deduced. This is similar to the observation of other properties such as internal energy and temperature.

We presented the argument directly in terms of entropy, in order to arrive at equation (21), but some readers may find the following approach more intuitive. First we write down a fundamental equation relating to chemical potential of a single component system:

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{T,V} - T \left(\frac{\partial S}{\partial N} \right)_{T,V}. \quad (23)$$

Next we use (10) and (11), to obtain

$$\mu = \frac{U_0}{N} + k_B T \left(\frac{\gamma}{\gamma - 1} - \ln \zeta - \ln \left[\frac{1}{n} \left(\frac{k_B T}{\gamma - 1} \right)^{1/(\gamma-1)} \right] \right). \quad (24)$$

This draws attention to the fact that ζ appears as an unknown offset in the equation for μ , just as it does in the equation for S . The essence of the argument is to see that we can obtain this unknown offset by using the fact that in chemical equilibrium the chemical potentials balance (equation (12)), in a situation where the contribution of potential energy to the energy per particle is known, equation (15), and this contribution has to be made up by the translational degrees of freedom in the chemical potential balance. By substituting (24) three times into (12) and employing (15), one obtains (22) as before.

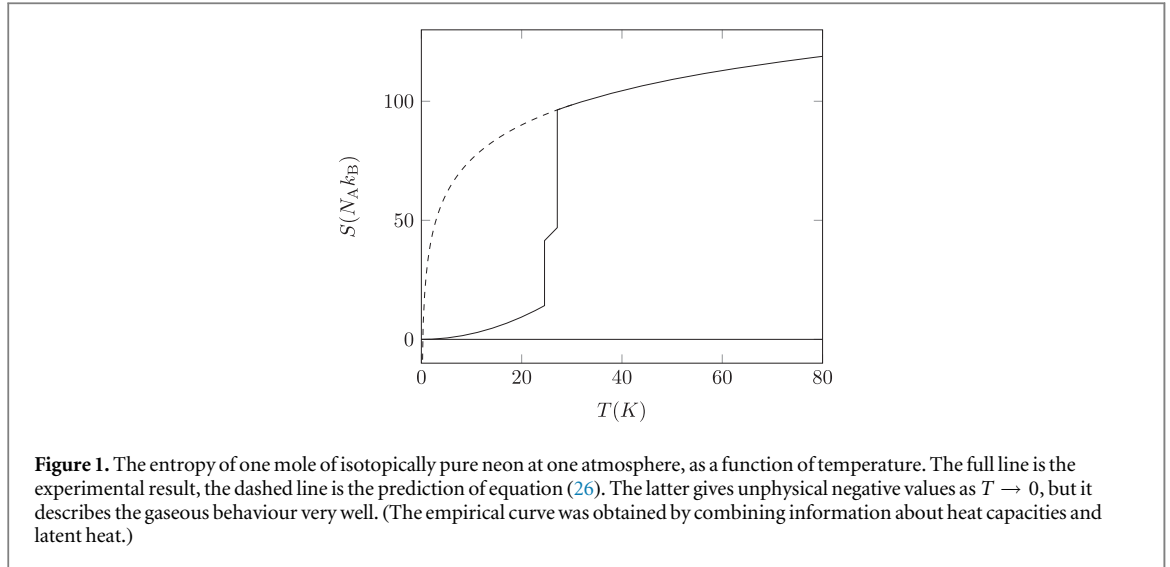


Figure 1. The entropy of one mole of isotopically pure neon at one atmosphere, as a function of temperature. The full line is the experimental result, the dashed line is the prediction of equation (26). The latter gives unphysical negative values as $T \rightarrow 0$, but it describes the gaseous behaviour very well. (The empirical curve was obtained by combining information about heat capacities and latent heat.)

The fact that no gas is ideal at low temperatures does not invalidate the method for measuring entropy that we have described. Indeed, equation (11) is completely wrong at low temperatures; this does not invalidate the argument but rather serves to emphasize that we have no need of the third law or heating from absolute zero in order to arrive at our result. Equation (11) is correct in its regime of validity (namely, low density, and over modest changes in temperature), and the observation of the ionization fraction will determine the constant ζ correctly. To illustrate this point, figure 1 shows the entropy of one mole of neon at one atmosphere, as a function of temperature. When we model neon as an ideal gas, we do not learn about its entropy at or below the boiling point, but this does not mean that our equation for the absolute entropy (not just entropy changes) lacks accuracy above the boiling point. This can be clarified by writing equation (20) another way:

$$\frac{n_p}{n_H} = \frac{1}{2e^{5/2}} e^{s_e/k_B} e^{-E_R/k_B T}. \quad (25)$$

With the benefit of statistical reasoning, we can interpret the right-hand side of this formula as the product of a number of states and a Boltzmann factor. The observation of the ionization fraction enables one to learn what the number of states is, when the energy E_R and the temperature are known.

We will now present the connection to statistical mechanics more fully. According to classical statistical mechanics, the entropy is given by Boltzmann's formula $S = k_B \ln W$, and W , the number of states available to the system, is counted by dividing the accessible phase space volume per particle by some constant h^3 whose value has to be determined empirically. Of course quantum theory comes in and tells us that this constant h is none other than Planck's constant that relates energy to frequency and momentum to wavelength of de Broglie waves, but one does not need to have that further information in order to make use of classical statistical mechanics combined with the empirically determined unit of volume in phase space. Whether a classical or a quantum treatment is adopted, one finds that in the case of a monatomic gas at low pressure (where particle interactions can be neglected), the entropy is

$$S = Nk_B \left(\frac{5}{2} - \ln n \lambda_T^3 \right), \quad (26)$$

where λ_T is the thermal de Broglie wavelength given by

$$\lambda_T = \sqrt{\frac{2\pi\hbar^2}{mk_B T}}. \quad (27)$$

This implies that for the monatomic gas, the constant ζ in (11) is $\zeta = e^{5/2} (3\pi\hbar^2/m)^{-3/2}$, where m is the mass of one atom. Hence the measurement of ζ can be regarded either as a way to obtain the entropy, or as a way to determine \hbar . Once this has been done in one case (such as the electron gas), one can then use the formula to find the entropy of any other ideal gas. In order to compare this result with equation (22) one should note that (22) includes the contribution from the spin degree of freedom for a gas of electrons, whereas (26) applies to a gas of spinless particles.

As an overall consistency check, we quote here the standard statement of the Saha equation in the case of hydrogen:

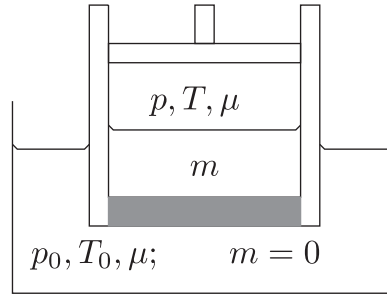


Figure 2. Experimental method to find the entropy of a nearly pure vapour. Here m is the concentration of a solute in a solvent and the barrier between the two chambers is a semipermeable channel that allows solvent but not solute to pass. Semipermeable membranes on each side of the channel support a pressure difference, and the channel is thermally insulating to good approximation (see main text). There is phase equilibrium between the solution and its vapour in the inner chamber. The fixed p_0, T_0 ensure that μ is constant in the outer chamber. By allowing the concentration m in the inner chamber to change, one adjusts the position of the phase equilibrium line as a function of pressure and temperature. This allows one to explore a range of p, T values all at the same μ . When the vapour pressure of the solute is low, the vapour is almost a pure substance, so one learns the entropy of that pure substance in its vapour phase. The vapour may have any equation of state.

$$\frac{n_p n_e}{n_H} = \left(\frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} e^{-E_R/k_B T}. \quad (28)$$

If one substitutes this into the right-hand side of (22) one finds $\zeta_e = 2e^{5/2}(3\pi\hbar^2/m_e)^{-3/2}$ which is the Sackur–Tetrode result for a gas of spin-half particles.

3. A more general system

We turn now to the case of a sample of ordinary matter (not radiation, and not necessarily an ideal gas). We will restrict our attention to a sample that can be treated as an ideal fluid, i.e., a system that exhibits pressure but not shear stress, but the sample need not be a gas and may have any equation of state.

Our proposed method is based on the Gibbs–Duhem relation. For an ideal fluid the Gibbs–Duhem relation reads

$$SdT - Vdp + \sum_i N_i d\mu_i = 0, \quad (29)$$

where the symbols have their usual meanings. N_i is the number of particles of the i th component, μ_i is the chemical potential per particle. In the case of a single component system, we have

$$S = V \left(\frac{\partial p}{\partial T} \right)_\mu \quad (30)$$

and

$$S = -N \left(\frac{\partial \mu}{\partial T} \right)_p. \quad (31)$$

Both of these equations offer ways to find S . The treatment of thermal radiation in section 1 can be regarded as an example of (30) if one models thermal radiation as a fluid at zero chemical potential. The argument from the Saha equation presented in section 2.2 could be regarded as indirectly or loosely connected to equation (31).

We now present a further application of equation (30).

We can apply (30) straightforwardly to any experiment in which the pressure and temperature of a fluid are caused to vary quasistatically, under conditions of constant chemical potential. Such conditions are not achieved under ordinary circumstances. An idealized particle reservoir can provide particles without also providing entropy, and such a reservoir is not ruled out in principle (Waldram 1985), but what one wants is a practical method. Figure 2 illustrates the main components of such a method.

A chamber of adjustable pressure and temperature p, T is surrounded by another whose pressure and temperature p_0, T_0 are maintained constant. The wall between the two chambers consists, in whole or in part, of a section that is permeable to a solvent such as water, but not to a solute such as common salt (sodium chloride). This section could consist, for example, of a short channel covered by semi-permeable membranes. The inner chamber contains a pool of solvent with solute dissolved, in phase equilibrium with its vapour. In this circumstance, solvent will move between the chambers until the chemical potential μ of the solvent is the same

in two chambers, and at equilibrium there will be a uniform temperature $T = T_0$, and a pressure difference owing to osmotic pressure, such that $p > p_0$.

We now change the concentration m and the temperature T in the inner chamber, by small amounts δm , δT , while keeping p_0 and T_0 fixed in the outer chamber. Owing to the fixed p_0 , T_0 , the solvent's chemical potential μ does not change in the outer chamber. Since the semi-permeable membranes allow solvent to pass, the condition of chemical equilibrium will be attained when μ is also unchanged in the inner chamber. Once this has happened, there will be a new value of the osmotic pressure, so p will have changed by some small amount δp . One then has a change in both p and T without a change in μ , so by measuring both for a few values and taking the limit, one obtains, subject to a *proviso* presented next, an empirical value for $(\partial p / \partial T)_\mu$ for the solvent in this experiment.

Before we can make such a claim, the following consideration has to be taken into account. At the new values $p + \delta p$ and $T + \delta T$, the fluid in the inner chamber will not be in a strict thermal equilibrium, because of heat transport to the outer chamber. One would like the semipermeable channel to be also thermally insulating, but this is not strictly possible, owing to heat transport by convection as the solvent passes between the chambers. However, one can have a case where there is a large ratio between the relevant relaxation times. There are three relaxation times to be considered. Let τ_μ be the time required for the equality of the chemical potential to be established, τ_T be the time required for the fluid in the inner chamber to attain its own thermal equilibrium if it were in complete thermal isolation, and τ_c be the time for temperature equilibrium to be established between the chambers in the actual system. If the channel has a low coefficient of thermal transport (including the contributions from both convection and ordinary thermal conduction) then one can have

$$\{\tau_\mu, \tau_T\} \ll \tau_c. \quad (32)$$

In this situation, the conditions in the inner chamber are close to thermal equilibrium conditions at the new temperature $T + \delta T$ for times t satisfying $\{\tau_\mu, \tau_T\} \ll t \ll \tau_c$.

We have now established that, as long as the condition (32) is satisfied, then the measurements of δT and δp can be interpreted in the ordinary way, and one can thus obtain an accurate measurement of $(\partial p / \partial T)_\mu$. It only remains to comment on the role of the vapour in the inner chamber. The chemical solution in the inner chamber is a system of two chemical components, and so equation (30) does not apply to it. Instead another equation applies, involving the chemical potentials of both the solvent and the solute. However, it is quite common for the vapour pressure of a solute to be very much lower than that of a solvent, so that the vapour consists almost entirely of the solvent. In this case the vapour is a one-component system to which (30) applies, and thus the experiment yields the absolute entropy of a given volume of the vapour (where we have used the fact that, in phase equilibrium, μ is the same for the two phases).

Note that although we assumed the vapour did not exhibit sheer stress, we did not need to assume anything about its equation of state. In short, it need not be an ideal gas. Also, although we have called it a vapour in the above, the second phase of the matter in the inner chamber need not be a gaseous phase; we only require that it be a phase to which the single-component Gibbs–Duhem equation can be applied to good approximation. This includes some solids as well as many liquids and gases.

The experimental method we have described is very closely related to the celebrated ‘fountain effect’ in liquid helium. Here, two chambers containing liquid helium below the lambda point are separated by a narrow tube or plug which is porous to the superfluid but not the ordinary component of the liquid. In the presence of a temperature difference between the chambers, superfluid moves from the colder to the hotter chamber until a pressure difference builds up, given by equation (30). One can use the equation in two ways. If the entropy is obtained by using the third law and integrating the heat capacity, one predicts the pressure difference for a given temperature difference. Alternatively, one may measure the pressure difference, and use it to obtain the entropy per unit volume of the liquid helium.

4. The third law

The third law of thermodynamics makes a statement about the absolute value of the entropy of any physical system, as explained in the introduction. The usual application of the third law is to say that since $S(0) = 0$, the right-hand side of expressions (1) and (2) can be used to determine $S(T_f)$. Expressions (11), (22) and (30) offer an alternative application. If, by using those equations, we learn $S(T_f)$ for a given system such as a mole of neon at some temperature, and then we use the third law to claim that $S(0) = 0$, then we obtain a *prediction* for the value of the right-hand side of equations (1) and (2). Note, this prediction is not about the gas alone, but about an integral involving the heat capacity of a solid and a liquid and a gas, and a sum involving the values of various latent heats and transition temperatures.

An alternative application of our results is to ignore the third law, and use (1) and (2) to determine the value of $S(0)$. For many systems, one will find the value $S(0) = 0$, and one will never find a negative value. It is not

necessary to invoke either classical or quantum statistical mechanics here; one simply makes the measurement. Of course, in this approach one will eventually formulate the third law as a useful summary of what is found in such experiments. It can be stated either as we have done, in terms of thermal equilibrium and the value $S(0) = 0$, or one may invoke quantum theory and discuss the ground state and its possible degeneracy. In either case one finds that, for any given system, the entropy in the limit $T \rightarrow 0$ takes a single value that does not change in isothermal processes, and one can use the results of this paper to discover what that value is. The point is, the value is fixed absolutely by a measurement at high temperature and the use of calorimetry to track the entropy reduction as the temperature falls.

It is sometimes asserted that the value of the constant towards which the entropy tends as $T \rightarrow 0$ is not fixed by thermodynamic arguments, and could in principle be some other value, as long as it is the same for all aspects of all systems. Such an assertion is in Adkins' book, for example (Adkins 1983). Callen (1985) makes a similar statement. One of the important features of the argument of this paper is that it shows that such is not the case. The value of $S(T)$ as $T \rightarrow 0$ is not arbitrary but can be ascertained by measurement, without requiring statistical or quantum theory. This does not mean the third law is not useful, but it does mean that the value of the entropy at absolute zero is a measurable, not an arbitrarily assigned, quantity, within classical thermodynamics.

All such arguments are not necessary to physics if one assumes that some fundamental theory, such as quantum theory and the Standard Model, is correct, and if one also assumes that we know how to apply such a model in order to gain understanding. However, thermodynamic arguments remain important because their role is, in part, to show us what must be true of the physical world, under a small number of assumptions, irrespective of our microscopic models. Their role is also, in part, to show us what concepts and ways of reasoning are fruitful.

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Appendix

Alternative derivation of equation (20)

Textbook derivations of the Saha equation often adopt a method slightly different to the one presented in section 2.2, as follows.

Consider first the definition of chemical potential

$$\mu_i \equiv \left(\frac{\partial U}{\partial N_i} \right)_{S,V,\{N_j\}}. \quad (33)$$

For a gas, the internal energy can be conveniently divided into the kinetic energy associated with translational motion of the particles, and the rest (potential energy and the energy in internal degrees of freedom of the particles themselves). Since the internal energy can thus be regarded as a sum of two parts, so can the chemical potential. Let us attach a star to the part associated purely with translational kinetic energy, giving

$$\mu_i^* \equiv \left(\frac{\partial U^*}{\partial N_i} \right)_{S,V,\{N_j\}}. \quad (34)$$

Then for a case where the internal degrees of freedom contribute negligibly to the heat capacity, we have $U^* = \sum_i U_i^*$ where

$$U_i^* = C_{V,i} T. \quad (35)$$

In the neutral hydrogen plasma, the energy required to remove one hydrogen atom and provide one proton and one electron, without changing the system entropy, is

$$-\mu_H^* + \mu_p^* + \mu_e^* + E_R. \quad (36)$$

The symbol μ_H^* here can be interpreted as the energy liberated when a hydrogen atom in its ground state is removed from the mix without first exciting it with the energy E_R that would be required for ionization. The binding energy E_R is normally associated with the hydrogen atom in equation (36), so one defines $\mu_H = \mu_H^* - E_R$ but this is not the only way to understand the situation: the energy E_R is an interaction energy so it really belongs to the electromagnetic field. For the purposes of book-keeping, it could be assigned to any one of the particles, or shared among them. The important point is to write down correctly what is the total energy conservation condition, allowing for all the energies involved. This is done by asserting that, in equilibrium, the chemical potentials are so arranged that the sum in (36) is zero. That is

$$\mu_p^* + \mu_e^* + E_R - \mu_H^* = 0. \quad (37)$$

This is another way of writing equation (12). Note that we have carefully avoided here any statements about partition functions. Indeed, the fact that the partition function for the electronic excitations of a single hydrogen atom in an infinite volume is itself infinite is commonly ignored or glossed-over in textbook treatments².

Equation (16) gives, for the contribution to chemical potential from translational kinetic energy

$$\mu_i^* = \left(k_B + \frac{C_{V,i}}{N_i} \right) T - T \frac{S_i}{N_i}. \quad (38)$$

By substituting this three times into (37) one obtains equation (20) as before.

Justification of $\zeta_H \simeq 2\zeta_p$

The fact that $\zeta_H \simeq 2\zeta_p$, that we used in order to obtain equation (21), is a standard part of the derivation of the Saha equation, but ordinarily it is justified by the use of Boltzman's statistical formula for the entropy, which we wish to avoid. To obtain it from thermodynamics alone, one may proceed as follows.

Consider the general problem of a gas of N particles with Z equally likely distinct internal states per particle, where the motion of each particle is independent of its internal state. The main concept we need is that such a gas has all the same thermodynamic properties as an equal mixture of Z gases of N/Z particles each, where each of the gases in the mixture is of the same type as the unpolarized gas, but fully polarized, that is, with all particles in the same internal state, and each of the Z cases appears equally in the mixture. Of course the counting of the internal states is explained by quantum theory, but all we need is the empirical fact that if one somehow prepares the mixture just described, then the system that results will be thermodynamically the same as the unpolarized gas.

Let S be the total entropy of the gas, and S_i the entropy of one of the components in the above model. Then $S = \sum_i S_i$. Applying equation (11) to each term in this equation, we find

$$Nk_B \ln \left[\zeta \frac{V}{N} \kappa \right] = \sum_{i=1}^Z N_i k_B \ln \left[\zeta_i \frac{V}{N_i} \kappa \right], \quad (39)$$

where $N_i = N/Z$ and $\kappa = [k_B T / (\gamma - 1)]^{1/(\gamma-1)}$. Here, ζ is the constant appearing in the formula for the entropy of the whole gas, and ζ_i are the constants appearing in the formulae for the entropies of the component gases. We now claim that all the ζ_i are the same, because the motions of the particles are independent of their internal state. Substituting this into (39) gives $\zeta = Z\zeta_i$. It follows that, for two gases that are identical except that one has 4 internal states per particle, the other 2, one will find the ζ of the first will be twice that of the second. QED.

References

- Adkins C J 1983 *Equilibrium Thermodynamics* 3rd edn (Cambridge: Cambridge University Press)
- Blundell S J and Blundell K M 2006 *Concepts in Thermal Physics* (Oxford: Oxford University Press)
- Callen H B 1985 *Thermodynamics and an Introduction to Thermostatistics* 2nd edn (New York: Wiley)
- Carrington G 1994 *Basic Thermodynamics* (Oxford: Oxford University Press)
- Fridman A A 2008 *Plasma Chemistry* (Cambridge: Cambridge University Press)
- Kingdon K H and Langmuir I 1923 *Phys. Rev.* **22** 148
- Saha M N 1920 *Phil. Mag. Ser. 6* **40** 472
- Waldram J R 1985 *The Theory of Thermodynamics* (Cambridge: Cambridge University Press)
- Wilks J 1961 *The Third Law of Thermodynamics* (Oxford: Oxford University Press)

² For a single hydrogen atom in an infinite volume, the partition function associated purely with the electronic excitations, even without ionization, is $Z = \sum_{n=1}^{\infty} 2n^2 \exp [(-E_0 + E_R/n^2)/k_B T]$, which is infinite. Setting this equal to 2 without a thorough argument is hardly justified!