

Entropy and the First Law of Thermodynamics

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Abstract: Planck's work on the Second Law of Thermodynamics in combination with a simple thermodynamic approach developed by Blinder show that the concept of entropy is introduced from the First and not the Second Law of Thermodynamics. In particular, it is proved that the First Law of Thermodynamics leads directly to the following statement: For every system of whatever complexity there exists an extensive function of state S defined from $dS = \delta q_{\text{rev}}/T$, where δq_{rev} is the infinitesimal quantity of heat exchanged reversibly between the system and the surroundings and T is the absolute temperature of the system. Thus, for reversible adiabatic processes we readily have from the First Law that $dS = 0$. Therefore, the Second Law should be properly reformulated, restricted to the inequality $dS > 0$ for irreversible processes only.

Introduction

The vast majority of textbooks of either Physical Chemistry or Thermodynamics point out that the First Law of Thermodynamics introduces the state function of the internal energy, U , whereas the Second Law defines the concept of another state function, the entropy, S . For example, the following two statements may express the second law [1–5]:

For every system there exists an extensive function of state, S , which is called the entropy of the system and is defined from

$$dS = \frac{\delta q_{\text{rev}}}{T} \quad (1)$$

where δq_{rev} is the infinitesimal quantity of heat exchanged reversibly between the system and the surroundings and T is the absolute temperature of the system.

When the system is isolated or adiabatically enclosed we have

$$dS \geq 0 \quad (2)$$

where the equality holds for reversible and the inequality for irreversible processes.

It is seen that the entropy is indeed introduced axiomatically by the Second Law; however, in many textbooks the Second Law is discussed after the Carnot cycle, which is a kind of introduction to the Second Law [3, 4, 6, 7]. The reason is that it can be explicitly proved that the integral of dq_{rev}/T around a reversible cycle of an ideal gas is zero, which means that dq_{rev}/T is an exact differential and therefore we can define a new function of state by means of eq 1, which we call entropy. It is seen that, at least for the special case of an ideal gas, the concept of the entropy arises directly from the First Law of Thermodynamics.

An alternative and elegant proof without the need of the Second Law that dq_{rev}/T is an exact differential for an ideal gas

may be found in some textbooks [7, 8]. In a reversible process of an ideal gas, the First Law gives

$$\delta q_{\text{rev}} = C_V dT + p dV \quad (3)$$

where C_V is the heat capacity at constant volume, V , and p is the gas pressure. C_V is constant and independent of the temperature, T . Thus, if eq 3 is divided by T , we obtain the linear differential form

$$\delta q_{\text{rev}}/T = (C_V/T)dT + (R/V)dV \quad (3)$$

which is an exact differential because

$$\left(\frac{\partial(C_V/T)}{\partial V} \right)_T = \left(\frac{\partial(R/V)}{\partial T} \right)_V = 0 \quad (4)$$

Therefore, according to the theory of linear differentials (see appendix), there exists a function $S(T, V)$ such that

$$dS = \delta q_{\text{rev}}/T \quad (5)$$

It is seen that both the Carnot cycle and the above proof show that for the case of an ideal gas the concept of the entropy arises directly from the First Law of Thermodynamics. Therefore, even an alert student could wonder whether the concept of the entropy arises from the First Law only for the special case of an ideal gas or for any thermodynamic system. A survey of the available literature reveals that there exists an interesting but rather forgotten paper by M. Planck [8], which proves that the First Law leads directly to the concept of the entropy for any system with two independent variables. Therefore, Planck's work extends the validity of eq 5 from an ideal gas to every real system of two independent variables. On the other hand Caratheodory's work [5, 9, 10, 11] clarifies that the purely mathematical extension of Planck's approach to systems of more than two independent variables is not possible

unless an additional principle, known as Caratheodory's principle, is adopted. Despite this, Planck's work can be extended to systems of whatever complexity on the basis of simple thermodynamic arguments, like those presented by Blinder in [9]. Thus, the already existing literature, that is, Planck's work in combination with that of Blinder's, leads to the unexpected conclusion that there is a strong connection between the concept of the entropy and the First Law, but this connection is completely ignored in the textbooks of Physical Chemistry and Thermodynamics.

In the present paper we re-examine this issue. In particular, we present Planck's work [8] in a rather simple but rigorous way suitable for teaching and prove that for every system of two variables there exists an extensive function of state, S , defined by eq 5. Next, Planck's work is combined with Blinder's thermodynamic approach [9] to extend the validity of eq 5 to any closed or open system of whatever complexity. Thus, we show that the concept of entropy is introduced from the First and not the Second Law of Thermodynamics.

Definition of Entropy in Closed Systems of Two Independent Variables

As discussed above, the derivation of eq 5 presented in several textbooks is restricted to the case of an ideal gas. Now let us consider a real thermodynamic system, for example a fluid, the properties of which can be expressed in terms of the temperature, T , and the volume V . In this case the total differential of the internal energy is given by

$$dU = (\partial U / \partial T)_V dT + (\partial U / \partial V)_T dV \quad (6)$$

which in combination with the first law ($\delta q_{\text{rev}} = dU + pdV$) yield

$$\delta q_{\text{rev}} = (\partial U / \partial T)_V dT + \{(\partial U / \partial V)_T + p\} dV = X_1(T, V) dT + X_2(T, V) dV \quad (7)$$

where $X_1(T, V)$ and $X_2(T, V)$ are functions of T and V . During an infinitesimal adiabatic change we have $\delta q_{\text{rev}} = 0$ and eq 7 results in the ordinary differential equation

$$X_1(T, V) dT + X_2(T, V) dV = 0 \quad (8)$$

All functions of physical variables, like $X_1(T, V)$, $X_2(T, V)$ and their ratio, are continuous functions with continuous and bounded derivatives, provided that the system does not undergo a phase transition. Therefore, if we exclude the possibility of occurring a phase transition, the fundamental theorem of ordinary differential equations given in the appendix is valid. This means that eq 8 is always integratable, and let $f(T, V) = \text{const}$ be a one-parameter set of solutions of this equation. As shown in the appendix, in this case there exists an integrating factor $\tau(T, V)$ such that eq 7 is written as

$$\delta q_{\text{rev}} = \tau(T, V) df(T, V) \quad (9)$$

It is seen that at least in the absence of phase transitions there exists an integrating factor, that is, a function that makes the ratio $\delta q_{\text{rev}} / \tau(T, V)$ an exact differential. The function $\tau(T, V)$ is not unique and we shall prove that a possible choice of $\tau(T, V)$ is the absolute temperature, T . The simplest way of doing this is to change the independent variables from T and V to T and σ , where σ is defined from $\sigma = f(T, V)$. This can be done by solving the equation $\sigma = f(T, V)$ with respect to V . If $V = g(T, \sigma)$, then $\tau(T, V) = \tau(T, g(T, \sigma)) = \tau(T, \sigma)$ and eq 9 becomes

$$\delta q_{\text{rev}} = \tau(T, \sigma) d\sigma \quad (10)$$

The properties of the integrating factor $\tau(T, \sigma)$ are further clarified if we consider an adiabatically enclosed system consisting of two parts, 1 and 2, in thermal equilibrium through a perfectly diathermic wall. For an infinitesimal reversible process, for example by slowly altering the volumes V_1 and V_2 of parts 1 and 2, we have

$$\begin{aligned} \delta q_{\text{rev}} &= \delta q_1 + \delta q_2 \\ &= 0 \Rightarrow \tau_1(T, \sigma_1) d\sigma_1 + \tau_2(T, \sigma_2) d\sigma_2 = 0 \end{aligned} \quad (11)$$

Note that eq 11 can be written as $d\sigma_1/d\sigma_2 = -\tau_2(T, \sigma_1)/\tau_1(T, \sigma_2)$, which shows that the ratio $\tau_2(T, \sigma_1)/\tau_1(T, \sigma_2)$ should depend only on σ_2 , σ_1 . This is possible if the functions $\tau_1(T, \sigma_1)$, $\tau_2(T, \sigma_2)$ either do not depend on T or, more generally, they both have the form $\tau_1(T, \sigma_1) = \tau(T) f_1(\sigma_1)$ and $\tau_2(T, \sigma_2) = \tau(T) f_2(\sigma_2)$. Therefore, eq 10 may be written as

$$\frac{\delta q_{\text{rev}}}{\tau(T)} = f(\sigma) d\sigma \quad (12)$$

However, the product $f(\sigma) d\sigma$ is the differential of the function $S = \int f(\sigma) d\sigma$. Thus we have

$$\frac{\delta q_{\text{rev}}}{\tau(T)} = dS \quad (13)$$

Note that because $\sigma = f(T, V)$, the function S depends also upon T and V ; therefore, it is a function of state of the system under consideration. The integrating factor $\tau(T)$ must be a universal function of T , because it has the same value for any arbitrary system and its arbitrary parts. The above treatment as well as all the approaches based on Caratheodory's principle cannot determine the mathematical expression of $\tau(T)$; however, because $\tau(T)$ is a universal function of T we need to determine this function only for one special case. Such a case is an ideal gas. Now it becomes obvious by comparing eq 13 with eq 5 that $\tau(T)$ is, in fact, identical to the absolute temperature T , that is, $\tau(T) = T$.

It is seen that at least for real systems of two variables, like fluids, and in the absence of phase transitions, the first part of the Second Law (eq 1) arises directly from the First Law by simple mathematical transformations. In the next section we shall prove that this holds for any multivariable closed system in the presence or absence of phase transitions.

Extension to Multivariable Closed Systems

As will be pointed out in the appendix, the direct extension of the above treatment to multivariable systems is not possible because there is need of Caratheodory's theorem [5, 9, 10, 11]. The extension, however, can be made on the basis of a very simple thermodynamic approach suggested by Blinder in [9]. Consider a multivariable closed system composed of one or more phases and in which chemical reactions may or may not take place. The properties of this system are expressed in terms of the temperature, T , and m other thermodynamic variables, say x_1, x_2, \dots, x_m . Let this system be in thermal contact with a two-variable system with independent variables T and V and let the composite system be adiabatically enclosed. We use again a composite system, which is adiabatically enclosed and consists of two subsystems in a perfect thermal contact. This system plays a central role in all approaches based on Caratheodory's principle [1, 5, 12], in Planck's work on the Second Law [8], as well as in Blinder's approach [9]. In such a system, as in every system described by equilibrium thermodynamics, the time effect is a priori excluded [12]. By definition a reversible (or quasistatic) process that can take place in this system is infinitely slow, is not a function of time, and proceeds via a continuous series of equilibrium states [12].

Consider an infinitesimal reversible process, which may occur by an infinitesimal change in the volume of one of the subsystems. We have

$$\delta q_{\text{rev},m} + \delta q_{\text{rev},2} = 0 \quad (14)$$

where $\delta q_{\text{rev},m}$ is referred to the multivariable system and $\delta q_{\text{rev},2}$ is the heat gained or lost by the two-variable system. That is, $\delta q_{\text{rev},2}$ is given by eq 7. We should point out that the process indicated by eq 14 may be any possible reversible process. If eq 14 is divided by T , we obtain

$$\frac{\delta q_{\text{rev},m}}{T} = -\frac{\delta q_{\text{rev},2}}{T} \quad (15)$$

and because $\delta q_{\text{rev},2}/T$ is an exact differential, $\delta q_{\text{rev},m}/T$ is also an exact differential.

Let us examine this point in more detail. The fact that $\delta q_{\text{rev},2}/T$ is an exact differential means that there exists a function of T, V , that is, a function of the independent variables of the two-variable system, the differential of which is equal to $\delta q_{\text{rev},2}/T$. This is a direct consequence of the properties of the exact differentials and because we denote this function by $S(T, V)$, we have $dS(T, V) = \delta q_{\text{rev},2}/T$; however, the meaning of $\delta q_{\text{rev},m}/T$ as also an exact differential is not so clear. It may show that there exists a function of T, x_1, x_2, \dots, x_m , that is, a function of the independent variables of the multi-variable system, the differential of which is equal to $\delta q_{\text{rev},m}/T$, but it may simply imply the trivial result $dS(T, V) = -\delta q_{\text{rev},m}/T$.

In order to clarify this point let us consider any arbitrary reversible cyclic process of the multivariable system by slowly altering some of its independent variables, x_1, x_2, \dots, x_m . Note that this system is neither isolated nor adiabatically enclosed,

because it may exchange heat through the diathermic wall and/or work through the adiabatic wall; therefore, it can perform any possible thermodynamic process. During the cyclic process of the multivariable system, the volume, V , of the two-variable system is kept constant but the temperature varies, being always equal to the temperature of the multivariable system. At the end of each cyclic process, however, the temperature, as all the other variables of the multivariable system, attains its original value, and due to the thermal equilibrium, the same is valid for the temperature of the two-variable system. It is seen that any reversible cyclic process of the multivariable system forces the two-variable system to execute also a reversible cyclic process because its volume is kept constant and its temperature always returns to its original value. Nevertheless, for a reversible cyclic process of the two-variable system we have

$$\oint \delta q_{\text{rev},2}/T = \oint dS(T, V) = 0 \quad (16)$$

In addition, due to the equality (eq 15), we have $\oint \delta q_{\text{rev},m}/T = 0$. It is seen that during any reversible cyclic process of the multiple-variable system the cyclic integral $\oint \delta q_{\text{rev},m}/T$ is equal to zero. This means that there does exist a function of T, x_1, x_2, \dots, x_m , the differential of which is equal to $\delta q_{\text{rev},m}/T$, i.e.

$$dS(T, x_1, x_2, \dots, x_m) = \delta q_{\text{rev},m}/T \quad (17)$$

The entropy of a system defined from eq 17 is an extensive property, because if we consider a composite system of two subsystems, 1 and 2, in thermal equilibrium and transfer to this system reversibly an infinitesimal quantity of heat δq_{rev} , then $\delta q_{\text{rev}} = \delta q_{\text{rev},1} + \delta q_{\text{rev},2}$, which readily yields $S = S_1 + S_2$. In this case the composite system is not adiabatically enclosed.

The combination of Planck's work with Blinder's thermodynamic approach readily proves that for every closed system of whatever complexity there exists a function of state S , which is an extensive property, and its total differential is given by eq 17. Note that a reversible phase transition occurring in a system is in fact an equilibrium process between two phases of this system and therefore our proof does not exclude the occurrence of phase transitions.

The Case of Open Systems

The treatment presented above for an arbitrary closed system is also valid for open systems. For example, consider that the closed composite system of the previous section consists of two open phases, 1 and 2. For this composite system there exists a function of state, S , which is defined from eq 17, and it is an extensive property. The latter property of S necessarily entails that $S = S_1 + S_2$, where S_1, S_2 are the entropies of the two open phases.

An alternative proof of eq 17 for open systems is the following. Consider a system composed of a simple closed system of T, V variables in thermal contact with two open systems that may exchange $m \geq 1$ component. Let the whole system be adiabatically enclosed and leave it undisturbed to

establish thermal and chemical equilibrium. Now, in an arbitrary infinitesimal reversible process we have

$$\delta q_{\text{rev,closed}} + \delta q_{\text{rev,open1}} + \delta q_{\text{rev,open2}} = 0 \quad (18)$$

which gives

$$\delta q_{\text{rev,closed}}/T = -(\delta q_{\text{rev,open1}} + \delta q_{\text{rev,open2}})/T \quad (19)$$

Eq 19 is valid for any open system of the composite system; therefore, it is also valid for the limiting case where the two open systems become identical to each other. Then eq 19 results in

$$\delta q_{\text{rev,closed}}/T = -2\delta q_{\text{rev,open}}/T \quad (20)$$

and because $\delta q_{\text{rev,closed}}/T$ is an exact differential, the same is valid for $\delta q_{\text{rev,open}}/T$. So, for any system closed or open of whatever complexity the ratio $\delta q_{\text{rev}}/T$ is an exact differential. This completes the proof of eq 17 on the basis of the First Law of Thermodynamics. It is interesting to point out that Blinder applied his method to an adiabatically enclosed system composed of an ideal gas in thermal equilibrium with a multivariable system. Due to the use of the ideal gas instead of a real fluid and because the ideal gas is strictly considered as an extrathermodynamic notion, Blinder did not consider his derivation of eq 17 in [9] as a rigorous result of the First Law.

To sum up, Planck's work on the entropy in combination with Blinder's thermodynamic approach clarify that the First Law of Thermodynamics introduces not only the concept of the internal energy but also that of the entropy. In particular, the First Law leads to the statement that for every system closed or open of whatever complexity there exists an extensive function of state, S , defined from $dS = \delta q_{\text{rev}}/T$. It is evident that for reversible adiabatic processes we have $dS = 0$. We must emphasize that the present treatment does not prove that the First Law leads to the second one. It simply shows that the concept of the entropy and in particular equations $dS = \delta q_{\text{rev}}/T$ and $dS = 0$ can actually be derived from the First Law of Thermodynamics. Finally, we should clarify that the statistical definitions of the entropy do not depend on its thermodynamic definition, that is, on whether it is introduced from the First Law or axiomatically from the Second Law.

Discussion

The treatment presented in this paper, that is, the combination of Planck's work on the Second Law with the corresponding Blinder's thermodynamic approach a) removes a misunderstanding about the concept of the entropy, b) calls for a reconsideration of the Second Law of Thermodynamics, and c) suggests an alternative approach in teaching this law. These topics are discussed further below.

a) In the majority of textbooks on thermodynamics and physical chemistry the concept of entropy is directly related to the Second Law; thus, in many of those books we can read or conclude that the Zeroth Law introduces the function of state we call empirical temperature, the First Law introduces the internal energy and the Second Law defines the entropy. The

treatment presented in the present paper, however, shows that this is a great misunderstanding because the concept of the entropy, as an extensive function of state, arises from the First Law of Thermodynamics.

b) I believe that the fact that the First Law leads to the concept of entropy calls for a proper reformulation of the Second Law. A physical law may in general be derived from another law or may be a limited case of a more general law; however, the fundamental laws of thermodynamics do not fall into this category. In many textbooks and papers the Zeroth, First, and Second Law are considered as postulates or principles or even as axioms. In this context the Second Law must not include parts that can be derived from the First Law; therefore, if we want to keep the postulate character of the fundamental thermodynamic laws, the statement of the Second Law should be restricted to the inequality $dS > 0$ for irreversible processes only.

c) The arguments presented in this paper indicate also the possibility of an alternative approach in teaching the Second Law, which might involve the following steps: First, within the framework of the First Law by means of eqs 3 to 5 or using the equivalent proof presented in [7] it is shown that for the special case of an ideal gas the quantity dq_{rev}/T is an exact differential and, therefore, defines a new function of state, the entropy. Next the proof may be extended to any two-variable real system following Planck's treatment, as given in the present paper. It is evident that, depending on the group of students, the detailed proof of eq. 13 might be omitted; however, the students must know that the proof of eq 5 is extended by strict mathematics to any two-variable real system. The extension to multivariable systems via Blinder's method is quite simple and it, therefore, may be presented as given in the sections "Extension to multi-variable closed systems" and "The case of open systems." Following this approach the concept of entropy is completely defined as a direct consequence of the First Law, and its changes may be studied during various reversible processes, as described in numerous textbooks. In addition, the need of a new law, the Second Law is now clear, because the extension to irreversible processes cannot be made within the framework of the First Law. The main advantage of this approach is that it presents a more natural connection of the Second Law to the First Law. Entropy is a function of state defined from the First Law and the Second Law defines its properties during irreversible processes.

Appendix

Here, we summarize the mathematical background necessary for a student to understand the treatment in this paper. The mathematics needed are associated with the properties of the linear differential forms

$$dz = P(x,y)dx + Q(x,y)dy \quad (A1)$$

These properties can be found in several textbooks [13, 14].

The differential form (A1) is an exact differential when P and Q obey the equation

$$\left(\frac{\partial P}{\partial y}\right)_x = \left(\frac{\partial Q}{\partial x}\right)_y \quad (A2)$$

In this case there exists a set of functions $f(x, y) + const$, such that $dz = df(x, y)$. Alternatively, dz is an exact differential when

the cyclic integral of dz over an arbitrary closed contour is equal to zero.

If eq A1 is not an exact differential, there may exist a function $\tau(x, y)$, called the *integrating factor*, such that the ratio $dz/\tau(x, y)$ is an exact differential, that is

$$dz/\tau(x, y) = df(x, y) \quad (\text{A3})$$

A necessary prerequisite for an integration factor to exist is the ordinary differential equation

$$dz = Pdx + Qdy = 0 \quad (\text{A4})$$

to be integratable. According to the fundamental theorem of ordinary differential equations [13–15], this happens when the function $g(x, y) = -P(x,y)/Q(x,y)$ is continuous and has continuous partial derivatives. Then the solution of eq A4 is a one-parameter set of curves

$$f(x, y) = \text{a constant} \quad (\text{A5})$$

Along any of these curves we have

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy = 0 \quad (\text{A6})$$

Now if we solve eq A4 and eq A6 with respect to dy/dx and equate the resulting expressions, we readily obtain

$$\frac{P(x, y)}{\partial f / \partial x} = \frac{Q(x, y)}{\partial f / \partial y} = \tau(x, y) \quad (\text{A7})$$

which in combination with eq A1 results in eq A3. This completes the proof that the fundamental theorem of ordinary differential equations leads to the existence of an integrating factor and therefore to the validity of eq A3.

The arguments presented above show that all differential forms with two variables have an integrating factor provided that P and Q are continuous functions with continuous partial derivatives. In contrast, for differentials of three or more variables this does not hold. For example, it can be proved that the differential expression $ydx + dy - dz$ does not have an integrating factor [9]. In fact in differentials of three or more variables the existence of an integrating factor is an exception.

In such differential forms the existence of an integrating factor is associated with the validity of Caratheodory's theorem of accessibility [5, 9, 10, 11]. The validity of this theorem necessarily requires the axiomatic acceptance of the following statement: "Arbitrarily close to a given thermal equilibrium state there exist equilibrium states that cannot be reached by an adiabatic change". This statement, known as Caratheodory's principle [5, 9, 10, 11], is an alternative formulation of the Second Law. Thus the purely mathematical proof of eq 17 from the First Law of Thermodynamics is not possible for systems of more than two variables. This can be attained by the proper combination of mathematical and thermodynamic arguments as shown in the main text.

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