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Commentary

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On the Relation between the Fundamental Equation of Thermodynamics and the Energy Balance Equation in the Context of Closed and Open Systems

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ABSTRACT: In this paper, we elaborate on the connection between the fundamental equation of thermodynamics, which is essentially the combination of the First and Second Laws of thermodynamics, and the energy balance equation in the context of closed and open systems. We point out some misinterpretations in attempts to derive the fundamental equation from these First and Second Laws of thermodynamics, which occur in several textbooks. These errors are connected with incorrect interpretations of heat and work terms in relation to changes of the entropy and internal energy change of the system. The consequences of matter transfer for the formulation of the First and Second Laws are often not properly taken into account, and there is a widespread misinterpretation of what is called 'chemical work'. In this paper, we present a correct derivation of the fundamental equation from the basic laws of thermodynamics, through a careful analysis of matter transfer to an open system. This provides insight into the meaning of 'chemical work'.

KEYWORDS: *Continuing Education, Second-Year Undergraduate, Chemical Engineering, Physical Chemistry, Misconceptions/Discrepant Events, Phases/Phase Transitions/Diagrams, Theoretical Chemistry, Thermodynamics*

The purpose of this paper is to address some errors in attempts to derive the fundamental equation for the energy from the basic laws of thermodynamics (eqs 1 and 2), which occur in several textbooks on thermodynamics for chemists and physicists, and to provide insight into the meaning of 'chemical work'. These errors are connected with incorrect interpretations of heat and work terms in relation to entropy and internal energy changes of the system, particularly when expressions for the First and Second Laws of Thermodynamics that apply to closed systems are used for open systems. Misinterpretation of what is called 'chemical work' and the denial of the contribution of matter exchange to the entropy change of an open system are responsible for this. We hope that this contribution will help teachers and lecturers to deal with these issues in a transparent way, and to avoid certain misinterpretations that can even be found in a number of otherwise excellent textbooks.

Traditionally, introductions to thermodynamics for chemists and physicists focus on closed systems, systems that do not exchange matter with their environment. These courses start out introducing the basics of thermodynamics in the context of closed systems. So, the First Law is introduced as

$$\mathrm{d}U_\mathrm{C} = đq + đw \tag{1}$$

Here, U_C is the internal[1] energy of the system. As the distinction between closed and open systems is central in this paper, we write the subscript C to emphasize that this is for a closed system. Furthermore, $đq$ is the heat transferred to the system, and $đw$ the amount of work done on the system upon some infinitesimal small change. In the present paper, we will deal with volume work only: $đw = -p\mathrm{d}V$, where p is the pressure and V is the volume of the system. Obviously, other work terms can be included in $đw$ when relevant, for example, for interfacial work or work of polarization.

It is one of the central messages of this paper that the mere inclusion of so-called 'chemical work' into $đw$ to account for the transfer of matter into or from an open system does not correctly take into account the energy change associated with exchange of matter between a system and its surroundings. Chemical work represents only part of the total energy change and ignores the contributions to the total energy related to entropy and so-called flow work.

We restrict the discussion to reversible processes, because it is sufficient for the points we want to make. For reversible changes of closed systems, the second law reads

$$\mathrm{d}S_\mathrm{C} = \frac{đq}{T} \tag{2}$$

Where S is the entropy and T is the temperature. Combination of the First and Second Law as given by eqs 1 and 2, substituting $T\mathrm{d}S_\mathrm{C}$ for the reversible heat exchange $đq$ and $-p\mathrm{d}V$ for $đw$, yields the expression for the total differential of U_C (often called the *fundamental* equation for the internal energy):

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$$dU_C = TdS_C - pdV \tag{3}$$

This is unproblematic but it applies to closed systems only, that is, systems that do not exchange matter with their environment.

Matter exchange, and the chemical potential are usually introduced and discussed in some later stage of a course on thermodynamics. Usually, little or no attention is devoted to the implications of matter exchange to the formulation of the First and Second Laws. We fear that with many students this may install the idea that eqs 1 and 2 apply just as well for open systems. As we will see, this misunderstanding has even transpired into some textbooks. Furthermore, it is most often merely postulated that μdn terms have to be added to the total differentials of a thermodynamic potential such as the energy. In this way, the fundamental equation for the energy of open systems, also denoted the *Gibbs equation*, is postulated correctly as[2]

$$dU = TdS - pdV + \sum_i \mu_i \, dn_i \tag{4}$$

Here, i stands for a particular substance, and μ_i and n_i denote chemical potential and amount (number of moles) of that substance, respectively. Most texts (e.g., 3−7) do not explicitly elaborate on the connection between the fundamental equation and the First and Second Laws. Instead, the extra $\mu_i dn_i$ terms are made acceptable by heuristic arguments, for example, by mentioning the analogy with the route leading to eq 3 and by emphasizing the analogy between terms $\mu_i dn_i$ and work terms such as $-pdV$, both being of the form "*intensive* d *extensive* ". Some other courses and textbooks provide some more background and first acknowledge that U is not only a function of S and V, but also of amounts of substances: $U = U(S,V,\{n_i\})$. From this, it follows immediately that

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,\{n_i\}} dS + \left(\frac{\partial U}{\partial V}\right)_{S,\{n_i\}} dV + \sum_i \left(\frac{\partial U}{\partial n_i}\right)_{S,V,\{n_{j\neq i}\}} dn_i \tag{5}$$

Subsequently, the identifications are made that $(\partial U/\partial S)_{V,\{n_i\}} = T$, $(\partial U/\partial V)_{S,\{n_i\}} = -p$. The new differentials $(\partial U/\partial n_i)_{S,V,\{n_{j\neq 1}\}}$ are then *defined* as μ_i. This derivation of the Gibbs equation (eq 4) is entirely correct and a perfect introduction of the chemical potential. However, in a course on thermodynamics one wants to also establish a connection with the First and Second Laws as well as to develop an intuition for the meaning of quantities such as the chemical potential.[8] A number of texts attempted to provide a derivation of the Gibbs equation from the First and Second Laws. Unfortunately, most accounts of these derivations that we have encountered are, quite frankly, incorrect.[7−13] Although there is some variation between these erroneous accounts, they all seem to have a number of features in common. They use for open systems versions of the First and Second Laws as given by eqs 1 and 2, which is incorrect. This is combined with a misinterpretation of what is called 'chemical work'. Owing to a wonderful cancelation of errors, yet the correct Gibbs equation is found, making it more difficult to uncover fallacious assumptions.

On the other hand, engineering-thermodynamics texts (e.g., 14−21) usually avoid such errors, probably because of their strong focus on open systems and on the consequences of matter transfer. They discuss rates of change of energy, entropy and other quantities in terms of *balance equations* and correctly include contributions owing to matter transfer. In fact, comparing texts on chemical thermodynamics and on engineering thermodynamics made us recognize the above-mentioned misinterpretations.

In the subsequent sections, we will pinpoint and discuss the misinterpretations in the above-mentioned erroneous derivations of the Gibbs equation. Furthermore, we will provide a correct derivation of the Gibbs equation from the First and Second Laws, involving a careful analysis of a process in which matter is added to a system. We will obtain the proper generalizations for open systems of eqs 1 and 2. These generalizations are consistent with the balance equations generally used in engineering thermodynamics. This derivation provides insight as to the meaning of the term 'chemical work'.

■ MISINTERPRETATIONS IN DERIVATIONS OF THE GIBBS EQUATION

The $\mu_i dn_i$ term has been interpreted as a work term as suggested by Gibbs himself.[22] Several texts followed this suggestion, including papers by Brønsted[23] and Gill,[8] and textbooks by Katchalsky and Curran,[24] and by Alberty.[25] Interestingly, Prigogine[26] included the effect of exchanging matter on the energy in a kind of extended $\text{đ}q$ term: $dU = d\Phi - pdV$, where $d\Phi$ is the sum of the heat exchange and the energy change due to the exchange of matter.

It is probably because of this tendency to interpret μdn as a work term that it is sometimes included in $\text{đ}w$ in an attempt to account for the energy change due to a change in the amount of i. Steps resembling those yielding eq 3 lead to (incorrect) equations of the type:[9−12]

$$dU = \text{đ}q - pdV + \sum_i \mu_i dn_i \tag{6}$$

or[13]

$$dU = \text{đ}q + \text{đ}w + \sum_i \mu_i dn_i \tag{7}$$

where $\text{đ}w = -pdV$. Combining these expressions for dU with the expression for the Second Law given by eq 2 yields the Gibbs equation (eq 4). Alternatively, but closely related, we came across:[12]

$$dU = \text{đ}q + \text{đ}w = TdS - pdV + \mu dn + ... \tag{8}$$

implying that the first equality (eq 1) applies to open systems, as the expression on the right-hand side has a μdn term.[27] Some texts avoid erroneous equations such as these, but include confusing (erroneous) verbatim 'explanations'. Reid (ref 7, section 7.1), for instance, makes the misleading suggestion that for open systems the first terms of eq 4 represent heat and work, respectively, just as for closed systems.

The above-mentioned 'derivations' of the Gibbs equation may seem straightforward at first sight, and it is perhaps reassuring that they indeed lead to the correct Gibbs equation. This is probably the reason why these misinterpretations found their way into several otherwise excellent textbooks.[7,9−13] We will show, however, that this fortuitous outcome is due to a cancelation of errors in the expression for the entropy change, and in the expression for the energy change, in combination with the treatment of μdn terms as work terms.

First of all, the expression for the second law for reversible processes, given by eq 2, does not apply to open systems. For an open system, undergoing a reversible change, the entropy is not just changed by transfer of heat, but also by transfer of matter. Hence, for open systems (O), the entropy change associated with a reversible process must be written as

$$\mathrm{d}S_\mathrm{O} = \frac{đq}{T} + \mathrm{d}_\mathrm{em}S \tag{9}$$

where $\mathrm{d}_\mathrm{em}S$ represents the entropy change as a result of the exchange of matter between system and environment. Some authors do state this clearly, for example, De Groot and Mazur:[28] 'For open systems, i.e., systems which may exchange heat as well as matter with their surroundings $\mathrm{d}_\mathrm{e}S$ (defined by De Groot and Mazur as the entropy supplied to the system by the environment, as opposed to d_iS, the entropy produced inside a system upon an irreversible change) contains also a term connected with the transfer of matter.' Equation 9 represents the proper expression for the second law of thermodynamics for reversible processes involving open systems. In the next sections, we clearly demonstrate that for open systems, $\mathrm{d}_\mathrm{em}S$ is nonzero and that it is therefore quite wrong to identify the $T\mathrm{d}S$ term with the reversible heat exchange, as was done in the above-mentioned fallacious accounts.

Analogously to the expression for the reversible entropy change, the energy change of an open system should be described as

$$\mathrm{d}U_\mathrm{O} = đq + đw + \mathrm{d}_\mathrm{em}U \tag{10}$$

where $\mathrm{d}_\mathrm{em}U$ represents the energy change as a result of the exchange of matter. In the next sections, we clearly demonstrate that $\mathrm{d}_\mathrm{em}U$ is *not* equal to $\sum_i \mu_i \mathrm{d}n_i$ but to $\sum_i h_i\ \mathrm{d}n_i$.[14−19,21] In the sections to follow, we show that h_i is a molar enthalpy for species i, which accounts for the added internal energy by injection of species i, plus the work done on the closed system to accomplish this. Equations 9 and 10 are consistent with the balance equations of engineering thermodynamics for the entropy and the internal energy, respectively. Evidently, authors of texts on engineering thermodynamics realize that for open systems an extra term $\mathrm{d}_\mathrm{em}U$ must be included in the expression for the First Law, whereas authors of texts on physical chemistry and chemical thermodynamics often erroneously believe that the contribution of matter exchange can be described by including an extra 'chemical-work' term in the First-Law equation.

THERMODYNAMICS OF MATTER TRANSFER

By careful examination of a process by which an amount of matter is isothermally and reversibly added to an open system containing some arbitrary mixture, we will now derive eqs 9 and 10, with the correct expressions for the matter-transfer contributions $\mathrm{d}_\mathrm{em}S$ and $\mathrm{d}_\mathrm{em}U$, as well as the Gibbs eq 4.

We consider an *open* system, O, that can exchange matter with its surroundings by means of an 'injector', I, that contains only one pure substance i, as illustrated in Figure 1. This is achieved by separating injector and open system by a semipermeable membrane that is only permeable to component i. This requires that the chemical potential of each species in the injector is almost identical to that of the corresponding species in the open system, that is, the difference between the chemical potential values must be infinitesimally small. For a real gas, this implies that the fugacity of component i on both sides of the membrane is almost identical. Also, the temperature of injector and open system is kept constant by means of a large reservoir surrounding the whole system. The open system contains component i in any mixture of substances. The pressure in the open system is maintained at p by means of a movable piston. Throughout the entire process, the open system and the injector together constitute a closed system with diathermal walls, kept at a constant temperature T by means of a large reservoir surrounding the whole system. The internal energy of this open system is denoted as U_O. Initially, the injector contains an amount (number of moles) Δn_i of component i in equilibrium with the open system and exactly this amount will eventually be brought into the open system by emptying the injector (that is why we use Δn_i and not just n_i). Volume, internal energy, and entropy of the injector system are $v_i\Delta n_i$, $u_i\Delta n_i$, and $s_i\Delta n_i$ respectively, where v_i is the molar volume of i, u_i its molar internal energy, and s_i its molar entropy. It is important to realize that the combination of the open system and the injector can be considered as a *closed* system. Therefore, we can use the expressions for the First and Second Laws given by eqs 1 and 2 for this combination of the open system and the injector. The relation between the initial internal energies of the closed and open systems is

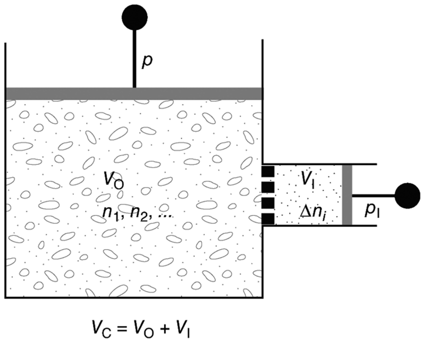

Figure 1. Open system of volume V_O separated from an 'injector' of volume V_I by a semipermeable membrane which is open to a substance i only. The open system contains i in an arbitrary mixture and is kept at a constant pressure p. The injector contains an amount Δn_i of pure substance i at pressure p_I, in equilibrium with the mixture. The content of the injector is reversibly (and isothermally) transferred to the open system. Throughout the entire process, the open system and the injector together constitute a closed system with diathermal walls, kept at a constant temperature T by means of a large reservoir surrounding the whole system.

$$U_\mathrm{C} = U_\mathrm{O} + u_i\Delta n_i \tag{11}$$

For the initial entropies, we have a similar relation

$$S_\mathrm{C} = S_\mathrm{O} + s_i\Delta n_i \tag{12}$$

The contents of the injector is reversibly pushed into the open system by the injector piston, thereby maintaining membrane equilibrium. After the injector has been completely emptied into the open system, we can write the following relation for the final entropies of the open and closed systems (the injector is now void):

$$S_\mathrm{C} + \Delta S_\mathrm{C} = S_\mathrm{O} + \Delta S_\mathrm{O} \tag{13}$$

where ΔS_C and ΔS_O are the changes in entropy due to injection process for the respective systems relative to the initial entropies S_C and S_O. Since $S_\mathrm{C} = S_\mathrm{O} + s_i\Delta n_i$, we come to the conclusion that $\Delta S_\mathrm{O} = \Delta S_\mathrm{C} + s_i\Delta n_i$. If this equation holds for a finite amount injected, it also holds for an infinitesimal small amount. So we can make the transition from finite differences to differentials:

$$\mathrm{d}S_\mathrm{O} = \mathrm{d}S_\mathrm{C} + s_i \mathrm{d}n_i \tag{14}$$

Furthermore, according to the Second Law for reversible changes of closed systems (eq 2), $\mathrm{d}S_\mathrm{C} = \text{đ}q/T$, so

$$\mathrm{d}S_\mathrm{O} = \frac{\text{đ}q}{T} + s_i \mathrm{d}n_i \tag{15}$$

where $\text{đ}q$ represents the possible heat exchange between closed system and surroundings.

Similarly as for the entropy, after the injector has been emptied into the open system, the internal energy of the open system equals that of the closed system (which consists of the contents of the open system and of the now empty injector): $U_\mathrm{C} + \Delta U_\mathrm{C} = U_\mathrm{O} + \Delta U_\mathrm{O}$. Here, ΔU_C and ΔU_O are the changes in energy due to the injection process for the respective systems relative to the initial energies U_C and U_O. Since $U_\mathrm{C} = U_\mathrm{O} + u_i \Delta n_i$, we come to the conclusion that $\Delta U_\mathrm{O} = \Delta U_\mathrm{C} + u_i \Delta n_i$. Hence, for the injection of an infinitesimal small amount:

$$\mathrm{d}U_\mathrm{O} = \mathrm{d}U_\mathrm{C} + u_i \mathrm{d}n_i \tag{16}$$

The change of the energy $\mathrm{d}U_\mathrm{C}$ of the closed system, comprising the open system plus injector, is given by the First Law for closed systems eq 1. Hence

$$\mathrm{d}U_\mathrm{O} = \text{đ}q + \text{đ}w + u_i \mathrm{d}n_i \tag{17}$$

Work is done on the open system by way of both pistons. The contribution from the piston of the open system is the familiar $\text{đ}w_\mathrm{O} = -p\mathrm{d}V_\mathrm{O}$, and the contribution from the injector's piston is $\text{đ}w_\mathrm{I} = -p_\mathrm{I} v_i \, \mathrm{d}n_i$ performed on the injector (the volume change of the injector is $-v_i \, \mathrm{d}n_i$). The latter contribution, associated directly with the transfer of i into the open system, is often called the 'flow work'. Substitution into eq 1 and subsequently into the above equation yields

$$\mathrm{d}U_\mathrm{O} = \text{đ}q + \text{đ}w_\mathrm{O} + u_i \mathrm{d}n_i + p_\mathrm{I} v_i \, \mathrm{d}n_i = \text{đ}q + \text{đ}w_\mathrm{O} + h_i \, \mathrm{d}n_i \tag{18}$$

Suppose that the reversible process is not carried out isothermally but adiabatically, implying that the walls of the closed system are insulating, so that $\text{đ}q = 0$. Also assume that the piston of the open system is fixed. In this case, the closed system's volume decreases upon injection and the injector volume ultimately becomes zero. This is in essence a reversible adiabatic compression of a closed system, implying that its entropy S_C cannot change. The entropy lowering associated with the volume decrease of the closed system is offset by an entropy rise as a result of the temperature increase due to the added energy from the external injection work. For the open system's entropy S_O, it follows from eq 13 that $S_\mathrm{C} = S_\mathrm{O} + \Delta S_\mathrm{O}$ because $\Delta S_\mathrm{C} = 0$. Since $-\Delta S_\mathrm{O} = -s_i \Delta n_i$ (see above after eq 13) and s_i and Δn_i are positive numbers, the negative of the entropy change of the open system $-\Delta S_\mathrm{O}$ must be smaller than zero. Hence, it is evident that the open system's entropy S_O must have increased in an amount that equals the entropy decrease $s_i \Delta n_i$ of the injector. This conclusion is at variance with the fallacious derivations of some authors[7−13] that would have concluded that $\Delta S_\mathrm{O} = 0$ because $q = 0$, as the different forms of the Second Law for closed and open systems are ignored in these derivations.

GENERALIZATION AND DISCUSSION

Equations 15 and 18 constitute the appropriate expressions of the First and Second Laws for reversible processes involving matter transfer of component i. This requires that the chemical potential of each species in the injector is almost identical to that of the corresponding species in the open system, that is, the difference between the chemical potential values must be infinitesimally small. Also, the temperature of injector and open system must be almost identical. We now generalize these results to the case where the injector is filled with an arbitrary mixture of species. Exchange of matter occurs for the species for which the membrane is permeable. As we only consider reversible changes, these species are in continuous membrane equilibrium with the open system. An infinitesimal volume change of the injector is now given by $-\sum_i v_i \, \mathrm{d}n_i$, where v_i is the partial molar volume of species i in the injector mixture. The internal energy of the mixture in this infinitesimally small volume is $\sum_i u_i \mathrm{d}n_i$, where u_i is the partial molar internal energy of species i in the injector mixture. So, by adding an infinitesimal small volume of injector mixture to the open system, an energy $\sum_i (u_i + p_\mathrm{I} v_i) \, \mathrm{d}n_i$ is transferred to the open system. Here, p_I is the pressure exerted on the injector piston. So,

$$\mathrm{d}U_\mathrm{O} = \text{đ}q + \text{đ}w_\mathrm{O} + \sum_i h_i \, \mathrm{d}n_i \tag{19}$$

Comparison with eq 10 reveals that the energy change associated with transfer of matter is $\mathrm{d}_\mathrm{em}U = \sum_i h_i \, \mathrm{d}n_i$. Clearly, $\mathrm{d}_\mathrm{em}U \neq \sum_i \mu_i \mathrm{d}n_i$ as is sometimes wrongfully assumed (see previous section). Equation 19 constitutes the correct expression for the first law for open systems.

The entropy of the volume $\sum_i v_i \, \mathrm{d}n_i$ is $\sum_i s_i \, \mathrm{d}n_i$, where s_i is the partial molar entropy of species i in the injector mixture. This entropy is transferred to the open system, so

$$\mathrm{d}S_\mathrm{O} = \frac{\text{đ}q}{T} + \sum_i s_i \, \mathrm{d}n_i \tag{20}$$

When we compare this equation to eq 9, we conclude that the contribution owing to matter transfer is $\mathrm{d}_\mathrm{em}S = \sum_i s_i \, \mathrm{d}n_i$. Equation 20 constitutes the appropriate expression of the second law for reversible processes involving matter transfer. According to this equation, the reversible heat exchange for a process involving matter transfer is not equal to $T\mathrm{d}S_\mathrm{O}$, as is sometimes assumed, but to $T\mathrm{d}S_\mathrm{O} - T\sum_i s_i \, \mathrm{d}n_i$. Substituting in eq 19, this correct expression for the reversible heat exchange for $\text{đ}q$, and $-p\mathrm{d}V_\mathrm{O}$ for $\text{đ}w_\mathrm{O}$, we obtain the fundamental equation for the internal energy:

$$\begin{aligned} \mathrm{d}U_\mathrm{O} &= T\mathrm{d}S_\mathrm{O} - p\mathrm{d}V_\mathrm{O} + \sum_i (h_i - Ts_i)\mathrm{d}n_i \\ &= T\mathrm{d}S_\mathrm{O} - p\mathrm{d}V_\mathrm{O} + \sum_i \mu_i \mathrm{d}n_i \end{aligned} \tag{21}$$

This brings us back to eq 4. The great benefit of the current derivation is that it clearly shows that the $T\mathrm{d}S$ term in the fundamental equation should not be identified with reversible heat exchange alone in cases involving matter transfer, and that $\sum_i \mu_i \mathrm{d}n_i$ should not be interpreted as a traditional work term in the sense that it represents an internal energy change adjusted for heat exchange and other types of work. Instead, $\sum_i \mu_i \mathrm{d}n_i$ represents an internal energy change due to mass transfer inclusive flow work, and adjusted for the 'material' part of the

TdS term only. That is the true nature of what is sometimes confusingly called 'chemical work'.

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Notes

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(1) We will not consider the kinetic energy associated with the velocity of the system as a whole, nor the potential energy of the system as a whole associated with the system being located somewhere in a gravitational field.

(2) Most texts introduce the Gibbs energy $G = U - TS + pV$ already in the context of closed systems, before they discuss matter transfer and the chemical potential. Then, the $\mu_i \mathrm{d}n_i$ terms are usually added to the total differential of the Gibbs energy yielding the Gibbs equation: $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \sum_i \mu_i \mathrm{d}n_i$. This is done because the expression for the total differential of G is of more direct practical relevance than the total differential of U. For our present purpose of clarifying the relation between the first and second laws and the Gibbs equation, it is more convenient to focus on the energy.

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