

# On the Irreversible Thermodynamic Framework for Closed Systems Consisting of Chemically Reactive Components

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A methodology has been described to develop an irreversible thermodynamic framework based on the laws of thermodynamics and exemplified by applying it to a spatially uniform chemically reacting closed system with no irreversibility in the energy exchanges. It is shown that if in the Gibbs relation the chemical composition determining extensive parameters appear as independent thermodynamic variables and if their variation includes the changes due to chemical reaction, then it, in fact, is an irreversible thermodynamic description. The de Donderian thermodynamic framework is basically a nonequilibrium description in which the chemical affinity containing term is the manifestation of the irreversibility in chemical interactions. This confirms that the Gibbs function primarily takes care of the chemical interactions and hence the quantification of the irreversibility in the latter need to be achieved through the former function by identifying its suitable expression.

## INTRODUCTION

Irreversible thermodynamics (IT) has made a considerable progress beyond the classical irreversible thermodynamics (CIT)<sup>1-11</sup> of Onsager-Prigogine-Meixner-deGroot. Recall that second law of thermodynamics directly provides an entropy function for equilibrium states<sup>12, 13</sup>. On the other hand, for nonequilibrium situations there, one has the Clausius' inequality and hence an entropy function for nonequilibrium states does not directly follow from the second law of thermodynamics<sup>13</sup>. This difficulty is sidlined in CIT by postulating a local equilibrium assumption (LEA).<sup>1, 2</sup> Therefore, it is natural to enquire whether an IT can be developed for the nonequilibrium situations beyond LEA. In this pursuit a good number of IT frameworks have been developed.<sup>14-36</sup> However, these developments also surface out certain incoherences in various perceptions of LEA<sup>37</sup> and there too emerged a hot debate on the concepts of temperature and entropy for nonequilibrium states<sup>38-46</sup>. We believe that the cause of the existence of such a state of affairs in IT, as spelt out earlier,<sup>17, 34</sup> lies in the fact that so far an *ab-initio* method based on the laws of thermodynamics has not been followed for developing an IT framework. The exception being the works of Eu<sup>17, 46, 47</sup> and of the present author<sup>31, 34, 35</sup> wherein a concern for this requirement has been spelt out. The present author has developed a generalized phenomenological

irreversible thermodynamic theory (GPITT) in which a universal inaccessibility principle (UIP) is identified which directly gives a position and time dependent entropy function<sup>31, 34, 35</sup>. Whereas Eu<sup>17, 46, 47</sup> has arrived at the entropy of non-equilibrium states by a suitable manipulation of the Clausius' inequality, the same we have reproduced with a few modifications in the preceding paper<sup>18</sup>. Notice that in this latter development one arrives at the rate of change of entropy both at the global and the local levels of descriptions whose complete quantification depends on an amicable handling of the uncompensated heat contained in the respective expressions<sup>48</sup>. We too have addressed ourselves to this problem. Thus in our pursuit to develop an IT framework starting from the laws of thermodynamics we have recently generalized the zeroth law of thermodynamics which brings in its fold the nonequilibrium states too and thus a thermodynamic establishment of the concept of temperature for nonequilibrium states is accomplished.<sup>49</sup> This in turn ensures that on suitable manipulation of the Clausius' inequality an entropy function is obtained by using the temperature function provided by the generalized zeroth law of thermodynamics. Next in combining the entropy expressions so obtained with the respective expressions of the first law of thermodynamics a basic IT framework would be obtained. In this way we would have an IT framework which is based on the laws of thermodynamics.

In this paper we are exemplifying the above described method by tackling a closed system having an irreversibility only on account of a chemical reaction occurring at a finite rate. This paper serves to establish that without retaining irreversibility on account of the occurrence of a chemical reaction at a finite rate no chemical composition determining extensive parameter of the system (closed) can be made to act as an independent thermodynamic variable. It is once again shown that without the validity of a Gibbs-Duhem equation no thermodynamic framework exists, whether an equilibrium or a nonequilibrium one.

### Quantification of Uncompensated Heat

We recall that for the spatially uniform closed system the rate of change of its entropy is given by eq. (19) of the preceding paper<sup>48</sup>, namely:

$$\frac{dS(t)}{dt} = \frac{1}{T(t)} \frac{dQ}{dt}(t) + \frac{1}{T(t)} \frac{dQ'}{dt}(t) \quad (1)$$

where  $S$  is the entropy of the nonequilibrium state of the system,  $T$  is the temperature of the system,  $dQ$  is the differential element of heat exchanged by the system,  $dQ'$  is the uncompensated heat and  $t$  is time. The second law of thermodynamics guarantees (cf. eq. 18) of the preceding paper<sup>18</sup>) that

$$dQ' \geq 0 \quad (2)$$

Next we require the corresponding expression for the first law of thermodynamics, which for the type of system under consideration reads as

$$\frac{dU}{dt} = \frac{dQ}{dt} - p \frac{dV}{dt} \quad (3)$$

where  $U$  is the internal energy of the system,  $p$  is the pressure and  $V$  is the volume

of the system. As the irreversibility in mechanical energy exchange is assumed as not involved, the work term in eq. (3) is only due to the p-V changes of the system. Also from eq. (2) onwards we are not depicting the time t dependence of the quantities for the sake of simplicity but it remains implied. On substituting eq. (3) into eq. (1), we have

$$\frac{dS}{dt} = T^{-1} \frac{dU}{dt} + pT^{-1} \frac{dV}{dt} + T^{-1} \frac{dQ'}{dt} \quad (4)$$

or equivalently,

$$\frac{dU}{dt} = T \frac{dS}{dt} - p \frac{dV}{dt} - \frac{dQ'}{dt} \quad (5)$$

Notice that in the first law of thermodynamics namely eq. (3), there we have two terms on its right hand side. One originates in the thermal interactions and the other in the mechanical interactions of the system with its surroundings. Hence, in eq. (5), T and S are the thermal and p and V are the mechanical parameters of the system. Also since the system under consideration is spatially uniform the thermal and the mechanical interactions, contained in eq. (5), are those which are determined by the interaction of the system at its bounding surface with its surroundings but no irreversibility is assumed to be existing therein too. Hence, dQ' of eq. (5) must have its origin in other than the thermal and mechanical interactions. However, since dQ' appears in the above description only on account of an irreversibility and the irreversibility in the present case is assumed to be existing only due to a chemical reaction occurring at a finite rate, hence dQ' must be a manifestation of a chemical interaction. Therefore, the quantification of dQ' needs to be accomplished through the chemical interaction determining parameters. However, there are two possible ways to do this which we are describing below.

### The Traditional Approach

When a chemical conversion within a system takes place its chemical composition changes which is the manifestation of the existing chemical interactions. Obviously, the mole numbers become the automatic choice for the composition determining extensive parameters. As we know, in the case of volume change the pressure is its conjugate thermodynamic potential, hence exactly on the same lines on taking  $n_k$ , the mole number of the component k, as the composition determining parameter at time t, the conjugate potential to  $dn_k$  would obviously be termed as the chemical potential, which we denote by  $\mu_k$ . Indeed, it turns out that this  $\mu_k$  is the same physical entity (with the same name) which appears in the traditional Gibbs relation valid for open systems carried reversibly<sup>12</sup>. However, herein we have introduced it for a nonequilibrium state.

The above discussion on the chemical interaction allows us to write the following expression for dQ' for the case under consideration, namely:

$$\frac{dQ'}{dt} = - \sum_k \mu_k \frac{dn_k}{dt} > 0 \quad (6)$$

Notice that the positive sign to the right hand side summational term of eq. (6) is guaranteed by the second law of thermodynamics, namely by eq. (2) above. Now on substituting eq. (6) into eq. (4), we obtain

$$\frac{dS}{dt} = T^{-1} \frac{dU}{dt} + pT^{-1} \frac{dV}{dt} - T^{-1} \sum_k \mu_k \frac{dn_k}{dt} \quad (7)$$

which is the Gibbs relation in the time rate form for closed systems. It needs to be remembered that  $dn_k$  of eq. (7) are the changes in mole numbers due to the participation of the components of the system in a chemical reaction. To describe this latter aspect explicitly we recall that no mole number change occurs independent of the others if these changes are due to their participation in a chemical reaction. The Dalton law of constant proportions relates them as<sup>50</sup>:

$$dn_k = \nu_k d\xi \quad (8)$$

where  $\nu_k$  are the stoichiometric coefficients taken positive for the products and negative for the reactants and  $\xi$  is the extent of chemical reaction. Thus on incorporating eq. (8) into eq. (6), we have

$$\frac{dQ'}{dt} = \mathcal{A} \frac{d\xi}{dt} \geq 0 \quad (9)$$

where the chemical affinity,  $\mathcal{A}$ , has been defined as usual as<sup>50</sup>:

$$\mathcal{A} = - \sum_k \mu_k \nu_k \quad (10)$$

The form of eq. (9) is a typical one.  $d\xi/dt$  is the rate of the chemical reaction and hence  $\mathcal{A}$  is obtained as its driving force. That is, eq. (9) consists of a force multiplied by the corresponding displacement. Finally, on using eqs. (8), (9) and (10), eq. (7) reads as

$$\frac{dS}{dt} = T^{-1} \frac{dU}{dt} + pT^{-1} \frac{dV}{dt} + \mathcal{A} T^{-1} \frac{d\xi}{dt} \quad (11)$$

which is the same equation derived earlier by the de Donderian school<sup>50</sup>. In their derivation they have used the following inequality, namely,

$$dS > \frac{dQ}{T} \quad (12)$$

whose origin, as elaborated in the preceding paper<sup>48</sup>, was not clear at that time (that is 5–6 decades ago). Perhaps it could be this very reason that though Prigogine and Defay in the introduction of their classic monograph<sup>50</sup> have asserted that the chemical thermodynamics needs to be an irreversible one but the text of the said monograph hardly makes a clear distinction between the thermodynamics of a chemically reactive closed system carried along a reversible and an irreversible path. Neither this latter aspect is attended to in any of the later expositions based on the de Donderian approach. Thus from the above it is clear in conformity with the Belgian school that if  $\xi$  appears as an independent variable in a thermodynamic description, then the latter is indeed an irreversible thermodynamic one.

### An Alternative method for the Quantification of $dQ'$

In this method (which is akin to the one followed in GPITT<sup>31, 34</sup>) we first rearrange eq. (4) which yields

$$-\frac{dQ'}{dt} = S \frac{dT}{dt} - V \frac{dp}{dt} + \frac{d(U + pV - TS)}{dt} \quad (13)$$

Notice that the term  $(U + pV - TS)$  in eq. (13) has not been supplied by us from outside but appears naturally on its own which is nothing else but the Gibbs function,  $G$ , namely:

$$U + pV - TS = G \quad (14)$$

Hence eq. (13) reads as

$$-\frac{dQ}{dt} = S \frac{dT}{dt} - V \frac{dp}{dt} + \frac{dG}{dt} \quad (15)$$

Recall that the last term on the right hand side of eq. (4), namely the uncompensated heat,  $dQ'$ , appears on account of irreversibility. In the case under consideration the origin of irreversibility lies in chemical interactions. Therefore, it is needed to manipulate the right hand side of eq. (15) so that there survive only those terms which primarily originate from chemical interactions. In the present case the chemical interactions are those by which the chemical composition of the system changes on account of a chemical reaction occurring at a finite rate. The chemical composition determining parameters obviously are the mole numbers,  $n_k$ , which need to be multiplied by the corresponding potentials which determine the intensity of chemical interactions. The latter ones in the present case are  $\mu_k$ 's. Moreover, let us rewrite eq. (14) as

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

which clearly states that the internal energy of the system is made up of the contributions originating in thermal ( $TS$ ) and mechanical ( $-pV$ ) interactions and the term  $G$  whose origin must lie in the chemical interactions. Thus it is clear that in thermodynamics  $G$  basically quantifies the chemical interactions. Recall that in the physical world there are only these three categories of interactions<sup>51, 52</sup> (the mechanical interactions in the most general case include contributions from the actions of body and contact forces on the system) and hence the thermodynamic description of a system needs to be based only on these three interactions whether it is the case of equilibrium or nonequilibrium.

Therefore, a proper expression for  $dQ'$  can only be arrived at if we use a correct expression for the Gibbs function,  $G$ . Thus in the present case in view of  $G$  being an extensive quantity it is expressed as

$$G = \sum_k \mu_k n_k \quad (17)$$

where as introduced herein the chemical potential,  $\mu_k$ , is the partial molar Gibbs free energy of the component  $k$ . Next on substituting eq. (17) into eq. (15) we obtain two relations. One is eq. (6) and the other is the time rate form of the Gibbs-Duhem equation, namely:

$$S \frac{dT}{dt} - V \frac{dp}{dt} + \sum_k n_k \frac{d\mu_k}{dt} = 0 \quad (18)$$

Notice that the extracting out of the Gibbs-Duhem equation from eq. (15) is not dictated by the fact that we already know the expression of eq. (6) by another method but there are two reasons of it. Firstly, if we do not extract it out then on substituting eq. (15) into eq. (4) an identity is obtained and not a functional dependence. Secondly, the incorporation of eq. (17) in eq. (15) produces an expression which has terms having their origin in thermal and mechanical interactions along with those determining the chemical interactions. But  $dQ'$  should consist of only those terms having their origin in chemical interactions and that too consisting of the corresponding extensive parameters as variables.

Thus, we have established that during the said irreversible evolution of the system the Gibbs-Duhem equation is rigorously followed. That is, no thermodynamic description exists without its Gibbs-Duhem equation which describes a unique mutual control on the variation of intensities of the system. This we have stressed earlier too<sup>34-36</sup>. From here onwards we arrive at eqs. (7) and (11) in identically the same steps as described in the preceding sub-section.

From the above discussion we see that in the case of nonequilibrium considered herein we have the following equation of state for the chemical potential (cf. eq. (7)), namely,

$$-\frac{\mu_k}{T} = \left( \frac{\partial S}{\partial n_k} \right)_{U, V, n_{j \neq k}} \quad (19)$$

This is identically the same expression, as far as the thermodynamic parameters involved are concerned, which one has in the thermodynamics of equilibrium states of open systems<sup>12, 52</sup> as described earlier.<sup>50</sup> The only difference is that all the quantities involved in eq. (19) are basically the time dependent ones. Also in eq. (19) we have a quantitative expression of component-wise chemical interaction because the thermal, the mechanical and the chemical interactions of rest of the components have been frozen by keeping  $U$ ,  $V$  and  $n_{j \neq k}$  constant. Thus eq. (19) establishes that the physical contents of  $\mu_k$  remain identically the same in going from an equilibrium to a nonequilibrium situation.

Since in the present case the chemical interactions are manifested in the occurrence of a chemical reaction at a finite rate, a single compositely quantifying expression of the chemical interactions is obtained from eq. (11) as

$$\frac{\mathcal{A}}{T} = \left( \frac{\partial S}{\partial \xi} \right)_{U, V} \quad (20)$$

which is the de Donderian equation of state of chemical affinity.

Similarly, on the front of thermal interactions let us compare the equation of state of temperature obtained in the thermodynamics of equilibrium states (closed systems), namely:

$$T^{-1} = \left( \frac{\partial S}{\partial U} \right)_V \quad (21)$$

with the one give by eqs. (7) and (11), namely,

$$T^{-1} = \left( \frac{\partial S}{\partial U} \right)_{V, n_k} = \left( \frac{\partial S}{\partial U} \right)_{V, \xi} \quad (22)$$

Recall that the partial derivative of eq. (21) is the tangent to the curve in  $S, U$  and  $V$  space. Since  $S, U$  and  $V$  are the time independent quantities (because it is the case of reversibility) any change in  $U$  and  $V$  along a reversible curve not only brings about a corresponding change in  $S$  but also if the closed system is chemically reactive its chemical composition will change due to the concomitant internal chemical conversion. But as can be seen from the above discussion that the internal chemical conversion does not remain an independent process along a reversible path. Therefore, on keeping  $V$  constant in a reversible transition one allows only the thermal interaction to cause a change in the state of the system. That is, eq. (21) is a thermodynamic quantification of the thermal interaction along a reversible path. Similarly, since  $n_k$  and  $\xi$  become independent variables in the respective thermodynamic set-ups in the case of the existence of an irreversibility due to the occurrence of a chemical reaction at a finite rate it is now required to specify the constancy of  $V$  and  $n_k$  or  $V$  and  $\xi$  in order that only the thermal interaction of the system with its surroundings is allowed to cause a change in the state of the system. This is what is precisely expressed in eq. (22). Indeed, since the nature of the thermal interaction cannot be of different type whether the system is in equilibrium or in nonequilibrium, hence the temperature  $T$  of eq. (21) is essentially the same physical entity as that of eq. (22). Moreover, notice that in the thermodynamic description of a closed system the chemical interaction remains submerged in the basic thermodynamic framework in the event of reversibility while it surfaces out only if there exists an irreversibility in it. This is so because the process occurring due to the chemical interaction is an internal one which in the present case is the process of chemical conversion.

### Some of the Thermodynamic Deductions

Equation (9) demands that the signs of  $\mathcal{A}$  and  $d\xi/dt$  has to be the same. It is, therefore, easy to deduce the following from it, namely:

- (a)  $\mathcal{A} > 0, \frac{d\xi}{dt} > 0$  net forward reaction
- (b)  $\mathcal{A} < 0, \frac{d\xi}{dt} < 0$  net reverse reaction
- (c)  $\mathcal{A} = 0, d\xi = 0$  chemical equilibrium
- (d)  $\mathcal{A} = 0, d\xi \neq 0$  the system is carried along a reversible path
- (e)  $\mathcal{A} \neq 0, \frac{d\xi}{dt} = 0$  a metastable state. The energy of activation is so high that no observable chemical conversion takes place

The Belgian school has already described<sup>50</sup> the deductions contained in (a) to (c) above. In (c) we have the well known condition of chemical equilibrium. However, the deductions (d) and (e) are stated for the first time. In (d) we have the description of reversibility, that is, when a chemically reactive closed system is carried along a reversible path its chemical composition will change con-

comitantly due to the internal chemical conversion. Surprisingly, no thermodynamic text describes this fact though it is so apparent in the de Donderian description. This fact can also be appreciated as follows. As is known, the equilibrium constant of a chemical reaction is a function of  $T$  and  $p$ . Hence at different sets of  $T$  and  $p$  values for a given chemical reaction there will be, in general, different chemical compositions at the respective equilibrium states. Hence, when a chemically reactive closed system in equilibrium at a given  $T$  and  $p$  is carried to another set of  $T$  and  $p$  values the internal chemical composition needs to and hence will change accordingly. But any two equilibrium states can be connected by a reversible path. Hence when a chemically reactive closed system is carried along a reversible path the chemical conversion within the system will take place to attain the chemical composition demanded by the change in the equilibrium constant. In (e) above we have a metastable state. One of the prominent examples of the chemical metastable state is the mixture of hydrogen and oxygen gases without a catalyst or an electric spark and not too high a temperature though the water formation is a thermodynamically favourable process.<sup>50, 52</sup>

The condition of (c) when imposed on eq. (10) yields the traditional condition of chemical equilibrium, namely,

$$\sum_k \nu_k \mu_k = 0 = \mathcal{A} \quad (23)$$

which according to (d) above needs to be true also along a reversible path<sup>53</sup> even if the chemical composition might be changing on account of the internal chemical conversion. This latter fact was pointed out earlier too.<sup>34, 35</sup>

An interesting case is that of the reversible adiabates. On imposing the condition of adiabaticity on eqs. (3) and (11), we have

$$\frac{dS}{dt} = \frac{\mathcal{A}}{T} \frac{d\xi}{dt} > 0 \quad (\text{adiabatic conditions}) \quad (24)$$

Notice that eq. (24) asserts the traditional thermodynamic deduction that the occurrence of a chemical reaction at a finite rate produces entropy. Hence if there exists an irreversibility on account of chemical reactions at finite rates then entropy of the system under adiabatic condition will increase with time. Now if we further impose the condition of reversibility (that is a reversible adiabatic transition) then eq. (24) produces

$$dS = 0 \quad \text{because } \mathcal{A} = 0 \text{ though } d\xi \neq 0 \quad (25)$$

Thus it is seen that the isentropicity gets perfectly maintained along a reversible adiabatic path even if the chemical composition is simultaneously changing due to the internal chemical conversion in the case of chemically reactive closed systems. This reveals that how strong are the reversible adiabates in maintaining the entropy of the system (closed) constant. This fact we have spelt out earlier too.<sup>34, 35</sup>

As pointed out in the past<sup>53</sup> it is often misinterpreted that the de Donderian eq. (11) is compatible with the Gibbs relation derived in equilibrium thermodynamics and vice-versa<sup>50, 54, 55</sup>. The reason for this falling prey to a trap is



twofold. Firstly, when the Belgian school derived eq. (11) using eq. (12), it seems that there was no clear idea whether the entropy function contained in the latter equation is of an equilibrium state or of a nonequilibrium state. Secondly, it is hardly realized that the traditional Gibbs relation, namely,

$$T dS = dU + p dV - \sum_k \mu_k dn_k \quad (26)$$

does not contain a contribution from mole number changes on account of the internal chemical conversion when the system is carried reversibly from one equilibrium state to another. Recall that the mole number change in the Belgian school notation is expressed as<sup>50, 54</sup>

$$dn_k = d_i n_k + d_e n_k \quad (27)$$

where the subscripts *i* and *e* refer to the internal and exchange respectively. Thus when an open system is carried along a reversible path the correct version of the Gibbs relation describing such transitions is

$$T dS = dU + p dV - \sum_k \mu_k d_e n_k \quad (28)$$

because eq. (23) obviously needs to be valid in this case too. Notice that on imposing the constraints of a closed system on eq. (28) one obtains the Clausius' differential relation (this name seems to have been coined by Blinder<sup>56</sup>) namely:

$$T dS = dU + p dV \quad (29)$$

which in standard steps is obtained for the closed systems carried along a reversible path, directly on combining the equilibrium parts of the mathematical statements of the first and the second laws of thermodynamics<sup>12, 13, 50, 52</sup> irrespective of the system being chemically reactive or not. Notice that eq. (26) when subjected to the closed system constraints yields eq. (7) in the following form, namely,

$$T dS = dU + p dV - \sum_k \mu_k d_i n_k \quad (30)$$

and not eq. (29). Therefore, eq. (26) as such is not a description of an open system carried along a reversible path. Since eq. (23) is rigorously followed along a reversible path eq. (28) and (29) do not exclude the concomitant chemical conversion taking place within the system when it is carried along a reversible path if the components comprising the system happen to be chemically reactive ones. Thus when  $d_i n_k$  is retained in eq. (26) it simply means that one is dealing with a chemical reaction occurring at a finite rate and hence one, in fact, is doing IT and not the equilibrium one. Therefore, it is clear that the chemical thermodynamics of a closed system in which the chemical composition determining extensive parameters are taken or appear as independent thermodynamic variables is indeed an IT description which, unfortunately, has not been emphatically acknowledged so far.

Finally, there we have one and the same accompanying Gibbs-Duhem equation to eqs. (26) and (28) to (30), namely,

$$S dT - V dp + \sum_k n_k d\mu_k = 0 \quad (31)$$

That is, there is no distinction between the reversible and irreversible transitions from the point of view of the validity and the contents of Gibbs-Duhem equation which indeed should be in the time rate form in the case of irreversibility. Notice that eqs. (26), (28) and (30) have  $(N + 2)$  independent extensive variables but correspondingly only  $(N + 1)$  conjugate intensive variables can be varied independently according to the Gibbs-Duhem equation. The latter deduction remains true also in the case of a  $N$ -component closed system carried reversibly though there we have only two independent extensive variables [cf. eq. (29)]. This latter conclusion holds good whether the closed system happens to be chemically reactive or not.

### Concluding Remarks

In our pursuit to develop an IT framework based on the laws of thermodynamics we have recently generalized the zeroth law of thermodynamics which brings in its fold the nonequilibrium states and hence the temperature concept for the nonequilibrium states gets a thermodynamic legitimacy<sup>49</sup>. In the preceding paper<sup>48</sup> we have described by using Eu's approach<sup>47</sup> how to arrive at the entropy function for nonequilibrium states. In this approach a proper manipulation of the Clausius inequality is undertaken which generates an entropy function for nonequilibrium states both at the global and the local levels of descriptions in which the temperature function guaranteed by the generalized zeroth law of thermodynamics appears. The rate of entropy change expression so obtained contains the Clausius unconsummated heat whose quantification and the coupling of the former with an appropriate expression of the first law of thermodynamics generate the corresponding basic thermodynamic framework. It gets revealed that the quantification of the uncompensated heat is intimately entwined in the identification of a proper expression for the Gibbs function. The latter function primarily takes care of the existing chemical interactions.

This methodology is exemplified by applying it to a spatially uniform closed system having irreversibility only on account of a chemical reaction occurring at a finite rate. This reconfirms that the de Donderian thermodynamic framework<sup>50</sup> is basically an irreversible one. Notice that we have used herein a proper version of the Clausius inequality whereas the approach described by the Belgian school<sup>50</sup> remains ambiguous on this count, as described in the preceding paper<sup>18</sup> with regard to eq. (12) of this paper. Moreover, we have also described some of the relevant deductions and clarified certain existing ambiguities. In a forthcoming paper the above methodology will be applied to a non-uniform system.

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