

THERMODYNAMIC STABILITY OF IRREVERSIBLE PROCESSES: A GIBBS-DUHEM TYPE THEORY AND THE FOURTH LAW OF THERMODYNAMICS

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ABSTRACT

The Gibbs-Duhem theory of stability of equilibrium states has been extended to determine the stability of irreversible processes. The basic concept of virtual displacement in the reverse direction on the real trajectory, which is involved in the celebrated Gibbs-Duhem theory, has been used. This establishes that all thermodynamically describable processes are thermodynamically stable. This outcome led us to reformulate the fourth law of thermodynamics. Moreover, our present investigations illustrate the basis of the universal inaccessibility principle formulated earlier by one of the present authors (AAB).

INTRODUCTION

To meet the global energy demands with the limited resources at our disposal, there is currently considerable pressure on sustainable energy management. To achieve this goal, thermodynamic considerations enjoy a vital status among other tools. Within this approach, the thermodynamic stability criterion plays a crucial role. To this day, we have only a very sound thermodynamic stability theory of equilibrium states, which is known as Gibbs-Duhem stability theory [1-4]. However, this theory applies only to a very limited extent to the real problems we encounter day to day. This is so because the said theory is centered on equilibrium states, whereas in real problems, one hardly deals with equilibrium situations. To remove this lacuna, we need a thermodynamic stability theory that works entirely within a nonequilibrium environment. The notable efforts are those of Prigogine and co-workers (see for example reference [4] and references cited therein), in which they have developed their stability theory for local thermodynamic equilibrium (LTE) states. In principle, this theory is not capable of handling those vast varieties of irreversible processes not expected to lie in the domain of LTE. Hence, a thermodynamic stability theory of a wider spectrum of applicability is required. To meet this requirement, we have extended the Gibbs-Duhem stability theory of equilibrium states to general nonequilibrium situations, in which no assumption like LTE is involved. Thus, it is a comprehensive thermodynamic theory of stability.

For the sake of self-sufficiency, let us first recall some basic aspects of the Gibbs–Duhem theory of stability of equilibrium states.

The thermodynamic description of the natural direction of irreversible evolution is [1– 4],

$$(\Delta S)_{U,V} > 0, \quad (\Delta A)_{T,V} < 0, \quad (\Delta G)_{T,p} < 0 \quad (1)$$

$$(dS)_{U,V} > 0, \quad (dA)_{T,V} < 0, \quad (dG)_{T,p} < 0 \quad (2)$$

where in eqs. (1) and (2) S is the entropy, G is the Gibbs free energy, A is the Helmholtz free energy, U is the internal energy, V is the volume, T is the temperature, and p is the pressure.

Hence the unnatural direction of processes obviously become described as,

$$(\Delta S)_{U,V} < 0, \quad (\Delta A)_{T,V} > 0, \quad (\Delta G)_{T,p} > 0 \quad (3)$$

$$(dS)_{U,V} < 0, \quad (dA)_{T,V} > 0, \quad (dG)_{T,p} > 0 \quad (4)$$

These inequalities constitute the Gibbs-Duhem thermodynamic theory of stability of equilibrium states [1– 4].

In essence, the above inequalities respectively describe the impossible changes of the state functions or virtual displacements to a neighboring nonequilibrium states. In other words, they are the expressions of unattainability (under the given conditions) of nonequilibrium states from an equilibrium state. The said nonequilibrium states are the ones through which the system naturally evolved to a final equilibrium state, as described in eqs. (1) and (2).

Let us recall that the inequalities of eqs. (1) and (2) describe the monotonic increase/decrease of the thermodynamic functions during the given irreversible processes.

Upon close scrutiny of the above thermodynamic inequalities, a few queries get raised. They are,

1. In the above inequalities, the change of state functions can be taken equally between two end equilibrium states, as well as between end equilibrium and nonequilibrium states. But when the latter is the case, then how does one arrive at these state functions for nonequilibrium states? This by itself is a thermodynamically (particularly at the times of Clausius, Gibbs and Duhem) obvious question.
2. The preceding query crops up because we have a rigorous thermodynamic definition of entropy, S , in equilibrium only, which is given by Clausius [5],

$$dS = \frac{dQ}{T} \quad (\text{for a closed system carried on a reversible path}) \quad (5)$$

3. In equilibrium we have the following definitions of Helmholtz free energy, A , and Gibbs free energy, G ,

$$A = U - TS, \quad G = U + pV - TS = H - TS \quad (6)$$

But when we consider that the above thermodynamic inequalities are between two end states, one equilibrium and the other nonequilibrium states, then it implies that there exists a function, S , also for nonequilibrium states and hence the definitions of eq. (6) hold true for nonequilibrium states as well.

4. It seems that the answer to the above question lies in the use of the inequality in differential form, stated by Clausius himself without its derivation [5,6],

$$dS > \frac{dQ}{T} \quad (\text{for a closed system}) \quad (7)$$

However, Meixner, as late as in 1973, argued that the entropy function appearing in eq. (7) must be that for the intermediate nonequilibrium states of an irreversible evolution of a system [6].

5. In particular, the inequalities in terms of the functions A and G are extensively used in chemical thermodynamics describing chemical reactions at non-vanishing rates, inter-

phase matter transfers, and matter diffusion (see for example [7–9]) starting with the inequality of eq. (7).

In spite of these ambiguities associated with the above stated inequalities, the crucial principle that is involved in the Gibbs-Duhem theory of stability of equilibrium states is the impossibility of traversing the path in the reverse direction. This basic element we have extended to irreversible processes. The conclusion reached is that irreversible evolutions describable thermodynamically are all stable ones.

In doing so, we take care of not getting trapped in the types of ambiguities mentioned above. Our investigations finally culminate into a formulation of the fourth law of thermodynamics.

The chronology of presentation is as follows. Next Section describes the thermodynamic theory of stability of (i) irreversible processes both under traditional conditions and general evolution, and (ii) nonequilibrium stationary states. In the following Section we formulate the *fourth law of thermodynamics*. The final Section contains concluding remarks.

ENTROPY BALANCE EQUATION AND THERMODYNAMIC STABILITY OF IRREVERSIBLE PROCESSES

Earlier we have developed a generalized phenomenological irreversible thermodynamic theory (GPITT) [10– 20]. We in particular refer readers to the paper cited at reference [18] wherein we have finally succeeded in identifying thermodynamic variables for spatially non-uniform systems (also in upcoming paper [21]). Using GPITT given Gibbs relation or from any of the other nonequilibrium thermodynamic frameworks such as classical irreversible thermodynamics (CIT), extended irreversible thermodynamics (EIT), etc. (reviewed in reference [22]), it is easy to recall that for an open system evolving irreversibly we have,

$$\frac{dS}{dt} = \frac{d_e S}{dt} + \frac{d_i S}{dt} \quad (8)$$

where dS/dt is the net rate of entropy change of the system, the net rate of entropy exchange is given by,

$$\frac{d_e S}{dt} = \int (\nabla \cdot \mathbf{J}_s) dV \geq 0 \quad (9)$$

and the total rate of entropy production reads as,

$$\frac{d_i S}{dt} = \int \sigma_s dV > 0 \quad (10)$$

where \mathbf{J}_s is the entropy flux density and σ_s is the entropy source strength. Notice that eqs. (8) – (10) are valid for a multicomponent multiphase system in nonequilibrium.

Thus, a complete and direct description of irreversibility is the rate of entropy production, eq. (10). Hence, Prigogine writes the second law of thermodynamics in the following words [23, 24]:

“Entropy of a system can change on two and only two counts, one by the exchange mechanism and the other by its production within the system.”

Although eq. (10) is an inequality, it *cannot* be used to deduce the thermodynamic stability of the corresponding irreversible processes along the lines of the Gibbs-Duhem theory of stability of equilibrium states. This is so because it is not a complete description of the change of state during an irreversible process. However, we notice that under certain conditions, the rate of

entropy production becomes a complete description of the change of state of a system. This approach is described in the following Subsection.

Thermodynamic Stability of Irreversible Processes Occurring in Systems with Conditions Imposed

Notice that once we have established an entropy function in nonequilibrium independently using Clausius' inequality, it then follows that we legitimately have the following standard relations at the local level too,

$$a = u - Ts, \quad \mathcal{G} = u + pv - Ts = h - Ts \quad (11)$$

where a is the per unit mass Hemholtz free energy and \mathcal{G} is the per unit mass Gibbs free energy. When T and p are uniform throughout a given system, we have the following standard relations at the global level,

$$A = U - TS, \quad G = U + pV - TS = H - TS \quad (12)$$

Notice that all the functions of eqs. (11) and (12) are time dependent, because in these expressions there appears the time dependent entropy in nonequilibrium.

Recall once again that the Gibbs-Duhem theory of stability of equilibrium states is based on the impossibility of a virtual displacement from an equilibrium state in the reverse direction on the trajectory of the natural evolution, to the final equilibrium state determined by eqs. (3) and (4). We are applying exactly the same method to the irreversible segments between two end nonequilibrium states that would determine the thermodynamic stability of irreversible processes.

Now it is ideal to start with closed systems evolving irreversibly under certain imposed conditions.

1. On imposing the condition of isolation on a system, all exchange mechanisms become forbidden, eq. (8) reduces to,

$$\left(\frac{dS}{dt}\right)_{U,V} = \left(\frac{d_i S}{dt}\right)_{U,V} > 0 \left\{ \begin{array}{l} \text{(natural direction of evolution} \\ \text{of an isolated system)} \end{array} \right. \quad (13)$$

This inequality describes the evolution towards a final equilibrium state. Also, the rate of entropy production monotonically decreases and finally becomes zero, and as a result of this, the entropy of the system maximizes at the final equilibrium state. Hence for its conjugate virtual displacement, eq. (13) guarantees,

$$\left(\frac{dS}{dt}\right)_{U,V} = \left(\frac{d_i S}{dt}\right)_{U,V} < 0 \left\{ \begin{array}{l} \text{(unnatural direction of} \\ \text{evolution of an isolated system)} \end{array} \right. \quad (14)$$

Therefore, *the irreversible processes in the natural direction under the condition of isolation are guaranteed to be thermodynamically stable ones.* The allowed irreversible processes are chemical reactions at non-vanishing rates, internal matter diffusion within and across the phases of the system, and due to the existence of heat and momentum fluxes within the system.

2. In this case, we impose on eq. (8) the condition of the constancy of H and p and we obtain,

$$\left(\frac{dS}{dt}\right)_{H,p} = \left(\frac{d_i S}{dt}\right)_{H,p} > 0 \left\{ \begin{array}{l} \text{(natural direction of isoenthalpic –} \\ \text{isobaric evolution of a system)} \end{array} \right. \quad (15)$$

In arriving at the result of eq. (15) we have also used the following identity obtained under the uniformity of p and the constancy of H and p from the first law of thermodynamics,

$$\left(\frac{dQ}{dt}\right)_{H,p} = \left(\frac{d_e S}{dt}\right)_{H,p} = 0 \left\{ \begin{array}{l} \text{(for isoenthalpic – isobaric} \\ \text{evolution of a closed system)} \end{array} \right. \quad (16)$$

The inequality of eq. (15) describes the evolution towards a final equilibrium state. It also demonstrates that the rate of entropy production decreases monotonically and becomes zero at the final equilibrium state, whereby the entropy of the system maximizes at the final equilibrium state. Therefore, for the conjugate virtual displacement eq. (15) guarantees,

$$\left(\frac{dS}{dt}\right)_{H,p} = \left(\frac{d_i S}{dt}\right)_{H,p} < 0 \quad \left\{ \begin{array}{l} \text{(unnatural direction of isoenthalpic -} \\ \text{isobaric evolution of a system)} \end{array} \right. \quad (17)$$

Thus, *the isoenthalpic-isobaric evolution of a system is guaranteed to be a thermodynamically stable one.* In arriving at the above inequality, the pressure and temperature were considered uniform throughout the system. Therefore, at constant pressure and enthalpy, the only irreversibility that can exist is due to chemical reactions at a non-vanishing rate and matter diffusion.

3. Let us consider a closed system evolving irreversibly under the uniform p within and across the boundaries of the closed system, with the only possible work being that due to $p - V$ changes. Hence the corresponding expression of the first law of thermodynamics is,

$$\frac{dU}{dt} = \frac{dQ}{dt} - p \frac{dV}{dt} \quad (\text{closed system}) \quad (18)$$

Further assuming uniformity of T within and across the boundaries of the given closed system, we can use the standard relation of Helmholtz free energy given in eq. (12), whose time rate variation reads as,

$$\frac{dA}{dt} = \frac{dU}{dt} - T \frac{dS}{dt} - S \frac{dT}{dt} \quad (\text{closed system}) \quad (19)$$

Notice that because now we have used the entropy function for nonequilibrium states, the function A is that for a nonequilibrium state. Next on substituting eq. (18) into eq. (19) yields,

$$\frac{dA}{dt} = \frac{dQ}{dt} - p \frac{dV}{dt} - T \frac{dS}{dt} - S \frac{dT}{dt} \quad (\text{closed system}) \quad (20)$$

which under the condition of constant T and V reduces to,

$$\left(\frac{dA}{dt}\right)_{T,V} = \left(\frac{dQ}{dt}\right)_{T,V} - T \left(\frac{dS}{dt}\right)_{T,V} \quad (\text{closed system}) \quad (21)$$

However, at constant T and V eq. (8) reads as,

$$\left(\frac{dS}{dt}\right)_{T,V} = \left(\frac{d_e S}{dt}\right)_{T,V} + \left(\frac{d_i S}{dt}\right)_{T,V} \quad (22)$$

The second law of thermodynamics for a system at uniform temperature throughout and across its boundaries gives,

$$\frac{dS}{dt} = \frac{1}{T} \frac{dQ}{dt} + \frac{d_i S}{dt} = \frac{d_e S}{dt} + \frac{d_i S}{dt} \quad (23)$$

so that from eq. (23) we have,

$$\left(\frac{d_e S}{dt}\right)_{T,V} = \frac{1}{T} \left(\frac{dQ}{dt}\right)_{T,V} \quad (24)$$

Thus, on substituting eq. (24) into eq. (21) and using eq. (22), yields the following inequality,

$$\left(\frac{dA}{dt}\right)_{T,V} = -T \left(\frac{d_i S}{dt}\right)_{T,V} < 0 \quad \left\{ \begin{array}{l} \text{(natural direction of evolution of a} \\ \text{closed system at constant } T \text{ and } V) \end{array} \right. \quad (25)$$

The inequality of eq. (25) describes the evolution towards a final equilibrium state. Also, the rate of entropy production decreases monotonically and finally becomes zero whereby the Helmholtz free energy of the system is a minimum at the final equilibrium state. Therefore, for its conjugate virtual displacement eq. (25) guarantees,

$$\left(\frac{dA}{dt}\right)_{T,V} = -T \left(\frac{d_i S}{dt}\right)_{T,V} > 0 \quad \left\{ \begin{array}{l} \text{(unnatural direction of evolution of} \\ \text{a closed system at constant } T \text{ and } V) \end{array} \right. \quad (26)$$

Thus, the *evolution of a closed system at constant T and V is guaranteed to be a thermodynamically stable one*. Arriving at the above inequalities, the uniformity of T and p was assumed, such that the irreversibility on account of heat transfer within and across the boundaries of the system, and that due to $p - V$ changes cannot exist anymore because volume is also kept constant.

4. Now let us consider uniformity of T and p within and across the boundaries of a closed system and also assume that only $p - V$ work is involved. Then the applicable expression of the first law of thermodynamics is,

$$\frac{dH}{dt} = \frac{dQ}{dt} + V \frac{dp}{dt} \quad (\text{closed system}) \quad (27)$$

Under these conditions we can use the standard expression of Gibbs free energy, G , given in eq. (12) and its time rate of change reads as,

$$\frac{dG}{dt} = \frac{dH}{dt} - T \frac{dS}{dt} - S \frac{dT}{dt} \quad (\text{closed system}) \quad (28)$$

which on combining with eq. (27) yields the following expression,

$$\frac{dG}{dt} = \frac{dQ}{dt} + V \frac{dp}{dt} - T \frac{dS}{dt} - S \frac{dT}{dt} \quad (\text{closed system}) \quad (29)$$

which at constant T and p takes the form,

$$\left(\frac{dG}{dt}\right)_{T,p} = \left(\frac{dQ}{dt}\right)_{T,p} - T \left(\frac{dS}{dt}\right)_{T,p} \quad (\text{closed system}) \quad (30)$$

while at constant T and p eq. (8) reads as,

$$\left(\frac{dS}{dt}\right)_{T,p} = \left(\frac{d_e S}{dt}\right)_{T,p} + \left(\frac{d_i S}{dt}\right)_{T,p} \quad (31)$$

Under these conditions, from eqs. (23) and (31) the rate of exchange of entropy reads as,

$$\left(\frac{d_e S}{dt}\right)_{T,p} = \frac{1}{T} \left(\frac{dQ}{dt}\right)_{T,p} \quad (32)$$

which on substitution into eq. (30) yields,

$$\left(\frac{dG}{dt}\right)_{T,p} = -T \left(\frac{d_i S}{dt}\right)_{T,p} < 0 \quad \left\{ \begin{array}{l} \text{(natural direction of evolution of a} \\ \text{closed system at constant } T \text{ and } p) \end{array} \right. \quad (33)$$

The inequality of eq. (33) describes the evolution towards a final equilibrium state. Also, the rate of entropy production decreases monotonically and finally becomes zero at equilibrium, and whereby the Gibbs free energy of the system is minimum at the final equilibrium state. Therefore, for its conjugate virtual displacement eq. (33) guarantees,

$$\left(\frac{dG}{dt}\right)_{T,p} = -T \left(\frac{d_i S}{dt}\right)_{T,p} > 0 \quad \left\{ \begin{array}{l} \text{(unnatural direction of evolution of a} \\ \text{closed system at constant } T \text{ and } p) \end{array} \right. \quad (34)$$

Thus, the *evolution of a closed system at constant T and p is guaranteed to be a thermodynamically stable one*. Arriving at the above inequalities, the uniformity of T and p was assumed such that the irreversibility on account of heat transfer within and across the boundaries of the system and that due to $p - V$ changes cannot exist. Thus, if viscous dissipation is also absent, then the only irreversibility that can exist is due to non-vanishing rates of chemical reactions and internal matter diffusion.

Now we see that the inequalities of eqs. (1) and (2) are in essence the assertions about the entropy production under the respective conditions.

Yet another deduction that follows from the conditional inequalities of eqs. (13) – (15), (17), (25), (26), (33), and (34) is that *they all guarantee that the respective evolution follows a passage through predestined nonequilibrium states to the final equilibrium state. Also as the*

system evolves, it passes successively from more unstable nonequilibrium states to less unstable nonequilibrium states. This then implies that during these conditional evolutions, the instantaneous rate of entropy production continuously decreases.

Thermodynamic Stability of Equilibrium States

In the preceding Subsection we have demonstrated the stability of irreversible evolution. This remains true throughout the irreversible evolution. Hence, at the ‘end segment’ of the irreversible evolution, the virtual displacement would be considered from the final equilibrium state to the same neighboring nonequilibrium states comprising forward motion, but in the reverse order. Since this reverse motion constitutes an impossible transition, the stability of the equilibrium state gets established. This is nothing else but the Gibbs-Duhem theory of stability of equilibrium states, and its specific descriptions get generated on integration of inequalities of this Section between the end equilibrium state and the neighboring nonequilibrium states. They are none else than the traditional ones given in eqs. (1) and (3). Correspondingly, if we consider the differential rates of this Section as the ones between the end equilibrium state and the infinitesimally away nonequilibrium state, then they are nothing else than those given in eqs. (2) and (4). This establishes the self-consistency of the present analysis of stability of irreversible processes.

Thermodynamic Stability of Nonequilibrium Stationary States (NSS)

Lavenda has claimed that it is not possible to thermodynamically assign maximum entropy to a nonequilibrium stationary state (NSS) (see Chapter 4 in [25]). However, it is possible to establish thermodynamic stability of NSS. Let us first elaborate the above assertion of Lavenda.

Thermodynamically at nonequilibrium stationary state we have from eq. (8),

$$\frac{dS^{nss}}{dt} = 0 = \frac{d_e S^{nss}}{dt} + \frac{d_i S^{nss}}{dt} \quad (35)$$

where on the right-hand side of the second equality, the first term is the rate of exchange of entropy, the second term quantifies the rate of production of entropy, and the superscript *nss* denotes nonequilibrium stationary state. Then the Taylor expansion of entropy about its value at NSS on a path that led the system to achieve the given NSS yields,

$$S(t) = S^{nss} + (\delta S)(t) + \frac{1}{2} (\delta^2 S)(t) + (\text{higher order terms}) \quad (36)$$

Notice that it is not possible to arrive at $(\delta S) = 0$ without imposition of some suitable conditions, but then under those conditions it would not be possible to attain a NSS. That is, one cannot assert that the entropy at NSS is maximum or in other words, the entropy about NSS is not obtained as a convex function. Hence on differentiating eq. (36) w.r.t. time we get,

$$\frac{dS}{dt} = \frac{d(\delta S)}{dt} + \frac{1}{2} \frac{d(\delta^2 S)}{dt} + (\text{higher order terms}) \quad (37)$$

Now eq. (37) needs to be compared with eq. (8) and we see in eq. (8) that the rate of entropy change is determined by the flow $(d_e S/dt) \geq 0$ and the non-flow $(d_i S/dt) > 0$ terms. Hence, eq. (37) needs to be composed of flow and non-flow terms. Therefore, eq. (37) gets expressed as,

$$\frac{dS}{dt} = \left(\frac{d(\delta S)}{dt} \right)_{flow} + \left(\frac{d(\delta^2 S)}{dt} \right)_{flow} + \dots + \left(\frac{d(\delta S)}{dt} \right)_{nonflow} + \left(\frac{d(\delta^2 S)}{dt} \right)_{nonflow} + \dots \quad (38)$$

where the first set of terms on the right-hand side of eq. (38) must measure the rate of exchange of entropy,

$$\frac{d_e S}{dt} = \left(\frac{d(\delta S)}{dt} \right)_{flow} + \left(\frac{d(\delta^2 S)}{dt} \right)_{flow} + \dots \geq 0 \quad (39)$$

and the second set of terms of eq. (38) must measure the rate of production of entropy,

$$\frac{d_i S}{dt} = \left(\frac{d(\delta S)}{dt} \right)_{nonflow} + \left(\frac{d(\delta^2 S)}{dt} \right)_{nonflow} + \dots > 0 \quad (40)$$

Because of the existence of a contribution from flow terms, we have no definite sign in eq. (38). Hence on the attainment of an NSS the entropy is not maximized in general.

As far as the *thermodynamic stability of NSS* is concerned, one needs to recall that when the constraints on the system are such that it finally attains a NSS, which is thermodynamically described by eq. (8) it finally reduces to eq. (35). This motion is unidirectional from nonequilibrium to the final NSS. Therefore, the reverse motion from the said NSS to any of the nonequilibrium states from which the said NSS was achieved is impossible. That is, if from eq. (36) for the forward motion we have $(S^{nss} - S) > 0$, then it is impossible to have a motion commensurate with $(S^{nss} - S) < 0$. This can also be understood by the fact that the exchange of entropy contribution to $(S^{nss} - S)$ would change sign on reversing the motion, while simultaneously the entropy production contribution cannot be made negative. Hence, the so called virtual displacement would carry the system on paper to some other succession of nonequilibrium states, but that cannot be taken as the reverse motion. In this way, we have proven the impossibility of virtual displacement described by $(S^{nss} - S) < 0$ and hence *all NSS are thermodynamically stable states*. This is the Gibbs-Duhem theory specialized for NSS.

Thermodynamic Stability of a General Irreversible Evolution

So far, we have demonstrated the thermodynamic stability of (i) conditional irreversible evolution of closed systems, (ii) equilibrium states, and (iii) nonequilibrium stationary states (NSS). However, it is possible to establish thermodynamic stability of a general irreversible evolution as follows.

Consider the general statement of eq. (8), which is valid for open systems too. It describes an irreversible motion and correspondingly establishes forward direction. This is demonstrated by proving that this description cannot be reversed. For a system to have a reversed motion all the terms of eq. (8) must be made to reverse their signs. However, $d_i S/dt > 0$ cannot be assigned a negative sign, because that will shatter the very definition of a nonequilibrium state. That means on changing the sign of $d_e S/dt$ the system would attain some other nonequilibrium state, which cannot be called a reverse motion. Alternatively, suppose that in a given irreversible motion $dS/dt > 0$ irrespective of the sign of $d_e S/dt$, then the envisaged reverse motion described by $dS/dt < 0$ is impossible because the rate of entropy production cannot change its sign. It thus establishes that eq. (8) indeed describes the forward motion that cannot be reversed. Thus, in general *no irreversible motion describable by eq. (8) can be reversed*. That means the virtual displacement in the reverse direction of a forward motion described by eq. (8) cannot be realized, and *every irreversible motion describable by eq. (8) is obtained as a stable one*. This also demonstrates the basis of the statement of the Universal

Inaccessibility Principle (UIP) [10, 12] formulated earlier by one of the present authors (AAB), which reads as,

“In every neighborhood of every equilibrium and nonequilibrium state of a system there exist states (both equilibrium and nonequilibrium ones), which remain unattainable by reversible or spontaneous paths.”

THE FOURTH LAW OF THERMODYNAMICS

The discussions and conclusions presented in the preceding Section lead us to formulate a new law of thermodynamics. That we term as the *fourth law of thermodynamics* that reads as,

“The irreversible processes describable by,

$$\frac{dS}{dt} = \frac{d_e S}{dt} + \frac{d_i S}{dt} \geq 0 \text{ and } \frac{d_i S}{dt} > 0,$$

cannot be reversed, hence they all constitute thermodynamically stable processes.”

In this connection we also recall that earlier, the fourth law of thermodynamics was proposed (for example, recently Kamal has described earlier attempts of formulation of the fourth law of thermodynamics [26]), but none of these proposals could advance beyond the proposal stage. However, the proposal originating from the works of Glansdorff and Prigogine on the stability of the so-called local equilibrium states merits mention herein [4, 27, 28]. They have proposed the following condition of stability of local equilibrium states,

$$\delta^2 s < 0 \text{ and } \frac{d}{dt} (\delta^2 s) > 0 \tag{41}$$

which seemingly resembles Lyapunov’s direct (second) method of stability of motion [29– 40]; Glansdorff and Prigogine claim the same. That is, $\delta^2 s$ has been assumed to serve as the thermodynamic Lyapunov function. The thermodynamic basis of the second inequality in eq. (41) has been questioned [25, 40], although the very assumption of local equilibrium allows one to consider the local entropy a convex upward function, so that the first inequality in eq. (41) is legitimized. It is pertinent to cite a very recent example wherein Sieniutycz and Kuran (private communication) have shown that far from equilibrium $\delta^2 s$ fails to serve as a Lyapunov function. Hence, the conditions of eq. (41) are not general and hence cannot be taken as the fourth law of thermodynamics.

However, in Lyapunov’s theory of stability of motion an act of sufficiently small perturbation from the real trajectory is involved, hence we have a perturbed trajectory distinctly different from the unperturbed trajectory. In this way, the identified Lyapunov function has to be a function of perturbation coordinates, not dependent only on the thermodynamic variables on the real trajectory. In view of this requirement, $\delta^2 s$ may perhaps be considered a Lyapunov function on the real trajectory, with the virtual displacement coordinates as the perturbation coordinate. But then the difficulty is that the virtual displacements, in principle, would carry the system on the real trajectory in the reverse direction. If so, how can we define corresponding perturbation coordinates distinctly different from the thermodynamic variables on the real trajectory? Yet another difficulty is that on a real trajectory, by the assumption of local thermodynamic equilibrium, each point is a local equilibrium state; or in other words, the real trajectory is made up of a succession of local equilibrium states. The perturbation, in principle, needs to carry the system to a neighboring nonequilibrium state, which is not a local equilibrium state. Otherwise, we will be guilty of questioning the very proposal of local equilibrium assumption. Therefore, the Lyapunov method of stability cannot be applied if it is a case of

virtual displacement in the reverse direction on a path consisting of a succession of local equilibrium states. Hence, the Glansdorff-Prigogine theory of stability of local equilibrium states *cannot* be considered as a thermodynamic Lyapunov theory. Thus, if it is a case of virtual displacement on the real trajectory in reverse direction, then there is no room to call δ^2s a Lyapunov function and then use its time derivative. Further, as stated above, in addition to these difficulties, no thermodynamic basis of the second inequality in eq. (41) could be established*. Of course, Landsberg [41] did suggest that it may be called a new “law” that appears to be the fourth law of thermodynamics. Unfortunately, his optimism did not stand the test of time.

In contrast, our formulation of thermodynamic stability theory and the fourth law of thermodynamics are based purely on a Gibbs-Duhem type stability theory for irreversible processes described in the preceding Sections— that is, it is based on the concept of virtual displacement in the reverse direction on the real trajectory.

CONCLUDING REMARKS

A long pending demand to have a thermodynamic theory of stability of irreversible processes has been met in this paper. It is in essence an extension of Gibbs-Duhem theory of stability of equilibrium states to systems evolving irreversibly. With the advent of this theory, almost all branches of science would benefit, such as industrial processes, energy optimization management, biophysics, processes affecting/maintaining ecology, physico-chemical processes, etc.

We notice that the inequalities of eqs. (1) – (4) can now be understood as describing natural and unnatural changes of closed systems (i) between end equilibrium states, (ii) between equilibrium and nonequilibrium states, and (iii) between end nonequilibrium states. This is easily demonstrated by appropriately integrating the inequalities of eqs. (13), (25), and (33) that yield the inequalities of eq. (1) for the categories (i), (ii), and (iii). Similarly, appropriately integrating the inequalities of eqs. (14), (26), and (34), yields the inequalities of eq. (3) for the categories (i), (ii), and (iii). On the other hand, for infinitesimally away states when we drop the dt from the denominator from the inequalities of eqs. (13), (14), (25), (26), (33), and (34), the inequalities of eqs. (2) and (4) are obtained for the categories (i), (ii), and (iii).

The striking outcome is that the irreversible processes describable by eq. (8) all become established as thermodynamically stable ones. On the face of it, it looks like a strange outcome, but we need to keep in mind that basically thermodynamics is not a constitutive theory, it only provides broad guidelines, and for example eq. (8) describes irreversible evolution of a system with its behavioral contents, but not the constitutive rates of the other properties of the system. Of course, on elaborating the rate of change of entropy in terms of the thermodynamic variables and then on supplying constitutive relations of the rates of change of thermodynamic variables, the corresponding thermodynamic predictions would be generated. To understand this, let us recall that in chemical thermodynamics, on providing the constitutive equations, say ideal gas law or van der Waals equation, the corresponding thermodynamic predictions get generated. Similarly, in the case of natural evolution of an isolated system, for example, if the irreversibility is on account of a simple bimolecular reaction at a non-vanishing rate, the rate of change of entropy is given by [8, 23, 24],

$$\frac{dS}{dt} = \frac{d_i S}{dt} = \frac{\mathcal{A}}{T} \frac{d\xi}{dt} > 0 \quad (42)$$

* Of course, even if at the global level under certain global conditions, such as isolation of the system where we have $\delta^2S < 0$, this does not guarantee, in general, $\delta^2s < 0$ at a local level because each local pocket behaves as a tiny open system.

where \mathcal{A} is the chemical affinity and ξ is the extent of advancement of the chemical reaction. Whereas from chemical kinetics [42] the rate of the chemical reaction, say



with the forward rate constant k , is given by,

$$\begin{aligned} \frac{d\xi}{dt} &= k C_A C_B, & \frac{d\xi}{dt} &= A \exp(-E_a/RT) C_A C_B, \\ \frac{d\xi}{dt} &= \frac{k_B T}{h} \exp(-\Delta^\ddagger G/RT) C_A C_B \end{aligned} \quad (44)$$

where C_A and C_B are the concentrations of the reactants A and B respectively, A is the Arrhenius pre-exponential factor, E_a is the Arrhenius energy of activation of the forward chemical reaction, k_B is the Boltzmann constant, h is Planck's constant, $\Delta^\ddagger G$ is the Gibbs free energy of activation in going from reactants to activated complex (\ddagger) at the top of the Gibbs free energy barrier of the chemical reaction, and R is the universal gas constant.

In eq. (44), the first expression of the rate of reaction is based on laboratory experiments, the second expression is the Arrhenius theoretical version [43], and the third expression is also a theoretical one based on the Eyring's theory of bimolecular reaction rates [43–49]. Thus, there are three possibilities to evaluate the rate of entropy change of eq. (42). In this way we will have corresponding thermodynamic predictions, as well as access to the respective control parameters.

The present study tells us that, to achieve stability, one needs to maintain inaccessibility in the reverse direction on the trajectory of a given motion. Thus, we learn that if the conditions of irreversible evolution are strictly and meticulously maintained, in reality the thermodynamic stability would be maintained. Hence, the challenge before us is to maintain those conditions rigorously during an irreversible process under investigation. However, the stability/instability obtained from non-thermodynamic means constitutes a constitutive theoretical investigation; indeed, they have their own practical advantages too. The distinction between the two is akin to the distinction between thermodynamics and statistical mechanics. Moreover, in order to retain the full thermodynamic character of the present theory, we have not incorporated the aspects dealing with the hydrodynamic stability, as Glansdorff and Prigogine have done in their proposal.

The present discussion also sheds light on the effect of the fluctuations about equilibrium and nonequilibrium stationary states on thermodynamic properties of a given system. Statistically, all possible fluctuations leading a system to neighboring nonequilibrium states are counted, but only overwhelmingly dominating fluctuations are those, which produce the virtual displacements in the reverse direction on the trajectory described by eq. (8) in the forward direction.

Though the present theory does not need the Lyapunov type of analysis, one would still be interested to know if there can be a thermodynamic tool akin to Lyapunov's theory of stability of motion [29–40]. Yes, one of the present authors (AAB) has already developed a comprehensive thermodynamic theory of stability of irreversible processes (CTTSIP) [50–54]. In CTTSIP we apply all the steps of Lyapunov's direct method of stability of motion to the defined thermodynamic Lyapunov function via the entropy production function on real and perturbed trajectories. This approach we are summarizing in the following paper [55].

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