AD NUMBER

AD848610

NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

Distribution authorized to U.S. Gov't. agencies and their contractors; Critical Technology; DEC 1968. Other requests shall be referred to Commanding Officer, Department of the Army, Fort detrick, Attn: SMUFD-AE-T, Frederick, MD 21701.

AUTHORITY

SMUFD, D/A ltr, 17 Feb 1972

AD848610

Best Available Copy

DEPARTMENT OF THE ARMY
Fort Detrick
Frederick, Maryland

14

ON THE DIFFERENTIAL PROPERTIES
OF ENTROPY PRODUCTION

by P. Glansdorff and I. Prigogine

Physica, 20, 773-780 (1954)

Faculte Polytechnique de Mons et Faculte des Sciences de l'
Universite Libre de Bruxelles, Belgium

SYNOPSIS

1. Introduction

The study of non-equilibrium stationary states constitutes a most
important domain of the thermodynamics of irreversible phenomena. These
states are characterized by the fact that intensive variables remain
constant in time. It has been established that they become established or
continue only under the effect of "constraints" imposed on the system and
which prevent it from attaining an equilibrium state, for example, the
systematic maintenance of a difference of temperature or of concentration,
of chemical affinity, of a heat flow or a diffusion flow within the system
represented. If the latter is a continuous medium, the constraints are the
conditions called "boundary conditions".

In 1945, one of us established a theorem according to which stationary
states of a system correspond to minimum entropy production, for a given
value of the constraints (1)(5). Throughout the proof the following
restrictive hypotheses were implied:

(1) Linear relations between generalized forces (or affinities)
and flows (or velocities) of irreversible phenomena.

(2)Validity of the Onsager reciprocal relations.

(3) Phenomenological coefficients considered to be constant. In case of continuous media it was necessary to assume in addition that mechanical equilibrium existed.

Various authors have since studied this problem (6,7,8) but the initial restrictions have continued. Recently, one of us has succeeded in eliminating them, but by utilizing an exceptional type of constraint from the point of view of applications (specific entropy and entropic flow imposed separately on the domaine boundary (9,10).

Therefore, the following two problems are posed:

(1) Independently of these restrictive hypotheses, what are the most general properties of entropy production?

(2) Does there exist another measure of entropy production which takes on a minimum value in stationary nonequilibrium states when at least one of these hypotheses does not hold?

The second question has been taken up recently (11) and has received an affirmative response in a certain number of simple cases. The present communication is devoted to the first question. We show that in reality the minimum of the variational law searched for represents only a particular case of a more general differential law. We conserve at all time the hypothesis of mechanical equilibrium (barycentric velocity zero at all points, or sufficiently small to be conformity with the classical hypothesis of small fluctuations).

2

2. __[Essential?] properties of the production of entropy.__ Let us adopt for the production of entropy, σ , per unit time and unit volume, the bilinear form between affinities or generalized forces X_j and their conjugate flows or generalized currents J^j, for irreversible phenomena (2,6)

$$\sigma = \Sigma_j X_j J^j \quad (j = 1,2,---) \tag{2.1}$$

In a continuous medium, σ represents the local specific volume entropy production rate, at a macroscopic point and at the instant considered. The entropy production relative to the entire system is then written

$$d_i S/dt = \int_v \sigma dv \tag{2.2}$$

We propose to abbreviate this as

$$P \equiv d_i S/dt \tag{2.2'}$$

Decomposing the total differential of the function σ into a sum of two linear partial differentials

$$d_j \sigma = \Sigma_j X_j dJ^j \quad \text{and} \quad d_X \sigma = \Sigma_j J^j dX_j \tag{2.3}$$

it becomes

$$d\sigma = d_j \sigma + d_X \sigma \tag{2.4}$$

Recall from above it follows immediately from the sign of (2.1) that for all variations $\underline{e}, \underline{e}'$, starting from the equilibrium state $\underline{e}$, one has

$$\Delta\sigma = \sigma_{\underline{e}'} > 0 \tag{2.5}$$

3

or again, indifferently, according to the choice of path of integration applied to (2.4),

$$\Sigma X_{j\underline{e}'} \; \Delta J^j \geq 0 \quad \text{or} \quad \Sigma_j J^j_{\underline{e}'} \; \Delta X_j \geq 0 \tag{2.6}$$

Inversely, and in particular for an elementary transformation terminating at equilibrium, one has at $\underline{e}'$ the first order conditions

$$d\sigma \leq 0 \; , \; d_j\sigma \leq 0 \; , \; d_{\underline{x}}\sigma \leq 0 \tag{2.7}$$

from which one deduces the known criteria of stability at equilibrium with regard to neighboring states (12). Likewise in a continuous medium the three inequalities (2.7) are written, respectively, using (2.2):

$$\partial P/\partial t < 0 \; , \; \partial P/\partial t < 0 \; , \; \partial_x P/\partial t \leq 0 \tag{2.8}$$

First let us consider the domain of validity of the restrictions recalled in Par. 1. We write the linear phenomenological relations

$$J^j = \Sigma_k L^{jk} X_k \tag{2.9}$$

With local Onsager's reciprocal relations,

$$L^{jk} = L^{kj} = \text{constant} \tag{2.10}$$

We will then have:

$$d_j\sigma = \Sigma_{jk} L^{jk} X_j \, dX_k = d_x\sigma \tag{2.11}$$

and also

$$d\sigma = 2d_j\sigma = 2d_x\sigma \tag{2.12}$$

By means of the restrictions (2.9)(2.10) the two differential forms (2.3) are the equal.

Consider for the moment the case of any elementary transformation whatever between two non-equilibrium states and not subjected to these restrictions. The conclusions (2.7) and (2.12) are no longer valid. Nevertheless we shall go on to demonstrate that the three relations (2.8) remain when the system considered is submitted to the conditions of fixed limits of temperature and chemical potential, μ.

In fact, all the calculations necessary to demonstrate this may be found in a study by P. Mazur, carried out for studying the minimum in the entropy production. (8) But the numerous restrictive conditions which accompany that development did not permit the author to bring out this general significance.

Consider in the first instance the simple case of heat transport by conduction in a solid ($J^j \equiv W^j$; $X_j \equiv \partial T^{-1} \partial x_j$). We have here

$$\frac{\partial_x P}{\partial t} = \int_V \tau_j W^j \frac{\partial}{\partial t} \left(\frac{\partial T^{-1}}{\partial x_j} \right) dV = \int_V \vec{W} \cdot \mathrm{grad} \left(\frac{\partial T^{-1}}{\partial t} \right) dV \qquad (2.13)$$

for all non-volatile solids, isotropic or not. Introduce, with the help of integration by parts, the integral over the boundary surface Ω of volume V. It becomes

$$\frac{\partial_\omega P}{\partial t} = \oint_\Omega W_n \frac{\partial T^{-1}}{\partial t} d\Omega - \int_V \frac{\partial T^{-1}}{\partial t} \mathrm{div} \vec{W} dV \qquad (2.14)$$

The boundary conditions being considered stationary, the surface integral vanishes. Bringing in the condition of local energy conservation,

$$\rho c_v \frac{\partial T}{\partial t} + \mathrm{div} \vec{W} = 0 \qquad (2.15)$$

5

we obtain for (2.14)

$$\frac{\delta x^2}{\delta t} = - \int_V \frac{\rho c_v}{T^2} \left(\frac{\delta T}{\delta t}\right)^2 dV \leq 0 \tag{2.16}$$

which demonstrates the stated property since specific heat is necessarily
positive as a result of the known condition of stable equilibrium, deduced
in addition by (2.7). Consider now the general case of an open system
which will be the seat of irreversible phenomena as a result of the
simultaneous effects of heat conduction, diffusion and of r chemical
reactions between the c constituents. The local production of entropy is
written, in this case (2-6)

$$\sigma = \vec{U} \cdot \text{grad } T^{-1} + \Sigma_\gamma \rho_\gamma \vec{\Delta}_\gamma [\vec{F}_\gamma / T - \text{grad}(\mu_\gamma/T)] + \Sigma_\rho v_\rho A_\rho \tag{2.17}$$

$$(\gamma = 1, \dots, c; \rho = 1, \dots, r)$$

where $\rho_\gamma \vec{\Delta}_\gamma$ represents the diffusion current of constituent γ.

The conjugated force is the affinity of diffusion which we assume to be
"conservative" (2). We admit in addition that the actions at a distance $\vec{F}_\gamma$
depend only on the position of the point considered ($\partial \vec{F}_\gamma / \partial t = 0$). Finally,
in the third term, v_ρ designates the rate of reaction ρ and A_ρ is the
corresponding chemical affinity; it is related to the potential μ_γ through the
intermediary of stoichiometric coefficients $\nu_{\gamma\rho}$ and molar masses M_γ through
the relation (2,6,13)

$$A_\rho = -\Sigma_\gamma \nu_{\gamma\rho} M_\gamma \mu_\gamma / T \tag{2.18}$$

By the same reasoning as in the proceeding example, we obtain this time,
after integration by parts and elimination of boundary terms,

$$\frac{\delta x^2}{\delta t} = \int_V \left[(\Sigma_\gamma \rho_\gamma \vec{\Delta}_\gamma \cdot \vec{F}_\gamma - \text{div } \vec{U}) \frac{\partial T^{-1}}{\partial t} - \Sigma_\gamma (\Sigma_\rho \nu_{\gamma\rho} M_\gamma v_\rho - \text{div } \rho_\gamma \vec{\Delta}_\gamma) \frac{\partial (\mu_\gamma T^{-1})}{\partial t} \right] dV \tag{2.19}$$

6

...introducing the c mass balances:

$$\rho \, \partial N_\gamma / \partial t = \Sigma_\delta \gamma_{\gamma\delta} M_\gamma v_\delta - \text{div } \rho_\gamma \vec{\delta}_\gamma \tag{2.20}$$

where N_γ represent the mass fraction of constituent γ and then, the internal energy balance, e:

$$\rho \cdot \frac{\partial e}{\partial t} = \Sigma_\gamma \rho_\gamma \vec{\Delta}_\gamma \cdot \vec{F}_\gamma - \text{div } \vec{W} \tag{2.21}$$

The relation (2.19) becomes:

$$\frac{\partial_x P}{\partial t} = \int_V \rho \left[\frac{\partial s}{\partial t} \ \frac{\partial T^{-1}}{\partial t} - \Sigma_\gamma \left(\frac{\partial N_\gamma}{\partial t} \right) \ \frac{\partial (\mu_\gamma T^{-1})}{\partial t} \right] dV \tag{2.22}$$

which, after several calculations previously developed in the study by P. Mazur cited above [loc. cit.(6), see especially transformation (4.20)-(4.23)]:

$$\frac{\partial_x P}{\partial t} = -\int_V \left[\frac{\overline{\rho c_v}}{T^2} \left(\frac{\partial T}{\partial t} \right)^2 + \Sigma_{\gamma\gamma'} \ \frac{\partial \mu_\gamma}{\partial \rho_{\gamma'}} \ \frac{\partial \rho_{\gamma'}}{\partial t} \ \frac{\partial \rho_\gamma}{\partial t} \right] dV \tag{2.23}$$

But since according to the stability criterion of diffusion equilibrium one must have (12):

$$\Sigma_{\gamma\gamma'} \ \frac{\partial \mu_\gamma}{\partial \rho_{\gamma'}} \ \frac{\partial \rho_{\gamma'}}{\partial t} \ \frac{\partial \rho_\gamma}{\partial t} > 0 \tag{2.24}$$

it becomes finally

$$\frac{\partial_x P}{\partial t} = \int_V \Sigma_j \ J^j (\partial X_j / \partial t) dV \leqslant 0 \tag{2.25}$$

the equal sign referring exclusively to the stationary state.

We have obtained therefore in this way a general principle of moderation of irreversible phenomena, according to which the variation in time of the affinities or generalized forces X_j in a system under the constraint of stationary behaves always in a manner such as to diminish entropy production.

No doubts on this subject, that thanks to the fluctuation theory, the reasoning presented above is also applicable in the neighborhood of mechanical equilibrium, the relations (2.17)-(2.25) not being modified provided that mechanical forces retain practically their equilibrium value during perturbations. (local isobaric transformations in fluids, viscous forces remaining zero as in the neighborhood of mechanical equilibrium). If, to the contrary, appreciable differences in velocities arise between neighboring particles, the law (2.25) will not be generally valid.

One knows, on the other hand, that in the expression (2.1) of the entropy production, the choice of fluxes and forces is not uniquely imposed; it suffices in general, that the choice leaves the entropy production invariant (6):

$$\sigma = \Sigma_j X_j J^j = \Sigma_j X'_j J'^j \tag{2.26}$$

In (2.25) on the contrary, the choice is no longer arbitrary. The flows must be those which appear explicitly in the balance of mass and energy (2.20) and (2.21). We hope to return eventually to this question.

We consider finally the particular case of the stationary state for which one has the equality sign in (2.25), $(\partial X_j/\partial t = 0)$.

We designate J^j_0 the flows relative to this state. They cancel the right-hand member of the balances (2.20) and (2.21). Therefore (2.19) gives:

$$\int_V \Sigma_j \, J^j_0 (\partial X_j/\partial t) \, dV = 0 \tag{2.27}$$

for all elementary displacements starting from any stationary state 0 whatever.

8

It follows that for any displacement (real or virtual) causing a departure from a stationary state, the limits remaining fixed, one has

$$\delta P = \delta_j P \qquad (2.28)$$

This equality shows a certain analogy with the Lagrangian principle in mechanics in the case of non-holonomic relations (14); (the equivalent of work of non-holonomic forces correspond to the term $\delta_j P$).

We note finally that the property (2.25) appears as a direct consequence of the stability conditions of equilibrium thermodynamics.

5. <u>Classification of stationary states.</u> In the particular case where the theorem of minimum entropy production is valid, the stability of stationary states is easily discussed (3). Those stationary states are stable which correspond to a minimum in entropy production (at uniform temperature).

The more general theorem which we are going to prove will permit a classification of stationary states from the point of view of stability although a little different. In effect, one requires that once the stationary state is attained, the system may leave that state in accordance with the macroscopic laws of evolution or only as a consequence of a fluctuation according to evolutionary laws.

Consider then any <u>small virtual displacement whatever, Δ,</u> starting from a stationary state 0, the state variables being held constant at the boundaries of the system (T and μ_γ in the preceeding example), and the conditions of mechanical equilibrium at the displacement, or in its neighborhood, remain satisfied as we have previously specified. Let us explain that none of the virtual displacements thus regarded can correspond to a real

transformation of the system. We obtain for those small displacements when having subtracted (2.27) from (2.25), the condition:

$$\int_V \Sigma_j \Delta J^j \Delta X_j \, dV \geq 0 \tag{3.1}$$

where the equality sign has been retained since, according to (2.13), it is unable to correspond to non-stationary transformation of the system. In addition, since the distribution law of displacement ΔX_j is random in volume V, one deduces immediately from (3.1) the local condition which we write to first-order approximation:

$$\Sigma_{jk} (\partial J^j / \partial X_k)_0 \, \delta X_k \delta X_j \geq 0 \tag{3.2}$$

or, in a more explicit manner:

$$\Sigma_{jk} (\partial J^j / \partial X_k)_0 \, \partial X_k \partial X_j \geq 0 \tag{3.3}$$

the index 0 referring to the stationary state.

When this relation is satisfied at all points of the system, it will then be unable to leave its stationary state according to the macroscopic laws of thermodynamics.

Such is notably the case when the phenomenological laws are linear, as in (2.9) for the condition (3.3) is verified identically and independently of the restrictive hypotheses repeated in part 2 and in part 3 of paragraph 1 (reciprocity and constancy of phenomenological coefficients). In fact, the entropy production (2.1) is then written:

$$\sigma = \Sigma_{jk} (\partial J^j / \partial X_k)_0 X_k X_j \geq 0 \tag{3.4}$$

which prescribes the sign of the quadratic form (3.3).

One notes that the classification of stationary states in accordance with condition (3.3) is relative to the mechanisms by which the system studied is able to enter or leave a stationary state. Nevertheless, this condition does not constitute a stability criterion properly speaking of the stationary state considered, except in the case when $d_x S$ is an exact total differential, for one is unable to deduce from it the evolution which the system will undergo as a result of local fluctuations, not related to the laws governing macroscopic transformations.

4. _Conclusions._ We may summarize as follows the most general thermodynamic properties of a system outside equilibrium prior to consideration of any particular phenomenological laws:

(a) the entropy variations may be decomposed into two parts:

$$dS = d_e S + d_i S \qquad (4.1)$$

the second term, due to the irreversible phenomena in the interior of the system being always positive (or zero at equilibrium):

$$d_i S \geqslant 0 \qquad (4.2)$$

(b) the variation of entropy production per unit of time:

$$P \equiv d_i S/dt \qquad (4.3)$$

decomposes also into two terms:

$$dP = d_J P + d_X P \qquad (4.4)$$

of which the second, due to the variation of generalized forces or affinities, is always negative along real transformations (or zero in the stationary state):

$$d_X P \leqslant 0 \qquad (4.5)$$

when the conditions imposed on the system at its boundary are stationary..

11

... limit ourselves at all times to systems in mechanical equilibrium or reduced to small fluctuations.

These two laws are expressed by non-total differentials. In the two cases, it is only as a consequence of special circumstances that one may reduce them to total differentials introducing potentials characteristic of the system's behavior and especially of its stability. In case (a), these circumstances depend essentially on exterior conditions imposed on the system (isolated system, isothermal, at constant volume, open or closed, ...). In case (b) these circumstances relate most precisely to the mechanism by which changes in the entropy production are effected (4.4).

The inequality (4.5) together with (4.4) permit foreseeing under what conditions entropy production itself decreases in the course of the change. This last point was developed in work with Dr. H. C. Mol (15), specifically for the case of chemical reactions.

We thank Dr. Mol with whom we have had fruitful discussions concerning the problem treated in this study.

References

1. PRIGOGINE, I., Ac. roy. Blg. Bull. Cl. Sc. 31 (1945) 600.

2. PRIGOGINE, I., Etude thermodynamique des phenomenes irreversibles Liege, Desoer, 1947; cf. specialement chap. V et pp 68-69.

3. PRIGOGINE, I., et DEFAY, R., Ac. roy. Blg. Bull. Cl. Sc. 32(1946) 694; 33(1947) 48.

4. PRIGOGINE, I., Colloque de thermodynamique, Union Internationale de Physique, Bruxelles, janvier 1948, p. 87.

5. PRIGOGINE, I. et WIAME, J. M., Experientia 2 (1946) 451.

6. DE GROOT, S. R., Thermodynamics of Irreversibles Processes, North
Holland Publ. Comp. Amsterdam, 1951.

7. DENBIGH, K. G., Trans. Far. Soc 48 (1952) 389.

8. MAZUR, P., Ac. roy. Blg. Bull. Cl. Sc. 38 (1952) 182.

9. GLANSDORFF, P., Physica 19 (1953) 757, 1029.

10. GLANSDORFF, P., Ac. roy. Blg. Bull. Sc. 39 (1953) 97.

11. PRIGOGINE, I., Ac. roy. Blg. Bull. Cl. Sc. 40 (1954) 471.

12. PRIGOGINE, I. et DEFAY, R., Thermodynamique Chimique, Liège, Desoer
1950, chap. XV.

13. DONDER, TH. de, L'Affinité, Paris, Gauthier-Villars, 1933.

14. Cf. Hamel, G., Theoretische Mechanik, Berlin, Springer, 1949.

15. NEL, H. C., Ac. roy. Blg. Bull. Cl. Sc. 40(1954).