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DATE: Dec 1968

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## ON A LAW OF MODERATION OF IRREVERSIBLE CHEMICAL TRANSFORMATIONS

By P. Glansdorff

Bull. de la Classe des Sciences, Acad. Roy. de Belgique, 42, 628-630 (1956)

Summary: <sup>A</sup> Simple demonstration, when chemical irreversibility is the sole cause, <sup>is given</sup> of a general theorem of moderation previously established by Prigogine and the author (1).

1. In a previous publication (1), Prigogine and the author have established the following quite general property, relative to moderation of irreversible evolutions: For all systems in mechanical equilibrium and subject to time-independent boundary conditions, the entropy production:

$$P = \sum_i X_i J_i \geq 0 \quad (1)$$

varies in the course of all real transformations, conforming to the condition of moderation:

$$P'_x = \sum_i X_i J_i \leq 0 \quad (2)$$

where  $P'_x$  designates the derivative with respect to time of  $P$ , taken at constant fluxes  $J_i$ . The sign of equality corresponds in (1) to the state of equilibrium, and in (2) to the stationary state. The domain of validity of (2) is that for which the physicochemical constants of the system satisfy the conditions usually deduced in studies of equilibrium stability.

This theorem, independent of all kinetic hypotheses, is demonstrated in a remarkably simple fashion in this specialized but important case, where

chemical irreversibility is the only cause. This is why we have become interested in describing separately this proof.

2. The generalized force  $X_i$  are here the affinities  $A_i$ , and the fluxes  $J_i$  are the reaction velocities  $v_i$  of the  $r$  chemical reactions of the system. The latter is open and in communication with exterior phases maintained in a time-independent state, characterized by fixed values of temperature, pressure and external chemical potentials. We assume uniform pressure and temperature so that these are then constant. On the other hand, the values imposed on the chemical potentials prevent the system from attaining a state of equilibrium, but permit it to attain perhaps a stationary state. If the system includes several phases we assimilate phase changes into the chemical reactions attaching distinct indices to the constituents using the same index for a constituent in the different phases.

Writing the mass balance of a constitute  $\gamma$ :

$$\frac{dn_\gamma}{dt} = \frac{d^e n_\gamma}{dt} + \sum_p v_{\gamma p} v_p \quad (3)$$

where  $d^e n_\gamma$  refers to the molar interchange, with the exterior and where  $v_{\gamma p}$  is the stoichiometric coefficient of constituent  $\gamma$  in the reaction with index  $p$ . Multiplying the two members of (3) by the derivative  $\mu'_\gamma$ , with respect to time, of the corresponding chemical potential, gives

$$\mu'_\gamma \frac{dn_\gamma}{dt} = \mu'_\gamma \frac{d^e n_\gamma}{dt} + \sum_p v_{\gamma p} \mu'_\gamma v_p \quad (4)$$

Observe that the first term on the right hand side vanishes since, under the imposed constraints, its first factor vanishes each time its second factor

is different from zero. Sum overall constituents  $\gamma$ . We obtain, since  $T$  and  $p$  are assumed constant:

$$\sum_{\gamma} \sum_{\gamma'} \mu_{\gamma\gamma'} \frac{dn_{\gamma}}{dt} \frac{dn_{\gamma'}}{dt} = \sum_{\gamma} \sum_{\rho} v_{\gamma\rho} \mu'_{\gamma\rho} \quad (5)$$

Introducing the affinity of reaction  $\rho$ :

$$A_{\rho} = -\sum_{\gamma} v_{\gamma\rho} \mu_{\gamma} \quad (6)$$

relation (5) becomes:

$$\sum_{\gamma} \sum_{\gamma'} \mu_{\gamma\gamma'} \frac{dn_{\gamma}}{dt} \frac{dn_{\gamma'}}{dt} = -\sum_{\rho} A'_{\rho} v_{\rho} \quad (7)$$

Now, the left-hand side of the equation is positive by virtue of the equilibrium stability which we assumed satisfied [1]. One has then

$$\sum_{\rho} A'_{\rho} v_{\rho} \leq 0 \quad (8)$$

confirming (2), in the particular case of chemical systems and taking into account in due course the affinities of phase changes. The equality sign refers to the stationary state ( $dn_{\gamma} = 0$ ).

May 1956

Bibliography

University of Brussels

[1] P. Glansdorff and I. Prigogine, *Physica*, 20, 773-780 (1954)