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ON THE DEFINITION OF THE *GIBBS* POTENTIAL

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The fundamental thermodynamic equation for an infinitesimal reversible change of a chemical system:

$$dE = TdS - pdv \quad (1)$$

where E , S , v , T and p stand for energy, entropy, volume, temperature and pressure respectively, applies only to a system through the boundaries of which no net transport of matter takes place. Such a system, in accordance with R. DEFAI¹, we shall term a closed system. If the system is open, i. e. if matter is allowed to pass through its boundaries, additional changes in the functions of the system may occur.

WILLARD GIBBS², in order to include in the thermodynamic treatment such systems of variable mass, introduced the conception of the chemical potential of a component by in equation (1) simply adding members to represent the energy changes due to the addition of each one of the components. Hence:

$$dE = TdS - pdv + \mu_1 dm_1 + \mu_2 dm_2 + \dots \quad (2)$$

where the μ 's and the m 's denote potential and mass of the various components. The potential as given by this equation is:

¹ R. DEFAI, Bl. Acad. Belg. (5) **15** 678 (1929).

² W. GIBBS, Trans. Conn. Acad. **3** 108 (1875) Coll. Works. **1** 55 (1928).

$$\mu_1 = \left(\frac{dE}{dm_1} \right)_{s, v, m}, \quad \mu_2 = \left(\frac{dE}{dm_2} \right)_{s, v, m} \quad (3)$$

i. e. the partial differential coefficient of the energy with respect to the mass of the component. The potential, therefore, equals the increase in energy caused by the addition of unit mass of the particular component, the entropy, volume and mass of all other components remaining constant during the process.

The extreme usefulness of the concept of potential thus introduced by GIBBS in thermodynamical science is generally acknowledged. However, the opinion is held by various authors that the method by which GIBBS introduced and defined the potential is unsatisfactory.

Thus E. A. MILNE¹ states: "WILLARD GIBBS simply introduces partial differential coefficients into a situation in which the ordinary "physical" notion of a partial differential coefficient is physically not realizable. He considered the increase of energy of a system, which occurs when its volume and entropy remain fixed, but the mass of a chemical constituent is altered. How on earth (or in physics, which is the same thing) one can experimentally import matter into a system without importing or exporting entropy, or indeed knowing what entropy has been imported or exported, I have never been able to see; and the difficulty is largely responsible for the obscurity which is felt when reading GIBBS."

TH. DE DONDER² speaks of the potential definition as the "hypothese" of W. GIBBS. R. DEFAI³ from a similar standpoint emphasises the lack of conclusiveness in the

¹ E. A. MILNE, "The Aim of Mathematical Physics". Oxford (1929).

² TH. DE DONDER, Bl. Acad. Belg. (5) **15** 615 (1929).

³ I. c.

GIBBS treatment: "W. GIBBS a donné les principales équations qui régissent les systèmes ouverts. Mais son exposé est celui d'une intuition géniale qui procède par bonds et que la logique, avançant pas par pas, ne peut suivre".

Quite recently thermodynamic relations of open systems have been deduced by J. GILLESPIE and J. R. COE¹. They avoid intentionally the GIBBS potential as a basis for their deductions, on account of the fact that "GIBBS' treatment has been held obscure by some authors". They say that GIBBS provides a physical interpretation (of the potential), but postpones it to a later part of his work.

In order to ascertain, whether by means of equation (2) a logical and unequivocal definition of the potentials is provided, it seems that the only question that needs consideration is whether the variables in this equation are independent or not. According to the above critics entropy, (volume?) and mass are not independent variables, because one cannot import matter in the system without at the same time importing entropy (and volume?). On the basis of this conclusion, one would deem the GIBBS deductions to be fallacious.

The question, however, is not, whether by some random addition of matter the entropy of the system may change or may remain constant, but whether it is possible to conduct the transport of matter to the system in such a way that no change in entropy takes place. There can be no doubt that such a process is actually practicable, since entropy may be varied unlimitedly by adding or subtracting heat, and any change in entropy on adding substance therefore can be cancelled merely by a thermal process.

This recognition is sufficient to explain and justify the

¹ J. GILLESPIE and J. R. COE, *J. Chemical Physics*. **1** 103 (1933).

definition of the potential in equations (2) and (3). For the determination of the numerical value of the potential of a component, knowledge, however, is required as to the amount of energy and entropy carried by unit quantity of the component added. This must be determined by reference to a standard state in which the amounts of energy and entropy of the component are fixed by convention. This necessity, however, is not confined to the determination of the potential, but is of course a typical requirement for the determination of any thermodynamic function pertaining to open systems.

The particular form of the relation by which the potential of the component in the mixture is correlated to its energy, entropy and volume in a standard state can be derived by various procedures, dictated by the GIBBS definition. The following seems particularly perspicuous.

Imagine a quantity of the mixture in thermal and chemical equilibrium (for instance through a semipermeable membrane) with the pure component K_1 . Add to the mixture, without changing its volume, the amount dm_1 of the pure component by a reversible and adiabatic process. Then, if ϵ_1 , s_1 and v_1 represent the energy, entropy and volume of unit mass of the component and p_1 its pressure, all for the given state of equilibrium, the increase in energy of the mixture by the process considered is:

$$(\epsilon_1 + p_1 v_1) dm_1.$$

At the same time, however, the entropy $s_1 dm_1$ contained in the amount dm_1 of the component has been added to the mixture, and since the addition of the component was conducted in a reversible and adiabatic manner this is the whole increase in entropy. In order to obtain the increase

in energy at constant entropy, as required by the definition of the potential, the entropy $s_1 dm_1$ carried by the mass dm_1 has to be eliminated at constant volume by removal of heat. The energy lost in this way by the system is:

$$Ts_1 dm_1.$$

The total increase in energy of the system due to the addition of the mass dm_1 of the component is therefore:

$$dE = (\epsilon_1 - Ts_1 + p_1 v_1) dm_1 \quad (4)$$

and since this process has been carried out at constant volume and entropy, by Equation (3):

$$\mu_1 = \epsilon_1 - Ts_1 + p_1 v_1. \quad (5)$$

By this equation the chemical potential of a component in a mixture is expressed in terms of the thermodynamic quantities of this component in a pure state and in equilibrium with the mixture. The significance of the potential for chemical equilibria appears immediately therefrom. As the energy, entropy and volume in the equilibrium state differs only by measureable quantities from the energy, entropy and volume in a standard state of the component, the calculation of the potential by means of Equation (5) is possible on the basis of a conventional fixation of these functions in the standard state. Accordingly, the potential on this basis is completely determined. It seems obvious, therefore, that the GIBBS definition, which leads up directly to Equation (5), does not suffer from any vagueness or obscurity, such as has been indicated by the various critics quoted above.

