J. N. BRØNSTED MEMORIAL ISSUE

**Equilibrium and Thermodynamic Functions
in a Gravitational Field ***

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The simplest systems dealt with in energetics and in the theory of physico-chemical equilibrium are composed of phases which are characterized by homogeneity in the energetic potentials of all pertinent quantities. If for instance the system is a liquid mixture of various chemical components, it will be a (necessary) condition of equilibrium that temperature, pressure, and the chemical potentials of the components have the same values throughout the mixture.

Furthermore, states of heterogeneous equilibrium are dealt with, in which each separate phase complies with the same conditions. These equilibria can be of two kinds: They may be either complete equilibria in which the homogeneity in potentials extends throughout the composed system, or they may be incomplete or partial equilibria, in which differences in one or more of the potentials are present between sharply defined phases. It is a condition for the establishment of the latter kind of equilibria that the system has been constructed in such a way that the free exchange of some of the energetic quantities is forbidden.

There are, however, other cases in which a certain kind of partial equilibrium is present, in spite of the fact that potential differences exist between parts of the system which are not separated from each other by any definite boundaries. Such conditions may prevail in systems of the most varied character. It is possible to divide them into two main groups: Systems in which the state is maintained through the presence of an outer field of force without requiring any further action from the surroundings, and: Systems in

* Translated from the Danish manuscript, left by Prof. Brønsted at his death, by J. Koefoed. For comments and references see the article by Th. Rosenberg, this issue p. 1215.

which the state is of a stationary character, and is existing, therefore, only by virtue of a flow which is maintained at the expense of constant changes in the surroundings.

Both kinds of systems are of great fundamental significance, and they have certain features in common in spite of their typical dissimilarities. In the present paper the first kind only will be dealt with. In another paper¹ the author has already contributed to the study of systems in stationary states, and it is intended to make them the object of more detailed investigation in a later publication.

1. THE THERMODYNAMIC FUNCTIONS IN A GRAVITATIONAL FIELD

The most important example of the energetic consequences of an outer field of force is the conditions in a system which is under the influence of gravitation. The process of transporting mass in a gravitational field has played an essential part in the establishment of the concept of 'work'. If a body of mass m is moved from one gravitational potential Φ_1 to another Φ_2 , a loss of work is said to have occurred in a system comprising only the transported body. This loss of work may be characterized as gravitational, and it can be expressed as:

$$A_{\text{grav}} = (\Phi_1 - \Phi_2) m \quad (2.1)$$

According to Gibbs the increase in energy of a system consisting of only one chemical component K , entropy S , and volume v , if gravitational forces can be neglected, is:

$$dE = TdS - pdv + \mu dn \quad (2.2)$$

n being the amount of K , and T , p , μ denoting temperature, pressure, and chemical potential, respectively. In the energetic theory this expression is derived from the definition of the energy of a system as the amount of work lost in an outer work reservoir when the system is built up reversibly from the component quantities, supplied from fixed standard reservoirs. We shall stick to this definition of energy, also where the definition of the system is influenced by a gravitational field.

In setting up (2.2) we have assumed energy to be a function of S , v , and n . The gravitational field taken into consideration, the supply of an amount of matter dn to the system will mean an increase in energy dependent on the gravitational potential as well as on the chemical potential, n and m being connected through the equation:

$$m = nM \quad (2.3)$$

where M is a constant characteristic of K , viz. the mass of unity of matter. Equation (2.2) is thus seen to need the addition of a term originating from the supply of mass and of the magnitude Φdm . It then becomes:

$$dE = TdS - pdv + \mu dn + \Phi dm \quad (2.4)$$

or:

$$dE = TdS - pdv + (\mu + \Phi M) dn \quad (2.5)$$

But the presence of the gravitational field will necessitate a further modification of (2.2): The term Φdm appearing in (2.4) takes into account the influence of the supply of matter to the system, but according to (2.1) it is necessary to add one more term connected to the possible movement of the system in the gravitational field. This term becomes $md\Phi$. Hence the complete expression for the energy will be:

$$dE = TdS - pdv + \mu dn + \Phi dm + md\Phi \quad (2.6)$$

or:

$$dE = TdS - pdv + (\mu + \Phi M) dn + nMd\Phi \quad (2.7)$$

or:

$$dE = TdS - pdv + \mu dn + d(\Phi m) \quad (2.8)$$

Integration of this equation gives for the energy:

$$E = TS - pv + \mu n + \Phi m \quad (2.9)$$

or:

$$E = TS - pv + (\mu + M\Phi) n \quad (2.10)$$

These equations differ from the usual energy expression in the appearance of the term Φm , or in the exchange of μ with $(\mu + M\Phi)$.

In (2.9) all quantities and potentials are entering in a completely symmetrical manner. In (2.6), however, m and Φ enter in a special way.

The lack of symmetry is due to the fact that T , p , and μ are 'internal potentials' and dependent on the relative amount of quantities in the system, while Φ is an external potential and as such does not depend on the composition of the system.

It is easily seen that the thermodynamic functions F , G , and H in a gravitational field are derived from the usual expressions in the same way as for E , by addition of the term Φm or by exchange of μ with $\mu + \Phi M$. Hence we obtain:

$$F = E - TS = -pv + (\mu + M\Phi)n \quad (2.11)$$

$$G = E - TS + pv = (\mu + M\Phi)n \quad (2.12)$$

$$H = E + pv = TS + (\mu + M\Phi)n \quad (2.13)$$

as well as the corresponding differential equations:

$$dF = -SdT - pdv + (\mu + M\Phi)dn + nMd\Phi \quad (2.14)$$

$$dH = TdS + vdp + (\mu + M\Phi)dn + nMd\Phi \quad (2.15)$$

$$dG = -SdT + vdp + (\mu + M\Phi)dn + nMd\Phi \quad (2.16)$$

and the expression for the chemical potential:

$$\mu + M\Phi = \left(\frac{\partial E}{\partial n}\right)_{S,v,\Phi} = \left(\frac{\partial F}{\partial n}\right)_{T,v,\Phi} = \left(\frac{\partial H}{\partial n}\right)_{S,p,\Phi} = \left(\frac{\partial G}{\partial n}\right)_{T,p,\Phi} \quad (2.17)$$

2. EQUILIBRIUM IN A GRAVITATIONAL FIELD

We shall consider the equilibrium condition in a column of an isotropic fluid of homogeneous temperature enclosed in a cylinder of fixed walls, and with its axis parallel to the direction of gravitation.

This system may be in equilibrium in spite of the presence of potential gradients in the axial direction for the relevant potentials: Chemical potential, pressure and gravitational potential. The reason why these gradients do not give rise to any transport of the corresponding quantities is that the practical definition of the system imposes a coupling on the possible basic processes, preventing them from taking place separately. The conditions are analogous to those in a system consisting of two equally heavy weights suspended from a cord running over a pulley. The lowering of one weight is inevitably connected with the raising of the other.

The active basic processes schematically possible in the fluid system considered, are the transports of matter, volume, and mass. It is not compatible with the existing state of equilibrium that any such process takes place isolatedly. The simplest total process possible is one in which two of these quantities are simultaneously transported. To define such a process completely we shall mark out two partial systems in the column between which the transports are taking place. Let these partial systems be the layers (1)

and (2) of the figure. If only one chemical component is present, their states will be defined by the potentials:

$$\mu_1, \quad p_1, \quad \Phi_1,$$

and:

$$\mu_2, \quad p_2, \quad \Phi_2,$$

respectively, the layers being assumed to be so thin that the potentials inside each of them can be taken as constant. It is a presupposition that in the processes we shall consider, the transported quantities are sufficiently small for the potentials not to change materially on account of the transport.

We shall first assume that matter and mass are transported, while volume is not, and that the transport is taking place from (1) to (2). This process is easily conceivable. At first sight one might even be inclined to believe that the transport of the chemical component from (1) to (2) would invariably involve a simultaneous transport of its mass. The loss of work in the chemical basic process is:

$$A_{\text{chem}} = (\mu_1 - \mu_2) \delta n \quad (3.1)$$

and that in the gravitational basic process:

$$A_{\text{grav}} = (\Phi_1 - \Phi_2) \delta m \quad (3.2)$$

Applying the work principle to the total process, we hence obtain as the condition of equilibrium in the system:

$$(\mu_1 - \mu_2) \delta n + (\Phi_1 - \Phi_2) \delta m = 0 \quad (3.3)$$

Next we shall assume that a volume transport is taking place in the way that the boundary of (1) is moved from b to b' . (1) then loses the volume δv . At the same time the boundary of (2) is shifted from a to a' , (2) thereby gaining the same volume δv . Volume (3) of the intermediate part of the column has

remained unchanged, and the spatial process has only consisted in the transport of δv from (1) to (2). Hence the spatial loss of work will be:

$$A_{sp} = -(p_1 - p_2)\delta v \quad (3.4)$$

No transport of matter is connected with this spatial process, but a gravitational process is seen to have taken place, as the mass in (3) has been lowered by a distance $aa' = bb'$.

If, however, the compressibility of the fluid is provisionally assumed to be infinitesimal, this movement in the gravitational field will be identical with the movement from (2) to (1) of the mass δm , contained in the volume δv . Consequently the gravitational loss of work is:

$$A_{grav} = -(\Phi_1 - \Phi_2)\delta m \quad (3.5)$$

From the work principle and on the basis of (3.4) and (3.5) we then obtain:

$$(p_1 - p_2)\delta v + (\Phi_1 - \Phi_2)\delta m = 0 \quad (3.6)$$

Finally, by a procedure equivalent to the successive effectuation of the above described chemical-gravitational and spatial-gravitational processes, it is possible to accomplish a spatial-chemical process, in which volume and matter are moved from (1) to (2) without involving any net transport of mass. For this process the work principle obviously furnishes the expression:

$$(\mu_1 - \mu_2)\delta n - (p_1 - p_2)\delta v = 0 \quad (3.7)$$

If layers (1) and (2) are infinitely close to each other in the column, expressions (3.3), (3.6), and (3.7) are reduced to:

$$d\mu + Md\Phi = 0 \quad (3.8)$$

$$Vdp + Md\Phi = 0 \quad (3.9)$$

$$d\mu - Vdp = 0 \quad (3.10)$$

when it has been introduced that mass and volume of unity of matter are respectively:

$$M = \frac{\delta m}{\delta n}, \quad V = \frac{\delta v}{\delta n} \quad (3.11)$$

These equations will, of course, hold regardless of any compressibility of the fluid. For the transport between layers of finite distance the corresponding expressions are obtained for compressible fluids by integrating (3.9) and (3.10), for which procedure it is necessary to know the relation between v and p .

All terms in equations (3.3), (3.6), (3.7), (3.8), (3.9), and (3.10) represent works of different kinds, and in each of these equations they are connected to two coupled basic processes, the equations expressing, in accordance with the work principle, that a sum of such works is zero.

But it is, of course, possible for all three basic processes to take place simultaneously, the chemical loss of work being recovered by equivalent spatial and gravitational gains of work, or in other ways.

REFERENCES

1. Brønsted, J. N. *Principer og Problemer i Energetiken. Københavns Universitets Festskrift*. Copenhagen (1946).