

J. N. BRØNSTED MEMORIAL ISSUE

Some Aspects of Brønsted's Energetic Theory¹⁻¹⁰

THOMAS ROSENBERG

Universitetets Fysisk-Kemiske Institut, København, Denmark

J. N. Brønsted considered his last work on the fundamentals of thermodynamics not only as a logical and consistent presentation of the traditional principles, but undoubtedly also, and primarily, as a possible way to cover new fields. His first papers seemed merely to be polemics on formulation, but to him the terminology of a science was the tools the quality of which will determine whether this science is facing stagnation or further progress. Already in the formulation of the basic concepts of a scientific discipline the solution of a certain part of the pertinent problems is inherent, and the desire to attack a wider field of problems may turn an otherwise satisfactory formulation into a hindrance both to the setting and to the solution of the new problems. And Brønsted did have new questions to ask, the solution of which called for a rearrangement of the bricks, so he tackled the very hard task of making such a rearrangement.

The completeness of the thermodynamic complex of thought, which is generally considered to be one of the most perfect achievements of science, Brønsted rather considered a restraining limitation. He had to attack established dogmas of classical thermodynamics, and also his own theses of yesterday. His remarkable ability to consider familiar problems with completely fresh eyes was once again of the utmost significance.

His latest writings and discussions with his collaborators at the Institute convey to us an idea of the goal towards which his theories were pointing. In the 'Festskrift' of the University of Copenhagen from 1946 he is dealing with certain stationary systems; and in the fragment which is published in this issue, and which is his last manuscript, he has taken the first step to provide a description of equilibria in systems which are not 'potential homogeneous' due to the effect of forces from outside, *i. e.* such systems as include gradients in for instance chemical potentials or pressure. Whereas the treatment of equilibria in such systems have for a long time been incorporated

in thermodynamics, considerable uncertainty has persisted about the relation to thermodynamics of the comparatively few theoretical approaches to the treatment of stationary states. In excluding all systems of non-equilibrium from the domain of thermodynamics, a severe restriction is introduced without obvious necessity, and work covering a great and possibly fruitful field is a priori renounced. Brønsted's work must be considered a preparation for the attack on this field.

One of the more important problems is the formulation of the thermodynamic conditions for stability in stationary systems. A system is called stationary if a state, invariable in time, is forced upon the system by a natural process taking place within the system, *e. g.* a current of matter, entropy ('heat') or other energetic quantities from a higher potential to a lower, the current being maintained through action on the system from outside.

As a definite and simple example we shall consider a tube containing a liquid mixture of uniform temperature and pressure, and consisting of two compounds *A* and *B*. A stationary state is maintained by continuous supply of *A* at one end of the tube and withdrawal of it at the same rate at the other end. If such a process has been going on for some time, the system will presumably attain a state of a certain stability compared to other states which comply with the same conditions of mass transport and of temperature and pressure homogeneity. In the stationary state the system will contain gradients in chemical potential for the diffusing as well as for the non-diffusing component, and the latter must have the same tendency to be transported in all directions whether it be along, against or orthogonal to the gradient in its potential. If the supply and withdrawal of *A* is stopped, all gradients will disappear, the free energy of the system decreasing to a minimum characteristic of the stability of the equilibrium state.

Thermodynamics has not yet produced a function to measure the relative stability of the stationary state in the same way as Gibbs' functions do for equilibria. There has even been a tendency to consider such a problem as being in principle unapproachable to a thermodynamic analysis, although no evidence has been given why it should not be solvable on a general thermodynamic basis. Similar problems appear with respect to the separate components in the stationary system. Obviously, the usual conditions of homogeneity in the potentials of all components do not apply: The distribution of a component in the various parts of the system, consequently, is not determined only by its chemical potential.

The combination of reversible and irreversible elements present in stationary states shifts the centre of concern from the surroundings into the interior of the very system. It is a characteristic of Brønsted's treatment that weight

is attached to thermodynamic causality in contradistinction to traditional thermodynamics, which aims at nothing more than to keep precise accounts of macroscopical changes and their mathematical relations. Consequently the concept of potentials plays a great rôle in his system.

Brønsted's principal instrument in the analysis of stationary systems is the fundamental equation of Gibbs:

$$SdT - vdp + \sum_i^n n_i d\mu_i = 0 \quad (1)$$

and this equation is considered an expression for the work connected with the transport of quantity between two adjacent cross-sections in the system. Between two such cross-sections certain processes may take place reversibly even in cases of incomplete equilibrium. Practically all previous treatments of stationary states have been based on this assumption in various formulations, but uncertainty about how to select the reversible elements have made former attempts unsatisfactory. Brønsted applies equation (1) to define the reversible elements: A process will be reversible if it consists in a shift from one of the adjacent cross-sections to the other of a *transport-complex* composed of entropy, volume, and matter in proportions corresponding to the quantities appearing in (1). The isolated movement of the individual quantities is restricted by their coupling into the transport-complex, the same coupling being a condition also for the particular, usually unequal, distribution of the component quantities in the stationary systems.

As (1) will hold also for systems in which the stationary state has not yet been attained, in so far as the potentials will then be defined, it is obvious, however, that the equation will not exhaustively describe the stability of the stationary state. The particular application of (1) is dependent only on continuity in the changes through the system. Hence the shift of the transport-complex will be a reversible process also in non-stationary systems.

Another fundamental principle was outlined by Brønsted in a private discussion on these topics. It can be formulated as follows:

The maintenance of a certain stationary state will be accompanied by the same external 'work effect', *i. e.* the same loss of work per unit time in the surroundings, irrespective of the nature of the external phenomena attached to the maintenance of stationarity.

For the sake of illustration we shall apply the principle to the above-mentioned system: s_A is the amount of matter flowing through any cross-section of the system in unit time, and μ_{A1} and μ_{A2} are the chemical potentials of A at the two end points I and II of the tube. The loss of work in unit time, w_A is then:

$$w_A = (\mu_{A1} - \mu_{A2}) s_A$$

If now the two end walls of the tube are arranged to be permeable to *B* and not to *A*, it will be possible to establish the same stationary state in the tube as before by letting *B* flow in the direction opposite to that of *A*'s flow in the first case. Then, the loss of work in unit time is:

$$w_B = (\mu_{B2} - \mu_{B1}) s_B$$

which, according to the above principle, will equal w_A . This loss of work is an entity which is measurable by the changes in the surroundings.

Brønsted, rather jestingly, mentioned this principle as the fourth law of energetics to indicate that according to his view it could not be derived from the other laws. Brønsted did not get time to verify this principle and to put it into a final formulation, and equally unfinished other thoughts remain which he occasionally mentioned in spite of his disinclination to speak about problems which he had not made finally clear to himself. His treatment of the stationary states is left, therefore, at a very preliminary stage, but his way of approach seems to us to be very appropriate to this special problem. The first experiments planned for the verification of the theory also dealt with stationary systems.

The field which it was intended to make accessible to an energetic analysis includes among many other phenomena: galvanic cells, thermocouples, the Soret effect, thermoosmosis, rectifying columns and stationary biological systems. Such subjects have, of course, been treated separately by other workers from various theoretical view-points. They seem particularly suited for approach through statistical thermodynamics, a science which never seems to have appealed very much to Brønsted. It was his opinion that none of the two sciences, statistical and classical formal thermodynamics, had any superiority over the other, and neither can make the other superfluous. No doubt he did appreciate the insight into the basic concepts of thermodynamics afforded by statistical analysis, but he maintained that the mixing up of the two view-points in the very establishment of the fundamental theories would not promote the progress of knowledge and understanding. He found the justification of the existence of thermodynamics as a separate science in the fact that it was able to rest entirely on the fundament developed by itself. The most favourable conditions for a mutually fructifying relation to statistics will be provided by allowing the two sciences to develop separately, either of them along its own lines.

His goal was to describe the separate phenomena under comprehensive view-points, and it is to be hoped that the impulses given by him will promote the solution of problems which are still obscure, and direct attention to phenomena still unknown.

Brønsted had recognized that an adequate treatment of all these problems could only be arrived at on the basis of a general analysis, particularly the simplest potential inhomogeneous systems. He, therefore, intended to treat all important systems of this kind, beginning with equilibrium systems. The above treatise on the state of fluid systems in a gravitational field represents the first part of this programme, and owing to his death it also became the last.

The results he arrives at concerning equilibrium conditions are identical with those of Gibbs's treatment, probably especially well known in Guggenheim's presentation¹¹. But as to the terms originating from the presence of a gravitational field, he is led to different thermodynamic expressions. Thus from his derivation it appears, that the fundamental equation (1) is valid in this form also for a system in a gravitational field, *i. e.* this equation does not contain a 'gravitational term'. This may prove significant for further theoretical development.

REFERENCES

1. Om relationen mellem varme og arbejde. *Kgl. Danske Videnskab Selskab. Mat. fys. Medd.* **XV** (1937) no. 4.
2. De thermodynamiske hovedsætningers grundlag og formulering. *Kgl. Danske Videnskab. Selskab Mat. fys. Medd.* **XVI** (1939) no. 10.
3. The Fundamental Principles of Energetics. *Phil. Mag.* (7) 29 (1940).
4. The Derivation of the Equilibrium Conditions in Physical Chemistry on the Basis of the Work Principle. *J. Phys. Chem.* 44 (1940).
5. On the Concept of Heat. *Kgl. Danske Videnskab. Selskab Mat. fys. Medd.* **XIX** (1941) no. 8.
6. Energitransformationen og den klassiske thermodynamik. *Fysisk Tids.* 43 (1945) 133—154.
7. Om grundlaget for energetiken. *Fysisk Tids.* 43 (1945) 155—188.
8. Principer og problemer i energetiken. *Københavns Universitets Festskrift nov. 1946.*
9. Rosenberg, Th. *Fysisk Tids.* 41 (1943) 1.
10. Koefoed, J. *Colloque de Thermodynamique* (Union Int. de Physique). Bruxelles (1948). p. 107.
11. Guggenheim, E. A. *Modern thermodynamics.* (1933).