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J. N. BRØNSTED MEMORIAL ISSUE

Some New Procedures in Thermodynamic Theory Inspired by the Recent Work of J. N. Brønsted *

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During the past decade, Professor J. N. Brønsted has been engaged in developing a new system for presenting the principles and concepts of thermodynamics. Cast into this form he called the subject *Energetics.* Instead of the traditional first and second laws he proposes two new principles; namely, the 'work principle', which is restricted to, and is sufficient for, an exhaustive treatment of all reversible processes, and the 'equivalence principle' which applies similarly to irreversible processes. These principles are expressed in compact analytical form in one equation (4.22) in the following text.

They are introduced as general postulates based upon experience just as the first and second laws of thermodynamics are introduced.

With the aid of the 'work principle' Brønsted achieves in a simple and elegant manner a uniform treatment of all reversible processes on the basis of the concepts of the extensive and the intensive energy factors, and 'work'***. without introducing the concept of heat. More especially all reversible thermal processes may be completely described in terms of temperature and entropy. It is only when proceeding to irreversible processes that phenomena occur which require a concept of 'heat', which embodies some but not all of the characteristics of the heat concept employed in the two classical laws. The

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*** Quotes will be used to designate Brønsted's use of these terms which often differ from their classical meanings.

various forms of the characteristic thermodynamic potentials introduced by Gibbs are defined as functions often more convenient for special applications, but their introduction like that of internal energy is not a necessary part of his system.

The basic ideas of Energetics appeared in two monographs [2,3] in Danish in 1937 and 1939. A brief summary, translated by R. P. Bell, appeared in English in 1940 [4], and also a short paper [5], in which the 'work principle' was used to derive the equilibrium equations for heterogeneous and homogeneous systems. An important monograph [7] clarifying criticisms [6] based upon misunderstandig of this paper [5] was published in 1941 (in English) under the title of 'The Concept of Heat'.

The fundamentals of Energetics were incorporated in the second Danish edition of the textbook of physical chemistry [8]. In his last monograph [9] (in Danish), Brønsted introduces the concept of 'transport complexes' and applies it together with the 'work principle' to the treatment of the reversible aspects (assumed isolable) of steady state processes in thermoelectric, electrochemical and thermal transpiration cells.

BRØNSTED'S ENERGETICS

The following is a brief perspective view of some of the ideas formulated by Brønsted.

Energetics is motivated by the symmetry existing between all of the various extensive energy factors (the quantities) and, likewise, between their conjugate intensive factors (the potentials). For example, in equations like

$$SdT - Vdp + \Sigma\, n_i d\mu_i + \varepsilon d\psi + \dots = 0$$

we find entropy and temperature, volume and pressure, number of moles and chemical potential, electric charge and potential, *etc.*, always in a conjugate relationship. All of the extensive properties are defined such that they are conserved, except for entropy in the special case of irreversible processes.

Next it is asserted that all the extensive factors, such as volume, mass, electrical charge, *etc.*, and also entropy always tend to occupy states of lowest accessible potential. Natural (spontaneous) and unnatural (imaginary) processes consist of the movement of the extensive factors between states of different potentials. Each individual transport is called a *basic process.*

Such processes involve respectively a positive or a negative *loss of ability to perform useful work.* This 'loss of work' in a process where an amount

δK_i of an extensive property of the i^{th} kind undergoes a transport from one potential to another, is defined as:

$$\delta A_i = (P_{i(1)} - P_{i(2)})\delta K_i$$

Here $P_{i(1)}$ and $P_{i(2)}$ are the potentials, conjugate to the quantity K_i, of the initial and final state of transport, respectively *.

When natural and unnatural basic processes are *coupled* and balanced to within an infinitesimal difference in net potential a reversible process results. Thus, Brønsted asserts that reversible processes are made up of coupled basic processes only, and conversely, that processes consisting of coupled basic processes only are reversible.

The 'work principle' states that in reversible processes the sum δA of the individual δA_i terms (*i. e.*, the sum of all the 'losses of work' in all of the coupled basic processes constituting the total reversible process) is zero:

$$\delta A = \Sigma_i \delta A_i = \Sigma_i\, (P_{i\,(1)} - P_{i\,(2)})\, \delta K_i = 0 \tag{2}$$

In irreversible processes the sum δA is not zero but positive; there is a positive loss of potential work.

The 'equivalence principle' states that:

$$\delta A = T\delta S'' \tag{3}$$

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* Brønsted recognized the necessity of broadening the concept and definition of work beyond the narrow limits it enjoys in the classical presentation in order to achieve the uniform and systematic treatment which he desired for all forms of energy.

In the classical presentation, the element of work DW is an inexact differential defined as

$$DW = PdK \tag{1}$$

Here d and D are symbols for exact and inexact differentials; P and K are the conjugate potential and quantity factors; thus $DW = pdV$ for volume work.

On the other hand Brønsted's 'loss of (potential) work', δA_i, ***always involves the difference between two potentials.*** In the reversible case, δA_i becomes a function of state and represents the maximum work the i^{th} natural process can perform upon the unnatural process with which it is coupled (see the following text paragraph). In spite of this similarity δA_i should not be confused with the Helmholtz free energy function bearing the same symbol.

For the transport of a finite amount of quantity between states the potentials of which differ only infinitesimally, the 'loss of work' assumes the form $\delta A = KdP$ but is not in general integrable. Also, in the special case where one of the potentials of a component process can be set equal to zero and the amount of quantity transported is infinitesimal the 'loss of work' assumes the same form and numerical value as the classical Eq. (1) but should not be confused with it.

where $\delta S''$ is the amount of entropy produced in the process. $T\delta S''$ is consequently the non-compensated heat of Clausius.*

We realize the difficulty of giving a satisfying exposition of Brønsted's fundamental ideas in a few introductory pages; we, therefore, refer the reader to the original articles, of which (4), (5) and (7) are in English, for the logical operational definitions of such topics as internal energy, the absolute temperature scale, entropy and heat in the system of Energetics.

Unfortunately, the very use of the terms 'work' and 'heat' in senses which often differ from the time honored and specific meanings of the classical presentation leads to confusion no matter how carefully they are defined. Also it is not easy to look with favor upon a summary replacement of the well established first and second laws by two new postulates. Only when the advantages of the replacement becomes evident can one expect approval.

When one examines the *direct* experimental evidence supporting the postulates of energetics, one will find that it is not abundant, because the attention of investigators has been directed over the past century to the justification of the two laws in their classical form. Although we believe no one, who will follow through the logical reasoning of Energetics, will question the validity of the postulates on these grounds, nevertheless, the critical reader and the student approaching the subject for the first time are justified in expecting to be led to Energetics from an abundance of direct experimental evidence with which he is familiar.

Consequently, many readers and particularly those who have had access only to the abbreviated presentations available in English have been unsympathetic. Some may have ceased reading before they have had an opportunity to assess the functional value of the ideas embodied in the new principles. As a result many real contributions contained within the manifold of Energetics have been ignored.

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* In order to distinguish reversibly transported (conserved) entropy from irreversibly *produced* entropy, as well as to distinguish reversibly absorbed heat from the non-compensated (irreversibly evolved) heat, Brønsted uses, when necessary, single and double primes, respectively. Thus:

$$\text{Heat reversibly communicated} \quad \delta Q' = T\delta S' \tag{4}$$

$$\text{Heat irreversibly evolved} \quad \delta Q'' = T\delta S'' \tag{5}$$

This notation is adopted in the following text.

The significance of including terms for the irreversibly produced entropy or the non-compensated heat of Clausius — which Brønsted does in his 'equivalence principle' — was pointed out in 1936[1]. It has been stressed recently by Tolman and Fine[10]. See also Eckart[11], Bridgman[12], De Donder and Van Rysselberghe[13]; Prigogine[14] and Leaf[15].

One of the objectives of this paper therefore is to show that the new postulates are completely equivalent to the classical laws, but that they have in addition certain valuable simplifying didactic merits. One of these is that the new system focuses attention upon the physical structure of the concepts and operations rather than upon the mathematical transformations.

Also, Energetics goes beyond Thermodynamics in furnishing a generalized model concerning which a universal statement; namely, our *rule of potentials* (see below) can be enunciated. This does not imply that more information is obtained but only that a concise and unequivocal form of statement results. Our original plans were to describe Brønsted's system in the manner in which he arranged it. Discussions with colleagues, as our manuscript took shape, demonstrated that confusion resulted from a new terminology. This and, in addition, the existence of a natural reluctance to base conclusions upon new postulates until their advantages are clearly evident. have led us to reverse the procedure.

Thus, in this paper, we abstract and emphasize only those facts which represent tangible contributions by fitting them into the established framework of classical thermodynamics to be used as additional tools.* When the reader becomes satisfied that the new treatment is fully equivalent to the old, and through use becomes more confident in its power and simplicity we hope he will be less reluctant to follow Brønsted's procedure and base all of the reasoning on the new postulates thus achieving a further gain in didactic simplicity.

To this end in what follows we have attempted to avoid objectionable terminology, but have retained the advantageous features of the 'spirit' of Energetics. They are listed in the chapter on assessment. In these respects. much of what follows cannot be imputed to Brønsted alone.

CONCEPTS AND DEFINITIONS

A thermodynamic system is defined as a geometric region whose boundaries may be fixed or variable, and which may contain matter, or energy, or both. The suitable description of such a system depends, in part, upon the specification of the amounts of certain components known as the extensive energy factors, which we shall call *quantities*, following Brønsted. Thus, it is customary to say that the system possesses certain amounts of volume, surface, matter, electric charge, entropy, moles of chemical components, *etc.*

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* For discussions of the relationship between Brønsted's Energetics and traditional Thermodynamics see Rosenberg [16] and Holtan [17].

Consider an isolated system, *i. e.*, one which cannot receive quantity from, or lose it to, the regions beyond its geometric boundaries. In addition, we shall at first be concerned only with a system in which no chemical reaction is occurring. Any infinitesimal variation which takes place within this system is limited, either to the *redistribution* of quantity among its physically distinct parts or to the *production* * of quantity *within* the system, or both. Call those variations, associated with redistribution, *transport* processes.

The comprehensive description of a thermodynamic system requires the numerical specification of another set of entities, known as *intensities* or *potentials*. In this set we include the familiar parameters, pressure, surface tension, gravitational potential, electrical potential, temperature, and chemical potential, *etc.*, which the reader will recognize are each conjugate respectively to the quantities above. During any infinitesimal change, involving the production and redistribution of quantity the potentials remain, sensibly, constant.

The transport of matter, charge, entropy, and moles of chemical constituent, *etc.*, between parts of the system requires no comment. The situation, in respect to volume and surface, is much the same. However, it is worth while to indicate clearly how these latter transports occur.

Imagine a box (Fig. 1) equipped with a movable partition (cross-hatched) which separates two gases at the pressures p_2 and p_1, respectively; $p_2 > p_1$.

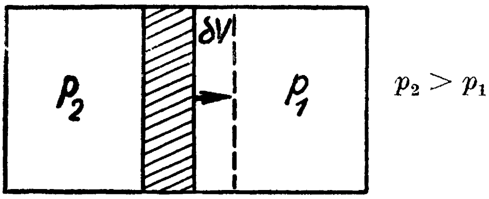

Figure 1.

The partition moves to the right, as indicated by the arrow, and the volume, dV, originally on the right of the partition, appears on the left. In this sense, the volume is transported from the region of lower pressure, p_1, to that of

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* The only quantity which can be produced, *i. e.*, which is not conserved, is entropy, in irreversible processes. In the reversible case, entropy and thermal processes can be treated in full conformity with other quantities and processes as emphasized by Brønsted.

higher pressure, p_2; *i. e.*, the potential conjugate to volume is negative pressure. Similarly, we can consider the transport of surface. Consider two films (Fig. 2)

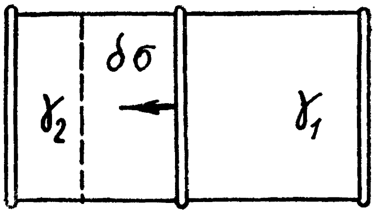

Figure 2.

having the tensions, γ_2 and γ_1; $\gamma_2 > \gamma_1$; which are distended between two fixed wires (extremes) and a wire free to move as the films demand (center). The center wire will move spontaneously to the left, as the arrow indicates, and the surface, $\delta\sigma$, will be transported from left to right, from the region of higher surface tension to that of lower.

THE BRØNSTED PRINCIPLES DERIVED FROM THE FIRST AND SECOND LAWS. THE NON-COMPENSATED HEAT OF CLAUSIUS *

Choose an isolated system which is not the seat of chemical reactions, and divide it into localities, in each of which the *potentials* are *uniform*. By combining the first and second laws of thermodynamics, we follow Gibbs and write for the variation δE_j of the internal energy of the j^{th} locality, during any infinitesimal change:

$$\delta E = T\delta S - p\delta V + \gamma\delta\sigma + \Sigma_i\mu_i\delta n_i + \varphi\delta m + \psi\,\delta\varepsilon \tag{4.1}$$

In Eq. (4.1) and in all of the following equations to (4.14) we have dropped, for simplicity, the subscript j which should modify every symbol in these equations to specify that it refers to the j^{th} locality.

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* Since the non-compensated heat measures the amount of energy that becomes unavailable as useful work in an irreversible process, and is zero for reversible processes, we prefer, for the present, to emphasize this concept also for reversible processes rather than the Brønsted concept 'loss of work' (which is defined differently from the traditional work of thermodynamics). The non-compensated heat as a measure for 'loss of potential work' has been emphasized by Tolman (see Ref. 10 and patents cited there).

Here T = temperature; p = pressure; γ = surface tension
S = entropy; V = volume; n_i = moles of the i^{th} species
m = mass; ε = electric charge; σ = surface

$$\mu_i = \frac{\partial E}{\partial n_i} = \text{chemical potential of a mole of the } i^{th} \text{ species}$$

$$\varphi = \frac{\partial E}{\partial m} = \text{gravitational potential of a gram of matter}$$

$$\psi = \frac{\partial E}{\partial \varepsilon} = \text{electrical potential of a coulomb of charge.}$$

Now:

$$\begin{array}{ll} m_i = n_i M_i & \delta m_i = M_i \delta n_i \\ \varepsilon_i = n_i Z_i F & \delta \varepsilon_i = Z_i F \delta n_i \\ \Sigma_i \delta m_i = \delta m & \Sigma_i \delta \varepsilon_i = \delta \varepsilon \end{array}$$

where M_i is the molecular weight, Z_i is the charge per molecule of the i^{th} species, and F is the Faraday constant.

Accordingly (4.1) can be rewritten as

$$\delta E = T\delta S - p\delta V + \gamma\delta\sigma + \Sigma_i (\mu_i + M_i \varphi + Z_i F\psi)\delta n_i \qquad (4.2)$$

where the sum $(\mu_i + M_i\varphi + Z_i F\psi)$ can be conveniently replaced by the symbol λ_i, where λ_i is a general component potential for the i^{th} species; *e. g.*, in the electrical case $(\mu_i + Z_i F\psi)$ becomes the now well-known electrochemical potential of Guggenheim[18] which Brønsted adopts and employs effectively in treating galvanic cells[1, 8, 9, 18, 19, 20].

$T\delta S$ represents the heat which could be absorbed by the locality if the variation were conducted reversibly. In order to calculate δE it is therefore demanded that the additional terms in (4.2) which indeed represent work terms, be those which would be obtained if the variation were conducted reversibly. In other words, p, γ, and λ_i must be equilibrium values. If we represent by $\delta Q'$ the heat which would be absorbed if the variation were conducted irreversibly, then we have

$$T\delta S - \delta Q' > 0 \qquad (4.3)$$

Accordingly, we write

$$T\delta S = \delta Q' + T\delta S'' \qquad (4.4)$$

where, by virtue of (3)

$$T\delta S'' > 0 \qquad (4.5)$$

in the irreversible case. In the reversible case equality exists for (4.5) and the double primed quantity vanishes. The term $T\delta S''$ is the so-called non-compensated heat of Clausius represented by $\delta Q''$, while

$$\delta Q' = T\delta S' \tag{4.6}$$

where $\delta S'$ is the entropy which is transported into the locality, through its boundaries. $\delta S''$ represents the entropy *produced within* the j^{th} locality by whatever irreversible phenomena are occurring there.

The variation of entropy, as ordinarily defined (no prime) is a sum given by

$$\delta S = \delta S' + \delta S'' = \frac{\delta Q'}{T} + \frac{\delta Q''}{T} \tag{4.7}$$

For an irreversible variation in the j^{th} locality, the first law gives

$$\delta E = \delta Q' - \delta W' \tag{4.8}$$

where $\delta W'$ is the work performed by the locality upon its surroundings. Substituting for $\delta Q'$ we get

$$\delta E = T\delta S - T\delta S'' - \delta W' \tag{4.9}$$

Eq. (4.9) indicates clearly that the non-compensated heat $T\delta S''$ represents work which is potentially available provided that the variation associated with δE is carried out reversibly. δE and δS have fixed values, being exact differentials, independent of whether or not the change occurs reversibly.

Therefore, the sum of the residual terms

$$-T\delta S'' - \delta W' \tag{4.10}$$

is fixed for the defined variation.

In the limit of reversibility, $\delta S''$ is zero and consequently $\delta W'$ has its maximum value. All of the non-compensated heat can be obtained as useful work in this limit.

Now (4.7) is substituted into (4.2), yielding

$$\delta E = T\delta S' + T\delta S'' - p\delta V + \gamma\delta\sigma + \Sigma_i \lambda_i \delta n_i \tag{4.11}$$

for each j^{th} locality.

To compute the variation of the total internal energy of the isolated system we sum over two types of localities. The first summation is over all of the j localities. Now the system may also contain localities whose quantities are invariant to any general change. Fixed weights or charges are examples. Eq. (4.11) cannot be used for the computation of the variation of the energy connected with the transport of such quantities, since all of its differentials are quantities, and consequently equal to zero. Instead

$$\delta E_k = m_k \delta \varphi_k \tag{4.12}$$

where φ is the gravitational potential and m is the mass, is suitable if we deal with a weight, while

$$\delta E_k = \varepsilon_k \delta \psi_k \tag{4.13}$$

is likewise suitable if we deal with an electric charge. Then the total variation δE in the internal energy of the isolated system is representable as

$$\delta E = \Sigma_j \delta E_j + \Sigma_k m_k \delta \varphi_k + \Sigma_k \varepsilon_k \delta \psi_k \tag{4.14}$$

and can be set equal to zero since the system is isolated. Accordingly from (4.11) we obtain (4.15)

$$\begin{aligned}\delta E = \Sigma_j T_j \delta S'_j + \Sigma_j T_j \delta S''_j - \Sigma_j p_j \delta V_j + \Sigma_j \gamma_j \delta \sigma_j + \Sigma_j \Sigma_i \lambda_{ij} \delta n_{ij} \\ + \Sigma_k m_k \delta \varphi_k + \Sigma_k \varepsilon_k \delta \psi_k = 0\end{aligned} \tag{4.15}$$

This equation can be rearranged immediately as follows:

$$\begin{aligned}-\Sigma_j T_j \delta S'_j + \Sigma_j p_j \delta V_j - \Sigma_j \gamma_j \delta \sigma_j - \Sigma_j \Sigma_i \lambda_{ij} \delta n_{ij} - \Sigma_k m_k \delta \varphi_k \\ - \Sigma_k \varepsilon_k \delta \psi_k = \Sigma_j T_j \delta S''_j\end{aligned} \tag{4.16}$$

Since we have excluded the possibility of chemical reactions, all of the quantities on the left in (4.16) satisfy the condition of conservation for reversible processes in the isolated system. Thus:

$$\Sigma_j \delta S'_j = 0, \quad \Sigma_j \delta V_j = 0, \quad \Sigma_j \delta \sigma_j = 0, \quad \Sigma_j \delta n_{ij} = 0 \tag{4.17*}$$

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[*] $\Sigma_j \delta S'_j = 0$ because $\delta S'_j$ is that part of entropy which is transported. $\Sigma_j \delta V_j$ and $\Sigma_j \delta \sigma_j$ can always be set equal to zero by defining, if necessary, transports to and from regions of zero pressure and zero surface tensions. Neither (4.15), (4.16) or (4.17) are affected by these transports because the terms referring to those localities of zero pressure and surface tensions necessarily have zero values. $\Sigma_j \delta n_{ij} = 0$ because we have excluded for the moment the possibility of chemical reactions.

A further rearrangement of the left terms of (4.16) can be effected in the following manner. Consider the sum $\Sigma_j p_j \delta V_j$ and specialize for simplicity to the case where it equals

$$p_1\delta V_1 + p_2\delta V_2 + p_3\delta V_3 \tag{4.18}$$

Then the isolated system is a box, similar to that used in Fig. 1, but having, in this case (Fig. 3), two movable partitions, separating regions having the pressures p_1, p_2, and p_3, respectively.

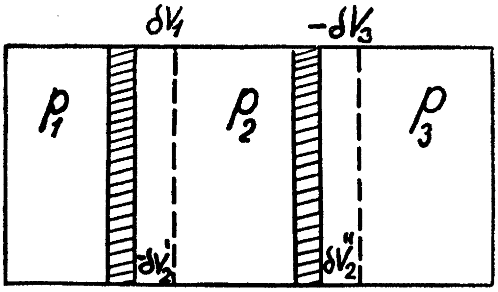

Figure 3.

Now by the conservation of volume

$$\delta V_1 + \delta V_2 + \delta V_3 = 0 \tag{4.19}$$

It is apparent from figure 3, in which $p_1 > p_2 > p_3$, that

$$\begin{aligned} \delta V_2 &= \delta V_2' + \delta V_2'' \\ \delta V_1 &= -\delta V_2' > 0 \\ \delta V_3 &= -\delta V_2'' > 0 \end{aligned} \tag{4.20}$$

so that (4.19) is satisfied. Using the notation of (4.20) we can write for (4.18) the expression

$$p_1\delta V_1 - p_2\delta V_1 + p_2\delta V_2'' - p_3\delta V_2''$$

or (4.21)

$$(p_1 - p_2)\delta V_1 + (p_2 - p_3)\delta V''_2$$

In other words (4.18) is identical with a sum, each term of which consists of the product of a potential difference, multiplied by the quantity which is transported through the potential difference.

By induction, this result is perfectly general, and can be applied to all of the sums on the left-hand side of (4.16). We thus effect the complete rearrangement, and write finally, the important equation:

$$\delta A = \Sigma_r \delta K_r \; (P_{r(\text{initial})} - P_{r\,(\text{final})}) = \Sigma_j \, T_j \, \delta S''_j \geq 0 \qquad (4.22)$$

(4.22) is the analytical form of the *combined* Brønsted principles. The equality applies to reversible processes, *i. e.*, the 'work principle', and the inequality to irreversible processes, *i. e.*, the 'equivalence principle'. δK_r symbolizes a transported quantity, while $P_{r\,(\text{initial})}$ is the conjugate potential in the locality from which and $P_{r\,(\text{final})}$ the conjugate potential in the locality to which the quantity is transported. δK_r is always greater than (or equal to) zero (see Eqs. (4.20)). The potential for volume always appears as negative pressure.

VIRTUAL CHANGES, COUPLING, AND THE RULE OF POTENTIALS

It is to be noted that all of the differentials in (4.22) are specified by the symbol, δ, which designates a virtual variation. The term, virtual, implies that the variation may be of the most general kind, and need not be physically realizeable. Although some of the most important phases of thermodynamic theory deal with the subject of virtual variations, very few authors have succeeded in presenting this subject clearly. The virtual variation is an important adjunct of the Brønsted treatment and hence requires discussion.

Any displacement from equilibrium subject to the same constraints which are imposed upon the system at equilibrium is, strictly speaking, impossible. A real displacement can only occur by the alteration of one or several of the constraints. In this sense, any displacement which a system in equilibrium undergoes is a virtual displacement. Let us confine our attention to displacements which are infinitesimal.

A system in equilibrium can experience two types of infinitesimal virtual displacements. The first type involves a displacement, joining equilibrium states (quasi-static), while the second involves a displacement which originates in equilibrium and terminates in non-equilibrium. The former is the assymptotic limit of some real process, while the latter has no basis in reality whatsoever.

The reader is undoubtedly familiar with many specific examples of quasi-static processes. Examples of this type will be given in the chapter on these processes.

For a concrete example of a *non*-quasi-static displacement, consider a liquid drop, in equilibrium, surrounded by its vapor. It would be impossible, unless the system were severely altered, to transport isothermally dn moles of the drop to the region of its vapor without, at the same time, transporting some of its volume and surface area. On the other hand, there is nothing to prevent us from *imagining* the physically impossible transport, during which the drop simultaneously dilates, so that its volume and surface area remain constant. It is evident that this would represent a displacement passing from an equilibrium to a non-equilibrium state.

In order to obtain a clear understanding of the usefulness of the method of virtual displacements, it is absolutely necessary to have a broader definition of a 'thermodynamic state' than the one ordinarily given. Usually a 'state' means an '*equilibrium* state' whose reproducible properties can be described by a minimum number of macroscopic parameters. Any function of state, *e. g.*, the free energy, has these parameters for arguments.

In a larger sense, a state can be defined as any *reproducible condition* of a system, either in equilibrium or in the process of change. A non-equilibrium state will, in general, require a larger number of parameters for its description than an equilibrium state. In the extreme case the dynamical specification of every microscopic particle in the system may be required. In any event, any function of state, *e. g.*, the free energy, will depend upon a larger number of variables, but will remain a defined function. From the operational point of view, an equilibrium state then becomes a special kind of state defined by the minimum number of parameters. It can be represented by a point in 'state-space', *i. e.*, the space whose coordinates are the parameters defining the state in the most general sense.

An infinitesimal displacement from equilibrium is represented by an infinitesimal path in 'state-space' originating at the point of equilibrium. A number of these paths will satisfy the condition that the temperature and pressure remain constant along them. It is a classical criterion of equilibrium that for an infinitesimal displacement along any one of these isothermal, isobaric paths the Gibbs free energy of the system remains unaltered. This free energy is understood to be defined in the larger sense, so that it remains a defined function of a non-equilibrium state. For the application of this criterion, it is inconsequential whether the displacement is or is not quasi-static. All that is demanded is that it be infinitesimal and that it originate in equilibrium. In particular, it may be of the type illustrated above in connection with the spherical drop.

The point that many fail to grasp is that one does not seek information about the condition of the system along the path of the infinitesimal displacement *but only about the condition at the origin of the path.* Others have difficulty in conceiving the significance of the free energy along a non-quasi-static path because the description of a 'state' as an equilibrium state has been overemphasized.

The Gibbs free energy has been chosen as an illustration because of its familiarity. However, all of these implications concerning virtual variations can be transferred in full to Brønsted's 'work principle', (Eq. 4.22), when employed as the criterion of equilibrium. This equation (like other criteria) imposes the demands of thermodynamics upon a system in equilibrium. Very often, however, certain extra-thermodynamic conditions are imposed upon the behavior of the system. When this is true, all of the virtual displacements must be consistent with these conditions.

For example, return to the consideration of the drop. We may impose an extra-thermodynamic condition upon the system represented by the drop and its vapor, namely, the geometric condition which specifies that the transport of volume from the drop to the vapor must occur in such a manner that the spherical shape of the drop is retained. It is then not permissible to carry out a virtual variation during which the volume, δV, is transported without the simultaneous transport of the surface, $\delta\sigma$, because both are connected by the geometrical relation

$$\delta V = \frac{r}{2}\,\delta\sigma \tag{5.1}$$

where r is the radius of the drop.

The equality and inequality (4.22) represents a compact and extremely useful expression of the laws of thermodynamics. In addition, it furnishes a very satisfying model for the internal behavior of a thermodynamic system. These contentions shall be demonstrated in detail.

From the nature of the rearrangement (4.22) it is clear that the potentials conjugate to the different quantities are, in order:

quantity	*potential*
volume	negative pressure
entropy	temperature
surface	surface tension
moles of chemical components	component potential [*]
mass	gravitational potential
charge	electrical potential

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[*] Note that we are replacing the ordinary Gibbs chemical potential μ by the more general component potential λ defined in the chapter on the derivation of the Brønsted principles.

In mechanics and field theory, potential has the significance of determining the direction of change. That this significance is retained, unaltered, in the above table can easily be shown.

To do this, consider a system undergoing a virtual change which consists of a single transport, such that all of the terms on the left of (4.22) with the exception of one, $\delta K_x(P_{x\,(\text{initial})} - P_{x(\text{final})})$, are zero. Then (4.22) reduces to

$$\delta A = \delta K_x(P_{x(\text{initial})} - P_{x(\text{final})}) = \Sigma_j\, T_j \delta S''_j \geq 0 \tag{5.2}$$

In (5.2) as in (4.22) the inequality corresponds to a *natural* irreversible change, *i. e.*, one which does occur spontaneously, and the equality corresponds to a reversible process, *i. e.*, to a displacement of a system in equilibrium. Since δK_x is arbitrary and positive, it follows that the expression in brackets (potential difference) is positively different from zero when a real change takes place. Finally, we observe that the potential difference is zero when no change takes place (when the system is in equilibrium). Therefore, a finite difference of potential bears a one-to-one correspondence to change, while no potential difference corresponds to no change. For this reason, potential difference may be regarded with complete consistency as the motivating factor for change. Taking account of the subscripts (initial) and (final) in (5.2), it is to be observed that all quantities tend to move from a higher to a lower potential. These conclusions which we have derived from the laws of thermodynamics, Brønsted introduces as observations of experience to justify the reasonableness of his principles.

The form (5.2) was achieved by restricting the virtual change to a single transport. But suppose this is not possible, as in the example offered previously, concerning the volume and area of a spherical drop. In that case, the quantities volume and area were *coupled* together so that the movement of one demanded the movement of the other. For such a case, the form (5.2) could not be achieved. Then it could not follow that the potential differences conjugate to the coupled quantities would be required to be zero at equilibrium.

We are thus led (quite rigorously) to a general rule which we shall call the *rule of potentials*, namely, that *all potential differences necessarily vanish at equilibrium except those corresponding to conjugate transported quantities which are coupled to other quantities.* In particular, since chemical components are never coupled so as to defy an *individual virtual transport*, the *component potential* λ_i corresponding to the i^{th} species is *identical in every locality when equilibrium has been attained.*

In the usual presentation of thermodynamics the rule of potentials enunciated above can only be proved by inventing a suitable characteristic function for each case and by setting in motion the machinery of the Lagrange method of undetermined multipliers. In the current presentation it has been obtained *rigorously* and in a *single stroke* by utilizing a satisfactory physical model for the thermodynamic system in which constraints can be described in terms of bonds; '*coupling*'.

This result constitutes part of the evidence for the contention that (4.22) is a compact and useful expression of the laws of thermodynamics and that it furnishes a good model of thermodynamic behavior. We will now proceed to examine the beautiful and consistent description which it provides for the state of internal equilibrium when 'coupling' exists.

A MODEL FOR INTERNAL EQUILIBRIUM

When coupling exists, the potential differences conjugate to the coupled quantities are not necessarily zero. If we write (4.22) for the process involving the reversible transport of these quantities, we retain only the equality, and have:

$$\sum_{\text{coupled}} \delta K_r(P_{r\,(\text{initial})} - P_{r\,(\text{final})}) = 0 \tag{6.1}$$

Physically, the situation in (6.1) can be described as follows. Each of the coupled quantities is invited by its conjugate potential difference to move, but the movement of one quantity, in the direction specified by its conjugate potential difference, compels (because of the bonds between quantities) other quantities to move in directions opposite to those specified by their own potential differences. At equilibrium, all of the opposing tendencies balance and this is signified by the condition (6.1).*

TREATMENT OF QUASI-STATIC PROCESSES

In the first place, it is to be noted that a quasi-static displacement is one along which the system remains in equilibrium. Consequently, all of the potentials in the system are subject to the restrictions of our rule of potentials. In addition, since a quasi-static displacement has a limit-basis in reality, we

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* This model of equilibrium (*i. e.*, coupling between basic processes) was applied in Brønsted's last monograph[9] to the treatment of the reversible aspects of steady staet processes; *e. g.*, in the thermoelectric cell he utilizes the coupling between a mole of electrons and the entropy associated with it. Similar procedures were employed for the gas transpiration cell.

shall consider it formally to be a real change and accordingly employ the symbol d rather than δ to symbolize differentials.

The reversible expansion of a gas

Consider a gas (Fig. 4) having the pressure p,

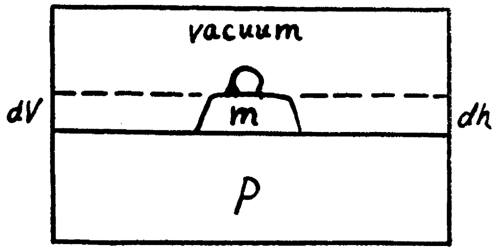

Figure 4.

separated from a vacuum by a partition upon which a weight, m, rests, which is almost but not quite heavy enough to maintain equilibrium. The containing vessel is surrounded by a reservoir of temperature, T. The isolated system which we need to consider consists of the reservoir and the container plus its contents.

Under the prescribed conditions, the partition will move upward the distance dh and the volume dV will be transported from the vacuum to the pressure, p. Corresponding to this transport the loss of spatial potential work is given by

$$dA_{\text{spat}} = -(0 - p)dV = pdV \tag{7.1}$$

There is an accompanying loss of gravitational potential work

$$dA_{\text{grav}} = [gh - g(h + dh)]\ m = -\ mgdh \tag{7.2}$$

There will also be a flow of entropy between the reservoir and the gas. The variation is quasi-static and the rule of potentials can be applied. Since there is no extra-thermodynamic relation coupling the transport of entropy to other processes, it follows that the potentials conjugate to the entropy, *i. e.*, the temperatures are the same in the gas and in the reservoir. For the thermal loss of potential work we obtain

$$dA_{\text{therm}} = 0 \tag{7.3}$$

However, there is an extra-thermodynamic, geometrical relation between dV and dh, and thus the spatial and gravitational processes *are* coupled. This is consistent with the rule of potentials; the corresponding losses of potential work do not have zero values.

Upon substitution of (7.1), (7.2) and (7.3) in the equality of (4.22), we obtain the result

$$pdV - mgdh = 0 \tag{7.4}$$

Brønsted has commented upon the fact that it is customary to regard the motivation of the quasi-static process just described as originating in the reversible flow of heat from the reservoir to the gas, or what amounts to the same thing, in the transport of entropy. He points out that it is more consistent to regard the transport of volume as the motivating factor since it is here that a finite potential difference exists (see Eq. (7.1)) and because we have considered a potential difference to be the motivating factor for change (see the chapter on virtual changes).

Carnot cycle — Coupling of thermal and mechanical basic processes

As an important example of the direct use of the equality in (4.22) we give Brønsted's treatment of the reversible Carnot engine. Let the heat absorbed by the engine at the upper temperature T_1 be $DQ_1 = T_1\,dS$ and that rejected at the lower temperature T_2 be $DQ_2 = T_2\,dS$:

$$dS = \frac{DQ_1}{T_1} = \frac{DQ_2}{T_2} \tag{7.5}$$

The thermal process in the heat engine thus consists in the reversible transport of an amount of entropy dS between the temperatures T_1 and T_2. The reversible mechanical work dA obtained from the engine may consist in the transport of a weight m from a lower height h to a higher height $h + dh$: $dA_{\text{mechanical}} = -mgdh$. In any case, regardless of the nature of the mechanical work, (4.22) gives:

$$(T_1 - T_2)dS + dA_{\text{mechanical}} = 0 \tag{7.6}$$

or, introducing (7.5):

$$|dA_{\text{mechanical}}| = DQ_1\,\frac{T_1 - T_2}{T_1} \tag{7.7}$$

To be consistent, the driving force may be considered to originate in the thermal process, *i. e.*, the tendency of the entropy to go from the higher to the lower temperature. Since this process is coupled and balanced through the engine to a mechanical process, it can only occur reversibly through the simultaneous performance of mechanical work.

The reader is referred to the original articles[4, 7] for Brønsted's objections to the Clausius' interpretation of the Carnot Cycle.*

THE GIBBS-DUHEM EQUATION

In treating problems of equilibrium, it is often necessary to have a differential relation which connects the real variations (symbol *d*) of the different potentials, rather than the extensive properties in a given phase. The general relation, which we shall call the ***generalized*** Gibbs-Duhem equation, has the following form:

$$SdT - Vdp + \Sigma_i n_i d\lambda_i = 0 \tag{8.1}$$

Equation (8.1) can be obtained in a simple and straight-forward manner by applying the equality contained in (4.22) to a selected reversible transport.

Consider a phase whose potentials are specified by the pressure, p, the temperature, T, and the ***component potential*** for the i^{th} species, λ_i. Consider another phase, having the potentials $p + dp$, $T + dT$, and $\lambda_i + d\lambda_i$, which contains the same chemical species as the first phase. Now, combine these two phases in a rigid, adiabatic shell, so that they form an isolated system. Since the potentials in the two phases differ infinitesimally, the transports which now occur do so reversibly. We can thus apply the equality contained in (4.22) to these transports.

$$[(T + dT) - T]\, dS + [p - (p + dp)]\, dV + \Sigma_i\, [(\lambda_i + d\lambda_i) - \lambda_i]\, dn_i = 0 \tag{8.2}$$

or

$$dSdT - dVdp + \Sigma_i\, dn_i d\lambda_i = 0 \tag{8.3}$$

This equation places no restriction upon the amounts of quantity dS, dV and dn_i which are transported, since there is only one dependent variable and we can always choose this to be one of the potential differences, *i. e.*, dT, dp or $d\lambda_i$. By suitably adjusting the amounts of quantity, originally present in the two phases, it is always possible to adjust the transport so that:

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* See, also: V. K. La Mer, 'Some current misconceptions of Carnot's Memoir and Cycle.' Paper read before American Physical Society, Jan. 29, 1949; to be published in Am. J. Phys.

$$dS : dV : dn_i = S : V : n_i \tag{8.4}$$

Here S, V, and n_i are the quantities in the first phase. This means that the quantities, transported combine to form a replica of a portion of the first phase. Because of (8.4), (8.2) can be multiplied by a constant to yield (8.1), which is the generalized Gibbs-Duhem equation for the first phase. Since the first phase was arbitrary, (8.1) is applicable to any phase.*

The derivation of (8.1) is again an illustration of the compactness and usefulness of (4.22). In the usual presentation of thermodynamics, it is necessary to invent a function of state and to apply Euler's theorem for homogeneous functions before (8.1) can be derived.

TREATMENT OF EQUILIBRIUM

We are now in position to apply (4.22) to the solution of problems of equilibrium. In a sense, we have already partially solved every conceivable problem of internal equilibrium by the use of (4.22), since we have been able to arrive at the conclusion that the component potentials are uniform throughout the system when equilibrium has been attained. To obtain a more tangible and comprehensive description of the interior of a system at equilibrium, we have only to proceed from this point by the usual methods of thermodynamics taking account of the manner in which the component potentials are related to the other parameters which determine the state of a given locality.

However, we have not exhausted the utility of the equality in (4.22) for in many cases it yields an immediately useful result over and above that pertaining to the equality of the potentials. As an example, compute the difference in pressures inside and outside of a drop having the radius, r. Choose for the isolated system the drop surrounded by its equilibrium vapor contained in a rigid, diathermic shell which is placed in a thermostat. Since the temperature is everywhere uniform, the terms referring to the transport of entropy vanish from (4.22). The same, of course, is true of the transport of material. Writing the equality (4.22) for the transports attending the transport of moles of material from the drop to its vapor, we find that only the terms corresponding to the transport of the 'coupled' quantities volume, δV, and surface, $\delta\sigma$, can have non-zero values. This follows from the rule of potentials. We thus have for (4.22):

$$-(p_1 - p_2)\delta V + (\gamma - 0)\delta\sigma = 0 \tag{9.1}$$

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* Our use of the equality (4.22) for the derivation of the generalized Gibbs-Duhem equation is slightly different from that of Brønsted [5].

Here p_2 is the pressure of the vapor outside the drop, p_1 the pressure inside the drop, 0 the surface tension of the hypothetical surface in the vapor, and γ the surface tension of the vapor-drop interface. Substituting (5.1) into (9.1) the familiar formula of Kelvin, specialized to a sphere, follows immediately.

$$p_1 - p_2 = \frac{2\gamma}{r} \tag{9.2}$$

CHEMICAL EQUILIBRIUM

Thus far, systems in which chemical reactions occur have been excluded from consideration. This was done as a matter of convenience only, and does not represent any fundamental insufficiency of the Brønsted treatment. The inclusion of the chemical reaction as a possible source of variation necessitates the introduction of a slight modification in Eq. (4.16).

The rearrangement of (4.16) to yield (4.22) is no longer valid since any particular type of molecular species entering into the reaction is not conserved. It is possible to modify (4.16) so that in place of the mole numbers the numbers of atoms of particular kinds contained in a particular molecular species inhabiting a given phase serve as parameters. It is also possible to use the masses of the various molecular species in this connection. Both atoms and mass are conserved even in the presence of a chemical reaction, and so a rearrangement of the desired type is possible.

However, it is more expedient, for chemical purposes, to define a pseudo quantity $\delta\alpha$, which is also conserved. Let ν_r and ν_p be the stoichiometric coefficients of the r^{th} reactant and p^{th} product in a given chemical reaction of the type:

$$\Sigma \nu_r R_r = \Sigma \nu_p P_p$$

where R_r and P_p are the molecular symbols of the r^{th} reactant and p^{th} product. Let ν_r and ν_p *both be positive.* Then *

$$\delta\alpha_R = \frac{\delta n_r}{\nu_r} \qquad \text{for all } r \tag{10.1}$$

$$\delta\alpha_P = \frac{\delta n_p}{\nu_p} \qquad \text{for all } p \tag{10.2}$$

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* It will be notes that α_P, but not α_R is the degree of advancement of reaction employed by De Donder.

From stoichiometric considerations, it is evident that

$$\delta\alpha_P + \delta\alpha_R = 0 \tag{10.3}$$

For simplicity let us restrict our attention to a system in which the mole numbers are varied by a single chemical reaction confined to a single phase. This result can be generalized easily, as the occasion requires.

Then the term, in (4.18), $-\Sigma_j\Sigma_i\lambda_{ij}\delta n_{ij}$, reduces to $-\Sigma_i\lambda_{ij}\delta n_{ij}$ and by virtue of (10.1) and (10.2) this becomes

$$-(\Sigma_r\lambda_r\nu_r\delta\alpha_R + \Sigma_p\lambda_p\nu_p\delta\alpha_p) \tag{10.4}$$

or

$$-(\delta\alpha_R\Sigma_r\lambda_r\nu_r + \delta\alpha_P\Sigma_p\lambda_p\nu_P) \tag{10.5}$$

and by the use of the new conservation condition (10.3), we obtain the form

$$-(\Sigma\lambda_p\nu_p - \Sigma\lambda_r\nu_r)\delta\alpha_P \tag{10.6}$$

If we define

$$\lambda_P = \Sigma\lambda_p\nu_p \tag{10.7}$$

$$\lambda_R = \Sigma\lambda_r\nu_r \tag{10.8}$$

as 'system potentials' for the pseudo-quantity $\delta\alpha_P$, (10.6) indicates that the form (4.22) can be extended to chemical reactions.

Indeed for any reaction proceeding isothermally and isobarically, the work principle now demands that at equilibrium

$$(\lambda_R - \lambda_P)\delta\alpha_P = 0 \tag{10.9}$$

or that the 'system potentials':

$$\lambda_R = \lambda_P \tag{10.10}$$

(10.10) yields the law of mass action when the individual potentials are substituted.

In closing, it is to be noted that the pseudo-quantity can be used as a measure (on stoichiometric grounds) of the rate of transport of the real quantity, mass, from reactants to products.

IRREVERSIBLE PROCESSES

The inequality contained in (4.22) provides a direct means for computing the production of non-compensated heat during an irreversible process, provided that the transports involved are recognizable and that the irreversible process conducts itself in such a way that each stage can be described by what are sensibly equilibrium parameters.

We shall consider one example of this type. A single thermostated phase, the seat of a chemical reaction, but nevertheless in *mechanical* and *thermal* equilibrium, represents a system satisfying the requirements just mentioned. The only transport having a non-zero term will be that corresponding to the transport of the pseudoquantity da_P. The system is out of equilibrium so that entropy is being produced. Eq. (4.22) then reduces to

$$(\lambda_R - \lambda_P)da_P = TdS'' \tag{11.1}$$

If we divide by dt and define the velocity of the reaction, v, as

$$v = \frac{da_P}{dt} \tag{11.2}$$

we obtain

$$(\lambda_R - \lambda_P)v = T\frac{dS''}{dt} \tag{11.3}$$

or

$$\frac{dS''}{dt} = \left(\frac{\lambda_R - \lambda_P}{T}\right)v \tag{11.4}$$

a result given by De Donder.

ASSESSMENT

The favorable points for equation (4.22) follow:

(a) It provides a satisfying model for the internal behavior of an isolated thermodynamic system.

(b) It leads simply and with a minimum of mathematical expenditure to a simple rule of potentials. As a corollary, the general result asserting that the component potentials are uniform at equilibrium is obtained. In the classical discipline the concepts and ideas are not available to make such a concise universal statement.

(c) The generalized Gibbs-Duhem relation is obtained with a minimum of mathematical expenditure.

(d) In cases of coupling (4.22) leads to an immediately useful result, concerning the features of equilibrium in a system where the coupling phenomena exist. By this it is implied that properties, other than the fact that the component potentials are uniform, are described.

(e) In some instances (4.22) affords a direct means of calculating the noncompensated heat evolved in an irreversible change.

Finally, we do not assert that (4.22) is the most convenient form for all thermodynamic purposes. Attention is always focused upon an isolated system, which means any system of physical interest *plus* its environment. In this way some of the detachment which is gained by defining thermodynamic potentials which are functions of the state of some particular nonisolated system is lost. However, by combining both methods of attack, fruitful results are obtained.

SUMMARY

A brief exposition of the salient features of Brønsted's Energetics is given. The complete equivalence of his basic postulates, namely, the 'work' and the 'heat and equivalence principles' in respect to the two laws of classical thermodynamics has been demonstrated by deriving his postulates from these laws. Some of Brønsted's fundamental conceptions, *e. g.*, the existence of a potential difference as the motivating factor for the occurrence of a basic process, balanced coupling of basic processes to produce reversible processes, the localized production of entropy in irreversible processes, *etc.*, emerge as necessary consequences in this derivation.

The compactness and elegance of Brønsted's approach are illustrated by simple examples using his 'work principle' and a new rule of potentials given by us. An assessment of the merits of the system is included.

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