

Brønstedian Energetics, Classical Thermodynamics and the Exergy. Towards a Rational Thermodynamics. I.

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A comparison between the process-oriented energetics of Brønsted and the system-oriented classical thermodynamics is carried out. It is shown that a unification can be made in terms of the exergy concept. The exergy is generally defined as the maximum available energy in the thermodynamic system which may be completely general with several temperatures, pressures, phases *etc.* The exergy is shown to be a non-additive energy function when subsystems are united. Under appropriate simplifying conditions the exergy specialises into the well-known Gibbsian Legendre-transformed energy functions. The “active variables” of the Legendre-transformations correspond to Brønstedian “neutral transports”.

As is well known the foundation of phenomenological thermodynamics were laid by Sadi Carnot with his famous treatise over cyclically operating heat engines in 1824.¹ Historically, the Carnot cycle was used in developing a statement of the second law of thermodynamics and to create the concept of entropy.^{2,3} This procedure cannot be said to be particularly expedient in chemical thermodynamics, however, and therefore the Carathéodory version of the second law is sometimes preferred.^{4–6} The present author does not feel, however, that an understanding of Carathéodory's theorem about Pfaffian forms is of much help in overcoming the didactic problems in teaching thermodynamics to chemists.

The reason is that there are a number of logical flaws and weaknesses in the definitions of “heat” and “work” of traditional thermodynamics, as pointed out by J. N. Brønsted many years ago. Brønsted tried to reformulate classical thermodynamics into a more precise and symmetrical structure named *energetics*

by himself.^{7–12} I would especially recommend the Philosophical Magazine article¹² as a short-hand introduction to Brønstedian energetics. The Brønsted energetics has obvious pedagogic advantages and permits replacement of lengthy considerations by short statements of immediate transparency.

In 1971 the author wrote an article¹³ trying to reconcile the *process-oriented* Brønstedian energetics with the *system-oriented* Gibbsian approach. Especially the connection between Brønsted's “neutral transports” and Gibbs' derived energy functions was pointed out. In the author's Ph. D. dissertation¹⁴ the analysis was carried somewhat further in an effort to establish a general *exergy* function (generalised free energy) on the basis of Brønsted's energetics. Actually, Brønsted never did integrate his work principle explicitly, although the mere mentioning of a work *loss* assumes the existence of a work *function*. Colmant has once pointed out¹⁵ that Brønstedian energetics in many respects is very similar to the “energetique” advocated earlier by Le Chatelier.¹⁶ The latter author bases, however, his entire theory on the “puissance motrice” which can be regarded as an exergy function.

The term “Exergie” was apparently introduced by Z. Rant in 1953 and has been used within the field of power station and refrigeration techniques.¹⁷ A quantity named “essergy” has been defined through the information theory by R. B. Evans in 1969,¹⁸ and this is also essentially an exergy function. Very recently a book about irreversible thermodynamics utilising the exergy concept has appeared.¹⁹ None of the above-mentioned exergy functions

Table 1.

Type of basic process	Potential	Quantity	Conserved/Not Conserved
Mechanical	Force (f)	Length (x)	C
Kinetic	$v^2/2$ (v = velocity)	Mass (M)	C
Gravitational	Gravitational potential (Φ)	Mass (M)	C
Spatial	Negative pressure ($-p$)	Volume (V)	C
Elastic	Stress tensor	Strain tensor ("length")	C
Interface	Interfacial tension (σ)	Interfacial area (A)	NC
Thermal	Temperature (T)	Entropy (S)	C Rev. processes NC Produced in irrev. processes
Chemical	Chemical potential (μ)	Number of moles (n)	C Physical transport NC Chemical reactions
Electric	Electric potential (Ψ)	Electric charge (q)	C
Dielectric	Electric field (\mathcal{E})	Dielectric polarisation (\mathcal{P})	NC
Magnetic	Magnetic field (\mathcal{H})	Magnetisation (\mathcal{M})	NC

have the generality and simplicity of the function defined on the basis of the work principle of Brønsted.

In the present article I shall try to formulate the main content of Brønstedian energetics and its extensions in the pious hope that there will be a renewed interest in this concise representation of the body of thermodynamic facts.

POTENTIALS, QUANTITIES AND THE WORK PRINCIPLE

Brønsted wished to expand the meaning of the term "work" beyond the narrow definition (force times length) in mechanics and classical thermodynamics. Just as the work done by lifting a weight may be calculated as the product of the mass and a difference in gravity potential, a number of other processes in nature may be described as transfer of quantities of an extensive nature between two potentials of an intensive nature (basic process of the first type) or the creation or destruction of a quantity at a single potential (basic process of second type). The work done by those basic processes is given by

$$\text{Type 1: } \delta W = -\Delta P \delta K \quad (1a)$$

$$\text{Type 2: } \delta W = -P \delta K \quad (1b)$$

δK represents a virtual variation of the amount of a quantity and P the conjugated potential. A list of some dual quantities and potentials is given in Table 1. Processes of type 1 may be considered to be the sum of a destruction and a creation process of the second type with the net result that quantities participating in processes of the first type are conserved. The *work principle* of Brønsted now states that when two or more of such basic processes are coupled together and when the transformations are reversible – that is their directions may be reversed without any supplementary help from outside – the sum of all the work done must be zero

$$\sum \delta W_i = -\sum P_i \delta K_i = 0 \quad (2)$$

The summation has to be carried out over all quantities and all localities with distinct potentials in the considered closed system. In case of continuous systems the summation must be replaced by an integration over the volume of the system.

Taking our departure in a simple mechanical basic process such as the lifting of a weight, we may define work done by thermal, electric, or other basic processes by successive coupling of the basic processes under study with the mechanical process. We notice that in cases

where we have already established the extensive quantity the intensive potential will be defined through the work principle. For example, with K being equal to the number of moles of a substance (n_i) we have a direct definition of the chemical potential μ_i . There is no need to make a *detour* over the internal energy or its Legendre-transforms as did Gibbs in his "Equilibrium of Heterogenous Substances"²⁰ in order to define this fundamental potential. On the other hand, for the thermal basic process the work principle uniquely defines the thermal quantity which is not heat, but entropy when some temperature scale has been established. The only net result of a Carnot cycle is a transfer of entropy from a heat reservoir (better: entropy reservoir) at one temperature to a reservoir at another temperature. A general Carnot cycle may be carried out with any reversibly functioning device with thermal communication during a part of the cycle with two thermal reservoirs. With this general definition of a Carnot cycle we have included cooling techniques such as the cyclical magnetisation and demagnetisation of paramagnetic salts.²¹ The definition from Brønsted's work principle of the entropy * reveals that quantity to be the real thermal quantity corresponding to other quantities in physical chemistry such as electric charge, volume, number of moles, mass and surface area.

The basic spatial process consists of moving a piston corresponding to an infinitesimal volume δV when the pressure on one side is p_1 and on the other side p_2 . If the piston is moved towards the p_2 side, the process may

be characterised as a transfer of δV from p_2 to p_1 . The work done is

$$\delta W_{\text{spatial}} = (p_1 - p_2)\delta V$$

Comparison with eqn. (1a) shows us that the potential in the spatial basic process should be put equal to the negative pressure.

One striking example of the fundamental manner in which Brønstedian energetics differ from traditional thermodynamics may be given at this stage. Consider an ideal gas confined in a cylinder with piston in thermal contact with an entropy reservoir. On the other side of the piston is vacuum, but a weight is placed on the piston. Now, traditional thermodynamics would maintain that the conversion of heat taken from a single reservoir into work is possible in a *non-cyclical* process. Heat flows into the gas and the piston with the weight goes up. As the internal energy of the gas remains constant in the isothermal expansion, the potential energy taken up by the weight corresponds to the heat absorbed. Brønsted finds this untenable. He maintains that the conversion of thermal energy at a single temperature into other kinds of energy is impossible under all circumstances. The two basic processes which are coupled together in the present example are the transfer of δV from zero pressure to p and the transfer of mass M from the gravitational potential ϕ to $\phi + d\phi$. The transfer of entropy from the entropy reservoir to the ideal gas is just a *neutral transport* without any energetic significance, because the transfer occurs between regions with the same temperature. The absorption of entropy is only a consequence of the special *constitutive relation* of the ideal gas (the ideal gas law). Consider that the material enclosed in the cylinder were water at 2°C. Now, when heat is absorbed, the piston goes down! The "tragicomedy of thermodynamics" – as Truesdell has put it²² – has been the persisting tendency to entangle in special constitutive relations, so that the purely *energetic* content of the theory becomes invisible.

We notice also that there is no need to speak about "heat" in reversibly coupled processes. Entropy is the useful thermal quantity which can be defined both when it is reversibly or irreversibly transported and as a static entropy

* Actually, Brønsted did first define the entropy and thereafter an "energetic temperature scale", see e.g. section 3 in Ref. 12. His arguments are somewhat circuitous, however, because he first defines a calorimeter as an energetic system with uniform potentials which is only in thermal contact with the surroundings. Then he measures some preliminary temperature of the calorimeter by any conventional thermometer and defines the change in entropy as being proportional to the change in temperature when they are both infinitesimal. Finally, he establishes the energetic temperature scale by means of the work principle. The arguments are much shortened and clarified if the order of definitions are reversed giving rise to an "energetic entropy definition" corresponding to any arbitrary temperature scale.

content of a body. The "heat" defined in traditional thermodynamics can only be defined when it is transported and it is not conserved in the basic thermal process: the Carnot cycle. Heat enters into Brønstedian energetics only in connection with *irreversible* processes as we shall see in the next section.

EXERGY AND BRØNSTED'S HEAT PRINCIPLE

We shall now proceed to define the exergy of an isolated thermodynamic system. By isolated we mean that it has no communication of work or any energetic quantities with the outside world. Such a system may be characterised by the set of two vectors (\mathbf{P}, \mathbf{K}) denoting the amount of different quantities at different "positions" (be it in physical space or in more abstract reaction spaces) and the conjugated potentials. Furthermore, there will be a set of *constitutive relations* given by the vector eqn. $\mathbf{C}(\mathbf{P}, \mathbf{K}) = \mathbf{0}$. By a constitutive relation we mean a relation between potentials \mathbf{P} and quantities \mathbf{K} , such as given by the dependence of heat capacity (better: entropy capacity) on temperature or the dependence of pressure on volume and temperature (eqn. of state). The constitutive relations for general thermodynamic systems will depend both on the materials constituting the system and on the specific arrangement of the quantity exchange and the energy conversion between the subsystems within the system. Most of such constitutive relations will possess what might be called the *local property*, i.e. only \mathbf{P} 's and \mathbf{K} 's at the same physical locality enter into the constitutive relation. Sometimes it will be necessary, however, to operate with quite complicated non-localised constitutive relations. For example when a charge distribution produces an electric field according to the eqn. of Poisson. This will be the case for, e.g., electrokinetic phenomena²³ or in electrolyte diffusion zones.²⁴

Imagine now that we allow for interaction of the system with an outside mechanical basic process. We proceed to move quantities between the different localities in a reversible manner by coupling with the exterior mechanical reservoir until the potential differences in the system cannot be further equalised. At that point – the *energetic zero point* of the system

– the state of the system will be ($\mathbf{P}_0, \mathbf{K}_0$). The state is not necessarily a state with all potentials of the same kind being identical at all localities. Different quantities are often linked together in fixed proportions in so-called *transport complexes*. For example, one mol of a given ionic species is linked to a charge $z_i F$ and a mass M_i , z_i being the number of elementary charges on the ion with sign, F the Faraday constant and M_i the ionic weight in Daltons. Thus, in electrical and gravitational fields equilibrium will be reached with the equalisation of the compound *electro-gravi-chemical* potential

$$\tilde{\mu}_i = \mu_i + z_i F \psi + M_i \Phi \quad (3)$$

in all regions of the system to which access of the i 'th ion is possible.

When the system has reached the energetic zero point some work has been received by the external mechanical reservoir and we shall term this work the *exergy* of the system and designate it by the symbol Ex . By the work principle we have

$$Ex = - \int_{\mathbf{P}, \mathbf{K}}^{\mathbf{P}_0, \mathbf{K}_0} \sum_{\text{system}} P_i \delta K_i \quad (4)$$

We can only carry out the integration having a knowledge of the set of constitutive relations $\mathbf{C}(\mathbf{P}, \mathbf{K}) = \mathbf{0}$. On the other hand it should be clear from the fundamental theorem of energy conservation in nature that the exergy of a given system must be independent of the integration path. Thus, the exergy must be a function of state of the system, a state being defined by the set (\mathbf{P}, \mathbf{K}). Clearly, this requires that the constitutive relations satisfy the requirement

$$\frac{\partial P_j}{\partial K_i} = \frac{\partial P_i}{\partial K_j} \quad (5)$$

When the constitutive relations possess the local property, eqn. (5) will be automatically satisfied for quantities and potentials which refer to two different regions, because the cross derivatives will be zero. *Within* the same region eqn. (5) will yield relations of the usual Maxwell type.

To give a specific example of an exergy calculation consider two blocks of the same material at atmospheric pressure and tempera-

tures t_2^i and t_1^i on any arbitrary temperature scale (superscript i stands for "initial"). We may put as constitutive relation

$$\delta S = c \delta t \quad (6)$$

where S is the entropy conjugate to the chosen temperature scale and c is an entropy capacity of the material which we for simplicity consider independent of temperature. By means of a Carnot cycle we transfer entropy from the upper temperature t_2^i to the lower t_1^i . When the amount of entropy transported has reached the value S , the two temperatures will be, respectively,

$$t_1 = t_1^i + S/c$$

$$t_2 = t_2^i - S/c$$

At the energetic zero point $t_1 = t_2$ and the transferred entropy equals to

$$S^0 = (c/2)(t_2^i - t_1^i)$$

The exergy can now be calculated from eqn. (4)

$$Ex = \int_{S=0}^{S^0} (t_2 - t_1) dS = \frac{c}{4} (t_2^i - t_1^i)^2 \quad (7)$$

We notice that the exergy is a minimum when the initial temperature difference is zero if $c > 0$ which is the condition of thermal stability of the material.

The exergies of subsystems have a remarkable property: they are *not additive*.¹⁴ Imagine a subsystem I with an exergy $Ex(I)$ and another subsystem II with an exergy $Ex(II)$. When the two subsystems are fused together after their exergies have been extracted, it will often be possible still to extract additional exergy from the total system, because there will still be unexploited potential differences *between* the two subsystems even if an *internal* equalisation of potentials (or transport complex potentials) has been carried out in each system *per se*. Symbolically we have

$$Ex(I + II) = Ex(I) + Ex(II) + Ex(I_0 + II_0) \quad (8)$$

a subscript 0 denoting that the system is at its energetic zero point. Thus, thermodynamics is *holistic* in its very nature, a feature which has been totally neglected in all traditional expositions of the subject.

Until now we have only considered reversible transformations. When irreversible processes have occurred in an isolated system, this is reflected by the fact that the system cannot be carried back to its initial state without mechanical and thermal manipulations from outside. The quantitative description is given by Brønsted's *heat principle*

$$-dEx = dQ \geq 0 \quad (9)$$

In words: the loss of exergy – Brønsted spoke about the loss of work – equals the *energetic heat evolution*. This quantity is always positive (zero only for strictly reversible transformation). It is called heat evolution, because it is accompanied by a *production* of the thermal quantity

$$dQ = T dS_{\text{prod}}, \quad dS_{\text{prod}} \geq 0 \quad (10)$$

For small changes there will be a simple proportionality between the heat evolution (or exergy loss) and the production of entropy. The proportionality constant T in eqn. (10) has the dimension temperature and it is found to vary with the arbitrary temperature t . Actually, it might quite as well be used as a measure of temperature as the arbitrary temperature. The positivity of T is assumed by the simultaneous positivity of the energetic heat evolution and the entropy production. The advantage of using T instead of t as a measure of temperature is, of course, that we now have an *absolute energetic temperature scale* defined solely through eqn. (10) and with no reference to statistical mechanics, extrapolation of ideal gas properties or properties of materials at very low temperatures. The arguments presented here are not circuitous, since the entropy produced may be measured using the work principle and the arbitrary temperature scale, and the loss of exergy may also be uniquely defined using the arbitrary temperature scale, *cf.* eqn. (7).

It is of course important not to confuse the energetic heat evolution with intuitive considerations, *e.g.* whether there is an increase in temperature or not. Brønsted⁹ investigated the heat concept in a number of monographs upon thermodynamics and found that it varied from author to author and from situation to situation. Vague words from the daily life are not suited to build a science upon, perhaps

it would be better to avoid the word "heat" altogether and use instead the word *energy* which is actually already in use.¹⁷ Energy is the "low quality" thermal energy into which exergy degrades during irreversible transformations. Further utilisation of this energy is not possible, if the system under consideration remains isolated from its surroundings. Utilisation is possible, however, if the gates open up to other systems with lower temperatures than the temperature prevailing in the original system. Then, suddenly, energy is converted to new exergy.

INTERNAL ENERGY, NEUTRAL TRANS-PORTS AND CONDITIONED EXERGY

An energy quantity as important as the exergy is the *internal energy* of the system (\mathbf{P}, \mathbf{K}). We shall designate that quantity by the letter E , but our internal energy is more generally defined than the one usually discussed in thermodynamics. Besides the system considered we need some standard reservoirs of the conserved energetic quantities (C) with fixed conjugate potentials. We start with an empty system and then slowly transfer the conserved quantities in a reversible manner from the standard reservoirs to their positions in the system. The work done in order to perform the operations described can be found from the work principle, and from the principle of conservation of energy we may also find it as a sum of the gain in internal energy of the system and the gain of the standard reservoirs

$$\sum (P - P_{st}) dK(C) + \sum P dK(NC) = dE + dE_{st} \quad (11)$$

The summation over non-conserved quantities (NC) represents the work absorbed by the reversible creation of quantities in the system itself, e.g. interfacial areas or mol of a chemical component produced from other components in internal chemical equilibria. The division of the internal energy between the system and the reservoirs is quite arbitrary, but it appears natural to take

$$dE = \sum_{\text{system}} P dK \quad (12a)$$

and

$$dE_{st} = \sum_{\text{reservoirs}} P_{st} dK_{st} = \sum P_{st} (-dK) \quad (12b)$$

The definition of the internal energy of a system is thus taken to be

$$E = \sum_{\text{system}} \int_0^{K_i} P_i dK_i \quad (13)$$

Clearly, we must assume a knowledge of the internal constitutive relations as the case is with the exergy, too. From the principle of conservation of energy or by comparison of eqns. (4) and (13) we immediately find the following connection between the exergy and the internal energy of a system

$$Ex = E - E_0 \quad (14)$$

where E_0 is the internal energy of the system at its energetic zero point. In contrast to exergy the internal energy *is* additive as a result of conservation of energy. Therefore, the fact that the total exergy is often greater than the sum of the exergies of the subsystems [cf. eqn. (8)] merely reflects the fact that the energetic zero point of the combined system is at a lower internal energy than the sum of the internal energies of the subsystems at *their* energetic zero points. It is also important to notice another fundamental difference between internal energy and exergy. When we differentiate eqn. (14) we have to take

$$dEx = dE - dE_0 \quad (15)$$

because the energetic zero point will change when irreversible processes are occurring in the system. This is so, because the system will not be the same before and after some irreversible transformations have taken place, since more entropy has been produced in the system. The change in internal energy in an isolated system during irreversible transformations will be zero, but the internal energy at the energetic zero point will be greater after the transformations than before, and therefore there has appeared a loss in exergy according to (15).

From the very general considerations given here it is possible to make a bridge to the specialised – but for chemists very useful – Gibbsian thermodynamics based upon Legendre transforms of the internal energy. We shall introduce the concept *conditioned exergy* of a thermodynamic system (\mathbf{P}, \mathbf{K}) which is permitted to exchange certain quantities with

outside reservoirs of infinite magnitude. Hereby the corresponding potentials – or transport complex potentials – at the localities where the exchanges occur will be fixed at the values P_{fix} of the external reservoirs. From eqn. (12a) we observe that terms $P_{\text{fix}}dK$ will contribute to the changes in internal energy of the system, but there can be no alterations in exergy, since all the transfers of quantities through the boundaries of the system take place over zero potential differences. This is precisely what Brønsted called *neutral transports*. It is interesting to observe neutral transport processes to be on the borderline between reversible and irreversible processes in Brønstedian energetics. They are processes which are not coupled to any other process, but their driving forces must of course be slight differences in potentials. So in a way they are irreversible processes, but the loss of exergy is zero because the difference in potentials is infinitesimal and the processes may equally well be reversed.

If we subtract the contributions $P_{\text{fix}}dK$ from the internal energy, we obtain the conditioned exergy in cases with no irreversible processes. In the general case with both reversible and irreversible processes we may write for the conditioned system instead of eqn. (15)

$$dEx(P_{\text{fix}}) = dE - \sum P_{\text{fix}}dK - dE_0 \quad (16)$$

with $Ex(P_{\text{fix}})$ being the conditioned exergy. Clearly, the conditioned exergy is the maximum amount of work which can be extracted from the open, conditioned system with the external constraints maintained.

In the very special, but important systems studied by Gibbs, the internal energy has the property of being multiplied by n if the amount of all quantities constituting the thermodynamic phase is multiplied by n . The integration in eqn. (13) may then be carried out by

means of Euler's theorem for homogeneous functions of the first degree with the result

$$E = \sum PK \quad (17)$$

Comparison of eqn. (17) with eqn. (12a) gives us the Gibbs-Duhem formula

$$\sum KdP = 0 \quad (18)$$

Now, consider the following Legendre transform of the internal energy

$$E(\mathbf{P}') = E - \sum P'K \quad (19)$$

The technique of Legendre transforms was well known in analytical mechanics before it was introduced into thermodynamics by Gibbs, see *e.g.* Lanczos' book.²⁵ The selected vector of potentials \mathbf{P}' constitutes the *active variables* of the transformation. Taking the differential on both sides of eqn. (19) and using (17) and (18) we obtain

$$dE(\mathbf{P}') = \sum PdK - \sum P'dK - \sum KdP' \quad (20)$$

If the \mathbf{P}' is chosen to be the vector of fixed potentials \mathbf{P}_{fix} , the third term on the r.h.s. of eqn. (20) will vanish and the second term will accomplish the required correction for neutral transports, so under the given external constraints and when no irreversible processes occur, the Legendre-transformed internal energy in eqn. (19) will be equal to the conditioned exergy, *i.e.* the Legendre transforms will correspond to the maximum work which can be withdrawn from the conditioned systems. Table 2 shows the constraints and the neutral transports in connection with the well-known Gibbsian functions.

CONCLUSION

The present way of presentation has distinct advantages in simplicity, symmetry and strength in comparison to traditional exposi-

Table 2. The Gibbsian Legendre-transformed internal energy functions.

Name	Conditioned exergy	Neutral transport of.	Constraints
Enthalpy	$H = E - (-p)V$	V	p and S const.
Helmholtz' free energy	$F = E - TS$	S	T and V const.
Gibbs' free energy	$G = E - (-p)V - TS$	V and S	p and T const.

tions of thermodynamics. Also, it gives to thermodynamics a much more general structure which might become of value in the analysis of complex thermodynamic systems, e.g. for analysis of exergy flow patterns in ecosystems. A paper on the rationalisation of irreversible thermodynamics along the lines of Brønsted energetics will be forthcoming.

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