

The Principles of Thermodynamics

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The Principles of Thermodynamics

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A formulation of thermodynamics has been developed which points out the restrictions of classical treatments. This formulation in terms of potential and charge concepts predicts the property ascribed to the entropy of increasing during thermodynamic processes and leads to an equation for entropy produced and heat dissipated in irreversible processes. The postulates of the treatment presented have allowed deduction of a generalized form of the second law of thermodynamics which applies to each energy field of the system. These concepts have been further developed in discussion of the phase rule; the functions H , A , and F ; a generalization of Kelvin's postulate; and a generalization of the Carnot cycle. The results obtained have permitted derivation of the principles of Brønsted's system of energetics.

IT is the purpose of this paper to investigate the basic assumptions of thermodynamics. The classical formulation of thermodynamics involves concepts which greatly restrict its generality. We shall attempt to develop a formulation of thermodynamics within the classical framework in such a way as to demonstrate the limitations of the classical treatment and possibly to indicate the approach to a more general treatment. Our results will enable us to derive the principles of energetics as enunciated by Brønsted¹ so that these principles will appear as special results of thermodynamics.

One of the first considerations in the classical treatment of thermodynamics is the definition of the system and the state of the system. The concept of the state of the system imposes serious limitations on the applicability of the results of the classical treatment. A thermodynamic system may be any portion of the universe we care to consider. The properties of a system are considered to be functions of a certain few variables, which are generally chosen to be the temperature, entropy, pressure, volume, composition, etc. When these functions are defined in the system, a set of values for these variables is said to describe a state of the system. Thermodynamic processes consist of the passage of the system from one state to another. The limitation imposed by this formulation is at once apparent; we are unable to treat the system when it is not in a defined state. This immediately precludes the possibility of treating flowing systems,

problems of diffusion, viscosity, or heat conduction, since in none of these instances do the systems considered have well-defined functions such as the pressure or temperature. Only when the system is static can we define such functions. Consequently, formulated according to the concept of the state of the system, thermodynamics is not designed to give information about flowing, non-static systems, or systems in the process of transition between initial and final states of a process.

It appears that in order to overcome the restrictions imposed by the classical treatment one must replace the concept of the state by something more general. This entails description of the region under consideration by means of differential equations giving the variation with time of the properties at each point in the various energy fields of the region. Such a method is illustrated in an article by Meixner.² Since, however, in this paper we desire to remain within the classical framework we will employ the concept of the state. We note that if we are content to consider only problems concerned with changes of a system between initial and final states the classical treatment is adequate.

Let us now consider a certain system which we will suppose to exist in a certain state. The intensity of energy is specified by the potential functions corresponding to the various forms in which energy may be manifest in the system, e.g., the temperature T , pressure P , chemical potential μ_i , etc. Corresponding to each potential

¹ J. N. Brønsted, *Phil. Mag.* [7] **29**, 449 (1940); *J. Phys. Chem.* **44**, 699 (1940).

² J. Meixner, *Ann. d. Physik* **39**, 333 (1941).

function for the system there exists an energy charge function, as for example, the entropy S corresponding to the temperature, the volume V corresponding to the pressure, the mass m_i of the i th chemical component corresponding to the chemical potential of component i . When a quantity of energy charge enters a system against the prevailing potential values, the energy of the system increases. The increase in energy of each homogeneous portion or phase of a system, characterized by a single value of each potential function, is given by the sum of the increases in energy in the various forms in which it may enter that phase. As the defining equation for the increase of energy of a phase during an infinitesimal change of state we write

$$dE = TdS - PdV + \sum \mu_i dm_i + \dots \quad (1)$$

The increase in energy of the whole system is the sum of the increases in the homogeneous portions. If the system is a single homogeneous phase its energy increase is given by (1).

About the system there exist homogeneous surroundings for which the increase of energy is given by

$$dE' = T'dS' - P'dV' + \sum \mu'_i dm'_i + \dots \quad (2)$$

It has been pointed out³ that in an actual instance, if a finite system at a certain set of potential levels is in contact with surroundings at a different set of levels then neither Eq. (1) nor Eq. (2) describes the detailed process that occurs. Local inhomogeneities will develop, first, at the boundary between system and surroundings and then these disturbances will spread throughout the system; finally, the disturbances will become uniformly distributed and the system is again homogeneous. As soon as the local inhomogeneities appear, however, the system is no longer in a thermodynamic state and cannot be treated in the classical manner. In order to treat the problem the method is to replace the actual path, traversed by the system in passing from initial to final states, by an idealized path in which a state is defined for the system at every point. Since classically we are interested only in the end states, such a method gives the correct result and the treatment is much simpler than

that required in a detailed description of the actual process. Equations (1) and (2) are therefore valid within the limits of utility of the classical treatment since they are equations defining energy changes along the idealized path.

There is an alternative method of viewing the limitations of Eqs. (1) and (2). The local inhomogeneities attend the transfer of energy charges between system and surroundings. If the rate of distribution of these charges throughout the system is rapid compared to our experimental observation of the system, the system will at every stage of the process appear homogeneous. Consequently, by being sufficiently slow in our measurements as to allow disappearance of the local disturbances we will find the changes of state of the system and surroundings to be described by Eqs. (1) and (2).

The range of validity of Eqs. (1) and (2) coincides with the range of applicability of the classical method using the state concept. To get a more detailed description of the process as a function of time one must resort to a more general method such as the use of differential equations for the various energy fields as indicated earlier.

Having defined the energy changes in the system and surroundings we can now formulate the law of conservation of energy. The composite system consisting of the system and its surroundings is isolated with respect to all forms of energy. The region designated as the surroundings during a process involving the system is always chosen large enough so that the composite system satisfies this condition. Since the total energy is conserved for the composite system

$$dE + dE' = 0. \quad (3)$$

In consideration of energy exchanges between system and surroundings it is necessary to distinguish between charge entering the system from the surroundings and increase in charge in the system resulting from processes within the system. If K is the charge corresponding to a particular form of energy, then δK , the charge entering the system, is equal to $-dK'$, the charge leaving the surroundings

$$\delta K = -dK'. \quad (4)$$

³F. H. MacDougall, private communication.

The total gain in charge of the system is written as dK and is the sum of the quantity δK entering from the surroundings and the charge produced in the system, during an infinitesimal process. For the surroundings no distinction is made between dK' and $\delta K'$. The surroundings may be imagined to be infinite reservoirs of the various forms of energy each at a certain potential level. It is only in the system that changes of energy involving charge production occur.

We can now demonstrate that the total charge function in the total energy field of a system must increase in the system and its surroundings. Let us consider a field of energy which we will designate as a ϕ - Z field. We shall assume that this field is conservative. This ϕ - Z field satisfies two conditions, namely:

(a) The total ϕ - Z energy in the system and the surroundings is conserved.

$$\phi dZ + \phi' dZ' = 0 \quad (5)$$

or
$$\phi dZ - \phi' \delta Z = 0. \quad (6)$$

(b) The gradient of the potential function ϕ determines the total force field on an element of charge δZ as it passes between system and surroundings and therefore determines the direction of flow of δZ .

$$(\phi - \phi')\delta Z = (\phi' - \phi)dZ' \leq 0. \quad (7)$$

According to relation (7) if

$\phi > \phi'$, then $\delta Z < 0$ and Z leaves the system.

$\phi < \phi'$, then $\delta Z > 0$ and Z enters the system.

From (6)

$$(\phi - \phi')\delta Z + \phi(dZ - \delta Z) = 0.$$

Hence

$$\phi(dZ - \delta Z) = -(\phi - \phi')\delta Z \geq 0 \quad (8)$$

$$dZ \geq \delta Z. \quad (9)$$

This interesting result shows that $dZ + dZ' \geq 0$ so that the charge in the ϕ - Z field must increase or reach a maximum in the system and its surroundings. If we suppose that the total energy field can be identified with the ϕ - Z field so that it satisfies relations (5) and (7) then we are led to expect the existence of a charge function with the property of always increasing. This property, of course, is associated with the entropy, so that

we anticipate one of the most important properties of the entropy.

The condition for equilibrium between system and surroundings is

$$\phi = \phi' \quad (10)$$

so that

$$dZ = \delta Z. \quad (11)$$

The identification of the total energy field with the ϕ - Z field which obeys relations (5) and (7) is permissible within the classical treatment based on the idea of the state of the system. In this treatment charges simply move from one potential level to another. Kinetic energy is excluded from consideration since a system with moving parts is not in a thermodynamic state. The entire energy field is therefore of the potential energy type for which there exists the potential function ϕ whose gradient determines the direction of motion of the total energy charge δZ . This charge is the sum of the charges for the individual component fields. For example, if the total field consists of thermal and electrical fields, the charge δZ is the sum of a certain number of entropy units and a certain number of electrical charge units. Corresponding to this composite charge the potential ϕ is a thermoelectric potential function.

Since we identify the total energy field with the ϕ - Z field

$$dE = \phi dZ. \quad (12)$$

We now suppose that the total energy field can be divided into two fields one of which is a T - S or thermal field for which

$$dS \geq \delta S \quad (13)$$

and the other of which is a ψ - Y or work field for which

$$dY = \delta Y. \quad (14)$$

Since $dZ = dS + dY$ this is consistent with (9). At equilibrium, therefore, according to (11)

$$dS = \delta S. \quad (15)$$

In subdividing the field we let

$$dE = \phi dZ = T dS + \psi dY \quad (16)$$

so that we see by comparison with Eq. (1) that

$$\psi dY = -PdV + \sum \mu_i dm_i + \dots \quad (17)$$

The ψ - Y field is really the aggregate of all the individual fields except the thermal field which we have singled out for special consideration here.

We can now obtain a very important relation giving the entropy produced during irreversible processes. From (6) and (14) we find

$$TdS - T'\delta S + (\psi - \psi')dY = 0. \quad (18)$$

This equation can be written, according to (13), as

$$T(dS - \delta S) = -(T - T')\delta S - (\psi - \psi')dY \geq 0. \quad (19)$$

Relation (19) is of fundamental importance. It can also be written

$$T(dS + dS') = (T - T')dS' + (\psi - \psi')dY' \geq 0. \quad (20)$$

The term $T(dS + dS')$ is an energy dissipation function representing energy of internal processes in the system. It represents energy converted into heat in the process of transferring charges dS' and dY' from potential levels T' and ψ' to T and ψ . Meixner² has related this dissipation function to the energy of diffusion, heat flow, and viscosity in the system during irreversible processes. As we shall see, this term has the properties of Brønsted's "energetic heat evolution."¹

Now we notice that the transfer of thermal charge δS and the transfer of work charge dY between system and surroundings are independent processes. Consequently from (19) we find an inequality on each of the two fields.

$$(T - T')\delta S \leq 0 \quad (21)$$

$$(\psi - \psi')dY \leq 0. \quad (22)$$

Relation (22) substituted into (18) shows that

$$TdS - T'\delta S \geq 0 \quad (23)$$

a relationship which, as we shall see, reduces to the ordinary statement of the second law of thermodynamics. At equilibrium, when, according to (15), $dS = \delta S$, we find from (19) that

$$T = T' \quad \text{and} \quad \psi = \psi'. \quad (24)$$

We define a reversible process between system and surroundings as one in which there are only infinitesimal differences between the potentials of the system and those of the surroundings. At any stage in the process, equilibrium conditions pre-

vail between system and surroundings so that $dS = \delta S$. Such processes, of course, take an infinite time. Notice that our use of the term equilibrium is in a different sense from its use in statements such as "Supercooled water is not at equilibrium." This statement is concerned with the stability of one state of the system as compared to another possible state. We allow the possibility of supercooling water reversibly with equilibrium prevailing between system and surroundings. It is only necessary that the temperatures (and other potentials) of the system and surroundings be in balance throughout the process. For any reversible processes the dissipation function is zero. The magnitude of the dissipation function is the criterion of the degree of irreversibility of a process.

According to (22) a directional condition governs the motion of dY between system and surroundings. Charge moves from higher to lower potential. This is similar to the condition in relation (7) for the motion of δZ in a conservative ϕ - Z field. However, ψ - Y energy is not conserved except for $\psi = \psi'$ or for $dY = 0$, when the equality holds in (22), so that

$$\psi dY + \psi' dY' = 0.$$

If this equation were true for $\psi \neq \psi'$ and $dY \neq 0$, it would follow from (22) that $dY > \delta Y$ which contradicts our assumption (14). Except when $\psi = \psi'$ or $dY = 0$ it is necessary to combine thermal energy with work energy to make a conservative energy field.

For thermal energy likewise, according to (21), a directional condition governs motion of entropy between system and surroundings. Entropy moves from higher to lower potential. From (20) we see that when $\psi = \psi'$ or $dY = 0$, the thermal energy is also conserved.

$$TdS + T'dS' = 0.$$

If we restrict the changes in the ψ - Y field to P - V changes only, then, according to (17), $dY = 0$ implies constant volume and $\psi = \psi'$ implies equality of pressure between system and surroundings. These are the conditions for constant volume and constant pressure (i.e., $P = P' = \text{constant}$) calorimetry, respectively, so that in ordinary calorimetric processes the thermal energy and work energy are individually conserved.

Let us now define two terms which will enable us to present the ordinary statements of the first and second laws of thermodynamics as results of our previous discussion. Define

$$\begin{aligned} dq &= -T'dS' & \text{or} & & dq &= T'\delta S \\ dw &= \psi'dY' & \text{or} & & dw &= -\psi'dY. \end{aligned} \quad (25)$$

dq is the heat entering the system from the surroundings and dw is the work done upon the surroundings. From (16) and (18) we find

$$dE = T'\delta S + \psi'dY \quad (26)$$

and therefore

$$dE = dq - dw \quad (27)$$

which is the usual formulation of the first law of thermodynamics. From (23) and (22) we find

$$dq \leq TdS \quad (28)$$

$$dw \leq -\psi dY. \quad (29)$$

Relations (28) and (29) are the usual expressions of the second law of thermodynamics. Each implies the other because of (18) which can be written

$$TdS - dq = -\psi dY - dw \geq 0.$$

At this point we have divided the total energy field into two parts. ψ - Y energy has been given the generic name of work energy to distinguish it from T - S or thermal energy. In the absence of other work terms it reduces to pressure-volume work. However, it is often necessary to subdivide the ψ - Y energy into several component fields as shown in Eq. (17). Let us designate as π - K fields the component fields of the ψ - Y work field. From (14)

$$\sum dK = \sum \delta K \quad (30)$$

and from (22)

$$\sum (\pi dK - \pi' \delta K) \leq 0, \quad (31)$$

the summation being over all the component π - K fields. Define

$$dg = \pi' dK' = -\pi' \delta K \quad (32)$$

so that

$$dw = \sum dg = -\sum \pi' \delta K. \quad (33)$$

Examples of various types of π - K energy are:

π	K	dK	dg	Type of Energy
P	V	$-dV$	$P'\delta V$	Pressure-volume
μ_i	m_i	dm_i	$-\mu_i'\delta m_i$	Chemical
\mathcal{E}	ϵ	$d\epsilon$	$-\mathcal{E}'\delta\epsilon$	Electrical.

It may often be true that $dK = \delta K$ as in the case where K represents the volume V . We shall assume

$$dV = \delta V \quad (34)$$

so that for P - V work

$$dg = P'dV. \quad (35)$$

Also, in the absence of chemical reactions in the system

$$dm_i = \delta m_i.$$

However, if reactions occur, dm_i , the gain in mass of substance i in the system, may be different from δm_i , the mass entering from the surroundings. But in either case

$$\sum dm = \sum \delta m_i \quad (36)$$

since in all ordinary processes mass is conserved. We readily see from this discussion that the logical unit of charge for chemical energy is the unit of mass. It is a widespread custom among chemists to take the mole as the unit of charge so that μ_i is a partial molal quantity rather than a partial mass-unit quantity. For many purposes this is satisfactory and advantageous. But if we replace m_i by n_i , the number of moles of substance i , none of Eqs. (14), (30), or (36) will hold.

Now if we write (31) in the form

$$\sum \pi(dK - \delta K) + \sum (\pi - \pi')\delta K \leq 0$$

we see that

$$\sum \pi(dK - \delta K) \leq 0 \quad (37)$$

and

$$(\pi - \pi')\delta K \leq 0 \quad \text{or} \quad dg \leq -\pi\delta K. \quad (38)$$

Relation (38) gives a directional condition governing motion of δK between system and surroundings. At equilibrium the equality holds in (37) and $\pi = \pi'$ in (38).

When $dK = \delta K$ for any of the π - K fields we find from (38) that

$$(\pi - \pi')dK \leq 0 \quad \text{or} \quad dg \leq -\pi dK. \quad (39)$$

Such a π - K field is independent of the other fields. The increase in charge results only from charge entering from the surroundings; none is formed within the system at the expense of the charge functions of the other π - K fields. The number of independent π - K fields in the total work field is the number of π - K fields for which

$dK = \delta K$. In the case of chemical fields this number is known as the number of "components" of the system. Relation (39) is a generalization to the individual π - K fields of the second law of thermodynamics given in (29). It is true only for those fields *for which* $dK = \delta K$ (as, for example, in the cases where K represents V or $\sum m_i$).

From this point on, whenever we refer to a π - K field we shall mean one for which $dK = \delta K$ so that relation (39) will apply.

We have now concluded the discussion of the principles of thermodynamics. The remainder of the paper will be concerned with application and development of the concepts already presented. Let us summarize the important postulates on which our formulation of thermodynamics is based.

1. A system is defined by its energy fields, each of which is characterized by a potential function and a charge function. This is the assumption which limits classical thermodynamics to treatment of systems in "states."

2. Energy is conserved according to Eqs. (3) or (5).

3. The total energy field is conservative in the sense of relation (7); i.e., there exists a potential function whose gradient regulates motion of the total charge function.

4. The total energy field can be subdivided into a thermal field and work fields, the thermal field having the property that $dS \cong \delta S$ and the work fields having the property that $dK = \delta K$.

Postulate (2) is, of course, equivalent to the first law of thermodynamics; postulates (3) and (4) imply the usual statement of the second law but also allow formulation of the important relation (19) for the dissipation function.

It was suggested by the reviewer of this article that reference be made to the formulation of thermodynamics presented by C. Caratheodory⁴ and by M. Born.⁵ These authors have shown that for reversible processes dq has the form of a Pfaff differential expression. A consequence of their statement of the second law (Caratheodory's principle) is that for reversible processes dq has an integrating factor which can be defined as the temperature T and that the resulting exact differential dq/T defines the entropy. By this

approach the authors are able to relate some problems of thermodynamics to the mathematical structure built around the Pfaff expressions. This development of the subject appears to have certain deficiencies:

1. It is not readily extended to give information about irreversible processes. For such processes, of course, dq does not have the form of a Pfaff expression. The important result in relation (19) for the energy dissipation, which clarifies the nature of irreversible processes, is not obtainable since the distinction between heat entering the system from the surroundings and the heat generated within the system is not made.

2. There is undue emphasis on the unique properties of heat. There seems to be little more reason to introduce the temperature as an integrating factor for the heat than to define the pressure, for example, as an integrating factor for pressure-volume work. We have, in this paper, introduced T and S on an equal basis with the other potentials and charges of the system.

THE PHASE RULE

If we consider a system whose energy is divided among T - S , P - V , and chemical energy fields, the number of chemical "components" C is one less than the number of π - K fields, the remaining π - K field being, of course, the P - V energy. C is the number of chemical fields for which we can write $dK = \delta K$. The total number of fields is therefore $C+2$. If the total energy of this system is specified, the energy of $C+1$ fields can be varied arbitrarily. The distribution of energy among the various fields determines the properties of the system. All the "intensive" properties of the system are determined when $C+1$ variables are fixed.

Our considerations so far have dealt with a homogeneous system characterized by a single value for each independent variable throughout. Consider now a system which is not necessarily a single phase but which may have different values for the potential functions within its boundaries. Assume there are p homogeneous phases in the system and that the system is so isolated that no form of energy is exchanged with the surroundings.

$$\sum_p T_p dS_p \cong 0, \quad \sum_p \pi_p dK_p \leq 0. \quad (40)$$

⁴ C. Caratheodory, Math. Ann. **67**, 355 (1909).

⁵ M. Born, Physik. Zeits. **22**, 218, 249, 282 (1921).

At equilibrium

$$\sum_p T_p dS_p = 0, \quad \sum_p \pi_p dK_p = 0, \quad (41)$$

and

$$\sum_p dS_p = 0, \quad \sum_p dK_p = 0. \quad (42)$$

Hence at equilibrium T and π are uniform throughout the system. Each form of energy is at one potential level in an isolated system at equilibrium.

Even though the system is not isolated the potentials must nevertheless be uniform throughout. This follows from the fact that the composite system formed of the system and its surroundings is itself completely isolated so that at equilibrium the potentials are uniform throughout the composite system. But the system considered is a part of the composite system and therefore at equilibrium it must be at constant potential.

This result enables us very simply to derive the phase rule. The number of independent variables in p separate phases is $p(C+1)$. If these phases are parts of a system at equilibrium they must all be at the same potentials, a condition which imposes $(C+2)(p-1)$ relationships on these variables. The number of independent variables remaining for the system is

$$f = p(C+1) - (C+2)(p-1) = C - p + 2. \quad (43)$$

DERIVED FUNCTIONS

As a result of our previous discussion certain facts about the derived functions H , A , and F are clearly brought out. Define

$$H = E + PV \quad (44)$$

$$A = E - TS \quad (45)$$

$$F = H - TS. \quad (46)$$

According to the first law and Eqs. (33) and (35)

$$dE = dq - dw = dq - P'dV - dw^*, \quad (47)$$

$$dE \leq TdS - dw = TdS - P'dV - dw^*, \quad (48)$$

where dw^* includes all the work done on the surroundings other than P - V work. If the system undergoes a change at constant volume with $dw^* = 0$, then $dE = dq$.

$$dH = dq - P'dV - dw^* + PdV + VdP \quad (49)$$

$$dH \leq TdS - P'dV - dw^* + PdV + VdP. \quad (50)$$

If the pressure of the system P equals the pressure of the surroundings P' and is constant, and if furthermore $dw^* = 0$, then $dH = dq$. The increase in enthalpy equals the heat of reaction for the type of reaction carried out in an open vessel so that the pressure of the reaction mixture is always atmospheric pressure and no work other than pressure-volume work against the atmosphere is performed.

$$dA \leq -SdT - dw. \quad (51)$$

At constant temperature

$$-dA \geq dw. \quad (52)$$

The increase in work function for a system in an isothermal process is the negative of the maximum work of the process. In an isothermal process for which $dw = 0$

$$-dA \geq 0. \quad (53)$$

Therefore, at equilibrium in a system at constant temperature which can do no work against the surroundings, $dA = 0$ and A is a minimum.

$$dF \leq -SdT - P'dV - dw^* + PdV + VdP. \quad (54)$$

If the temperature of the system is constant and if the pressure of the system P equals that of the surroundings P' and is constant then

$$-dF \geq dw^*. \quad (55)$$

If we use the term "available work" to describe dw^* , then the increase in free energy of a system in an isothermal process such that the pressures of the system and surroundings are equal and constant is equal to the negative of the maximum available work. If $dw^* = 0$ in such a process then

$$-dF \geq 0. \quad (56)$$

Therefore, at equilibrium in a system at constant temperature and pressure (where $P = P'$) which can do no work other than pressure-volume work against the surroundings, $dF = 0$ and F is a minimum.

GENERALIZATION OF KELVIN'S POSTULATE

We shall now investigate certain consequences of our generalized statement of the second law as given in relation (39).

Let a system operate through a cycle.

$$\oint dS = \oint dq_{\max}/T = 0.$$

If the cycle is performed at constant temperature

$$\oint dq_{\max} = 0.$$

Hence, for any isothermal cycle

$$q = \oint dq \leq \oint dq_{\max} = 0.$$

Since $\Delta E = 0$ for the cycle

$$w = q \leq 0.$$

Both w and q must be negative or zero. Heat cannot flow into the system and serve as a source of energy to do work upon the surroundings in an isothermal cycle. This statement of the second law is known as the Kelvin postulate.

Similarly during the cycle

$$\oint dK = \oint -dg_{\max}/\pi = 0.$$

If the cycle is performed at constant potential π

$$\oint dg_{\max} = 0.$$

Hence, for any cycle at constant potential π

$$g = \oint dg \leq \oint dg_{\max} = 0.$$

Therefore, it is impossible to extract any form of work from a system operating through a cycle at constant value of the corresponding potential. This generalization of the Kelvin postulate is a consequence of the generalized statement of the second law. If all the potentials are constant during a cycle, no work whatsoever can be extracted for use in the surroundings.

GENERALIZATION OF THE CARNOT CYCLE

Let a system operate through a cycle, absorbing heat q_1 reversibly at T_1 and rejecting $-q_2$ reversibly at T_2 . The process can be considered

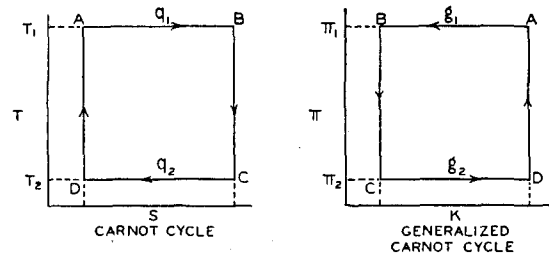


FIG. 1.

to occur in four steps as shown in the diagram: by two reversible isothermal steps AB and CD and two reversible adiabatic steps BC and DA (see Fig. 1).

$$\oint dS = q_1/T_1 + q_2/T_2 = 0. \quad (57)$$

Since $\Delta E = 0$ for the cycle

$$w_{\max} = q_{\max} = q_1 + q_2.$$

If $T_1 > T_2$ then $q_1 > -q_2$ so that $w_{\max} = q_{\max} > 0$. Heat is converted into work during the operation of the cycle. If $T_1 < T_2$ then $q_1 < -q_2$ and work is converted reversibly into heat.

$$w_{\max} = q_{\max} = q_1(T_1 - T_2)/T_1 = q_2(T_2 - T_1)/T_2. \quad (58)$$

These are the conditions obtaining in a Carnot cycle. Now

$$q_{\max} = T_1 \Delta S_1 + T_2 \Delta S_2.$$

But

$$\Delta S_2 = -\Delta S_1.$$

Let

$$\Delta S = \Delta S_2 = -\Delta S_1.$$

Then

$$q_{\max} = -(T_1 - T_2) \Delta S. \quad (59)$$

This is the expression for the maximum heat energy available for conversion into other forms of energy in the process of transfer of a charge ΔS from temperature T_1 to T_2 . The quantity q_{\max} does not depend at all on the nature of the system undergoing the cyclic operation. It depends only on the existence of the temperatures T_1 and T_2 between which the system operates. It is represented by the area $ABCD$ on the diagram with a sign depending on the relative values of T_1 and T_2 .

If the system undergoes a cycle in which it performs work g_1 reversibly at π_1 and receives

work $-g_2$ reversibly at π_2 as shown on the diagram, where AB and CD are two reversible changes at constant potential and BC and DA occur reversibly at constant charge, then

$$\oint dK = -g_1/\pi_1 - g_2/\pi_2 = 0. \quad (60)$$

$$g_{\max} = g_1 + g_2 = g_1(\pi_1 - \pi_2)/\pi_1 = g_2(\pi_2 - \pi_1)/\pi_2. \quad (61)$$

If $\pi_1 > \pi_2$, then $g_{\max} > 0$ so that π - K energy leaves the system. If $\pi_1 < \pi_2$, then $g_{\max} < 0$ so that π - K energy enters the system. Now

$$g_{\max} = -\pi_1 \Delta K_1 - \pi_2 \Delta K_2.$$

But

$$\Delta K_2 = -\Delta K_1.$$

Let

$$\Delta K = \Delta K_2 = -\Delta K_1.$$

Then

$$g_{\max} = (\pi_1 - \pi_2) \Delta K. \quad (62)$$

This is the expression for the maximum π - K work done in the transfer of charge ΔK from potential π_1 to π_2 . The quantity g_{\max} does not depend on the nature of the system undergoing the cyclic operation; it depends only on the existence of the potential levels π_1 and π_2 between which the system operates. It is represented by the area $ABCD$ on the diagram with a sign depending on the relative values of π_1 and π_2 .

That (62) is the expression for the maximum work can be verified by use of the generalized Kelvin postulate. Suppose that some more effective cycle could be found that would perform the same amount of work g_1 at π_1 but would receive less work $-g_2^0$ at π_2 . Let this cycle operate the reversible Carnot cycle in reverse. It will extract $-g_2^0$ at π_2 and deliver g_1 at π_1 . The reversed Carnot cycle will take up $-g_1$ at π_1 and deliver g_2 at π_2 . The net effect of the combined operation is to deliver $g_2^0 + g_2 > 0$ to the surroundings at a constant potential π_2 during a cyclic process. This contradicts the generalized Kelvin postulate.

It may be pointed out that just as a thermodynamic temperature scale can be defined as proportional to the absolute values of q_1 and q_2 in a thermal Carnot cycle, so a thermodynamic potential scale for any π can be defined proportional to the absolute values of g_1 and g_2 in a generalized Carnot cycle. We followed the reverse

procedure, introducing the temperature and other potential functions from the start. These functions we now see from (58) and (61) have the property of being proportional to the absolute values of the corresponding charges exchanged in a Carnot cycle.

BRØNSTED'S SYSTEM OF ENERGETICS¹

Let us write Eqs. (59) and (62) as

$$dq_{\max} = (T_2 - T_1) dS, \quad (63)$$

$$dg_{\max} = -(\pi_2 - \pi_1) dK, \quad (64)$$

$$\text{or} \quad dw_{\max} = -\sum (\pi_2 - \pi_1) dK. \quad (65)$$

We have here represented the maximum heat lost from the surroundings and the maximum work gained in the surroundings during the transfer of infinitesimal amounts of charge from one set of potential levels to another. The maximum energy which the surroundings can lose in these transfers is therefore

$$dE = (T_2 - T_1) dS + \sum (\pi_2 - \pi_1) dK.$$

But since these transfers are accomplished by systems operating through cycles, $dE = 0$, and therefore

$$(T_2 - T_1) dS + \sum (\pi_2 - \pi_1) dK = 0. \quad (66)$$

Equation (66) can be written

$$\begin{aligned} (T_2 - T_1) dS - (T_2 - T_1) \delta S \\ = -(T_2 - T_1) \delta S - \sum (\pi_2 - \pi_1) dK. \end{aligned}$$

But

$$\begin{aligned} (T_2 - T_1)(dS - \delta S) = T_2(dS_2 - \delta S_2) \\ + T_1(dS_1 - \delta S_1) \geq 0. \end{aligned}$$

Therefore, if we let $Q = (T_2 - T_1)(dS - \delta S)$

$$Q = -(T_2 - T_1) \delta S - \sum (\pi_2 - \pi_1) dK \geq 0. \quad (67)$$

We see at once the similarity between (67) and (19). Q is interpreted as the energy dissipation during charge transfer. If the transfer of charge occurs reversibly all the charges are transported unchanged in amount from one set of potentials T_1, π_1 to another set T_2, π_2 , and $Q = 0$. However, if the transfer is not reversible then entropy is produced and heat Q is evolved. In the reversible transfer of δS and dK , the potentials of the operating system are equal to those of the surroundings and no energy dissipation occurs. But

in the irreversible transfer, the potentials of the system and surroundings are not equal; the transfer of the same quantities of charge between the same potential levels in the system is accompanied by evolution of heat in the system.

Brønsted has made these results the basis of his system of energetics. He considers a "basic energetic" process to consist of the transfer of an amount of charge from one potential to another. The maximum energy of such a process is given by (63) or (64). In a reversible process, basic energetic processes are coupled so that the energy output of one drives another in reverse. The net effect is expressed by the equality sign in (67). This equation Brønsted calls the "work

principle." If the process is not reversible, not all the energy of one basic process is utilized in driving others in reverse, but part of the energy is dissipated as heat. This effect Brønsted calls the "heat principle." It is expressed by the inequality in (67). Hence we see that the fundamental postulates of Brønsted's formulation are direct consequences of our treatment. Brønsted's conception of thermodynamics appears entirely within the classical framework of the state of the system. It places needed emphasis on the dissipative aspect of energy processes. But it also is restricted to description of processes between definite states of the system, and is not designed to treat non-static systems with kinetic energy.

Frequency Spectrum of Crystalline Solids. III. Body-Centered Cubic Lattices

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This is a study of the dynamics of a Born-Karman atomic model of a body-centered cubic lattice developed with the assumption that only interactions between nearest and next nearest atomic neighbors are significant. The equations of motion of these systems are derived and the secular equations are given from which one can calculate the frequencies of the crystal's normal modes of vibration. From the secular equations the moments of the frequency spectrum are determined and by solving the "moment problem" the frequency spectrum itself is obtained as a function of the force constants of the lattice. There are two maxima of approximately equal height in the frequency spectrum. Asymptotic expressions are derived for the specific heat of a body-centered cubic lattice which are valid at high and low temperatures.

INTRODUCTION

IN this paper we shall present a theory of atomic vibrations in a body-centered cubic lattice and use this theory to develop equations for the thermodynamic properties of solids with such lattices. First the equations of motion for atoms in body-centered lattices will be derived under the assumptions: (a) that the interatomic forces are sufficiently short ranged so that only interactions between nearest and next nearest neighbors contribute to the total potential energy of the crystal; (b) the temperature of the crystal is low enough so that all internal vibrations are

essentially harmonic. Then we shall find the moments of the frequency spectrum and, in the manner described in the other papers of this series,¹ we shall find the frequency spectrum as a function of the lattice constants. From these quantities, expressions will be obtained for the specific heat at high and low temperatures.

I. EQUATIONS OF MOTION

Let us consider a monatomic crystal with a body-centered cubic lattice containing N lattice points in each direction and a total of $2N^3$ atoms. Such a lattice can be conceived of as two inter-

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¹ E. Montroll, *J. Chem. Phys.* **10**, 218 (1942); **11**, 481 (1943).