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Entropy: A Modern Discussion

Recently it occurred to the writer that a basic method of measuring entropy changes appears to be incongruent with its definition. Indeed, we determine the temperature dependence of the entropy of an object in a calorimeter by introducing energy with the aid of an electric coil and dividing the energy increase by the temperature. But conventionally one defines the entropy increase as the quotient of the *reversibly* introduced *heat* and the temperature. What we actually are doing is introducing not heat but *electric energy* in an *irreversible* process.

To be sure, the calorimetric method is not contradictory to the definition and can be justified by an appropriate discussion. But this procedure inevitably contributes to the impression that thermodynamics is a collection of tricks. Circuitous arguments should be replaced by a straightforward presentation which leads directly to the desired result without the necessity of introducing restrictive or enlargening afterthoughts.

Essentially such a presentation has been possible since the first decade of this century. But Carathéodory[1] as well as Buchdahl[2] concentrated on mathematical problems and did not make use of the opportunity of developing a clear and simple presentation. The following discussion attempts to develop the seed planted by Carathéodory. Our objective is a logically straight path between traditional sloppy thinking and unnecessary formal encumbrances.

It has not always been realized how wide the scope of thermodynamics is. Actually it encompasses all physical sciences as far as equilibrium or changes near equilibrium are concerned. The special sciences branch out in the investigation of kinetic and dynamic problems. But the traditional method of discussing relations between volume, pressure, and temperature and then cavalierly applying the results to entirely different questions must be replaced by the introduction of non-prejudicial, sufficiently general terms. This will be done in the two following sections.

The State of an Object

An *object* can be isolated from all influences of the environment; it also can be changed according to our pleasure by specific interactions with other objects. We can reduce the volume of a gas enclosed in a cylindrical vessel by putting a weight on a piston. Or we can charge a storage cell by connecting it with another galvanic cell or with a generator. Thus we select a set of independent variables that describe the object. They are called *generalized coordinates.* We restrict this term to properties that can be individually changed by means of a proper interaction mechanism while at the same time all others are kept unchanged. In addition to the volume and the electric charge, a number of other properties satisfy the requirements of generalized coordinates, e.g., the amounts (numbers of moles) of any components, the altitude, the length of a coil spring, the surface (interface) area, and so on.

In the investigation of a physical problem it is usually helpful to ask for the number of independent variables. Obviously this number cannot be smaller than the number h of the generalized coordinates that we have introduced to describe the object. We have to ask whether the number of independent variables describing the state of an object for a given problem is equal to h or greater. In other words, if we have attained a set of desired values for the h generalized coordinates (by interaction with other objects) and we keep these coordinates constant, can we still change the properties? The answer is yes, namely, by contact with another object or *thermal interaction.* We have no generalized coordinate for this kind of interaction. We can prevent it (ideally) by enclosing the object in a vacuum jacket; any change of the object under these conditions is called *adiabatic.* Thermal interaction gives us an opportunity to vary the state of an object at constant coordinates. But now the interaction possibilities are exhausted: The number of independent variables is $h + 1$. They determine the *state* of the object.

In addition to the generalized coordinates, one more property must be chosen as an independent variable.

Work and Energy

If we establish interaction between two objects with respect to one coordinate, one of three changes can occur: a change in one direction, in the opposite direction, or no change at all. For instance, if the objects are weights that we put on the pans of a balance, the left pan can go down or up, or stand still. We say that the gravitational force acting on the left-hand weight is greater or smaller than that on the right-hand weight, or that the two gravitational forces are equal. In another example we connect a capacitor and a galvanic cell and observe the transfer of charge. We say that the original voltage of the capacitor was higher or lower than, or equal to the voltage of the galvanic cell.

Thus we may define *generalized forces* (gravitational force, voltage, and so on), conjugate to generalized coordinates (altitude, electric charge, and so on). It can be shown[3] that these observations (higher, lower, or equal) are sufficient for a definition of the generalized forces.

If we wish to change an object to a certain state (e.g., compress a gas to a certain volume V), the force f^e (pressure) we must apply by means of a second object is a natural measure of the instantaneous effort we have to make. It must be equal to or larger than the force f exerted by the object. This holds for any generalized force f and its conjugate coordinate x. The total external effort for changing an object from an initial state I to a final state F along the coordinate x^e of the second object is

$$w = -\int_I^F f^e \mathrm{d}x^e \qquad (1)$$

If the interacting system is sufficiently close to equilibrium at every instant during the change, the force f exerted by the object under consideration is equal to the external force f^e. In this case the change is called *reversible* and the reversible work done upon the object is

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[1] Carathéodory, C., *Math. Ann.*, **67,** 355 (1909).

[2] Buchdahl, H. A., *Amer. J. Phys.*, **17,** 41,44,212 (1949); **22,** 182 (1954); **23,** 65 (1955); *Z. Phys.*, **152,** 425 (1958); Buchdahl, H. A., and Greve, W., *Z. Phys.*, **168,** 386 (1962).

[3] Redlich, O., *J. Phys. Chem.*, **66,** 585 (1962); *Rev. Mod. Phys.*, **40,** 556 (1968); J. CHEM. EDUC., **49,** 222 (1972).

$$w_{\text{rev}} = \int_{x_I}^{x_F} f\mathrm{d}x \tag{2}$$

The positive sign results from the fact that in the interaction[3] the external coordinate x^e changes in the direction opposite to the internal coordinate x.

The first law can now be formulated in this way: The work required to change an object *adiabatically* from a state I to a state F is always the same. We call this adiabatic work the *energy* change $E_F - E_I$ and note that the energy E is a function of the state as soon as a zero level is arbitrarily fixed. For any non-adiabatic or *diathermane* change one defines the heat q introduced into the object by

$$q = E_F - E_I - w \tag{3}$$

or, for a small change,

$$q = \mathrm{d}E + f^e\mathrm{d}x^e \tag{4}$$

If the change is reversible, we may write

$$q_{\text{rev}} = \mathrm{d}E - f\mathrm{d}x \tag{5}$$

In this case the heat can be expressed by the variables of state of the object under consideration.

A Single Coordinate

The preceding discussions have introduced, in a very abbreviated way, the concepts that we need for the main problem, the direction of the change occurring after interaction between two objects has been established. Actually this question has been settled before for changes depending on a single generalized coordinate by the introduction of the concept of force. The problem of many coordinates cannot be solved by a plain generalization of the simpler case, but a discussion of this case will be useful.

If in a process only a single coordinate is to be introduced, then the state of the object depends, according to the section The State of an Object, on two independent variables. All states therefore can be represented in a plane. In the figure we take the coordinate x (e.g., the electric charge of a galvanic cell) as the abscissa, the energy as the ordinate. Starting from an initial state I we may represent an adiabatic-reversible change by the curve F_a; the slope of the curve is according to eqn. (5) the generalized force f (i.e., the voltage of the cell).

If we take a galvanic cell as an example, the part of the curve F_a to the right of the initial point I represents a reversible charging process (reversible increase of energy); the part of curve F_a to the left of I represents reversible discharging. Such reversible changes can be closely approximated with a lead storage cell.

This example, however, serves only as an illustration. The diagram represents just as well the bending of an elastic rod, the compression of a gas, the extension of a soap film, the formation of ammonia from the elements, and any other change proceeding near equilibrium.

The diagram also shows irreversible-adiabatic changes. Such changes are indicated by the two arrows in the figure. Along the horizontal arrow the energy does not change, i.e., no work is done although the coordinate decreases. In our example this means that the charge decreases without the cell doing any outside electric work; in other words, there is a short circuit, which may be accompanied by irreversible chemical reactions or simply by warming up. The vertical arrow signifies energy increase at constant coordinate. This happens if electric energy is impressed on a storage cell that does not accept any charge; here again chemical reactions (hydrogen evolution) and warming up take place.

Since a plane furnishes a complete representation of all states of an object characterized by a single coordinate, the diagram must also show diathermane changes. Such a change, the conduction of the heat q (fig.) into the object without change of the coordinate x, is shown by the vertical arrow. If heat is conducted away from the object, the change is represented by a vertical arrow down. These diathermane changes may be reversible or irreversible; the diagram does not show any difference. If we include diathermane changes, every point in the diagram can be reached from any other point by means of changes of the coordinate and thermal interaction.

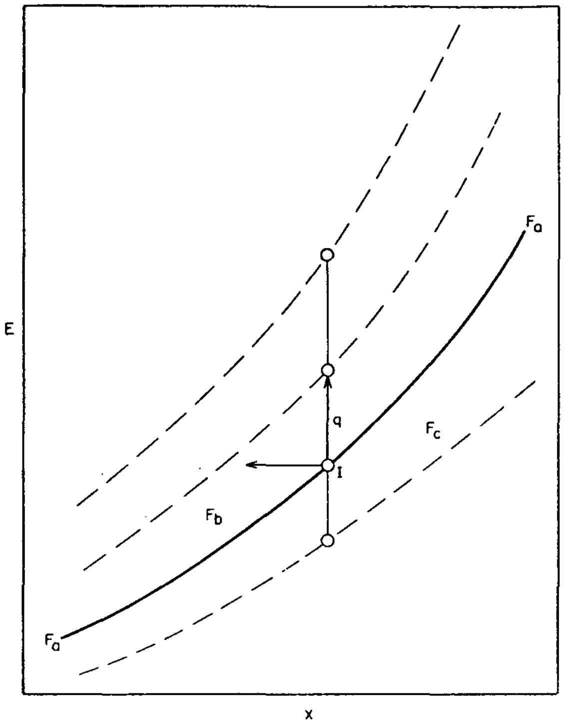

Diagram of the energy E and a single coordinate x.

In an adiabatic change, however, the representative point is restricted: If the change is adiabatic-reversible, it can move only along the curve F_a. In an adiabatic-irreversible change it can move, as we have seen, in the direction of either of the two arrows. By a combination of irreversible changes (not excluding reversible changes) it may also move in any direction between the two arrows or between an arrow and the curve F_a. In other words, from the initial state I the object may change adiabatically to any state in the field F_b (fig.) lying above the curve F_a. But in any *adiabatic* change it *cannot* change to a state in the field F_c lying below the curve F_a. The curve F_a is the border line between the states F_b that are adiabatically accessible from I and the states F_c that are adiabatically inaccessible.

In this discussion we have made use of the first law, but we have nowhere introduced the second law.

Entropy

It is obvious that we should like to generalize the results of this discussion to the case of more than one coordinate. Instead of the plane of the figure we should introduce a spatial diagram with a surface taking over the properties of the reversibility curve F_a, and two half-spaces replacing the fields F_b and F_c. This indeed can be done for two coordinates, but for three or more coordinates the possibility of such a generalization depends on the existence of certain relations between the generalized forces and coordinates ($\partial f_i/\partial x_k = \partial f_k/\partial x_i$) which do not necessarily follow from the definitions.

We adopt, however, as the principle[4] of the *second law*,

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[4] The principle goes back to Carathéodory (see footnote 1). His formulation is more elegant but less suitable for a plain presentation.

derived from observation, that all states of an object belong to one of three classes: (1) States F_a that can be reversibly-adiabatically reached from an initial state I. (2) States F_b that can be irreversibly-adiabatically reached. (3) States F_c that cannot be reached adiabatically.

Now we may adopt the figure as a symbolic representation of the general case of $h + 1$ dimensions. The reversibility line F_a becomes a hyper-surface which divides the multidimensional space into two half-spaces F_b and F_c.

We have not introduced any restrictive assumption concerning the state I. For this reason, a hyper-surface F_a goes through every point. A few such hyper-surfaces are indicated by broken lines in the figure. No two of the hyper-surfaces can cross; if they did, all points of both would be reversibly-adiabatically accessible from every other point, i.e., they would belong to the same hyper-surface.

Since the hyper-surfaces F_a are distinct from one another, we can assign a different number to each one. We call the number the *entropy* S; the reversibly adiabatic hyper-surfaces are called isentropics. The entropy has a definite value at every point of the state space spanned by the state variables E and x, and may therefore be regarded to be a function of these variables.

The direction of the numbering of the isentropics is at first arbitrary; it has been fixed in such a way that an entropy value $S_F > S_I$ is assigned to an isentropic that can be reached adiabatically (irreversibly) from an isentropic with the entropy S_I. In other words, the entropy of an adiabatically enclosed object increases in an irreversible change, and it stays constant in a reversible change; but it cannot adiabatically decrease.

The entropy of a system consisting of two objects with the entropies S' and S'' is chosen[5] to be

$$S = S' + S'' \tag{6}$$

Thus we make sure that the entropy of the system increases if either of the (adiabatically enclosed) objects undergoes an irreversible change.

Temperature

The vertical distance between two isentropics in the figure varies from point to point. If we denote by $\mathrm{d}S$ the (small) difference in S of two neighboring isentropics, the vertical distance $\mathrm{d}E$ may be represented with the aid of a new state function T as $T\mathrm{d}S$. Thus we define the temperature

$$T = (\mathrm{d}E/\mathrm{d}S)_x \tag{7}$$

and we have to show that T has indeed the qualities which we are used to ascribing to the temperature. This means that in thermal contact energy flows from the higher to the lower temperature.

We consider two heat reservoirs with the energies E' and E'', the entropies S' and S'', and the temperatures T' and T''. The system is isolated so that for any change, in view of eqn. (7)

$$\mathrm{d}E = \mathrm{d}E' + \mathrm{d}E'' = 0 \tag{8}$$

$$\mathrm{d}S = \mathrm{d}S' + \mathrm{d}S'' = \frac{\mathrm{d}E'}{T'} + \frac{\mathrm{d}E''}{T''} \tag{9}$$

Introducing eqn. (8) into eqn. (9) we have

$$\mathrm{d}S = \mathrm{d}E'\left(\frac{1}{T'} - \frac{1}{T''}\right) \tag{10}$$

Since the total entropy S can only increase, $\mathrm{d}E'$ is positive if $T'' > T'$. This means that the energy E' of the first object goes up if it is at the lower temperature.

Thus the temperature behaves similarly to a generalized force.

State Functions and Processes

For an object described by several generalized coordinates x_i and forces f_i we derive from eqn. (5)

$$(\partial E/\partial x_i)_S = f_i \tag{11}$$

because $q_{\mathrm{rev}} = 0$ for a change proceeding in an isentropic, i.e., reversibly-adiabatically. We may combine this relation with eqn. (7) to

$$\mathrm{d}E = T\mathrm{d}S + \Sigma f_i \mathrm{d}x_i \tag{12}$$

This relation does not contain any reference to a process, reversible or irreversible. It is a relation between state variables and is meaningful if all variables are well defined. This condition is *not* satisfied, for instance, while we drop a hot metal into a cold liquid as in an old-fashioned method for determining heat capacities; it is *not* satisfied during the expansion of a gas into an evacuated vessel because the pressure of the gas is not defined.

But one should not conclude that relation (12) can be applied only to reversible processes. The flow of water in a pipe may be irreversible; but we can measure the pressure at any point by means of a U-tube or any other gauge. The flow of heat in a copper rod between two heat reservoirs is irreversible; but suitable thermocouples tell us the temperature at any point. In a calorimeter we introduce the energy $\mathrm{d}E$ by means of an electric heating coil; at constant volume ($\mathrm{d}x_i = 0$) we calculate $\mathrm{d}S$ as $\mathrm{d}E/T$. At constant pressure or under other conditions we still use eqn. (12) for the computation of the entropy increase even if the process is irreversible, provided only that the quantities in eqn. (12) are well defined.

The present definition is immediately applicable in irreversible thermodynamics and furnishes there a starting point which is not subject to any question.

By means of eqn. (12) we have released the entropy from the burden of a connection with reversible processes. The conventional definition

$$\mathrm{d}S = q_{\mathrm{rev}}/T \tag{13}$$

follows of course from eqns. (5) and (12), but it is unnecessarily restrictive. It is a residue from the old times when all fundamental relations in thermodynamics were derived from reversible cycles. It is time to throw off this burden.

The author appreciates an interesting discussion with Professor Richard T. Beauboeuf, University of Houston.

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[5] This is the simplest choice satisfying the necessary condition of combination. Other choices would be possible but they would not change any of the essential conclusions. The only effect would be a complication.

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