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The Thermodynamics of Plastic Deformation and Generalized Entropy

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INTRODUCTION

THE entropy of classical thermodynamics is defined only as a difference for a final and an initial state of a system, subject to the restriction that the final state can be reached by some reversible process from the initial state. Classical thermodynamics has had comparatively little to say about irreversible processes and that little has been of a qualitative character, to the effect that during an irreversible process there is an ineradicable increase of the total entropy of the universe. But how much the increase is or where it is located is not specified, and in fact the increase of entropy itself has meaning and is defined only if reversible processes exist by which every part of the universe may be brought back from its final to its initial state. But it is safe to say that the majority of actual processes are irreversible, and worse still, most of the objects of daily life, such as a plastically strained metal exhibiting hysteresis, are completely surrounded by irreversibility, it being impossible to leave the present state of the body by any path whatever that is not irreversible in detail. The classical entropy concept is thus a concept which is applicable only to a highly idealized set of conditions and is not applicable, *in principle*, to the commonest situations of daily life. Yet the entropy concept and the associated second law of thermodynamics are commonly thought to formulate one of the most sweeping generalizations that can be made.

Recently there has been a growing feeling that some extension of the methods and definitions of classical thermodynamics should be possible in order to deal more adequately with irreversible phenomena. Physics, whether we choose to call it thermodynamics or not, should not be impotent in the face of any situation which can be completely characterized by measurements with macroscopic instruments. Yet many essentially irreversible processes can be completely characterized in terms of a few simple measurements. For instance, the irreversible process of heat conduction is exhaustively characterized in terms of a temperature gradient and the thermal conductivity of the material, and the irreversible generation of Joulean heat is fixed by current density and specific electrical resistance. A number of years ago[1] I attempted to generalize the thermodynamic method of attack by postulating that each of these essentially irreversible processes always has associated with it its own characteristic rate of entropy increase, whether or not other processes are occurring simultaneously. It was easy to write a detailed quantitative expression for this characteristic entropy increase. An application of this point of view to the thermoelectric circuit made possible a deduction of the Kelvin relations free from the universally recognized logical objections to Kelvin's analysis. The application of this method to the thermoelectric problem was later reformulated in my book, *The Thermodynamics of Electrical Phenomena in Metals*, and applied to several other situations presented by electrical phenomena in metals. Eckart[2] later discussed the processes of flow in a viscous liquid and of diffusion down a concentration gradient, two essentially irreversible processes which can be exhaustively described in terms of a few simple measurements. In proving in detail that these processes are always accompanied by an increase of entropy, he found the characteristic increase of entropy to be associated with them. More recently, Tolman and Fine,[3] in a summarizing article dealing with irreversibility, have explicitly adopted the point of view that there are characteristic increases of entropy and have discussed the application to the sort of examples just mentioned.

The same method of approach should be applicable to every other situation in which there are reproducible phenomena which can be described in terms of finite measurements with finite instruments. One, of course, makes the first attack on the simple situations. In this paper I discuss some of the aspects of extending this point of view to certain irreversible processes taking place in solids. The cases previously considered have had this simplifying feature in common, namely, that the body which is the seat of the irreversible phenomena is itself in a steady state, so that its entropy can be taken as constant, as e.g., a piece of metal in which heat is steadily flowing down a constant temperature gradient. We now desire to extend the treatment to such systems as a metal showing hysteresis in the relation between stress and strain, where part of the problem is to assign an entropy to the body which is the seat of the irreversibility. There is a twofold problem here—the problem of extending the conceptual machinery so as to be capable of handling the new situations, and the experimental problem of finding what the facts are in the new domain. We shall be concerned almost not at all with the latter aspects of the problem, mostly for the reason that there is practically no experi-

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[1] P. W. Bridgman, Proc. Nat. Acad. Sci. **15**, 765 (1929); **18**, 242 (1932); *The Thermodynamics of Electrical Phenomena in Metals* (Macmillan Company, Ltd., London, 1934), especially Chapter II and pp. 120–122, 136, 141, and 147.

[2] C. Eckart, Phys. Rev. **58**, 267, 269 (1940).

[3] R. C. Tolman and P. C. Fine, Rev. Mod. Phys. **20**, 51 (1948).

mental knowledge of the properties of plastically strained bodies over the range of conditions demanded by a thermodynamic approach. For instance, probably no attempt has been made to find whether there is any connection between stress hysteresis and temperature hysteresis.

Apart from the experimental problem, there is a very real conceptual problem here, as has already been suggested by the fact that the entropy concept is not applicable in principle to a system completely surrounded by irreversibility, as is any plastically deformed solid. In the following I shall endeavor to show that the concept of entropy and related points of view may be plausibly extended to handle what we may anticipate to be the experimental situation in the domain of certain irreversible phenomena in solids. There will be a certain intrinsic interest in this; it will at least show that the method of attack of thermodynamics does not lead to a logical impasse when applied to common situations. Whether the conceptual extensions which we find suggested will prove to be the best possible with which to meet the actual experimental situation will have to await more adequate experimental knowledge.

GENERALIZED "STATE"

The recognition that there may be states completely surrounded by irreversibility makes necessary a reexamination of the concept of "state" on which thermodynamics is based. Ordinarily the state of a body is characterized by all the measurable properties of the body. The dilemma which presents itself when the state is completely surrounded by irreversibility is how to assign operational meaning to "*all* the measurable properties" when measurement of a single property such as thermal expansion, for instance, which involves a displacement of temperature, removes the body irreversibly from its initial state so that we may not then return to the initial state to measure some other property. The dilemma may be resolved by the assumption of the possibility of an indefinite number of replicas of the original system, all in the same state. Any desired property which determines the state may then be found, in spite of the island of irreversibility, by making the appropriate measurement on a fresh replica. Identical replicas may be prepared by starting each replica from the same initial condition (the initial condition by hypothesis not being subject to insular irreversibility) and subjecting it to the identical history. For instance, the "state" of a given piece of plastically deformed steel is described in terms of the measurements which can be made on a number of replicas prepared by starting from similar pieces all cut from the same homogeneous cast ingot and subjected to the same subsequent history. The "state" is determined by the instantaneous values of certain parameters *and their history.* It is instructive to see how in a situation like this we have extended the ordinary operational meaning of such a concept, for example, as "sameness." For by hypothesis, we are estopped from applying our ordinary operational test to check whether all the properties of the so-called "identical" replicas are the "same," and can only say that they must be the same because we see no reason why they should be different. We have here a situation where a desired extension in meaning demands the cooperation of the "principle of sufficient reason." We have not thereby, however, departed from our operational requirement on our concepts, because we give an operational characterization of the conditions under which we say that the principle of sufficient reason applies.

One is strongly reminded here of the situation in wave mechanics where the only meaning that can be given to "identical" systems is, systems that have been identically "prepared." I suspect there are other situations where dilemmas which are apparently forced on us by wave mechanics could be shown by a more searching analysis to already exist in classical physics.

We recognize, then, that the possibility of insular irreversibility demands an extension of the fundamental notion of "state," and that this extension can easily be made in the framework of traditional points of view. In extending classical thermodynamics to irreversible systems and processes, we shall now assume that the difficulties all arise from the entropy concept and the second law, and that the first law is valid. In particular, we shall assume that the system has an internal energy, and that this energy is recovered when and if the state is recovered. "Insular irreversibility" does not necessarily mean non-recoverability, but it is possible that the intial state may be recovered under proper conditions by a finite excursion. The simplest example is of a material which has been put into a steady state by being put through many cycles of stress—each cycle is accompanied by a hysteresis loop, and any displacement from any point of the loop is essentially irreversible, but the body may be restored to its state at any point of the loop by carrying the stress through a complete cycle.

BODY WITH STRESS-STRAIN HYSTERESIS CYCLE

Let us consider more in detail the case of a body so conditioned as to perform a repeatable stress-strain hysteresis loop under the same repeated cycles of stress at constant temperature (Fig. 1). Associated with every point of the loop we assume there is an internal energy. This means that the energy at any point of the loop may be assigned arbitrarily and that the energy at any other point may then be found in terms of the experimentally determined mechanical work and heat absorbed in passing from the initial point to the chosen point. Since the mechanical work and heat along the hysteresis loop have an independent operational meaning it is a question for experiment to decide whether the total energy change is zero on describing a complete loop from any point and returning to the initial point.

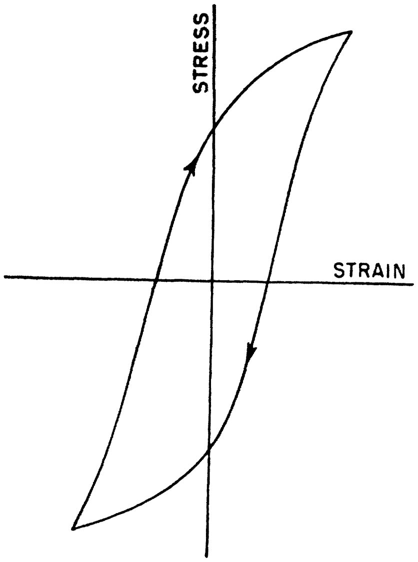

FIG. 1. Repeatable stress-strain loop.

Strictly the experimental confirmation should be given, for it is conceivable that our extended notion of "state" is not adequate under our broader conditions, but I imagine that few physicists would anticipate that there is any difficulty here or would be unwilling to examine the consequences of assuming the first law and putting the brunt on the second.

Assuming, then, the first law, what shall we say about the entropy associated with the body at various points of the loop? It would be in the spirit of thermodynamics to say that when the body returns to its initial state the entropy returns to its initial value. Hence, although strictly the entropy at every point of the loop is undefined under our conditions, nevertheless we would like to be able to say that at *every* point entropy is restored after performance of a complete loop—that is, from this point of view it appears that the essential thing in determining whether entropy is definable or not is the *restorability* of a state, not the reversibility. This point of view has been considerably elaborated in my *Nature of Thermodynamics*. The immediate question now is, can we extend the entropy concept so that entropy is restored after a complete cycle?

In order to make the extension we introduce the other classical attribute of entropy in addition to its being a state function, namely, that every irreversible process is accompanied by an increase of entropy of the universe. If this is applicable in the present situation, and it is under this fundamental assumption that we are trying to extend the entropy concept, then we must say that after the performance of every closed hysteresis cycle, starting from any initial point on the hysteresis loop, the entropy of the outside universe, which in this case may be a temperature bath in which the body is immersed, is increased by a definite amount, since the entropy of the body itself does not change after a cycle. Performance of the cycle demands the continual performance of mechanical work. What we have, therefore, in the outside universe is a weight continually lower after each cycle, and a reservoir continually increasing in heat content after each cycle (manifested perhaps by mounting the body in an ice calorimeter), whereas at each cycle the work and the heat received by the body exactly balance. At intermediate stages we would like to say that the entropy of the whole universe is continually increasing because of irreversibility. We can say this at the termination of each cycle starting from any arbitrary initial point. We cannot say it for intermediate points, however, unless we have some way of defining the difference of entropy of the working body between different points of the loop. Suppose that we can do this, and that we have an entropy and an energy at all points of the loop. Then what sort of picture do we get of the energy and entropy changes during the performance of successive cycles? Figure 2 shows qualitatively the nature of the relations. For comparison in the same diagram are shown the relations for a perfectly elastic body. The diagram makes plain the mechanism of the changes of entropy. During the part of the cycle during which heat would be flowing in from the outside if there were no hysteresis, less heat flows in than otherwise would because the irreversible internal generation of heat takes the place of the heat of external origin, so that during this part of the process the entropy of the external universe decreases less than it otherwise would (that is, there is an equivalent algebraic increase). On the other hand, during the part of the process during which without hysteresis heat would flow out of the body to the surroundings, more heat flows out than otherwise would, the excess being generated by the irreversible transformation within the body. Again the result is a greater than normal increase of entropy of the external universe. On balance, therefore, the total entropy increases as it should after every cycle. We ought to be able to describe the phenomena at all intermediate stages, and we seem almost forced to try to extend the entropy concept so as to be applicable to all intermediate stages.

Is there any simple and natural quantitative way in which entropy can be associated with the material undergoing hysteretic straining at every stage of the process? A natural working-out of the qualitative ideas just mentioned at once presents itself. We demand, in the first place, a complete knowledge of the properties of the body which are pertinent to a thermodynamic analysis. This means knowledge of both mechanical and thermal properties. If, for instance, the system is a simple one in which the body is subjected only to changes of mechanical tension and to temperature changes, then we demand to know how the length changes under arbitrary changes of temperature and of tension and also how much heat is adsorbed under the same changes. Now if the body is the seat of only reversible changes, not all these quantities are independent, but the second law imposes certain conditions. In particular, the heat absorbed when the stress changes at constant temperature is simply connected with the change of length when temperature changes at constant tension:

$$(\partial Q/\partial T)_\tau = \tau(\partial l/\partial \tau)_T,$$

or

$$(\partial Q/\partial l)_\tau = \tau(\partial l/\partial \tau)_T \cdot (\partial T/\partial l)_\tau.$$

In virtue of this relation, not all the heats have to be determined experimentally for reversibly strained bodies, but only the heats involving temperature changes. If the body is the seat of irreversibility, the basis for the above relation fails, and we have to suppose that in fact it does fail, making necessary the actual experimental determination of the heat absorption corresponding to an isothermal change. This experimentally determined heat we may write for emphasis as $(\partial Q/\partial T)_{\tau,\ \mathrm{exp}}$. The heat that would have been absorbed if the relations demanded by reversibility held we may write by contrast as $(\partial Q/\partial T)_{\tau,\ \mathrm{ther}}$. This is equal to $\tau(\partial l/\partial \tau)_T$ by the relation above, and may be expressly evaluated, because $(\partial l/\partial \tau)_T$ is an experimentally determinable quantity.

Let us now consider what relation we are to expect between the two known quantities $(\partial Q/\partial T)_{\tau,\ \mathrm{exp}}$ and $(\partial Q/\partial T)_{\tau,\ \mathrm{ther}}$. We expressly limit ourselves here to isothermal cycles. The body is the continued seat of irreversibility, which expresses itself as a continual internal generation of heat at all stages of the cycle. In virtue of this irreversible internal generation of heat, less heat has to flow in from outside to maintain the system isothermal than otherwise would during those parts of the cycle when heat is flowing in (here, during increasing tension) and conversely during those parts of the cycle when heat would otherwise have to flow out to maintain temperature constant (here, during decreasing tension), more heat has to flow out than otherwise would. The continued result is that the outside reservoir is always gaining more heat than it otherwise would, which results in a continued increase of entropy of the universe.

This simple picture at once provides a possible answer to our two questions as to what is the precise entropy increase associated with the irreversibility and as to how an entropy may be associated with the irreversibly strained body at all stages of the process. The difference between the "thermodynamic" and the "experimental" heats represents the heat generated internally by irreversibility. The associated characteristic entropy is this heat divided by temperature. Or in other words

$$\Delta S_{\mathrm{irrev}} = (1/\tau)[(\partial Q/\partial T)_{\tau,\ \mathrm{ther}} - (\partial Q/\partial T)_{\tau,\ \mathrm{exp}}]\Delta T,$$

or, in our particular case:

$$\Delta S_{\mathrm{irrev}} = (1/\tau)[\tau(\partial l/\partial \tau)_T - (\partial Q/\partial T)_{\tau,\ \mathrm{exp}}]\Delta T.$$

With regard to the body itself, all our demands will be met if we say that the entropy of the body changes at every stage of the cycle by

$$(1/\tau)(\partial Q/\partial T)_{\tau,\ \mathrm{ther}}\Delta T,$$

or here,

$$(\partial l/\partial \tau)_T \Delta T.$$

Obviously this integrates to zero for any complete stress cycle, at least to the approximation to which $(\partial l/\partial \tau)_T$ may be taken as constant, and our demand on the body is met.

There is nothing in our analysis to compel this as a unique solution, but we would obviously be going out of our way not to take the simplest solution that presents itself. When the experimental data are sufficiently well known, there will be the possibility of an experimental check, for this point of view demands that

$$(1/\tau)[(\partial Q/\partial T)_{\tau,\ \mathrm{ther}} - (\partial Q/\partial T)_{\tau,\ \mathrm{exp}}]\Delta T$$

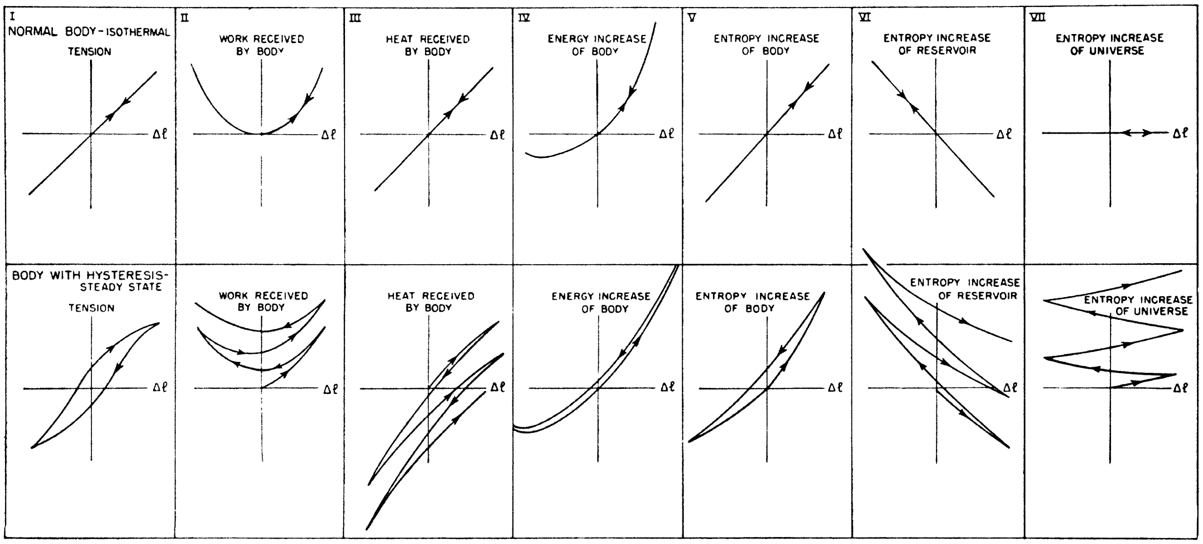

FIG. 2. The qualitative relations in a repeatable stress-strain loop compared with those in the corresponding elastically stressed body.

be intrinsically positive (or zero) at all stages of any actual operation.

It may seem surprising at first that the "generalized" entropy which we have been led to associate with the body which is the seat of the irreversibility bears no trace of the irreversibility, but is

$$(1/\tau)(\partial Q/\partial T)_{\tau,\,\mathrm{ther}}\Delta T,$$

or in other words, the entropy change that would have been associated with it had the phenomena been reverisble and the second law applicable. On second consideration, however, I think this appears natural and unavoidable. For we are assuming that the condition of the body can be completely specified in terms of two (or a finite number) of large scale parameters and their history. In these parameters and their smooth history there is nothing of the chaos or disorder associated with entropy, so that we would not expect any corresponding term in the entropy. The irreversible generation of entropy manifests itself exclusively in an altered flux of heat. This altered heat flux is such that the final abiding place of the entropy of irreversibility is in the heat reservoir surrounding the working body, the entropy of the reservoir increasing steadily above that which it would otherwise be as the process proceeds.

It is evident that the argument just presented is in no way restricted to bodies which have settled down to a steady state or which are performing closed hysteresis loops. Formally, we may extend this point of view to any sort of irreversible isothermal change such as bodies with strain hardening. If the parameters of the system are specified, then we may calculate by conventional thermodynamic methods, assuming reversibility, what would be the heat associated with any isothermal change of parameter. This we may call the "thermodynamic heat." The actual "experimental heat" may then be found by measurement corresponding to the same change of parameter. The difference of the two may be described as the heat generated by the irreversibility, and this divided by the temperature may be taken as the characteristic increase of entropy to be associated with the irreversibility. This we expect to be always positive (or zero), thus affording the possibility of an experimental check. And we may associate with the substance in which the irreversible change is occurring a "generalized entropy" change equal merely to that which would be deduced thermodynamically assuming reversibility. In order that this "generalized entropy" satisfy our demands it is necessary that the integral over any path which restores the body to its initial state vanish. It is obvious that this requirement is met to a first approximation, for the integral of

$$\frac{1}{\tau}\oint dQ_{\tau,\,\mathrm{ther}}$$

over a complete isothermal path for any body which remains reversible everywhere is automatically zero, and it is only departures from this behavior that are going to make trouble. This is not likely to be the case to a first approximation. Thus in the specific example used above, of a system under tension, the requirement is automatically met over the range in which the thermal expansion may be taken to be a constant. It is to be recognized, however, that there is no automatic reason why

$$\frac{1}{\tau}\oint dQ_{\mathrm{ther}}$$

has to vanish over every closed cycle, since dQ_{ther} may in general refer to effectively different bodies at different stages of the cycle. There is here, therefore, an additional requirement which may have to be checked by experiment. In view, however, of the complete absence of any suitable experimental material, we may for the present defer the exceedingly complicated task of working out theoretically the additional demands thereby placed on the experimental data, and content ourselves with the observation that at least we have here no evidence of inconsistency. It is further to be remembered that it is by no means true in general that the body has been restored to the initial state when the controllable parameters have been carried through a closed cycle.

IDEAL PLASTIC BODY

Let us now inquire how our point of view may be applied to the case of an ideal plastic body, which has the sort of ideal stress-strain diagram shown in Fig. 3. The body may be brought to any point D in the stress-strain plane within the band of plasticity by a combination of inclined paths, corresponding to elastic deformation, with horizontal paths at the plus or minus plastic stress level. We assume that the "state" of the body is fixed at the point D. If the body is brought to a given point D by different paths, its energy must be the same, independent of the path, because of the first law. We are also going to try to make the same requirement of its generalized entropy. The requirement of the first law means that the total heat absorbed in any possible loop is equal to the mechanical work done during the same loop. Since, by the thermodynamics of

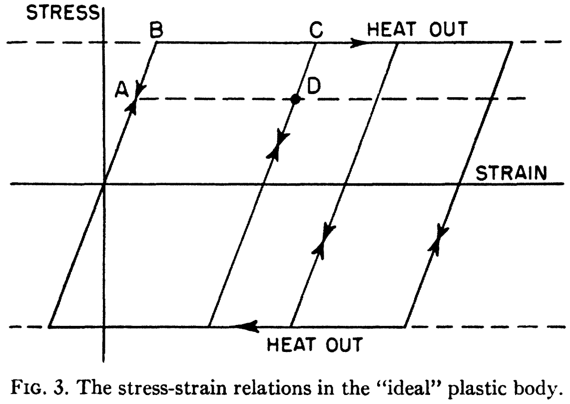

FIG. 3. The stress-strain relations in the "ideal" plastic body.

reversible bodies the heats and works are equal on the two elastic branches of any complete loop, this means that on the horizontal, plastic, branches, the work and heat are equal in detail. Or in other words, for this kind of a plastic body the work of plastic deformation is completely converted into heat, which forthwith flows out of the body, thereby increasing the entropy of the external universe. The characteristic increase of entropy to be associated with this sort of plastic deformation is, therefore, merely the work of deformation divided by the temperature. Here we have a possibility for about the only experimental check which at present seems feasible in this field. Taylor and Quinney[4] found that during the torsional deformation of rods of copper or iron, substances which roughly approximate to this sort of a plastic diagram, the larger part of the work of deformation, approximately 85 percent, forthwith flows out of the specimen in the form of heat.

We next have to ask whether a "generalized entropy" can be assigned to the body at *D*. We attempt to apply the same method as before, namely, to assign the entropy which it would have had if it had reached *D* by a reversible path. This indicates at once that the entropy in the body arising from the plastic deformation itself is zero, so that the entropy at every point on the horizontal line passing through *D* is the same as that at the point *A*, where it is to be calculated by the methods of reversible thermodynamics. That is, the integral of $dQ_{\tau,\text{ ther}}$, along the plastic path *BC* is identically zero, because on this path the stress does not change, or the analog of ΔT in our previous analysis is zero. Or if we take *l* as the independent variable, we have

$$(\partial Q/\partial l)_{\tau,\text{ ther}}=\tau(\partial l/\partial\tau)_T\cdot(\partial T/\partial l)_\tau,$$

which vanishes because $(\partial T/\partial l)_\tau$ vanishes. This again is all as it should be, because our assumption that the body recovers its state when the point *D* is recovered means that there is no progressive disorganization within the body as it is carried through one plastic cycle after another. The behavior is what would be produced by internal slippage on one or another well organized plane, that is, a purely mechanical affair with no associated change of entropy.

BODY WITH SINGLE PARAMETER OF IRREVERSIBILITY

We now turn to the consideration of an entirely different sort of irreversible process within solids, such as is met with in changes from order to disorder. A typical example would be a binary alloy, in which the atoms of the two elements may be either arranged regularly on the space lattice, each element being confined to one sort of site, or else in which the two elements may occupy either sort of site at random. We suppose that the degree of internal disorder may be specified by a parameter α in addition to the ordinary pressure (p) and temperature (τ) which we will suppose necessary for the description of this system. The parameter α is not directly connected to any additional external force variable, so that we cannot directly alter α as we wish by appropriate external manipulation. It is, however, a property of the system that at any temperature and pressure the system slowly assumes an equilibrium condition with the appropriate value of α. If pressure and temperature of the system are rapidly changed, α does not change and ordinary reversible thermodynamics applies. If, on the other hand, pressure and temperature are changed infinitely slowly, the system is always in equilibrium, with equilibrium values of α, and again reversible thermodynamics applies, but naturally with different values for the physical constants of the system. By combining rapid changes with waiting until equilibrium has completely or partially reestablished itself, we obviously acquire control over the variable α within the limits set by its equilibrium values. What the values are at any stage of the process we suppose ascertainable by some process, such as x-ray analysis, which has no thermodynamic coupling, so that the parameter α has an "operational" significance.

The problem we now set ourselves is a discussion of the entropy changes associated with the irreversible changes of α as it slowly assumes its equilibrium values. It is obvious that "rapid" and "slow" as characterizations of the changes have no absolute significance but depend on the dimensions of the system and the thermal conductivity of the surroundings.

Let us first consider the consequences of assuming in addition to p and T such a concealed parameter, α, in a conventional reversible thermodynamic system. There is to be no new external "force" associated with this parameter, so that we have the canonical expression for the work, namely $dW=-pdv$. Taking τ, p, and α as independent variables, we now have the formal expressions for heat and work:

$$dQ=(\partial Q/\partial\tau)_{p,\alpha}d\tau+(\partial Q/\partial p)_{\tau,\alpha}dp+(\partial Q/\partial\alpha)_{\tau,p}d\alpha$$

$$dW=-p[(\partial v/\partial\tau)_{p,\alpha}d\tau+(\partial v/\partial p)_{\tau,\alpha}dp+(\partial v/\partial\alpha)_{\tau,p}d\alpha].$$

Since the system is assumed reversible, dW must be a perfect differential at constant temperature. This gives at once:

$$(\partial v/\partial\alpha)_{\tau,p}=0.$$

Furthermore, dQ/τ is an exact differential. A trifling manipulation, replacing dQ by its equivalent $dE-dW$, yields at once:

$$(\partial Q/\partial\alpha)_{\tau,p}=0.$$

These two equations state that there is neither volume change nor absorption of heat on changing α alone. In other words, *in a reversible system*, the assumption of a third concealed parameter of this sort is entirely sterile and conventional, with no *thermodynamic* consequences whatever. A third parameter has thermodynamic consequences in a reversible system only if it carries with it a new kind of "force" so that an additional term appears in the work. There are, of course, many ex-

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[4] G. I. Taylor and H. Quinney, Proc. Roy. Soc. 143, 307 (1933–34).

amples in which a new kind of force does enter, as for instance, in systems the seat of magnetic phenomena.

If, however, we assume that changes of the third concealed parameter α are associated with irreversible changes, we do not have degeneration to a triviality. To show this, subject the system to a cyclic process as follows. It will be sufficient to suppose the pressure negligible, so that we consider only changes of temperature; this is the sort of change that we usually encounter in practise. We now start the system at τ_1 and α_1, the equilibrium value of α at τ_1. We rapidly raise the temperature to τ_2, α remaining constant. At τ_2 we wait until α has slowly assumed its equilibrium value α_2. We then bring the system rapidly back to τ_1, α remaining constant at α_2. Finally we allow α to slowly assume its equilibrium value α_1. There are two irreversible processes here, associated with the slow change of α at the two temperatures. These two irreversible processes we must assume to be associated with thermal effects, as a result of which the heat content, and so the entropy content, of reservoirs at τ_1 and τ_2 have been altered. We may for this purpose neglect the specific heat of the body, or better, assume it to be independent of α. This means that the heat absorbed irreversibly at τ_2 while α changes from α_1 to α_2 is equal to the heat given out irreversibly at τ_1 while α changes irreversibly from α_2 to α_1. This is because the first law applies, the body having recovered its initial condition, so that the total heat absorbed is zero, there being by hypothesis no work. In other words, under these conditions the heat associated with the given change of α is independent of the temperature at which it occurs. We may represent the total heat absorbed under these conditions by

$$\int_{\alpha_1}^{\alpha_2} \frac{\partial Q}{\partial \alpha} d\alpha \equiv q(\alpha_2) - q(\alpha_1).$$

Since closed cycles may be described not only between the equilibrium values of α at the two temperatures but also between intermediate values of α, it follows not only that $q(\alpha_2)-q(\alpha_1)$ is independent of temperature, but that also $\partial Q/\partial\alpha$ is independent of temperature, or a function of α only. An extension of the same argument, utilizing the condition that dE is a perfect differential in $d\tau$, dp, and $d\alpha$, and v is not a function of α, shows that $\partial Q/\partial\alpha$ is independent of pressure also.

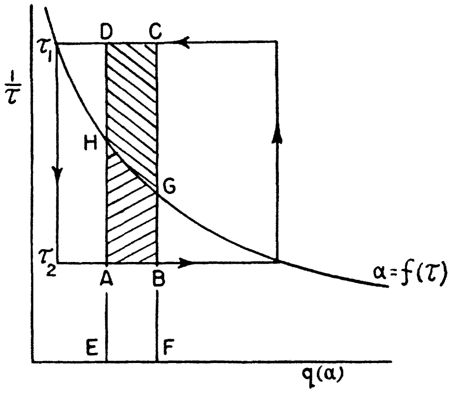

FIG. 4. Diagram showing the entropy relations (areas) in a body with one internal parameter of irreversibility.

We now see at once where the ineradicable increase of entropy associated with the irreversibility is located. Since the body has returned to its initial condition we must say that its entropy has not changed. The entropy change of the universe is located in the reservoirs. The reservoir at the higher temperature loses

$$[q(\alpha_2)-q(\alpha_1)]/\tau_2$$

and the reservoir at the lower temperature gains

$$[q(\alpha_2)-q(\alpha_1)]/\tau_1,$$

making a net gain of

$$[(\tau_2-\tau_1)/\tau_2\tau_1][q(\alpha_2)-q(\alpha_1)].$$

It is obviously demanded that $q(\alpha_2)-q(\alpha_1)$ be positive. This is already demanded by classical thermodynamics, because we know that if an equilibrium is shifted by an increase of temperature it is shifted in such a direction that heat is absorbed when equilibrium automatically restores itself.

We have then found the entropy increase associated with the net irreversibility of the total cycle. It remains to discover a possible distribution of this in detail, so that we may attach its own characteristic ineradicable increase of entropy to every infinitesimal change of α, and also so that we may associate with the body in which α is changing the proper change of entropy at every intermediate stage of the cycle.

The problem of the ineradicable entropy increase of the universe may be solved at once by a simple graphical construction. We assume that the heat $q(\alpha)$ is known as a function of α and also that α at equilibrium is known as a function of temperature, $f(\tau)$. Plot the curve giving equilibrium $\alpha[\equiv f(\tau)]$ as function of temperature in a plot in which $q(\alpha)$ is taken as abscissa and $1/\tau$ as ordinate (Fig. 4). Any admissible change in the body at constant temperature corresponds to motion along the q axis in Fig. 4 to the right (heat absorbed) below the curve, and along the q axis to the left (heat given out) above the curve. Counterclockwise cycles subject to this restriction, as *ABCDA*, represent possible processes. It is at once obvious that the area of the cycle *ABCDA*, which by construction is

$$[q(\alpha_B)-q(\alpha_A)][(1/\tau_1)-(1/\tau_2)],$$

is the ineradicable increase of entropy of the universe associated with the cycle. Because of the additivity of areas a possible increase of entropy to be associated with the single process *AB* is the area between *AB* and the equilibrium curve, or *ABGHA* as indicated by the cross hatching, and the entropy associated with the corresponding reverse process, *CD*, by the area *CDHGC*.

The graphical construction is obviously applicable to any shaped cycle or part of a cycle instead of to the rectangular path indicated in Fig. 4. The result may be formulated analytically as follows:

$$\left(\begin{array}{c}\text{Total irreversible entropy}\\ \text{increase of universe}\end{array}\right)=-\int_{q_1}^{q_2}\left[\frac{1}{\tau}-\frac{1}{\tau_{\text{equi}}}\right]dq,$$

where τ is the actual temperature at which the absorption of dq is taking place, and τ_{equi} is the temperature at which the value of α corresponding to the running q is the equilibrium α. The factor $[(1/\tau)-(1/\tau_{\text{equi}})]$ may be described as a measure of the degree of irreversibility under which dq is absorbed, this measure of irreversibility vanishing when $\tau=\tau_{\text{equi}}$. Our expression for the irreversible generation of entropy thus has a form which appears intuitively natural.

It is to be noticed that dq is only the part of the heat absorbed corresponding to the irreversible α. The separation of total absorbed heat into two parts, one corresponding to the ordinary specific heat, must be made experimentally by methods suggested above.

We now can find the entropy to ascribe to the body which is the seat of the irreversible process. We consider at first only the entropy changes associated with the irreversible change of α. The relations are clear from Fig. 4. Consider the change of α represented by AB, during which irreversible heat is absorbed from the reservoir at τ_2. The decrease of entropy of the reservoir is the area $ABFEA$ and the total increase of entropy of the universe is the area $ABGHA$. Hence the entropy increase of the body is $EFGHE$. Similarly for the reverse process CD. The increase of entropy of the reservoir at τ_1 is the area $EFCDE$ and the total increase of entropy of the universe the area $CDHGC$. Hence the body decreases in entropy by the area $GHEFG$. Hence, in general, the entropy change of the body is the area between the equilibrium curve and the axis $(1/\tau=0)$, taken positive if the change is from left to right, corresponding to absorption of heat, and negative if from right to left with liberation of heat.

Superposed on the entropy changes due to the changes of α are the normal entropy changes due to change of pressure and temperature, which are unaffected by those due to α. This means that we can write the total entropy as $S=S(p,\tau)+S(\alpha)$, where

$$S(\alpha)=\int\frac{dq(\alpha)}{\tau(\alpha)}.$$

Notice that $\tau(\alpha)$ is the temperature on the equilibrium curve, not the current τ, so that $S(\alpha)$ is formally not the same as for a reversible process. We can obviously write a similar equation for the energy, or

$$E=E(p,\tau)+q(\alpha).$$

No new information can be extracted from these equations from the conditions that dS and dE are perfect differentials; the information has already been utilized in deducing the functional forms.

Having now found a possible solution, we are now presented with the question of experimental check of its correctness. From one point of view the check is superfluous, because the solution has been so drawn that the only conditions on the entropy which have operational meaning are automatically satisfied, namely, the condition that the total entropy of the universe continually increase during all stages of the performance of an irreversible process, and the condition that the entropy of the working body, the seat of the irreversibility, return to its initial value when the body returns to its initial state. The most important question for experiment to decide here is whether the scheme of description adopted is adequate, especially whether, in addition to pressure and temperature, a single internal parameter associated with the irreversibility is sufficient. This means that the total energy absorption in any closed cycle of pressure, temperature, and parameter must be zero, and this may be checked by experiment. If the check fails, the natural conclusion is that other parameters are necessary, and experimental search for them may be initiated. Other parameters are to be handled by a straightforward extension of the methods applied above to one.

From the immediate point of view of this paper the analysis of this particular situation only reinforces the conclusion from the analysis of the two other situations, namely, that it is possible to generalize the entropy concept so as to apply to intrinsically irreversible processes, and employing only the macroscopic methods and instruments of classical thermodynamics, without entering the domain of the microscopic analysis of statistical mechanics, provided that the irreversible process is simple enough to be characterized in terms of a small number of macroscopic measurements. One may anticipate that the extension of the entropy concept to more complicated phenomena, perhaps including ultimately the biological phenomena of life, is coextensive with the discovery of macroscopic parameters adequate for the exhaustive description of these phenomena. In the extension to biological phenomena the method of identical replicas may be expected to play an important part. It is apparently possible to prepare identical replicas of the simpler biological systems in spite of the fact that the changes which such systems experience are all irreversible. Some such method as this seems necessary to avoid the dilemma which otherwise arises in applying the concept of entropy to biological systems because of the fact that at present life cannot be applied or withdrawn reversibly.

Note added on reading proof: Since writing this article I have become better acquainted with the work of the Belgian school of thermodynamicians, founded by DeDonder and especially the recent work of I. Prigogine. His thesis: "Etude Thermodynamique des Phénomènes Irréversibles," Liege, 1947, deals with many aspects of irreversibility, with the chief emphasis on chemical reactions, but including also thermo-electric phenomena and the diffusion phenomena discussed by Eckart and Tolman and Fine. As far as I know, however, all the examples treated by the Belgian school are such that some reversible method exists for getting from any state of the system to another, so that the entropy is defined and may be evaluated by conventional methods. The extension of the entropy concept to situations in which the entropy may not be so defined does not appear to have been considered.