ON ENTROPY.

BY W. S. FRANKLIN.

IT has perhaps occurred to every student of thermodynamics that there might be a simple and direct method of establishing the quantitative idea of entropy, considering that the idea is so widely applicable and that it is independent of the properties of particular substances and independent of particular processes. The difficulty is that the definite forward movement in nature which has been formulated as the law of increase of entropy is mixed up inextricably with changes of state of physical substances. This difficulty is met in the argument of Clausius by considering a cyclic process where no change of state is left outstanding, but it is apparently an unnecessary complication to base the discussion of a definitely forward moving quantity like entropy upon a cyclic process. Clausius's integral, moreover, is strictly applicable to reversible processes only, and in Clausius's argument, when limited in this way, the law of increase of entropy makes its appearance as follows: Consider a state B which is reached from state A by an irreversible process, then Clausius's integral extended over a reversible process leading from state A to state B gives a positive result. For example, a gas issues from an orifice in a high pressure tank, and if the gas is brought from its initial condition to its final condition by a reversible process, Clausius's integral extended over this reversible process gives the increment of entropy which is associated with the original irreversible process. To base the discussion of the law of increase of entropy upon reversible processes only (and this is substantially what Clausius's original argument does, considering that the application of Clausius's integral to irreversible processes is not legitimate) would seem to be to ignore a most important physical element, because the quantitative idea of entropy gains its significance chiefly in its application to irreversible processes.

The object of this paper is to call attention to a class of irreversible processes which are permanent or steady and therefore susceptible to quantitative treatment, and which lead to no change of state of any kind so that the entropy changes which are involved are associated solely with energy transformations. By a careful consideration of an irreversible process of this type the quantitative idea of entropy may be established in the most direct possible way. The quantitative idea of entropy when established in this way is quite primitive and highly generalized and it refers to the entropy increment involved in the conversion of work into heat or to the entropy increment involved in the flow of heat from a high-temperature region to a low-temperature region, and a further development of the idea of entropy is of course necessary in order to establish a measure of the entropy differences which are associated with changes of state. This extension of the primitive idea of entropy can be established only by a consideration of a cyclic process.

A further object of the paper is to discuss an apparent close relationship between entropy and time.

The simplest kind of irreversible process is that which takes place in an isolated system while the system is settling to thermal equilibrium. Such a process has a certain impetuous quality as, for example, in a conflagration, when a house is settling to thermal equilibrium with the surrounding air, and perhaps the physical nature of an irreversible process is most clearly and strongly suggested by speaking of such a process as a *sweeping process* or as a *sweep*. A careful consideration of the various sweeping processes which take place in nature leads to the recognition of three distinct types as follows: (*a*) Sweeping processes which take place in a closed system, (*b*) sweeping processes which take place in a system which is subjected to rapidly varying external action, and (*c*) sweeping processes which are perfectly steady and which involve no changes of state of any kind in the system under consideration. The first type is exemplified by the explosion of a mixture of hydrogen and oxygen in a closed vessel. The second type is exemplified in the departure from thermal equilibrium of a gas which is rapidly compressed under a piston or by the departure from thermal equilibrium of a vessel of water which is heated on a stove. In both cases the system never catches up, as it were, with the changing conditions but trails along behind them. The third type is exemplified by the flow of electric current through a wire from which heat is abstracted by a steady stream of air or water, and by the steady flow of heat from a region of high temperature to a region of low temperature. A number of years ago I suggested the terms "simple sweep," "trailing sweep" and "steady sweep," respectively, to designate these three types of irreversible processes. The entropy change which accompanies a simple sweep is involved in or associated with the change of state of the substance. The entropy change which accompanies a trailing sweep is associated in part with the conversion of work into heat, in part with the flow of heat from a region of high temperature to a region of low temperature, and in part with the changes of state of the substance. The entropy change which takes place in a steady sweep is due solely to the conversion of work into heat or to the transfer of heat from a region of high temperature to a region of low temperature, or both. Therefore a careful consideration of a steady sweep is the simplest basis for the discussion of the idea of entropy.

In establishing the idea of entropy it seems to be necessary to start out with the assumption that the entropy function exists, and then to justify this assumption by logical deductions and experimental verifications. Clausius, indeed, starts with the assumption that a non-compensated transfer of heat from a cold region to a hot region is impossible. This form of assumption may seem to obviate initial reference to the entropy function but it is not accompanied by a clear and complete definition of compensation in the thermodynamic sense, and indeed such a definition cannot be stated without the introduction of the idea of entropy. It is evident, therefore, that the idea of the entropy function is really involved at the very beginning of Clausius's classical argument, and a logical development of the second law of thermodynamics might perhaps be made less indefinite and more intelligible by frankly introducing the idea of entropy at the start in explicit terms. Indeed this is the procedure which is adopted by Professor Planck. It is difficult, however, to give a preliminary definition of entropy which is correct as far as it goes and which carries an appeal to one's primitive sense of physical things. Such an appeal is greatly to be desired and it is certainly possible because there is perhaps a more widespread intuitive sense touching the second law of thermodynamics than in the case of any other of the generalizations of physics.

Fire is the most familiar example of a sweeping process and its most striking characteristic is that its progress is not dependent upon any external driving cause; when once started it goes forward of itself and with a rush. Everyone perhaps will admit that the impetuous character of fire suggests a certain havoc, a certain degeneration or waste in the system in which the fire takes place, and the same is true of every sweeping process. Consider, for example, a charge of gunpowder which has been exploded in a large empty vessel; everything is there after the explosion, all of the energy is there and all of the material substance is there, and yet it cannot be exploded a second time! But the man on the street has heard so much during recent years of the conservation of energy and of the conservation of mass that the old proverb that "You can't eat your cake and have it" presents to his mind a very simple and inevitable fact or condition which he is at times tempted to ignore when he turns his attention to an unfamiliar matter like the steam engine; he tries in vain to rationalize steam engine theory in terms of the principles of conservation alone. Nearly all of the intuitive sense of the man on the street concerning such matters (and he has a great deal) is involved in the second law of thermodynamics which is not a law of conservation at all; it is a law of waste.

It may be assumed that every sweeping process brings about a definite amount of degeneration, an amount that can be expressed numerically. Thus a certain amount of degeneration may be assumed to be brought about when a compressed gas escapes through an orifice, when heat flows from a region of high temperature to a region of low temperature, when work is converted into heat by friction or by the flow of an electric current through a wire, and so on. In a simple sweep the degeneration lies wholly in the relation between the initial and final states of the substance. In a trailing sweep the degeneration may lie partly in the relation between the initial and final states of the substance which undergoes the sweep, partly in the conversion of work into heat, and partly in the flow of heat from a high temperature region to a low temperature region. In a steady sweep, however, the degeneration lies wholly in the conversion of work into heat, in the transfer of heat from a region of high temperature to a region of low temperature, or in both. Therefore the idea of thermodynamic degeneration as a measurable quantity can be reached in the simplest possible manner by a careful scrutiny of a steady sweep.

Proposition (*a*).—The thermodynamic degeneration which is represented by the direct conversion of work into heat at a given temperature is proportional to the quantity of work so converted. Consider, for example, a steady flow of electric current through a wire from which the heat is abstracted continuously so that the temperature of the wire remains constant. This is a steady process, that is to say, it remains unchanged during successive intervals of time, and therefore any result of the process must be proportional to the time. Thus the amount of degeneration occurring in a given interval of time is proportional to the time, but the amount of work which is degenerated into heat is also proportional to the time. Therefore the amount of degeneration is proportional to the amount of work which is converted into work at the given temperature.

Proposition (*b*).—The thermodynamic degeneration which is represented by the transfer of heat from a given high temperature T_1 to a given low temperature T_2 is proportional to the quantity of heat transferred. Consider a steady flow of heat from temperature T_1 to temperature T_2 constituting a steady sweep, a sweep which remains unchanged in character in successive intervals of time. Any result of this sweep must be proportional to the time and therefore the degeneration which takes place in a given interval of time is proportional to the time; but the quantity of heat transferred is also proportional to the time. Therefore the amount of degeneration is proportional to the quantity of heat transferred from temperature T_1 to temperature T_2.

According to proposition (*a*), above, the thermodynamic degeneration which is involved in the conversion of work into heat at a given temperature is proportional to the amount of work so converted and the proportionality factor depends upon the temperature only. Therefore we may write

$$\varphi' = m_1 W, \tag{1}$$

$$\varphi'' = m_2 W, \tag{2}$$

in which φ' is the degeneration involved in the conversion of an amount of work W into heat at temperature T_1, and φ'' is the degeneration involved in the conversion of an amount of work W into heat at temperature T_2, and m_1 and m_2 are factors which depend only upon T_1 and T_2, respectively. An amount of work W having been converted into heat at temperature T_1, imagine the heat to flow to a lower temperature T_2, thus involving an additional amount of degeneration according to proposition (*b*) above. The conversion of work W into heat at temperature T_1 and the subsequent flow of this heat to a lower temperature T_2 gives the same result as would be produced by the conversion of the work into heat at the lower temperature directly. Therefore the lower the temperature at which work is converted into heat the greater the amount of degeneration involved. That is to say, the factor m_2 in equation (2) is larger in value than the factor m_1 in equation (1), temperature T_1 being higher[1] than temperature T_2. Therefore, since m_1 and m_2 depend only upon T_1 and T_2, respectively, it is permissible to adopt the equation

$$T_1/T_2 = m_2/m_1, \tag{3}$$

as the definition of the ratio T_1/T_2.

Another way to express the definition which is involved in equation (3) is as follows: Considering that the factor m_1 is the smaller the higher the temperature T_1, we may adopt k/m_1 as the measure of the temperature T_1, and k/m_2 as the measure of the temperature T_2, giving

$$m_1 = k/T_1, \tag{4}$$

$$m_2 = k/T_2, \tag{5}$$

where k is an indeterminate constant. Therefore equations (1) and (2) may be written in the general form

$$\varphi = kW/T, \tag{6}$$

[1] The idea of higher and lower temperature is not dependent upon any method of measuring temperature.

where φ is the thermodynamic degeneration involved in the conversion of an amount of work W into heat at temperature T, and k is an indeterminate constant.

Since the factor k in equation (6) is indeterminate, we may adopt as the unit of thermodynamic degeneration the amount which is involved in the conversion of one unit of work into heat as a temperature of one degree on the absolute scale; then the value of k is unity and equation (6) becomes

$$\varphi = W/T, \tag{7}$$

in which W is expressed in joules, T in degrees centigrade and φ in joules per degree. Thus one joule per degree is the degeneration involved in the conversion of one joule of work into heat at 1° C. on the absolute scale.

To convert an amount of work W into heat at temperature T_1 involves W/T_1 units of degeneration. To convert the same amount of work into heat at temperature T_2 involves W/T_2 units of degeneration. Therefore to transfer an amount of heat equal to W from temperature T_1 to temperature T_2 must involve an amount of degeneration equal to the excess of W/T_1 over W/T_1, or an amount equal to $W(1/T_2 - 1/T_1)$, or $H(1/T_2 - 1/T_1)$, where H is the amount of heat transferred.

The word degeneration as used in the above discussion means the same thing as entropy increment, and the word degeneration is used because it carries with it a suggestion of irreparable waste. Furthermore, it is desirable to reserve the word entropy until with the help of Clausius's integral we are able to assign a definite entropy-difference to a given difference of state of a substance so that, choosing a zero state of the substance arbitrarily, we may speak of the entropy-of-the-substance in any other given state.

Starting with the above ideas of thermodynamic degeneration and remembering that such degeneration occurs only in sweeping processes, it is easy to establish the important proposition that the efficiency of a reversible engine depends only upon the boiler and condenser temperatures, and it is easy also to transform the above definition of temperature ratio as given in equation (3) to the form in which it was originally given by Lord Kelvin.[1]

The Relationship of Entropy and Time.

The above propositions concerning the entropy increment which is associated with a steady sweep suggest a relationship between entropy and time, and it is desirable to carry the inquiry further to determine whether this relationship is a fundamental one or not. It seems, indeed, at first sight, as though there could be no fundamental relationship between entropy and time because entropy increases with the utmost irregularity in different parts of the universe whereas time is thought of as a universal steady flux.

Imagine an isolated mechanical system involving no irreversible processes. After a sufficient length of time, using that term in the commonly accepted sense, the system returns to identically its initial state, and when the system has returned to its initial state it is unjustifiable to project into the system the idea that there has been a lapse of time. It seems, of course, absurd to make this statement because everyone realizes in looking at the ideal mechanical system that time has elapsed between its initial and final state, but this view of the matter involves the inclusion in our ideal system of one's own physical body and the projection of one's own consciousness into the aggregate of phenomena under consideration. Let us, therefore, consider our ideal system apart from its relation to any outside condition whatever. Then, to say that time has elapsed when the system has returned to its initial state is to introduce an arbitrary and meaningless difference between the initial and final state.

Consider a system in which no changes whatever are taking place. What we call the lapse of time finds no basis for its application to such a system because no progressive change of any kind is taking place in the system.

Consider a purely mechanical system (one in which no irreversible action takes place). Any change in state of this system after the lapse of what we call time can be completely specified in terms of

[1] These arguments are outlined in a very simple way in an article by W. S. Franklin in Popular Science Monthly, March, 1910.

the positions and velocities of the component parts of the system, and it must be remembered that in specifying the velocities of the component parts of the system no reference need be made to the time which has elapsed since the beginning. That is to say the complete specification of the change of state of the system may be made without reference to the lapse of time, and to say that time has elapsed is to introduce an arbitrary and meaningless difference between the initial and final states of the system in addition to the differences already completely specified in mechanical terms.

Consider a system in which irreversible processes take place. Such a system departs further and further from its initial condition without possibility of return and in this case a complete specification of change in the system can be made in terms of mechanical specifications and entropy specifications, and it would seem to be meaningless to add the further specification of lapse of time to what is otherwise complete.

What we call time, when reduced to its simplest terms, is a phenomenon of consciousness. And our sense of the inevitable forward movement of time is dependent upon the existence of irreversible processes everywhere about us, and especially inside of us. That is to say, our sense of the forward movement of time and the law of increase of entropy are based upon or grow out of the same fundamental conditions in nature.

The above argument would seem to indicate that the universal steady flux of time is an idea, and not a physical fact; although, taking the universe as a whole, local irregularities become individually negligible and the entire process of nature may be thought of as one vast steady sweep in which increase-of-entropy and passage-of-time, much as they differ in our local methods of measuring them, refer fundamentally to the same thing. The extent to which the idea of the steady flux of time pervades our habitual modes of thought seems to be an outgrowth of the methods that we have come to use in the expression of our rather complicated experiences relating to what we call coincidences in time. Indeed some of the most pervasive things of the human mind are the ideations which have been developed as bases for our system of language, and to make due allowance for them in a physical discussion is sometimes very difficult indeed, partly because we fail to recognize the ideations as such and partly because we are left without any adequate forms of expression if we set them aside. We always make time specifications with respect to a recurrent phenomenon like the rising of the sun, with finer gradations based upon the oscillations of a pendulum; our time specifications are simple counts of these recurrent phenomena; and the requirement of simplicity and directness of speech has led to the development of the idea of the steady flux of time and to the habitual projection of this idea into every objective condition we encounter in nature.

Two phases of two systems are simultaneous or coincident in time when they involve the loss of energy by one of the systems and the gain of energy by the other system. Thus it seems that the idea of simultaneity rests fundamentally upon the principle of the conservation of energy. If energy could be taken from one system, temporarily annihilated, and later delivered to another system, our idea of simultaneity would have to be modified; or if energy is taken from one system and if some time must elapse before its delivery to another system, as in the case of the transmission of energy by a beam of light, then again a modified conception of simultaneity would have to be developed. Indeed, this modified idea of simultaneity is already accomplished in terms of the idea that light has a definite velocity, and it seems as if the modern principle of relativity may lead to another solution of the same problem. The idea that it is everywhere *now* cannot be justified in the physical nature of things although an assumption to that effect is extremely convenient in speech. Also the idea that time is a universal steady flux cannot be justified in the physical nature of things although an assumption to that effect is extremely convenient in speech. Indeed, throughout the above discussion modes of expression are used which involve the common idea of time as a steady flux and to avoid the use of these common modes of expression would make the discussion extremely difficult to follow.

LEHIGH UNIVERSITY,
February 22, 1910.