SCIENCE

A WEEKLY JOURNAL DEVOTED TO THE ADVANCEMENT OF SCIENCE, PUBLISHING THE
OFFICIAL NOTICES AND PROCEEDINGS OF THE AMERICAN ASSOCIATION
FOR THE ADVANCEMENT OF SCIENCE.

FRIDAY, NOVEMBER 20, 1903.

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MSS. intended for publication and books, etc., intended for review should be sent to the responsible editor. Professor J. McKeen Cattell, Garrison-on-Hudson, N. .

*THE MISUSE OF PHYSICS BY BIOLOGISTS AND ENGINEERS.**

THIS somewhat informal paper is preliminary to a paper which I have in preparation on statistical physics. My chief object in presenting this preliminary paper is to call attention to some of the precise notions of thermodynamics and to point out the essential limitations of that subject. Gibbs, for example, raises the question repeatedly in his writings as to the legitimacy of the thermodynamic discussion of things, such as thermoelectricity, which are associated necessarily with irreversible processes. What I have in mind concerning thermodynamics proper and concerning statistical physics is a general point of view which completely elucidates this question of Gibbs, setting precise limits not only to systematic thermodynamics, but to systematic physics in the broadest sense, and marking sharp boundaries between systematic physics and what we may call statistical physics.

A great deal is, I think, to be gained for science at the present time by insisting upon the sharp delimitation of those general ideas in physics which are related primarily to thermodynamics just as a great deal has been gained in the last half century by the sharp delimitation of those general ideas which relate primarily to

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* A paper read before the American Physical Society on October 31, 1903.

mechanics. There is, I think, a widespread confusion of boundaries which makes this sharp delimitation a thing greatly to be desired, and I have chosen as the title of this preliminary paper 'The Misuse of Physics by Biologists and Engineers' for the reason that, in my opinion, these men, more than any others, violate in their philosophy the essential limitations of systematic physics and confuse the boundaries between systematic physics and statistical physics.

I do not wish this title to be taken as a challenge to biologists and engineers, but rather as suggesting, in a general way, the error of the indiscriminate application of the philosophy of the exact sciences in the study of natural phenomena. I do not expect, indeed, to make my position entirely clear until I have finished with what I have to say about statistical physics, but my position in brief is this, that the idea of quantitative relationships and the idea of one-to-one correspondence in general, as these ideas are known in physics, are inapplicable and necessarily fruitless in such fields as physical psychology and meteorology.

I am led to present this preliminary paper at this time from having read the recent presidential address of James Swinburne before the British Institution of Electrical Engineers and a subsequent paper on thermodynamics presented by Mr. Swinburne at the Southport meeting of the British Association in September.

Mr. Swinburne believes, apparently, that the precise ideas and methods of thermodynamics are unconditionally applicable to irreversible processes in general. I do not agree with him in this, and I do not think that the legitimacy and precision of the accepted ideas of thermodynamics especially as represented in the writings of Willard Gibbs can be questioned; but I do think that the notions of thermodynamics are precisely applicable to those types of irreversible processes which constitute permanently varying states, and approximately applicable to those irreversible processes which involve either approximate states of thermal equilibrium or approximately permanent states of variation. I shall point out the precise application of the ideas of thermodynamics to permanently varying states in this preliminary paper, reserving the discussion of approximate applications for a subsequent paper.

The fact is that the precise notions of systematic physics in general are essentially inapplicable in the world of actual phenomena, except in so far as these phenomena can be approximately correlated to *states of equilibrium* and to *permanently varying states* of material systems. I remember very distinctly the incredulity with which I first encountered, in my early study of physics, the unguardedly sweeping generalizations in the treatises which I then read, for example, on the elementary mathematical theory of electricity and magnetism. I could not believe that the phenomena of electricity and magnetism were quantitative in the sense that my then highly abstracted ideas of mechanical phenomena were quantitative.

In order to give some sort of a preliminary notion of what I have in mind in using the terms systematic physics and statistical physics I shall resort to classification.

Physics is divided into two branches, namely, systematic physics and statistical physics.

Systematic physics is again divided into mechanics and thermodynamics.

Mechanics, in the broad sense here defined, treats of those phenomena which can be to a high degree of approximation correlated in one-to-one correspondences to states of equilibrium and to simple types of sensible motion such as translatory motion, rotatory motion, motion involved in simple types of elastic distortion, steady types of fluid motion including wave motion and the corresponding types of force action. This definition of mechanics includes a large portion of the subjects of electricity and magnetism and of light. Mechanics, as here defined, includes all phenomena which involve action between bodies and regions of finite size, which action can be perceived directly or indirectly as a unit.

Thermodynamics treats of those phenomena which can be to a high degree of approximation correlated in one-to-one correspondences to states and processes involving thermal equilibrium and involving those permanently varying states which I have called steady sweeps. Thermodynamics involves much mechanics, but mechanics proper ignores everything which pertains strictly to thermodynamics. Thermodynamics includes all portions of the subjects of electricity and magnetism and light which are not completely defined in mechanical terms.

Statistical physics is the study of all the actual physical phenomena of nature, some of which, indeed, may be described in terms of the notions of ideal mechanics to a high degree of approximation, and some of which, indeed, may be described in terms of the notions of ideal thermodynamics to a high degree of approximation, but all of which are more or less erratic and in their minute details infinitely manifold, and in all of which the notion of one-to-one correspondence or of cause and effect, if one prefers that mode of expression, fails.

A clear understanding of the essential limitations of systematic physics is important to the engineer; it is, I think, equally important to the biologist, and it is of vital importance to the physicist, for in the case of the physicist, to raise the question as to limitations is to raise the question as to whether his science does after all deal with realities, and the conclusion which must force itself on his mind is, I think, that his science, the systematic part of it, comes very near, indeed, to being a science of unrealities. This is not necessarily to the discredit of the physicist, provided he knows it.

The engineer is not far wrong in his application of the principles of mechanics, for the engineer is chiefly concerned with integral relationships between finite things. Nevertheless, I think that the engineer frequently attempts to carry his mechanics too far, when, for example, he attempts anything but the crudest correlation in his studies of such things as friction and fluid motion. The phenomena of friction and of fluid motion can not be correlated—I do not mean by human means, conditionally as it were, but I mean that they absolutely can not be approximately correlated by any means in one-to-one correspondences. I discussed this matter briefly in some remarks before the American Institute of Electrical Engineers on December 19, 1902.* In studies which require the application of the principles of thermodynamics, on the other hand, engineers are, I think, frequently in error. Thus, Mr. Swinburne's difficulty—his statements, being partly right and partly wrong, may be taken to indicate a difficulty—seems to me to lie in an improper application of the principles of thermodynamics.

The biologist, on the other hand, is, I think, usually illogical when he attempts to make use of the ideas of systematic physics. The biological sciences, in so far as they are related to systematic physics at all, are related primarily to thermodynamics, and in so far as the biologist is unfamiliar with the principles of thermodynamics he can not make proper use of

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* See *Trans. A. I. E. E.*, January, 1903, pp. 79–80.

any of the generalizations of systematic physics. I shall consider later the relations of biology and statistical physics, not, of course, from the point of view of the biologist, for this would be to discuss the relation of organism to environment, but in the light of some of the ideas of thermodynamics.

The biologist and the engineer need to have precise knowledge of thermodynamics, inasmuch as it is thermodynamics chiefly which determines the limits of correct application of the ideas and methods of systematic physics to natural phenomena.

This subject of thermodynamics is so little understood that I am not willing to proceed to a precise discussion of the questions set forth in a general way above, without first giving an outline of the fundamental ideas of thermodynamics, which I shall give as concisely and concretely as possible. I feel justified in taking your time in this way for the reason that here and there throughout my presentation you will find that the ideas are new, and, furthermore, I wish this paper to be readable by biologists and engineers.

In some instances I shall insist upon what may seem to be unnecessarily fine distinctions; but Whewell says very aptly that 'In order to acquire any exact solid knowledge the student must possess with perfect precision the ideas appropriate to that part of knowledge.' If there is any branch of physics where perfect precision of ideas is demanded it is, I think, in the subject of thermodynamics, especially if the boundaries between the legitimate realm of thermodynamics and the almost untouched realm of statistical physics are to be sharply defined.

Perfect precision of ideas is tested, as Whewell says, by the extent to which one perceives axiomatic evidence in a subject, and I give this sketch of thermodynamics exactly with the view of setting forth axiomatic evidences.

1. THERMAL EQUILIBRIUM.

When a substance is shielded from outside disturbance it settles to a state in which there is no tendency to further change of any kind. Such a state is called a state of *thermal equilibrium.*

When a substance has settled to thermal equilibrium it is said to have a definite temperature. The notion of temperature, that is the precise idea of temperature, as a physical fact is derived from the notion of thermal equilibrium. Also the idea of differences of temperature as physical facts (not as quantities) is derived from comparisons of states of thermal equilibrium.

The idea of thermal equilibrium applies to a limit which is never realized. It is impracticable to shield a substance completely. Failure of two kinds occurs, namely, failure to prevent exchange of energy between one system and another, either in the form of mechanical work or in the form of heat, and failure to prevent exchange of matter between one system and another. This second failure is very marked in the case of radioactive substances. Furthermore, our accepted notions as to the quickness with which a gas, for instance, settles to thermal equilibrium may be altogether wrong, for Boltzmann has pointed out that even a small mass of gas shielded completely in a vessel may, for all we know, require months to settle to anything approaching complete thermal equilibrium.

Before proceeding with this outline of thermodynamics I wish to state what is my opinion as to the influence which the kinetic theory (of gases) is destined to have upon the subject of thermodynamics. Several years ago, in writing a review of Duhem's elaborate mathematical development of thermodynamics, 'Mechanique Chemique,' I contrasted the purely sensible basis and the abstract but inevitable mathematical structure of thermodynamics, on the one hand, with the mathematical theory of electricity and magnetism as it stands in Maxwell's 'Treatise,' on the other hand. Maxwell's theory is, of course, largely based on sensible things, but sensible things which are more or less inadequate to determine the essential elements of the theory, so that conception enters as an important and vital part of the theory. I stated that perhaps we are to have in thermodynamics a branch of physics which is to remain independent of conceptions, to remain, in other words, a purely algebraic structure resting upon an adequate foundation of axiomatic evidence which may be directly perceived. I do not now think that this is to be the case, but I think that the ideas of the kinetic theory, or, as Gibbs puts it, the ideas of statistical mechanics, are destined to become vital in the subject of thermodynamics; and I think that it is of the greatest importance in the treatment of thermodynamics, to reach conceptions of every fundamental notion with the help of the kinetic theory (statistical mechanics).

In view of my opinion as to the vital importance of statistical mechanics in thermodynamics, I shall suggest, whenever I can do so briefly, the molecular conceptions of the various notions of thermodynamics.

The Molecular Conception of Thermal Equilibrium.—The molecular motion at a given point in a gas (and no doubt in any substance) in thermal equilibrium is entirely erratic; an irregular and extremely rapid succession of fits and starts occurs as the molecules collide against each other, and the character of the molecular motion at the point is still further complicated by the fact that different molecules are continually passing the given point from every direction and with every variety of speed and oscillatory motion. Because of the enormous number of molecules in any perceptible volume of a substance it is the *average character* of the molecular motion, only, which has to do with temperature and pressure and in general with all thermal properties of substances; and, because of the enormous number of molecules, this average character of molecular motion is constant and uniform throughout a substance when the substance is in thermal equilibrium.

2. REVERSIBLE PROCESSES.

A substance in thermal equilibrium is generally under the influence of external agencies. Thus, surrounding substances confine the given substance to a certain region of space and they exert upon the given substance a constant pressure; surrounding substances are at the same temperature as the given substance and the molecules of the given substance rebound from surrounding substances with their motion, on the average, unchanged; surrounding substances may exert constant magnetic or electric influences upon the given substance, and so on. However, a substance can not be in thermal equilibrium when work is continually done upon or done by it, or when heat is continually given to or taken from it.

If the external influences which act upon a fluid in thermal equilibrium are made to change *very slowly,* causing the pressure and volume of the fluid to pass very slowly through a continuous series of values and in general involving the doing of work upon or by the fluid and the giving of heat to or taking of heat from the fluid, the fluid will pass slowly through *a process consisting of a continuous series of states of thermal equilibrium.* Such a process is called a *reversible process,* for the reason that the fluid will pass through the same series of states in reverse order if the external influences are changed slowly so as to make the pressure and volume of the fluid pass through the same series of values in reverse order.

The characteristics of a reversible process are therefore as follows:

(*a*) A substance which undergoes a reversible process must be under varying *external* influence. A closed system can not perform a reversible process.

(*b*) A substance as it undergoes a reversible process is at each instant in a state of thermal equilibrium; and if, at a given instant during a reversible process, the external influences should cease to change, causing a sudden cessation of the doing of work on or by the substance, and of the interchange of heat between the substance and its surroundings, no commotion would be left in the substance.

(*c*) A reversible process must take place slowly, strictly with infinite slowness. An actual process, that is, a process which actually does proceed, can be only approximately reversible. Examples of reversible processes are given in the article on trailing sweeps, for it is important that it be clearly recognized that a reversible process is the limit which a trailing sweep approaches when it is performed more and more slowly.

3. SWEEPING OR IRREVERSIBLE PROCESSES.

While a substance is settling or tending to settle to thermal equilibrium it may be said to undergo a process. Such a process can not, in general, be arrested and maintained at any stage short of complete thermal equilibrium, but always and inevitably proceeds towards that state. Such a process is, therefore, called a *sweeping process* or simply a *sweep.*

A sweeping process takes place in one direction only, that is, if *A* and *B* are two successive stages of a sweep, stage *B* following stage *A,* then stage *B* grows out of stage *A* inevitably, but stage *A* can not be made to follow or grow out of stage *B* by any means whatever. A sweeping process, therefore, is irreversible.

Molecular Conception of the Sweeping Process.—While a gas (and perhaps any substance) is settling to thermal equilibrium, immediately after an explosion, for example, the character of the molecular motion at a given point changes rapidly from instant to instant and the character of the molecular motion at a given instant varies greatly from point to point in the gas; in other words, the gas is the seat of more or less violent turbulence while it is settling to thermal equilibrium.

The effects of mutual collision among the molecules, the effects of the collision of the molecules against the walls of the containing vessel and the effects of the confused movement* of the gas molecules from one part of the vessel to another part are always to even up the differences in the character of molecular motion in different parts of the vessel. On the other hand, the external influences which can be brought to bear on a substance act on all the molecules in the same general way, so that the tendency of a turbulent state of a gas to die away on account of the internal actions just pointed out can not be counteracted by external influences,† and,

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* If a great number of white and black balls are placed in a box and shaken up, the confused motion tends to cause an even distribution of white and black balls throughout the box, for the reason, that, of all possible arrangements of the balls, approximately even distribution is the most probable.

† The maintenance of an unending state of turbulence in a trailing sweep because of rapidly changing external influence is by no means a case in which the tendency of a turbulent state to die away is counteracted by external action, but rather a case in which the goal, namely the final state of thermal equilibrium, is made to recede continuously.

therefore, a sweeping process can not be arrested nor reversed by any means.

Note 1.—A fluid not in thermal equilibrium has no definite pressure, temperature or volume. The volume of a turbulent gas pertains only to the containing vessel. Any one, for example, who reads the reports of the measurement of the Holton and St. Albans base lines by the U. S. Coast and Geodetic Survey will appreciate the necessity of the projection of a region of thermal equilibrium into a space which is to be measured, and any one of course knows that the reality of the results of these measurements depends upon the fact that the earth's crust is approximately in thermal equilibrium.

One error in Mr. Swinburne's discussion of thermodynamics is in the extension of the notions of volume, pressure, temperature and entropy to substances not in thermal equilibrium. Points in Watt's diagram can represent only states of equilibrium, and lines in Watt's diagram can represent only reversible processes. I shall indicate in a subsequent paper the method which must be used when one wishes to extend engine calculations, for example, so as to include sweeping processes.

Note 2.—Writers on thermodynamics who are obliged to deal with irreversible processes or sweeping processes, that is to say, steam engineers, frequently introduce the notion of the integration of entropy and temperature. Thus Mr. Swinburne enlarges upon this procedure. He would assign a definite entropy and a definite temperature to each volume element of turbulent steam, and by integration arrive at the notion of total entropy and mean temperature. Now in the first place, when this method appears to give results a legitimate mode of calculating sweeps is really used, and the legitimate ideas involved are illogically expressed in terms of temperature and entropy. In the second place, *temperature and entropy have no meaning as applied to the elements of volume, even of a substance in thermal equilibrium,* not to mention the question of their application to the volume elements of a turbulent substance. This is a limitation of the ideas of thermodynamics which is indicated by the ideas of statistical mechanics. Whether this limitation can be justified independently of statistical mechanics I am not prepared to say with certainty. Thermodynamics has to do only with finite portions of matter, and infinitesimals have no meaning except as increments of finite quantities.

4. SIMPLE SWEEPS.

The settling of a closed system to thermal equilibrium is called a *simple sweep.*

Example.—The equilibrium of a mixture of oxygen and hydrogen in a closed vessel may be disturbed by a minute spark, and the explosion and subsequent settling of the aqueous vapor to a quiescent state without loss of heat constitute a simple sweep. The equilibrium of a gas confined under high pressure in one half of a two-chambered vessel may be disturbed by opening a cock which connects the two chambers, and the rush of gas into the empty chamber constitutes a simple sweep.

5. TRAILING SWEEPS.

When external influences change continuously, a substance in its tendency to settle to equilibrium never catches up, as it were, with the changing conditions, but trails along behind them, and we have what is called a *trailing sweep.*

Examples.—The rapid expansion or compression of a gas in a cylinder is a trailing sweep. So long as the piston moves at a perceptible speed, the gas, in its tendency to settle to equilibrium, never catches up with the varying conditions. This is evident, for any one can see that a sudden stoppage of the piston would leave some slight turbulence in the gas, which would not be the case if the gas were in equilibrium at the instant the piston is stopped. When the piston is moved more and more slowly, the departure of the gas from strict thermal equilibrium at each stage of the expansion or compression becomes less and less, and the expansion or compression approaches more and more nearly to a reversible process.

The rapid heating (or cooling) of a gas in a closed vessel is a trailing sweep. So long as heat is given to the gas at a perceptible rate there will be perceptible differences of temperature in different parts of the gas; the gas in its tendency to settle to thermal equilibrium never catches up with the increasing temperature of the walls of the containing vessel.

When the gas is heated (or cooled) more and more slowly, that is, when heat is given to the gas at a rate which becomes more and more nearly imperceptible, then the departure of the gas from strict thermal equilibrium at each stage of the heating process becomes less and less, and the heating (or cooling) approaches more and more nearly to a reversible process.

6. STEADY SWEEPS.

A substance may be subjected to external action which, although unvarying, is incompatible with thermal equilibrium. When such is the case the substance settles to a permanent or unvarying state which is not a state of thermal equilibrium. Such a state of a substance is called a *steady sweep*.

Examples.—The two faces of a slab or the two ends of a wire may be kept permanently at different temperatures. When this is done the slab or wire settles to an unvarying state which is by no means a state of thermal equilibrium. Heat flows through the slab or along the wire from the region of high temperature to the region of low temperature, *never* from the region of low temperature to the region of high temperature. This flow of heat through the slab or along the wire is an irreversible process and it constitutes a steady sweep.

The ends of a wire may be kept permanently at different electric pressures, for example, by connecting the wire to the terminals of a battery or dynamo. When this is done a steady electric current flows along the wire, the battery does work steadily on the wire, and this work reappears steadily as heat in the wire. Reversal of the current *does not* reverse this process and cause heat energy to disappear in the wire (cooling the wire) and reappear as work done on the battery by the wire, but the process is irreversible and it constitutes a steady sweep.

The notion of steady sweeps is of the utmost importance in thermodynamics inasmuch as thermodynamics treats directly of states of thermal equilibrium and of steady sweeps only.

The notion of entropy is involved in the notion of a steady sweep; and the notion of temperature is involved in the notion of thermal equilibrium.

7. THERMODYNAMIC DEGENERATION AND REGENERATION.

A sweeping process always plays a certain havoc, or effects a certain *degeneration* in a system. Thus, there is a certain degeneration associated with the escape of a compressed gas through an orifice; there is a certain degeneration associated with the flow of heat from a region of high temperature to a region of low temperature; there is a certain degeneration associated with the direct conversion of work into heat, and so on.

In a simple sweep the degeneration lies wholly in the relation between the initial and final states of the substance which undergoes the sweep, inasmuch as, in a simple sweep, no outside substance is affected in any way, no work is done on or by the substance which undergoes the sweep, and no heat is given to or taken from it.

In a trailing sweep the degeneration may lie partly in the relation between the initial and final states of the substance which undegoes the sweep, partly in the direct conversion of work into heat and partly in the direct transfer of heat from regions of high temperature to regions of low temperature.

In a steady sweep the substance which undergoes the sweep remains entirely unchanged as the sweep proceeds, and the degeneration lies wholly in the direct conversion of work into heat, in the direct transfer of heat from a region of high temperature to a region of low temperature, or both.

A substance which has undergone a sweeping process may be brought back to its initial state, or *regenerated,* by a reversible process; but when a substance is regenerated by a reversible process, the external action necessary to bring about the reversible process involves an equal degeneration of some external substance; that is, the regeneration of a substance by a reversible process always involves the creation of an equal external regeneration. This is, in fact, a statement of the second law of thermodynamics.

The entire subject of thermodynamics, in so far as it does not have to do with the specific thermal properties of particular substances, is based upon the consideration of the two kinds of thermodynamic degeneration which are involved in steady sweeps, that is, upon: (*a*) The thermodynamic degeneration which is represented by the direct conversion of work into heat, and the thermodynamic regeneration which is represented by the conversion of work into heat by a reversible process; and (*b*) The thermodynamic degeneration which is represented by the direct transfer of heat from a region of high temperature to a region of low temperature, and the thermodynamic regeneration which is represented by the transfer of heat from a low temperature region to a high temperature region by a reversible process.

The following two propositions concerning the two kinds of thermodynamic degeneration (*a*) and (*b*) follow at once from a consideration of steady sweeps.

PROPOSITION (A).—The thermodynamic degeneration represented by the direct conversion of work into heat at a given temperature is *proportional* to the quantity of work so converted.

Proof.—Consider a steady flow of electric current in a wire. This process being steady, the amount of degeneration occurring in a given interval of time must be proportional to the time. The amount of work converted into heat is also proportional to the time. Therefore the amount of degeneration is proportional to the amount of work converted into heat. Of course the temperature must be invariable, or the process can not be thought of as remaining identically the same from instant to instant. The dependence of this kind of degeneration upon temperature will be considered later.

Corollary.—The thermodynamic regeneration which is represented by the conversion of heat at a given temperature into work by a reversible process is proportional to the heat so converted.

PROPOSITION (B).—The thermodynamic degeneration represented by the direct 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.

Proof.—Consider a steady flow of heat

from temperature T_1 to temperature T_2 constituting a steady sweep. This process being steady, the degeneration occurring in a given interval of time must be proportional to the time. The quantity of heat transferred is also proportional to the time. Therefore, the amount of degeneration is proportional to the quantity of heat transferred. The dependence of this kind of degeneration upon temperature will be considered later.

Corollary.—The thermodynamic regeneration which is represented by the transfer of heat from a low temperature T_2 to a high temperature T_1 by a reversible process is proportional to the heat transferred.

8. THE SECOND LAW OF THERMODYNAMICS.

(*a*) The degeneration of a system which accompanies a sweeping process can not be directly repaired, nor can it be repaired by any means without the creation of a compensating degeneration in some other system.

This is an entirely general statement of the second law. The *direct repair* of the degeneration due to a sweeping process means the undoing of the havoc wrought by the sweep by allowing the sweep to *perform itself backwards!* This notion of *direct repair* is introduced into this general statement of the second law in order that each of the following particular statements of the law, namely, (*b*), (*c*) and (*d*) may correspond exactly in form to the general statement (*a*). A slightly modified general statement of the second law is the following:

(*a*) Thermodynamic degeneration and regeneration are always balanced in a reversible process, while degeneration always exceeds regeneration in any process which is in any way sweeping in character.

(*b*) Heat can not pass directly from a cold body to a hot body, nor can heat be transferred from a cold body to a hot body by any means without compensation.

(*c*) Heat can not be converted directly into work, nor can heat be converted into work by any means without compensation.

The direct conversion of heat into work (see discussion following (*a*) above) would be simply the reverse of any of the ordinary sweeping processes which involve the degeneration of work into heat. Thus, work is degenerated into heat in the bearing of a rotating shaft, and we all know that to reverse the motion of the shaft will not cause the bearing to grow cold and the heat so lost to appear as work helping to turn the shaft!

(*d*) A gas can not pass directly from a region of low pressure to a region of high pressure, nor can a gas be transferred from a region of low pressure to a region of high pressure by any means without compensation.

The compensation involved in the transfer of a gas from a region of low pressure to a region of high pressure by means of a pump is the degeneration into heat of the work spent in driving the pump.

The repeated statement of self-evident facts in these statements of the second law of thermodynamics may seem ridiculous to the intelligent reader, but it must be remembered that but few persons realize that the second law of thermodynamics is a statement of a fact which every one knows, together with a generalizing clause which when once thoroughly understood is almost if not quite self-evident. I can not refrain from one more statement of the second law, the oldest English version of it:

Humpty Dumpty sat on a wall.
Humpty Dumpty had a great fall.
All the King's horses and all the King's men
Can not put Humpty Dumpty together again.

This is perhaps the most dignified of all the statements of the second law of thermodynamics, inasmuch as it omits all nonsense about *direct repair* and refers at once to external means.

The reader must not imagine, however, that thermodynamic degeneration has anything to do with structural degeneration or dissolution, which is the most prominent feature of the calamity which befell Humpty Dumpty, but, to put the case concretely, if one shakes up a quantity of pure and homogeneous water in a bottle, one plays that irreparable havoc which constitutes thermodynamic degeneration.

9. ENGINES.

The further development of the subject of thermodynamics depends upon the establishment of the exact relation between the degeneration which is represented by the transfer of heat from a high to a low temperature and the degeneration which is represented by the conversion of work into heat. To establish this relation it is necessary to consider a *reversible process* in which the degeneration of heat from high to low temperature is compensated by the regeneration of heat into work, or *vice versa*.

The engine is a machine which determines such a process. The ordinary engine, indeed, is subject to friction, and the steam as it passes through the engine does not undergo a reversible process; but if the engine were frictionless, if it were driven slowly, if the cylinder were prevented from cooling the steam, if the steam were expanded sufficiently to prevent puffing and if the feed water were heated, in a 'regenerative' feed water heater, to boiler temperature before entering the boiler, then the processes involved in the operation of the engine would be reversible. Such an ideal engine we will call a *reversible engine* or a *perfect engine*.

During a given interval of time the engine takes an amount of heat H_1 from the boiler at temperature T_1, it converts into work W a certain fractional part of H_1 and delivers the remainder H_2 to the condenser at temperature T_2.

The work W done by the engine is equal to the difference $H_1 - H_2$ according to the first law of thermodynamics. That is,

$$W = H_1 - H_2. \tag{1}$$

Now, all the heat used in the engine comes from the region at temperature T_1, and the net result of the operation of the engine is: (a) to convert the quantity $W(=H_1 - H_2)$ of heat from temperature T_1 into work, and (b) to transfer the quantity H_2 of heat from temperature T_1 to temperature T_2. The result (a) involves an amount of regeneration which is proportional to W, temperature being given; this regeneration may, therefore, be represented by mW where m is a constant depending *only* on the temperature T_1. The result (b) involves an amount of degeneration which is proportional to H_2, temperatures being given; this degeneration may, therefore, be represented by nH_2 where n is a constant depending *only* on the temperatures T_1 and T_2. If the engine is reversible we must have

$$mW = nH_2, \tag{2a}$$

or, using the value $(H_1 - W)$ for H_2, and solving for W we have

$$W = \frac{n}{m+n} H_1, \tag{2b}$$

in which $n/(m+n)$ depends on T_1 and T_2, *only*, irrespective of the kind of engine and of the physical properties of the fluid employed in the engine, provided, only, that the engine is reversible. The fractional part $n/(m+n)$ of the heat H_1 which the engine converts into work is called the efficiency of the engine, and from equation (2)b it follows that *the efficiency of all reversible engines is the same for given values of the temperatures T_1 and T_2.*

If the operation of the engine involves sweeping processes of any kind then the degeneration nH_2 exceeds the regeneration mW or

$$mW < nH_2,$$

or, using the value $(H_1 - W)$ for H_2, and solving for W we have

$$W < \frac{n}{m+n} H_1, \tag{3}$$

in which m and n have the same values as in equation (1). Comparing this with equation (2)*b* it follows that *any irreversible engine working between given temperatures T_1 and T_2 has less efficiency than a reversible engine working between the same temperatures.*

10. THERMODYNAMIC DEFINITION OF THE RATIO OF TWO TEMPERATURES.

According to article 9 the ratio, H_1/H_2, of the heat taken from the boiler to the heat given to the condenser by any reversible engine working between the given temperatures T_1 and T_2 is invariable, and it can be easily shown that this ratio approaches unity as T_1 and T_2 approach equality. Therefore, the ratio of the two temperatures T_1/T_2 may be defined as the ratio of the two heats H_1/H_2. That is:

$$\frac{T_1}{T_2} = \frac{H_1}{H_2}. \tag{4}$$

11. ENTROPY. THERMODYNAMIC DEGENERATION.

The statement of the second law of thermodynamics can scarcely be looked upon as complete until a precise and complete numerical measure of thermodynamic degeneration has been established. This numerical measure of thermodynamic degeneration is called entropy. The notion of entropy may be completely developed by consideration of steady sweeps. I will give this development first and I will give Clausius's development afterwards in order to point out an error in Clausius's discussion.

Referring to article 9 we may write the expression for the regeneration mW in the form $f(T_1) \cdot W$ inasmuch as m is a function of T_1 only.

The degeneration nH_2 may be written

$$[f(T_2) - f(T_1)]H_2,$$

inasmuch as the degeneration associated with the transfer of the heat H_2 from T_1 to T_2 may be thought of as (*a*) the regeneration of H_2 from temperature T_1 to work, and (*b*) the degeneration of this resulting work to heat at temperature T_2; in which case the regeneration (*a*) is $f(T_1) \cdot H_2$ and the degeneration (*b*) is $f(T_2) \cdot H_2$.

Therefore, equation (2)*a* may be written

$$f(T_1) \cdot W = [f(T_2) - f(T_1)]H_2.$$

Using equation (1) and equation (4) we have

$$\frac{f(T_2) - f(T_1)}{f(T_1)} = \frac{T_1 - T_2}{T_2}.$$

From which the function f is to be determined. Differentiating with respect to T_2 we have

$$\frac{f'(T_2)}{f(T_1)} = -\frac{T_1}{T_2^2} = -\frac{\frac{1}{T_2^2}}{\frac{1}{T_1}};$$

and, therefore, since T_1 and T_2 are independent of each other we have

$$f(T_1) = \frac{1}{T_1}.$$

That is to say, the thermodynamic degeneration associated with the conversion of an amount of work W into heat at temperature T_1 is equal to W/T_1, and the thermodynamic degeneration associated with the transfer of an amount of heat H_2 from temperature T_1 to temperature T_2 is

$$\frac{H_2}{T_2} - \frac{H_2}{T_1}.$$

Clausius's derivation of the numerical measure of entropy is based upon the idea that degeneration and regeneration are balanced in a reversible process. In this derivation it is necessary to consider a cyclic process (reversible) in order that no outstanding change of state may be left as a result of the process, so that one need consider only the exchange of work and heat between the substance which is being studied and external substances, and in particular one is not under the necessity of considering the amount of degeneration or regeneration involved in the change of state of a particular substance.

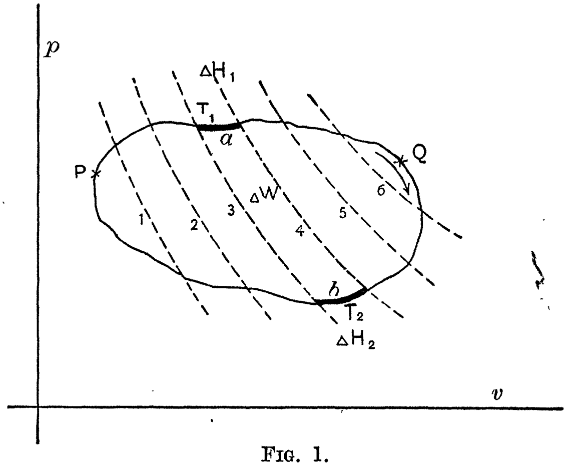

FIG. 1.

Consider a fluid, which, starting from the state *P*, Fig. 1, is made to pass through a reversible cyclic process and return to the state *P* by any combination whatever of slow heating and cooling, expanding and compressing. The closed curve represents the cyclic process, and the moving point *Q* as it moves along the process curve represents the changing state of the fluid.

A clear idea of the external actions which take place may be obtained by drawing a series of adiabatic or isentropic lines (an isentropic line represents the variation of pressure with volume when the fluid neither gives off nor receives heat). The fluid is receiving heat while *Q* is crossing isentropic lines from small numbers to large numbers in Fig. 1, and giving off heat while *Q* is crossing isentropic lines from large numbers to small numbers. The fluid is expanding and doing external work when *Q* is moving to the right, and contracting and having work done upon it when *Q* is moving to the left. The fluid is in general at high temperature for those positions of *Q* where *p* and *v* are both large, and at low temperatures for those positions of *Q* where *p* and *v* are both small.

Consider two portions, *a* and *b*, of the given process curve which lie between a pair of isentropic lines. Let T_1 be the high temperature of the fluid when *Q* is passing along *a*, and let dH_1 be the amount of heat taken in by the fluid while *Q* is passing along *a*. Let T_2 be the low temperature of the fluid when *Q* is passing along *b*, and let dH_2 be the amount of heat given off by the fluid while *Q* is passing along *b*.

Consider the reversible cyclic process which is represented by the two portions *a* and *b* of the given process curve, together with the isentropic lines between which *a* and *b* lie. We will call this cyclic process an elementary cyclic process to distinguish it from the given process. The net result of the elementary cyclic process would be the taking in of the quantity dH_1 of heat at T_1, the conversion of a definite fraction dW of this heat into work and the giving off of the remainder, dH_2, of the heat at temperature T_2. Therefore, according to Arts. 9 and 10 we have

$$\frac{dH_1}{dH_2} = \frac{T_1}{T_2}. \qquad \text{(i)}$$

Now, dH_1 is heat received by the fluid, and dH_2 is heat given off by the fluid, and one or the other should be considered as negative, say dH_2, then equation (i) should be written:

$$-\frac{dH_1}{dH_2}=\frac{T_1}{T_2}, \qquad \text{(ii)}$$

or

$$\frac{dH_1}{T_1}+\frac{dH_2}{T_2}=0. \qquad \text{(iii)}$$

The whole of the given cyclic process may be broken up into pairs of corresponding parts like *a* and *b*, so that the entire heat taken in and given out by the fluid during the given process consists of parts which correspond in pairs like dH_1 and dH_2, and each pair of heat parts satisfies an equation like (iii). Therefore, *the sum of all quotients obtained by dividing the heat taken in by a fluid at each step of any reversible cyclic process by the absolute temperature of the fluid at the step is equal to zero.* That is

$$\Sigma\frac{dH}{T}=0 \qquad (5)$$

for any reversible cyclic process.

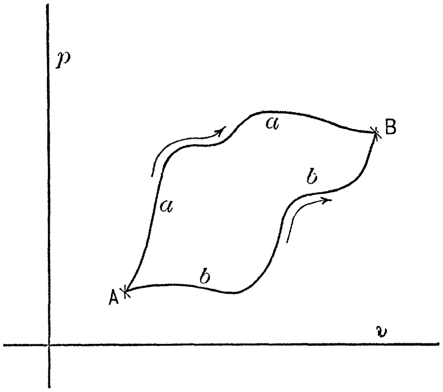

Fig. 2.

Consider two states of thermal equilibrium of a fluid represented by the points *A* and *B*, Fig. 2. Let the lines *a* and *b* represent any two different reversible processes leading from *A* to *B*. Then process *a* together with process *b reversed* constitute a cyclic process starting from *A* and returning to *A*. Therefore the sum $\Sigma\, dH/T$ is equal to zero when it is extended over process *a* and over process *b reversed.* Putting this into symbolic form we have:

$$\Sigma_a\frac{dH}{T}+\Sigma_{-b}\frac{dH}{T}=0, \qquad \text{(iv)}$$

in which the subscript *a* indicates that the first summation is extended over process *a,* and the subscript —*b* indicates that the second summation is extended over process *b reversed.*

But

$$\Sigma_{-b}\frac{dH}{T}=-\Sigma_b\frac{dH}{T}. \qquad \text{(v)}$$

That is, the summation $\Sigma\, dH/T$ extended over the process *b reversed* is equal but opposite in sign to the value of this summation $\Sigma dH/T$ extended over the process *b* not reversed, that is, when process *b* leads from state *A* to state *B*.

Substituting the value of $\Sigma dH/T$ from equation (v) in equation (iv) we have

$$\Sigma_a\frac{dH}{T}=\Sigma_b\frac{dH}{T}. \qquad (6)$$

That is, *the sum ($\Sigma\, dH/T$) has the same value for any two, and therefore, for all reversible processes which lead from one given state of thermal equilibrium A to another given state of thermal equilibrium B.*

If the state *B* is one which can be reached from state *A* by a sweeping process, then the sum ($\Sigma dH/T$) extended over a reversible process leading from *A* to *B* is *positive* in value. Therefore the value of the sum ($\Sigma dH/T$) extended over any reversible process leading from state *A* to state *B* of a substance *may be used as a measure of the thermodynamic degeneration* which is associated with the change of the substance from state *A* to state *B*. This sum is called the *increase of entropy* of the substance. When the sum ($\Sigma\, dH/T$) is negative it measures a thermodynamic regeneration and is called a *decrease of entropy.*

Examples.—A gas is allowed to sweep through an orifice and increase in volume from v to V with imperceptible change of temperature. The same gas is then expanded slowly in a cylinder from volume v to volume V without change of temperature. To prevent change of temperature heat must be given to the gas at each step of the expansion (dH positive), and therefore the sum ($\Sigma\, dH/T$) is positive.

A gas is heated at constant volume by the degeneration of work into heat. The same result may be accomplished reversibly by heating the gas slowly on a stove. In this latter process dH is positive at each step and the sum ($\Sigma dH/T$) extended over the slow heating process is positive.

The creation of an external compensating degeneration (decrease of entropy) when the effect of a sweeping process is repaired by a reversible process may be expressed by the entropy change of external substances. Thus in each of the above examples the reversible process involves the taking of heat from external substances so that the sum ($\Sigma dH/T$) is negative as applied to the external changes which are involved in the reversible processes mentioned, or in other words, external substances suffer an increase of entropy when a given substance has its entropy decreased by a reversible process.

In general the thermodynamic degeneration associated with a sweeping process can be represented as an increase of entropy (summation of dH/T as above explained) only by devising a reversible process which produces the same change as the given sweep so far as the substance under consideration is concerned. In the case of steady sweeps, however, it is not *necessary* to devise a reversible process for producing the same result in order to represent the result of a steady sweep as an increase of entropy. The entropy increase which is associated with a steady sweep may be derived from a consideration of the reversible processes which always accompany a steady sweep, using Clausius's summation $\Sigma\, dH/T$, as follows:

Consider the *slow* flow of heat from a body A at temperature T_1 to a body B at temperature T_2. The transfer of heat being slow, the cooling of A and the heating of B are reversible processes, and A and B are at each instant in thermal equilibrium.

While an amount of heat H is transferred the decrease of entropy of body A is $\Sigma dH/T = H/T_1$ and the increase of entropy of body B is $\Sigma dH/T = H/T_2$, so that the net increase of entropy due to the steady sweep is $(H/T_2 - H/T_1)$.

Consider a fine wire submerged in a large vessel of water at temperature T, heat being slowly generated in the wire by an electric current. Then the water will be at each instant in thermal equilibrium, that is, the heating of the water will be a reversible process to which Clausius's summation may be applied. Thus, while the water receives an amount of heat W (measured in terms of the work lost in the wire), the value of $\Sigma dW/T$ will be W/T, which is the increase of entropy of the water. In this case there is no decrease of entropy anywhere; so that W/T measures the thermodynamic degeneration involved in the conversion of the work W into heat at temperature T.

Absolute Values of Entropy.—Entropy changes or entropy differences only have real physical significance. However, a certain state of a substance may be arbitrarily chosen as a zero state or reference state and the absolute value of the entropy of the substance in any other given state may be defined as the value of Clausius's summation extended over any reversible process leading from the zero state to the given state. This is equivalent to assigning arbitrarily the value zero to the entropy of the substance in the zero state.

The entropy of a substance in a given state is proportional to the mass of the substance, for doubling the mass will double the value of dH for each step of any reversible process. Entropy is, of course, expressed in *units of heat per degree of temperature.*

Remark.—Equation (5), due to Clausius, was further generalized by Clausius so as to apply in his opinion to cyclic processes which are not reversible, in which case, according to Clausius, equation (5) becomes

$$\Sigma\frac{dH}{T} > 0.$$

This extension of the integral $\Sigma dH/T$ to include sweeping processes is incorrect except in so far as steady sweeps are concerned as explained above.

12. SUMMARY.

The precise idea of temperature is associated with the notion of thermal equilibrium, and the precise idea of temperature has nothing to do with the sensations of hot and cold. The electric arc, for example, is very hot, but it has no temperature.

The error of Clausius in extending his summation to irreversible processes lies in the fact that in general the idea of temperature utterly fails in such cases, and the summation $\Sigma dH/T$ has no meaning whatever. Of course, this summation may always be applied to the reversible changes (when they exist) which take place in the external substances which envelop the substance which is undergoing the irreversible process.

Not only is the precise idea of temperature limited to substances in thermal equilibrium, but it applies only to a finite portion of a substance. It is meaningless to speak of the temperature of a molecule.

There are many cases of steady sweeps, such as thermal conduction in a gas, steady electric discharge through a gas, steady radiation from a hot to a cold region, in which the sweeping substance, be it material or ether, is far from being in thermal equilibrium, although in a permanent or unvarying state. The precise idea of temperature is not applicable to such states. Thus radiation in space has no definite temperature unless the space is enclosed in an envelope which is in thermal equilibrium, in which case the radiation is the normal radiation for the given temperature, and the space occupied by the radiation has, in fact, the same temperature as the adjacent material.

When normal radiation issues from an aperture in an enclosure it becomes attenuated as it travels farther and farther from the aperture, and this attenuated radiation (absorption of medium supposed to be nil), although conforming to a simple law of distribution of energy among its various phases, has not a definite temperature. Neither does a monochromatic beam of light have a definite temperature.

In general, all cases of molecular motion and of ether motion (radiant heat) in which some definite and unvarying function exists expressing the distribution of energy among the various phases of the motion, are to be classed as steady sweeps. In all such cases the precise idea of temperature is inapplicable to the sweeping substance or space. Still, all such processes are amenable to precise and systematic treatment. This systematic treatment always depends upon a knowledge of the function of distribution of energy among the phases, *and the characteristics of the sweeping substance or space are properly described in terms of this function, not in terms of temperature and entropy.*

It is true, however, that a generalized idea of entropy, for example, can be applied to steadily sweeping substances. Thus Boltzmann's H function, which has a minimum value and closely corresponds to entropy when a gas is in thermal equilibrium, has a definite value for any steady state of a gas other than thermal equilibrium.

Entropy always increases in natural phenomena, and the notion of entropy is, perhaps, much more intimately related to the notion of time than any other physical notion whatever. The notion of entropy seems to me, indeed, to be the very foundation of the notion of time as a physical fact, although the numerical evaluation of time depends, in practice, upon the approximate realization of some of the precise ideas of mechanics.

This intimate relationship of the notions of entropy and time gives very great emphasis to the two propositions A and B in article 7 in which increase of entropy appears as measured by elapsed time.

Heretofore the idea of the increase of entropy associated with a sweeping process has been thought by the ablest writers on thermodynamics, such as Willard Gibbs, to be dependent upon the devising of a reversible process which leads to the same change of state as the given irreversible process. This is, I think, true in regard to sweeping processes in general, but it is not true in regard to steady sweeps.

The characteristic features of irreversible processes are, in my opinion, very clearly suggested by the term sweep and by the special terms simple sweep, trailing sweep and steady sweep, and I urge the adoption of these terms.

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METEOROLOGY AT THE BRITISH ASSOCIATION.

CONTRARY to custom, meteorology took foremost place at the Southport meeting of the British Association. This was largely due to the efforts of Dr. W. N. Shaw, the head of the British Meteorological Office, by whose invitation the International Meteorological Committee met with the British Association for the Advancement of Science and for the first time in England since 1876. The attendance of a majority of the members of the committee justified the innovation, and before going to Southport they were able to meet some representative British men of science at a dinner in London given by Dr. Shaw. Of the seventeen members constituting the International Meteorological Committee, the following ten were present at Southport: the president, Professor Mascart, of Paris; the secretary, Professor Hildebrandsson, of Upsala; Dr. Shaw, of London; Dr. Paulsen, of Copenhagen; Professor Mohn, of Christiania; Dr. Snellen, of Utrecht; General Rykatcheff, of St. Petersburg; Professor Pernter, of Vienna; Professor Hellmann, of Berlin; and Professor Moore of Washington. Although the United States has had a representative in the committee for twelve years, only now, for the first time, was a meeting attended by the chief of the Weather Bureau, indicating the present desire of this country to cooperate in international meteorology. Besides the above, there came for the discussion of meteorological telegraphy, Professor van Bebber from Hamburg and Captain Chaves from the Azóres; and of the sub-committee for scientific aeronautics its chairman, Professor Hergesell from Strasburg, M. Teisserenc de Bort from Paris, and the writer. The sessions of the committee lasted five days and the questions considered related principally to details of administration, publication and observation. Of greater scientific interest was an apparatus, shown by Dr. Paulsen, for the collection of atmospheric electricity by the employment of radioactive salts, and a