

On the Irreversible Production of Entropy

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The importance of irreversible entropy production is emphasized. The first and second laws of thermodynamics are both expressed by equalities by giving due recognition to the irreversible production of entropy. By specialization and combination of these equations, an "efficiency equation" is derived, applicable to cyclical and steady-state processes, and useful in studying the efficiency of practical processes. The thermodynamic theory involved in determining amounts of entropy produced by irreversible processes is investigated, and six cases of irreversible entropy production are treated in detail. The "efficiency equation" is applied to four practical processes to illustrate its usefulness in analyzing the causes of inefficiency in practical situations. The first and second law equations are directly applied to two theoretical problems so selected as to illustrate differences in the theoretical importance of being able to express the second law in the form of an equality. The concept of temperature is discussed, and the extent of its validity under non-equilibrium situations is analyzed.

1. INTRODUCTION

IN analyzing the thermodynamic behavior of physical chemical systems, it is essential to give due consideration to the production of entropy by irreversible processes that take place inside the system. Such considerations are very important from a practical point of view, since a determination of the different irreversible processes that lead to the production of entropy inside a heat engine or other kind of industrial apparatus makes it possible to evaluate the relative contribution of these irreversible processes to the inefficiency of the over-all process, in terms of useful work lost or made necessary by their occurrence. This possibility has already been investigated by one of the present authors.¹ Such considerations are also significant from a theoretical point of view, since the inclusion of appropriate terms for the irreversible production of entropy makes it possible to express the second law of thermodynamics in terms of an equation, rather than by an inequality, as is usually done in the case of irreversible processes. This possi-

bility, which is not a new one,² has recently been investigated in some detail by Eckart,³ and its importance stressed by Bridgman.⁴

In Part I of the present article, we shall express the first and second laws of thermodynamics in a form suitable for our later use, with the second law as well as the first written in the form of an equality by giving due recognition to the irreversible production of entropy. These equations will then be specialized so as to apply particularly to cyclical processes such as are carried out by a heat engine, or to steady-state processes such as are carried out in continuous flow production plants. By combination we then obtain an "efficiency equation" in a form specially adapted to show the usefulness of the idea of irreversible entropy production in providing a means for measuring the various inefficiencies encountered in practical operations.

In Part II of the article, we shall investigate the rigor with which the irreversible production of entropy can be computed, consider the different types of irreversible processes that can take place in nature, and obtain expressions for the

¹ A study of the irreversible increases in entropy encountered in the production of helium from natural gas was made by one of the present authors in 1922, and formed the basis for the government owned patents on helium production, Nos. 1,676,225 and 1,728,947, taken out by a government appointed committee, under the names of Richard C. Tolman, W. L. DeBaufre, John W. Davis, and Montague H. Roberts. A somewhat similar study has been made by W. L. DeBaufre in "Analysis of power-plant performance based on the second law of thermodynamics," *Mech. Eng.* **47**, 426 (1925).

² See, for example, DeDonder and Van Rysselberghe, *Affinity* (Stanford University Press, Stanford University, 1936), Eq. (2.17) p. 9, which introduces the DeDonder "uncompensated heat" dQ' ; Weber *Thermodynamics for Chemical Engineers* (John Wiley and Sons, Inc., New York, 1939), Eq. (33), p. 141; Keenan, *Thermodynamics* (John Wiley and Sons, Inc., New York, 1941), Eq. (150), p. 294.

³ C. Eckart, *Phys. Rev.* **58**, 267, 269, 919 (1940).

⁴ P. W. Bridgman, *Phys. Rev.* **58**, 845 (1940) and *The Nature of Thermodynamics* (The Cambridge University Press, Teddington, England, 1941).

amounts of entropy thereby produced. These expressions will, in general, not be new, but the point of view used in obtaining them will be more rigorous than is often the case, and their deduction from this point of view should increase confidence in the application of the idea of irreversible entropy production. In addition, it is useful to have an assembly of expressions for irreversible entropy increases available for studying the behavior of physical chemical systems.

In Part III of the article, we shall then make specific application of the "efficiency equation" to two cyclical and to two steady-state processes, all of them of some practical importance. This will lead to the deduction of useful formulae valid for these processes, and will show in detail the usefulness of the idea of irreversible entropy production in studying the causes of inefficiency.

In Part IV, we shall examine the theoretical significance of being able to express the second law of thermodynamics in the form of an equality instead of in the usual form of an inequality. To study this question, we shall apply our first and second law equations to the treatment of two specially selected problems, that of the theory of viscous flow and that of the theory of thermo-electromotive force. These cases have been selected to illustrate two different possibilities. In both cases we shall find that the second law equality supplies valid information. However, in the case of viscous flow we shall find that this information is already available from mechanical principles combined with the first law of thermodynamics, while in the case of thermo-electromotive force we shall find that the information supplied by the second law equality is essential for the treatment. The significance of this will be pointed out.

Finally, in Part V we shall present some theoretical considerations of the concept of temperature which will be of help in obtaining a full understanding of the preceding work and of thermodynamic theory in general. The considerations include discussion of the different roles of temperature, as a measurable property of a system at equilibrium, as related to driving force for thermal flow, and as used in the calculation of entropy transfer.

PART I. FORMULATION AND CONSEQUENCES OF THE FIRST AND SECOND LAWS

2. The First Law of Thermodynamics

In accordance with the principle of the conservation of energy, any change ΔE in the energy content of a system must be brought about by the transfer of energy between the system and its surroundings. For the purposes of thermodynamics we may regard this as taking place by one or more of the following three processes: (a) by the flow of matter across the boundary of the system which may be in either direction and may carry internal, kinetic, or other forms of energy, (b) by the flow of heat across the boundary which may also be in either direction, and (c) by the performance of work by the system on its surroundings or by the surroundings on the system.

In agreement with the foregoing, we shall find it convenient to write the first law of thermodynamics in the following form

$$\Delta E = \sum_m E_m + \sum_n Q_n - W, \quad (2.1)$$

where we equate the increase in energy of a system, ΔE , which occurs in any selected time interval of interest, to the net sum of quantities of energy E_m carried into the system by transfers of matter, plus the net sum of quantities of energy Q_n carried in by transfers of heat, minus the net work W done by the system on its surroundings, all taken for the selected time interval, with positive or negative signs for the quantities summed according to the direction of transfer.

This form of expression for the first law of thermodynamics is obviously correct and has been chosen so as to be convenient for our later use. We consider the change in energy ΔE , for a selected time interval, instead of the rate of change of energy with time dE/dt , since we shall later wish to be able to choose the time interval as that corresponding to a particular change in the system or its surroundings. The quantity on the left-hand side of (2.1) could be expressed if desired in the form of an integral, taken over the time interval of interest and over the volume of the system, and the quantities on the right-hand side could be expressed by integrals taken over the time interval and over the surface between

the system and its surroundings in such a way as to give a detailed evaluation of the energy transported through the surface by the flow of matter, flow of heat, and performance of work. (Compare Eckart³ and Bridgman,⁴ and also §18.)

3. The Second Law of Thermodynamics

In accordance with the second law of thermodynamics, entropy is not a quantity which obeys a conservation law, and it is hence necessary to relate the change in the entropy of a system ΔS , not only to the entropy crossing the boundary between the system and its surroundings, but also to the entropy produced by processes taking place inside the system. Processes taking place inside a system may be either reversible or irreversible. Reversible processes inside a system may lead to the transfer of entropy from one portion to another of the interior but do not generate entropy. Irreversible processes inside a system, however, lead to the generation of entropy, and hence in computing the change in the entropy of a system we must take into account the entropy ΔS_{irr} produced inside the system by such irreversible processes.

In agreement with the foregoing, we may now express the second law of thermodynamics in the form

$$\Delta S = \sum_m S_m + \sum_n \frac{Q_n}{T_n} + \Delta S_{\text{irr}}, \quad (3.1)$$

where we equate the increase in entropy of a system ΔS , which occurs in any selected time interval of interest, to the net sum of quantities of entropy S_m carried into the system by transfers of matter, plus the net sum of quantities of entropy Q_n/T_n carried in by transfers of heat, plus the entropy ΔS_{irr} produced by irreversible processes taking place inside the system, all taken for the selected time interval, with positive or negative signs for the quantities summed according as the transfer of entropy is into or out of the system.

The quantities occurring in (3.1) could be expressed, if desired, with the help of integrals taken over the time interval of interest, and over the volume of the system or over the surface separating it from the surroundings. (Compare Eckart³ and Bridgman,⁴ and also §18.)

The above formulation of the second law of thermodynamics (3.1) makes use of expressions of the usual form Q/T , valid under equilibrium conditions, for the entropy transferred across a boundary by the transfer of heat Q at temperature T . The extent of the validity of such expressions, under non-equilibrium conditions, will be discussed in §22, Part V of this article. The formulation (3.1) expresses the second law of thermodynamics by an equality rather than by an inequality, even when irreversibility is involved. This is made possible by the inclusion of the term ΔS_{irr} for the entropy produced inside the system by irreversible processes. The validity and character of expressions for irreversible entropy increase will be discussed in Part II of this article.

4. Application to Cases of Cyclical and Steady-State Processes

The foregoing expressions for the first and second laws, (2.1) and (3.1), assume a specially simple and easily usable form, in the case of cyclical processes where the system of interest returns to the same state at the end of each cycle, and also in the case of steady-state processes where the system of interest does not change with time although matter, energy, and entropy may be flowing through it. Under such circumstances it is expedient to choose the time interval of interest, to which the equations are applied, in the case of a cyclical process as the time necessary to complete one cycle, and in the case of a steady-state process as any interval that proves convenient, for example, unit time or the time necessary for the passage of unit amount of matter. With such a choice of time interval, the changes of energy ΔE and of entropy ΔS to which the equations apply evidently become zero, and we can write the two equations in the forms

$$\sum_m E_m + \sum_n Q_n - W = 0, \quad (4.1)$$

and

$$\sum_m S_m + \sum_n \frac{Q_n}{T_n} + \Delta S_{\text{irr}} = 0. \quad (4.2)$$

These equations may now be combined to eliminate any desired one of the quantities of heat Q_n that appear in both expressions. For

practical applications it often proves useful to eliminate the total heat Q_0 which may be regarded as transferred, either by design or by accident, between the system and bodies at the general temperature T_0 prevailing in the surroundings. In this we include heat transferred by intent to cooling water supplied at temperature T_0 , and heat leaking spontaneously between the system and portions of the surroundings at temperature T_0 .

To make the suggested elimination we may multiply (4.2) by T_0 and subtract from (4.1). Doing so, we obtain the useful result

$$\sum_m (E_m - T_0 S_m) + \sum_n \frac{T_n - T_0}{T_n} Q_n - W - T_0 \Delta S_{\text{irr}} = 0, \quad (4.3)$$

as an equation applicable to cyclical or to steady-state processes.

5. The Efficiency Equation

The physical significance of Eq. (4.3) can be more easily appreciated if we solve for W in the form

$$W = \sum_m (E_m - T_0 S_m) + \sum_n \frac{T_n - T_0}{T_n} Q_n - T_0 \Delta S_{\text{irr}}. \quad (5.1)$$

This equation may be called the "efficiency equation," since it correlates the net work W done by the system on its surroundings, in a cyclical or a steady-state process, (a) with quantities of energy E_m and entropy S_m transferred from surroundings to system by the passage of matter, (b) with quantities of heat Q_n transferred at temperatures T_n other than the temperature T_0 prevailing in the surroundings, and, finally, (c) with the entropy ΔS_{irr} produced inside the system by irreversible processes. Since ΔS_{irr} is necessarily positive, the equation clearly shows the effect of irreversibility in cutting down the work done by a system, or in making additional, external work on the system necessary. By analyzing ΔS_{irr} , and determining the amounts arising from the different irreversible processes involved, we can calculate the loss in horsepower correlated with each process and thus

obtain useful information for attacking problems of improving efficiency.

In using Eq. (5.1), in cases where heat leak is involved, it is to be remembered that we have included such heat in the quantity Q_0 which is transferred between the system and surroundings at the temperature T_0 prevailing in the surroundings. This means that we have included as part of our system regions where the leaking heat is being transported between the interior of the system at some temperature T and the surroundings at temperature T_0 . Hence we must include in the entropy ΔS_{irr} , produced by irreversible processes inside the system, the irreversible increase that accompanies this spontaneous flow of heat between temperatures T and T_0 . For the calculation of such increases in entropy see §8.

If for any reason we wish to choose the boundary between system and surroundings in such a way that a particular quantity of heat Q_l is treated as leaking between the system and surroundings at some temperature T_l intermediate between T and T_0 , then the irreversible entropy increase associated with the transfer of Q_l between T_l and T_0 is not to be included in evaluating $T_0 \Delta S_{\text{irr}}$, but to compensate for this an equivalent term $Q_l(T_l - T_0)/T_l$ will now be found to appear in the second summation on the right-hand side of (5.1). Hence the results of applying (5.1) will not be altered by our changed point of view, in satisfactory agreement with our certainty that the behavior of the system cannot depend on our arbitrary choice of place where we take the boundary between system and surroundings.

In considering the application of the efficiency equation (5.1) to practical problems, it is useful to emphasize a general principle which results from the form of the term $T_0 \Delta S_{\text{irr}}$, which expresses the loss of potential work which accompanies the irreversible production of entropy inside the system. In accordance with the circumstance that entropy is a quantity having extensive magnitude, it is evident that this term can be calculated by adding together separate terms of the form $T_0 \Delta S_{\text{irr}}$ for each of the irreversible processes that accompany a total operation. This then allows us to take each of these separate terms $T_0 \Delta S_{\text{irr}}$ as a measure of the loss in potential

work that results from the corresponding particular irreversible processes in the total operation. This is an important principle, since it allows us to determine the reduction in efficiency resulting from any particular cause without making an analysis of the whole operation. For example, we can separately calculate the loss of potential work caused by the irreversible transfer of heat from the high temperature of the fire bed to the lower temperature of the boiler in a steam power plant, without making an analysis of the whole power plant operation.⁵

PART II. EXAMPLES OF IRREVERSIBLE ENTROPY PRODUCTION

6. Method of Treatment

In order to obtain useful results from the foregoing formulation of the second law of thermodynamics as given by Eq. (3.1), and from the efficiency equation as given by Eq. (5.1), it is necessary to have specific expressions for the amounts of entropy produced by various irreversible processes. Without such expressions, it would not be possible to give actual content to the terms ΔS_{irr} and to $T_0 \Delta S_{\text{irr}}$ that appear in these equations, and these quantities would have to be regarded merely as correction terms defined by the equations themselves. It is our present task to obtain such expressions for a number of typical irreversible processes.

In carrying out this task, we shall make use of thermodynamic considerations, and it will be our primary concern to provide a logically satisfactory basis for the thermodynamic treatment of irreversible entropy production, rather than to provide new results. Many of the expressions that we obtain for the amounts of entropy produced by irreversible processes will already be familiar, but their validity from the point of

view of thermodynamic theory has not always been made clear. Indeed, we shall find that only a restricted measure of validity can be claimed for certain very familiar expressions for the rate of irreversible entropy production. At the end of the section we shall call attention to a theoretical possibility of extending the methods of calculating irreversible entropy production with the help of the statistical mechanical interpretation of entropy.

The need for careful consideration, in using thermodynamic methods to obtain expressions for the entropy produced by irreversible processes, arises from the circumstance that the entropy of a system is a quantity which must be taken as thermodynamically defined by its increase in the case of reversible rather than of irreversible processes. For the processes to be considered, we shall in every case be able to carry out our initial calculations of irreversible entropy production with the help of a method of treatment which is based strictly on the accepted thermodynamic expression

$$\Delta S = \int \frac{dQ}{T} \quad (6.1)$$

for changes in entropy accompanying reversible processes. This equation states that the increase in the entropy S of a system, when it changes from one state to another by a reversible path, can be computed, in terms of temperature T and heat absorbed Q , by taking the integral $\int dQ/T$ over the reversible path. Since the entropy of a system is a function of its state, this equation makes it possible to determine increases in entropy, even when resulting from irreversible processes, provided only that we can compute the integral $\int dQ/T$ over some conceivable reversible path connecting the initial and final states of the system, in which the irreversibly produced entropy is located. This possible procedure provides the primary method for the treatments of irreversible entropy production which we are going to undertake.

Certain limitations on the use of this method for the determination of irreversible entropy production are implied by the circumstance that we must compute the integral $\int dQ/T$ for a conceivable reversible process connecting the initial and final states of the system where the

⁵ The use of the quantity $T_0 \Delta S_{\text{irr}}$ as a measure of loss in potential work was introduced by one of the present writers in the investigation of the efficiency of helium production mentioned in reference 1. It is to be noted that the quantity $T_0 \Delta S_{\text{irr}}$ measures the loss in potential work which arises, in the case of *cyclical* or *steady-state* processes, from the irreversible production of entropy in amount ΔS_{irr} inside the system proper, and does not include losses caused by irreversible processes going on in the surroundings. It should be distinguished from the quantity $T_0 \Delta S_{\text{net}}$ recently introduced by Weber (see reference 2, p. 140), where, for any kind of process, ΔS_{net} is the net increase in entropy inside the system proper plus its surroundings, treated together as isolated from the rest of the universe.

irreversible increase in entropy takes place. Since a reversible process must consist in the passage of a system through a succession of equilibrium states, this then requires that the initial and final states of the systems that we treat shall themselves be states of equilibrium.

In the first place, it is to be noted that this feature of the method limits its application to the determination of irreversible entropy production in systems which are initially at equilibrium before the irreversible entropy production starts and are again at equilibrium after the irreversible process has been completed. It is to be specially emphasized, however, that this implies no limitation on the application of the method to cases where the system actually passes through states that are violently disturbed from equilibrium conditions, during the period of irreversible behavior intervening between the initial and final equilibrium states. Indeed, a very important characteristic of the method is just this circumstance that it does make it possible to calculate the total entropy produced as the end result of violent irreversible processes which have run to completion.

In the second place, it is to be noted that the method provides no expressions for the rate of entropy production during the progress of an irreversible process, but only gives a value for the total entropy which has been produced by a completed process of transition from an original to a final state of equilibrium. Methods for determining the amounts of entropy produced at each stage during the course of an irreversible process cannot, in general, be readily placed on an entirely satisfying theoretical basis. Nevertheless, at least tolerably satisfactory methods for calculating the rate of irreversible entropy production can be found in certain situations where the actual conditions in the system where entropy is being produced are appropriately related to equilibrium conditions. We turn to a brief discussion of some of these situations.

Entirely satisfactory treatments of the rate of entropy production can be given in the case of certain steady-state processes, in which matter or energy is transferred at a steady rate, between two reservoirs in states of substantial equilibrium, through a connecting region in a state that remains constant in time but is a non-equilibrium

condition leading to the continuous generation of entropy as the matter or energy passes through. Under such circumstances, since the condition of the connecting region does not change with time, the rate of production of entropy can be equated to the net rate of change in the entropies of the two reservoirs, which can be readily calculated since changes in the reservoirs take place substantially under equilibrium conditions. Examples of such situations are provided by the slow passage of gas through a porous plug between reservoirs maintained at constant uniform pressure as in the Joule-Thomson experiment, by the passage of gas through the front of a plane shock wave, and by the flow of heat between heat reservoirs of sufficiently large heat capacity through a heat conductor of sufficiently low thermal conductivity so that the reservoirs can be regarded as remaining substantially at constant temperatures.

Somewhat satisfactory treatments of the rate of entropy production can be given whenever the major portions of the system of interest are in homogeneous states that change slowly enough with time so as to remain close to conditions of equilibrium. Under such circumstances we can make an approximate calculation of the rate of entropy production, by treating these major portions of the system as though they were changing under strict equilibrium conditions, and by neglecting the effect of changes in any small portions of the system that are not close to equilibrium. Examples are provided (a) by the dissipation of mechanical or electrical energy in a medium most of which can be regarded as merely subjected to a gradually rising temperature, (b) by the equalization of gas pressure between two containers joined by a connector, of high enough resistance so that the contents of the containers are kept always practically at equilibrium, and of small enough volume so that changes in the entropy of its contents can be neglected, (c) by the equalization of temperature between two bodies through a thermal conductor of negligible heat capacity and at a slow enough rate so that the bodies at each instant can be regarded as nearly at equilibrium, (d) by the progress of a homogeneous chemical reaction at a slow enough rate so that we can regard the reacting mixture at each instant as practically

equivalent to a non-reacting mixture of definite composition and temperature, the entropy of which could be investigated by usual procedures.

An extension of the above type of treatment can sometimes be successfully made to systems or portions thereof which are in non-homogeneous states, provided the portion can be regarded as composed of infinitesimal elements each itself in a condition close enough to equilibrium to permit the specification of its entropy as a function of its state. As an example, we have the calculation of irreversible entropy production in the interior of a thermally conducting medium by treating the heat flow as taking place between elements having lower and lower but well defined temperatures in the direction of flow. Nevertheless, as will be discussed again later in Part V, it becomes more and more difficult to ascribe unique and appropriate values of temperature as the rate of heat flow becomes greater and greater.

No satisfactory treatment of the rate of entropy production, by the above methods, can be given in the case of violent irreversible processes where the system passes through states sufficiently removed from equilibrium conditions so that their thermodynamic specification is not possible. For example, the violent process may involve the transport of matter by unrelated streams of high velocity particles of various kinds—molecules, atoms, ions, and electrons—and may involve the transport of energy not only by the motion of matter but also by the flow of radiation of a variety of unrelated frequencies and intensities. Under such circumstances it may be difficult or impossible to apply our usual methods of thermodynamic specification. It may again be emphasized that a breakdown in the concept of temperature accompanying violent processes leads to a breakdown in the usual thermodynamic treatment of entropy. Discussion of the concept of temperature will be found in §§20, 21, and 22 of Part V.

It will be appreciated from the foregoing that it is not always possible to use thermodynamic methods to calculate rates of entropy production, especially in the case of violent irreversible processes. It is hence of interest to point out a theoretical possibility of extending the methods of entropy calculation with the help of the statistical mechanical interpretation of that quantity

given by⁶

$$S \rightleftharpoons -k \sum_n P_n \log P_n, \quad (6.2)$$

where the thermodynamic quantity entropy S is related to the statistical mechanical coarse-grained probabilities P_n for the different states n in an appropriate representative ensemble for the thermodynamic system of interest. Since changes with time in the quantities P_n would be determined by mechanical principles, an acceptance of this interpretation would make the rate of entropy production theoretically calculable in cases where purely thermodynamic considerations fail. This would then permit us to regard Eqs. (3.1) and (5.1) as having theoretical significance also when the values of the quantities ΔS_{irr} and $T_0 \Delta S_{\text{irr}}$ therein are not calculable by thermodynamic methods.

Several remarks must be made, however, in connection with this possibility. In the first place, it will be appreciated that this theoretical possibility is not of great practical importance at the present stage in the difficult development of the applications of statistical mechanics to irreversible processes.⁷ In the second place, it will be realized that the circumstance that we cannot now always assign values to the quantities ΔS_{irr} and $T_0 \Delta S_{\text{irr}}$ in Eqs. (3.1) and (5.1) does not interfere with the usefulness of those equations when appropriate values can be substituted. Finally, it may again be emphasized that thermodynamics is adequate for the exact treatment of irreversible entropy production on passage from an initial to a final state of equilibrium, without reference to the violence of the intervening irreversible behavior, and this is often all that is needed.

We now turn to a consideration of specific examples of irreversible entropy production. In the case of each example, we shall first apply our primary thermodynamic method of treatment which gives a completely valid expression for the irreversible increase in entropy accompanying passage from an initial to a final state of equilibrium. This will then usually be followed by a

⁶ See Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, London, 1938), Chapter 13.

⁷ For important recent advances in the application of statistical mechanics to irreversible processes, see Kirkwood, *J. Chem. Phys.* 14, 180 (1946); *ibid.*, 15, 72 (1947).

somewhat less satisfactory treatment leading to approximate expressions for instantaneous rates of irreversible entropy production.

7. Degradation of Energy

As a simple and fundamental example of processes leading to irreversible entropy production, we may first consider the degradation of energy from a form where it could be used for the performance of mechanical work to a form where it is dissipated as part of the internal energy of a material body. As illustrations we have the dissipation of mechanical energy through the action of friction or viscosity, and the dissipation of electrical energy by the passage of electric current through a resistance. Such processes are accompanied by irreversible entropy production, since the change in state of the body, in which the mechanical or electrical energy is dissipated, is a change in state which could also be brought about by the reversible absorption of heat.

To apply our proposed method for calculating the amounts of entropy produced by irreversible processes, let us assume that the body in which the degraded energy is dissipated is originally in a state of equilibrium at temperature T_1 and is again in a state of equilibrium at temperature T_2 after the energy has been dissipated, the rise in temperature being determined by the amount of energy dissipated. This is a change in state, however, which could also be brought about by the reversible absorption of heat. Hence, applying our method of calculation, we can evidently equate the irreversible increase in entropy ΔS_{irr} that actually occurs to the reversible increase $\int dQ/T$ that would be brought about by such a reversible absorption of heat. This then leads to the desired expression for the irreversible increase in entropy

$$\Delta S_{\text{irr}} = \int_{T_1}^{T_2} \frac{C}{T} dT, \quad (7.1)$$

where C is the heat capacity of the body in which the energy is dissipated.

This expression for the increase in entropy of the body receiving the dissipated energy applies to the over-all change from the initial equilibrium state originally set up at temperature T_1 to the

final equilibrium state ultimately established at temperature T_2 , and does not require equilibrium for the intermediate states through which the body passes. When the process does have such a character that we can regard each particular element of dissipated energy dE as having approximately the same effects as the absorption of that same amount of energy dQ in the form of heat at an equilibrium temperature T , we can write,

$$\left(\frac{dS}{dt}\right)_{\text{irr}} = \frac{1}{T} \frac{dE}{dt}, \quad (7.2)$$

as an expression for the corresponding rate of irreversible production of entropy. In the case of the dissipation of mechanical energy by friction or viscosity, this expression assumes the form,

$$\left(\frac{dS}{dt}\right)_{\text{irr}} = \frac{1}{T} \frac{dF}{dt}, \quad (7.3)$$

where dF/dt is the rate at which work is being done against frictional or viscous forces. And in the case of dissipation of electrical energy, by the flow of current I through a resistance R in material at temperature T , the expression assumes the form,

$$\left(\frac{dS}{dt}\right)_{\text{irr}} = \frac{I^2 R}{T}. \quad (7.4)$$

8. Irreversible Heat Flow

As a second example of a fundamental kind of process leading to irreversible entropy production, we may now consider the flow of heat from higher to lower temperatures. To apply our method of calculating irreversible entropy production, let us assume two heat reservoirs R and R' , of heat capacities C and C' , initially at equilibrium at temperatures T_1 and T_1' , and again at equilibrium at temperatures T_2 and T_2' after the flow of heat has ceased or been interrupted.

For the corresponding irreversible increase in entropy we can evidently write

$$\Delta S_{\text{irr}} = \int_{T_1}^{T_2} \frac{C}{T} dT + \int_{T_1'}^{T_2'} \frac{C'}{T} dT, \quad (8.1)$$

since this is obviously the net increase in entropy of the two reservoirs that would be calculated if we changed them reversibly from their initial to their final states. Moreover, we can evidently use the equation

$$\int_{T_1}^{T_2} C dT + \int_{T_1'}^{T_2'} C' dT = 0 \quad (8.2)$$

as an expression determining the relation between the two final temperatures T_2 and T_2' .

The expression for the irreversible increase in entropy given by Eq. (8.1) applies to the over-all result of the change from one equilibrium condition to another, and does not assume equilibrium conditions during the process of heat transfer. When heat flow does take place, however, under conditions such that we can regard the elements of the conducting medium as substantially at equilibrium temperatures which decrease in the direction of the flow, we can write

$$dS_{\text{irr}} = \left(\frac{1}{T'} - \frac{1}{T} \right) dQ, \quad (8.3)$$

as an expression for the irreversible production of entropy associated with the transfer of an amount of heat dQ through the medium from a place where the temperature has the higher value T to a place where the temperature has the lower value T' . Hence taking $\mathbf{q}$ as a vector which expresses the rate of heat flow per unit area per unit time, we can write

$$\left(\frac{dS}{dt} \right)_{\text{irr}} = \mathbf{q} \cdot \text{grad} \left(\frac{1}{T} \right) = -\frac{\mathbf{q}}{T^2} \cdot \text{grad} T \quad (8.4)$$

as an expression for the rate of irreversible production of entropy per unit volume at any point in a conducting medium for which temperature has a sufficiently well defined meaning. Or when heat flow can be expressed in terms of temperature gradient and thermal conductivity by the Fourier expression,

$$\mathbf{q} = -\kappa \text{grad} T, \quad (8.5)$$

we can take

$$\left(\frac{dS}{dt} \right)_{\text{irr}} = \frac{\kappa}{T^2} [\text{grad} T]^2 \quad (8.6)$$

as an appropriate expression for the rate of irreversible production of entropy per unit volume of the conducting medium.

More rigorous consideration of the limits of validity for Eqs. (8.4), (8.5), and (8.6) will be given in §§21 and 22 of Part V.

9. Free Expansion

As our next example of a process leading to irreversible entropy production, we may consider the free expansion of a gas, without absorption of heat, under conditions, as in the Gay-Lussac experiment, such that the gas does not perform the external work that would be possible if it were made to exert its pressure against a movable piston, rather than allowed to expand freely. This process leads to the irreversible production of entropy, since a reversible change from the same initial to the same final state would be accompanied by the performance of work and by a corresponding absorption of heat, which would lead to a calculable increase in entropy.

For simplicity let us assume that the gas is a perfect one, and let us consider the result of the free expansion of one mole, without absorption of heat, from an initial state of equilibrium in the volume v , at pressure p , and at temperature T , to a final state of equilibrium in the larger volume v' , at the lower pressure p' , and in accordance with the properties of perfect gases at unchanged temperature T . For the irreversible increase in entropy we can then immediately write

$$\Delta S_{\text{irr}} = R \log \frac{v'}{v} = R \log \frac{p}{p'}, \quad (9.1)$$

since the heat absorbed in a reversible isothermal expansion from the same initial to the same final state would have the well-known value $RT \log v'/v$, where R is the gas constant per mole.

This expression for ΔS_{irr} applies, of course, to the over-all change from the initial to the final state of equilibrium, and is independent of the way in which the expansion actually takes place, except that it shall be without net performance of work or absorption of heat. If the expansion takes place sufficiently slowly, for example, through a porous plug, so that we can treat the major portions of the system as passing through

a succession of equilibrium states, we can easily follow the rate of production of entropy in detail. If the expansion takes place suddenly, for example, through the removal of a partition separating the original volume v from the total volume v' , a complicated process will ensue, which would make it difficult to follow the rate of production of entropy in detail. In such a sudden expansion, acoustic waves will be set up; the accompanying interchanges of energy among internal, kinetic, and potential forms will lead to temperature changes in different portions of the gas; damping of the acoustic waves will take place through viscosity; this will also lead to changes in gas temperatures; and during the process heat will flow from regions in the gas of higher to those of lower temperature until the new state of equilibrium is reached.

In the case of the slow expansion through a porous plug, neglecting changes in the small amount of gas inside the plug, one could evidently write

$$dS_{\text{irr}} = RdN \log \frac{p_1}{p_2}, \quad (9.2)$$

as an approximate expression for the irreversible increase in entropy accompanying the transfer of any particular element of the gas, consisting of dN moles, from pressure p_1 to pressure p_2 . In the case of the sudden expansion, we should have to consider the entropy produced by the degradation of the mechanical energy of the acoustic waves, and by the flow of heat from regions of higher to lower temperature in the gas, in order to try to follow the irreversible production of entropy in detail. Nevertheless, both in the case of the slow and of the sudden expansion of the gas, the final total irreversible production of entropy would be correctly given by Eq. (9.1), since a definite change in state is necessarily accompanied by a definite change in entropy.

10. Diffusion of a Solute

The diffusion of a solute from regions of higher to those of lower concentration in a solution is an irreversible process similar to that of the diffusion of gas through a porous plug. In the case of isothermal diffusion, we may write in

analogy with Eqs. (9.1) and (9.2)

$$\Delta S_{\text{irr}} = R \log \frac{c}{c'}, \quad (10.1)$$

for the irreversible increase in entropy accompanying the dilution of a mole of solute from concentration c to c' , and

$$dS_{\text{irr}} = RdN \log \frac{c_1}{c_2} \quad (10.2)$$

for the irreversible increase in entropy accompanying the transfer of dN moles of solute from concentration c_1 to c_2 . These equations may be taken as valid or approximately valid for ideal dilute solutions. For actual concentrated solutions a knowledge of specific properties of the solution is necessary for an exact calculation of the increase in entropy resulting from dilution.

11. Passage Through a Shock Wave Front

An extremely interesting example of processes leading to the irreversible production of entropy is provided by the passage of shock waves through air or other gases. Elaborate experimental and theoretical investigations of shock waves have been made during the war because of their military importance. We give here a treatment of simple aspects of the phenomenon, not to make a new contribution to shock wave theory, but to emphasize the aspects related to irreversible entropy production.

Shock waves are characterized by a steep wave front, traveling through the gas with supersonic velocity, with an abrupt change in the state of the gas between the two sides of the front. Shock waves can be produced in air by the detonation of a mass of high explosive, in which case the wave travels out from the explosion with supersonic velocity. They can also be produced by the action of projectiles moving through air with supersonic velocity, or can be set up in supersonic wind tunnels.

On the passage of gas through a shock wave front, there will be sudden changes in the density ρ of the gas, in its pressure p , in its internal energy ϵ per unit mass, and in its velocity u —taken for definiteness as measured relative to the shock front and as positive in the direction

of motion through the front. Applying the principles of the conservation of mass, of momentum, and of energy to the passage, we can at once write the following equations,

$$\rho_1 u_1 = \rho_2 u_2, \quad (11.1)$$

$$p_1 + \rho_1 u_1^2 = p_2 + \rho_2 u_2^2, \quad (11.2)$$

$$p_1 u_1 + \rho_1 u_1 (\epsilon_1 + \frac{1}{2} u_1^2) = p_2 u_2 + \rho_2 u_2 (\epsilon_2 + \frac{1}{2} u_2^2), \quad (11.3)$$

connecting the values of the above-mentioned quantities, before and after passage through the front, as indicated by the subscripts (1) and (2). In using these equations to study the changes in condition that take place on passage through the shock front, we may supplement them by an equation of state for the gas involved, and by an equation giving its internal energy as a function of its state. For our purposes it will be sufficient to treat the gas involved as a perfect gas, with a constant specific heat. We may then write the following additional equations

$$p_1 = \rho_1 r T_1, \quad p_2 = \rho_2 r T_2, \quad (11.4)$$

$$\epsilon_1 = c_v T_1, \quad \epsilon_2 = c_v T_2, \quad (11.5)$$

where r and c_v are the gas constant and the heat capacity at constant volume for unit mass of the gas, and T_1 and T_2 are the temperatures before and after passage through the shock front. This then provides us with a total of seven equations connecting the ten quantities labeled with subscripts, and we can, if desired, solve for seven of them in terms of any three that we wish to regard as given.

We are now ready to investigate the change in entropy that takes place in the gas on passage through the shock front. This change, if any, can only be an irreversible increase in entropy, since in the absence of external bodies there is no opportunity for an element of gas passing through a uniform segment of the shock front to interchange heat with its surroundings.

Assuming a plane wave of constant intensity, it will be noted that we are dealing with a steady-state situation, of the kind discussed in §6, where an entirely satisfactory treatment of the instantaneous rate of irreversible entropy production can be given, since there is a transfer of matter from one equilibrium condition to another

through a transition region (the shock wave front) which is in a condition that does not change with time. Hence, for the rate of irreversible production of entropy per unit area of the front, we can evidently write

$$\left(\frac{dS}{dt} \right)_{\text{irr}} = \rho_1 u_1 \left\{ c_p \log \frac{T_2}{T_1} - r \log \frac{p_2}{p_1} \right\}, \quad (11.6)$$

where $\rho_1 u_1$ is the mass of gas passing through the front per unit time per unit area, and the quantity in brackets, with $c_p = c_v + r$, is the known expression for the change in entropy per unit mass of gas on changing from equilibrium at pressure and temperature p_1 and T_1 to equilibrium at pressure and temperature p_2 and T_2 .

The circumstance that this expression for the rate of irreversible increase in entropy cannot be negative, now makes it possible to draw some important conclusions as to the character of shock waves. Since $\rho_1 u_1$ is necessarily positive, it is evident that the quantity in brackets cannot be negative. Re-expressing this quantity with the help of Eqs. (11.1) to (11.5), we then obtain

$$\begin{aligned} & \left\{ c_p \log \frac{T_2}{T_1} - r \log \frac{p_2}{p_1} \right\} \\ &= \left\{ c_p \log \frac{p_2}{p_1} \frac{p_2/p_1 + (2c_p/r - 1)}{p_1 p_2/p_1 (2c_p/r - 1) + 1} \right. \\ & \quad \left. - r \log \frac{p_2}{p_1} \right\} \geq 0 \quad (11.7) \end{aligned}$$

as a necessary condition on the pressures before and after passage through the front. Analyzing this result, it can readily be shown that the condition can only be satisfied with p_2 equal to or greater than p_1 , and combining this finding with the relations between quantities given by (11.1) to (11.5), we then obtain

$$p_2 \geq p_1, \quad T_2 \geq T_1, \quad \rho_2 \geq \rho_1, \quad u_2 \leq u_1, \quad (11.8)$$

as necessary conditions for the existence of a shock wave, where the equality signs apply at the limit where the shock wave ceases to exist. We thus find that the concept of irreversible entropy production leads to the conclusion that the passage of gas through a shock front must be accompanied by an increase in pressure, tempera-

ture, and density and a consequent decrease in velocity. This is in agreement with the empirical discovery of the existence of compression but not of rarefaction shock waves.

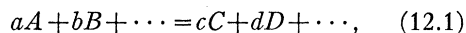
The results just obtained also make it possible to draw an important conclusion as to the actual velocity with which shock waves travel. Solving Eqs. (11.1) to (11.5) for u_1^2 in terms of p_1 , p_2 , and T_1 , we can obtain the result

$$u_1^2 = \frac{c_p r T_1}{c_v} \left\{ \frac{p_2}{p_1} - \frac{1}{2} \frac{r}{c_p} \frac{p_2}{p_1} + \frac{1}{2} \frac{r}{c_p} \right\}, \quad (11.7)$$

which shows that the velocity with which the shock front travels into the gas at temperature T_1 is greater than the ordinary velocity of sound $(c_p r T_1 / c_v)^{1/2}$ in gas of that temperature, by a factor which increases with the "strength" of the shock wave as measured by the ratio p_2/p_1 .

12. Chemical Reaction

As our final example of processes leading to the irreversible production of entropy, we shall consider chemical reaction under non-equilibrium conditions. For the sake of definiteness, and to correspond to a situation of common interest, let us assume that the reaction takes place in a thermally isolated system, under constant external pressure p , for example, that of the atmosphere. And let us take the reaction as corresponding to the chemical equation



in accordance with which a moles of the substance A react with b moles of the substance B , etc., to form c moles of the substance C , plus d moles of the substance D , etc.

Following our fundamental plan of treatment, let us assume that the system in which the reaction is going to occur is initially at equilibrium at pressure p and temperature T_1 , and that after the reaction has occurred the system is again at equilibrium at pressure p and at some new temperature T_2 . The initial equilibrium must be a metastable one, since we have the possibility for occurrence of the chemical reaction of interest. If desired, this can be thought of as set off by the introduction of a small amount of catalyst. The final equilibrium can be metastable or stable according to the extent to which the reaction

has proceeded. The final temperature T_2 will be higher or lower than T_1 , according as the reaction is exothermal or endothermal, the magnitude of the difference depending not only on the extent to which the reaction proceeds, but also on the heat capacity of the system which may contain inert material as well as the reacting substances of interest.

To calculate the entropy increase which accompanies the change from the initial to the final state, let us consider a succession of two steps by which the change could in principle be carried out. In the first step let us allow the chemical reaction to proceed under constant pressure to the same extent as in the over-all process of interest, but at the end of this chemical change let us set the temperature at its initial value T_1 rather than allow the change that will actually occur in the isolated system. For the increase in entropy of the system, we can then write in accordance with a familiar expression

$$\Delta S_1 = \frac{\Delta H_1 - \Delta F_1}{T_1}, \quad (12.2)$$

where ΔH_1 and ΔF_1 are, respectively, the increase in the enthalpy and in the thermodynamic potential of the system when the reaction occurs at T_1 . In the second step—since there must be no change in enthalpy for the over-all process on account of the assumed thermal isolation—let us heat or cool the system at constant pressure to a final temperature T_2 such as to satisfy the relations,

$$\Delta H_2 = -\Delta H_1 = \int_{T_1}^{T_2} C_p dT, \quad (12.3)$$

where C_p is the heat capacity of the system at constant pressure, *after the chemical reaction has occurred*. For the entropy increase accompanying this heating we can evidently write

$$\Delta S_2 = \int_{T_1}^{T_2} \frac{C_p}{T} dT. \quad (12.4)$$

Making use of the fact that the increase in entropy of the system in going from the given initial to the given final state must be equal to $\Delta S_1 + \Delta S_2$, without reference to the nature of the process by which the change is brought

about, and substituting for ΔH_1 from (12.3), we can then write

$$\Delta S_{\text{irr}} = -\frac{\Delta F_1}{T_1} + \int_{T_1}^{T_2} C_p \left(\frac{1}{T} - \frac{1}{T_1} \right) dT, \quad (12.5)$$

as the desired expression for the irreversible production of entropy when the reaction occurs spontaneously.

This expression (12.5) applies to the entropy produced as a result of the over-all change from the original metastable equilibrium state at pressure p and temperature T_1 to the final equilibrium state at pressure p and temperature T_2 , and does not assume equilibrium conditions during the course of the chemical reaction, which might actually take place in a very violent and irregular manner, once it has been started. When, however, the reaction does take place in such a manner that we can regard the system at each stage as substantially in a state of metastable equilibrium at a definite temperature T , we can then evidently write

$$\left(\frac{dS}{dt} \right)_{\text{irr}} = -\frac{1}{T} \frac{dF}{dt}, \quad (12.6)$$

as an expression for the rate of irreversible production of entropy at each stage of the reaction. Furthermore, in accordance with the known results of chemical thermodynamics, we can substitute for the rate of change of thermodynamic potential at temperature T , the expression

$$\frac{dF}{dt} = -RT \left(\log K_p - \log \frac{f_c^c f_d^d \cdots}{f_A^a f_B^b \cdots} \right) \frac{dx}{dt}, \quad (12.7)$$

where K_p is the equilibrium constant for the reaction at temperature T , $f_A f_B \cdots f_c f_d \cdots$ etc., are the actual instantaneous values of the fugacities of the reacting substances appearing in the chemical equation (12.1), and dx/dt is the factor by which we must multiply the numbers of moles $a, b, \cdots, c, d, \cdots$ etc., appearing in (12.1) to get the molal rate at which the corresponding substances are being used up or formed. Substituting (12.7) in (12.6), we then obtain

$$\left(\frac{dS}{dt} \right)_{\text{irr}} = R \left(\log K_p - \log \frac{f_c^c f_d^d \cdots}{f_A^a f_B^b \cdots} \right) \frac{dx}{dt}, \quad (12.8)$$

as an expression for the rate of irreversible entropy production in terms of chemically familiar quantities.

When the heat capacity of the system is sufficiently large, compared with the thermal effects of the reaction, so that we can regard the temperature of the reacting system as remaining constant, Eqs. (12.5) and (12.6) both lead to the simplified result

$$\Delta S_{\text{irr}} = -\Delta F/T, \quad (12.9)$$

as an approximately correct expression for the total irreversible production of entropy.

PART III. APPLICATIONS OF THE EFFICIENCY EQUATION

13. Nature of Applications

In Part I of this article, we have derived Eq. (5.1) which can prove useful in analyzing the efficiency of cyclical and steady state processes. This equation has the form

$$W = \sum_m (E_m - T_0 S_m) + \sum_n \frac{T_n - T_0}{T_n} Q_n - T_0 \Delta S_{\text{irr}}. \quad (13.1)$$

It correlates the external work W done in the process by the system on its surroundings, (a) with the quantities of energy E_m and entropy S_m brought into the system by the transfer of matter from the surroundings, (b) with the quantities of heat Q_n transferred into the system at temperatures T_n other than the temperature T_0 prevailing in the surroundings, e.g., the temperature of the cooling water available, and (c) with the entropy ΔS_{irr} produced inside the system by irreversible processes. In the case of cyclical processes the quantities W , E_m , S_m , and ΔS_{irr} are to be taken per cycle. And in the case of steady-state processes, they can be taken over any convenient interval of time, for example, one second.

In Part II of the article, we have discussed methods of calculating the amounts of entropy produced by irreversible processes, and have shown how these methods can be applied in a considerable number of typical cases. Hence we are now in a position to understand the possibilities for obtaining values of ΔS_{irr} to substitute

into the efficiency equation (13.1), and thus to make use of this equation to understand the losses in potential external work W that arise from the various sources of irreversibility that contribute to the term $T_0\Delta S_{\text{irr}}$.

In the present part of the article, we shall consider four typical examples of the method of applying the efficiency equation. Two of the applications will be to cyclical processes and two to steady-state processes.

14. Simple Heat Engine

We may first consider a simple heat engine, which uses the same working fluid over and over again, for example, in a cylinder provided with a movable piston, and operates by absorbing heat Q per cycle at temperature T , transforming part of it into work W , and giving up the remainder at the lower temperature T_0 . Applying Eq. (13.1), noting that there is no transfer of matter between the engine and its surroundings, we then obtain for the work done by the engine per cycle

$$W = \frac{T - T_0}{T} Q - T_0 \Delta S_{\text{irr}}, \quad (14.1)$$

where the first term is the well-known Carnot expression for the work that would be done if the engine operated reversibly, and the second term gives the work lost by the irreversible production of entropy ΔS_{irr} which actually accompanies its operation.

The causes contributing to the irreversible production of entropy include the dissipation of mechanical energy by friction and by viscous forces, the transfer of heat through finite temperature intervals inside the engine, and the transfer of leaking heat from the temperature of the engine to that of the surroundings. By analyzing the contributions of these different causes to the total irreversible production of entropy ΔS_{irr} , we can then obtain figures for the loss in horsepower arising from each cause, and thus essential information for studying the possibilities of more efficient design.

15. Heat Engine with Return of Working Fluid to Boiler

We may next consider a heat engine, such as a steam engine, having a cylinder and movable

piston carrying out a cycle in which vapor is withdrawn from a boiler at temperature T , expanded to a lower temperature and pressure, condensed to liquid form with the help of cooling water at temperature T_0 , and then returned as condensate to the boiler. In analyzing the operation of such an apparatus we are at liberty to choose the boundary separating system from surroundings in such a way as to include any part of the total apparatus in whose performance we may at the moment have special interest.

Let us first consider the operation of the engine proper, as separate from the boiler. We then have a system, undergoing a cyclical change, in which matter enters the system in each cycle in vapor form at temperature T carrying the energy E and entropy S , and leaves the system in liquid form at temperature T_0 , carrying the energy E_0 , and entropy S_0 . Substituting in Eq. (13.1), we then obtain for the work done per cycle

$$W = (E - E_0) - T_0(S - S_0) - T_0\Delta S_{\text{irr}}, \quad (15.1)$$

where the term $T_0\Delta S_{\text{irr}}$ expresses the loss of work resulting from the production of entropy by irreversible processes accompanying the operation of the engine. These irreversible processes would be similar to those already mentioned in the case of a simple heat engine.

In the absence of irreversibility, the last term in the above equation disappears. Furthermore, in the absence of irreversibility, the next to the last term can be set equal to the latent heat L_0 given out on condensation at temperature T_0 , since the working fluid will still retain its original entropy content S , until the time of condensation, owing to the reversible and adiabatic character of the process to which it is subjected. Hence, under reversible conditions, the equation reduces to the simple form

$$W = (E - E_0) - L_0, \quad (15.2)$$

in obvious agreement with the first law requirement that the work done should be equal to the net energy carried into the system by matter diminished by the heat given out.

Let us now consider the operation of the apparatus as a whole, including the boiler. Since the condensed liquid from the engine is returned to the boiler, we then have a closed

system, which does not take in or give out matter, but does absorb energy in the form of heat at elevated temperature, give out part of this in the form of heat at lower temperature, and transform the remainder into the form of work.

For the heat absorbed per cycle we have in the first place the latent heat of vaporization L of the vapor delivered to the engine per cycle, and in the second place the heat $\int_{T_0}^T C dT$ necessary to raise the temperature of the return feed to that in the boiler, C being the heat capacity of the liquid condensed in each cycle. We can take both of the quantities of heat as supplied approximately at the temperature T , if, for sake of definiteness, we assume that the condensate is fed back into the boiler without preheating. Substituting in Eq. (13.1), we then obtain as an expression for the work done per cycle

$$W = \left[L + \int_{T_0}^T C dT \right] \frac{T - T_0}{T} - T_0 \Delta S_{\text{irr}}, \quad (15.3)$$

where once more a quantity of the form $T_0 \Delta S_{\text{irr}}$ expresses the loss in work resulting from irreversible processes taking place in the system.

In the evaluation of ΔS_{irr} for use in Eq. (15.3), it is to be noted that we must now add to the irreversible increases of entropy which result from the operation of the engine proper and which have to be considered in connection with Eq. (15.1), the further irreversible increases in entropy which result from the operation of the boiler. These will include the entropy produced by the irreversible heating of the return feed from T_0 to T with heat supplied at temperature T , and such additional increases in entropy as are produced by heat flow and fluid friction inside the boiler, and by heat flow from the temperature of the boiler to that of the surroundings.

The above analysis, in which we first treated the results of irreversibility in the engine proper by itself and then in the engine plus boiler, illustrates the general principle discussed at the end of §5, in accordance with which we can give separate treatment to the loss in potential work W , correlated with the contribution to the term $T_0 \Delta S_{\text{irr}}$ from each particular source of irreversible entropy production.

16. Steady Flow of Fluids

As a first example of a steady-state process, let us consider the application of Eq. (13.1) to the steady flow of a homogeneous fluid through an apparatus, provided with a turbine (or rotary pump) for the transfer of work between system and surroundings, and involving differences in height and hence in the potential energy of the fluid entering and leaving the apparatus.

Let m be the mass of the fluid, for example, one mole, which passes through the apparatus in the time interval of interest, and let W_{turbine} be the work done by the turbine during this time interval. Furthermore, let us take the fluid as entering at height h_1 , with the velocity u_1 , under the pressure p_1 , having the volume v_1 and carrying the internal energy E_1 and entropy S_1 , and as leaving with the values h_2 , u_2 , p_2 , v_2 , E_2 , and S_2 for these same quantities. Substituting in Eq. (13.1), under the assumption that there is no transfer of heat between system and surroundings except at the temperature T_0 prevailing in the surroundings, we obtain the result

$$\begin{aligned} W_{\text{turbine}} - p_1 v_1 + p_2 v_2 \\ = (E_1 + mgh_1 + \frac{1}{2}mu_1^2 - T_0 S_1) \\ - (E_2 + mgh_2 + \frac{1}{2}mu_2^2 - T_0 S_2) \\ - T_0 \Delta S_{\text{irr}}, \end{aligned} \quad (16.1)$$

where the left-hand side expresses the total work done on the surroundings, including the net work done against the external fluid pressure as well as that done by the turbine, and the right-hand side includes obvious expressions for the potential and kinetic energies of the fluid entering and leaving the apparatus. We note once more the effect of the irreversible production of entropy in reducing the external work done by the system.

Using the symbol Δ to denote differences between the values of quantities applying to the leaving and entering fluid, and rearranging, the above equation can be written in the shorter form

$$\begin{aligned} W_{\text{turbine}} + \Delta E + \Delta(pv) - T_0 \Delta S + mg\Delta h \\ + \frac{m}{2} \Delta u^2 + T_0 \Delta S_{\text{irr}} = 0. \end{aligned} \quad (16.2)$$

This may be spoken of as a generalized Bernoulli equation. It would be valid in cases where the fluid enters and leaves the apparatus at tem-

peratures different from T_0 , and where chemical reaction takes place in the fluid during passage. In applying it to such cases, however, we must include in the term $T_0\Delta S_{\text{irr}}$ the irreversible increases in entropy that accompany heat transfer between the temperatures in the interior and in the surroundings, and that accompany chemical change under non-equilibrium condition, as well as those caused by friction and viscosity.

If we consider cases where the fluid enters and leaves the apparatus, in a condition of internal equilibrium, at the temperature T_0 prevailing in the surroundings, we can substitute in accordance with well-known relations

$$\Delta F = \int_1^2 v dp = \Delta E + \Delta(pv) - T_0\Delta S, \quad (16.3)$$

where ΔF is the difference in thermodynamic potential of the mass m of fluid on leaving and entering the apparatus, a quantity which can be set equal to the integral $\int v dp$ taken for a reversible isothermal path at temperature T_0 connecting the two conditions. Substituting in Eq. (16.2), we can then rewrite this in the form

$$W_{\text{turbine}} + \int_1^2 v dp + mg\Delta h + \frac{m}{2}\Delta u^2 + T_0\Delta S_{\text{irr}} = 0, \quad (16.4)$$

where, in the absence of chemical change, the term $T_0\Delta S_{\text{irr}}$ will now depend only on irreversibilities arising from friction, viscosity, and internal heat flow. Calling this term the work lost by friction, we thus obtain the ordinary form of Bernoulli's equation applicable under the specialized conditions.

17. Continuous Flow Processing Plant

As a final example of the application of Eq. (13.1), let us now consider the steady-state operation of an apparatus into which certain chemical substances are continuously fed for processing and from which the resulting products are continuously withdrawn. The operation of such an apparatus may be physical in character as in the separation of helium from natural gas by fractional condensation or of alcohol from admixture with water by fractional distillation,

or it may involve chemical change as in the production of ammonia gas by passage of hydrogen and nitrogen at elevated pressure and temperature through a catalyst. We shall make our treatment adequate to cover both types of operation.

For the sake of definiteness, and also to correspond to the situation of usual interest, we shall assume that differences between the kinetic and potential energies of the substances entering and leaving the process are negligible, and shall take the substances as entering and leaving at the temperature T_0 prevailing in the surroundings. We shall denote by v_i , E_i , S_i , and v_o , E_o , S_o , respectively, the volumes, energies, and entropies of the substances going into and coming out of the apparatus, in the time interval of interest, and shall take them as supplied and withdrawn under the pressures p_i and p_o .

Turning our attention once more to Eq. (13.1), we shall now be able to substitute for the work done by the system on its surroundings

$$W = -W_{\text{pump}} - \sum_i p_i v_i + \sum_o p_o v_o, \quad (17.1)$$

where W_{pump} is the extra mechanical work necessary to keep the process running, and the other terms give the work done due to the pressures acting on the substances entering and leaving the apparatus. Furthermore, we shall be able to substitute for the terms involving energy and entropy

$$\begin{aligned} \sum_m (E_m - T_0 S_m) &= \sum_i (E_i - T_0 S_i) \\ &\quad - \sum_o (E_o - T_0 S_o). \end{aligned} \quad (17.2)$$

Making these substitutions, we obtain after some rearrangement of terms

$$\begin{aligned} \sum_o (E_o - T_0 S_o + p_o v_o) - \sum_i (E_i - T_0 S_i + p_i v_i) \\ = W_{\text{pump}} + \sum_n \frac{T_n - T_0}{T_n} Q_n - T_0 \Delta S_{\text{irr}}, \end{aligned}$$

or, using a well-known relation, we can write

$$\Delta F = W_{\text{pump}} + \sum_n \frac{T_n - T_0}{T_n} Q_n - T_0 \Delta S_{\text{irr}}, \quad (17.3)$$

where ΔF is the increase in the thermodynamic potential of the substances leaving the apparatus over that of the original substances entering.

In accordance with the above result, the increase in thermodynamic potential, needed to go from the substances at our disposal to those we wish to produce, is equal to the mechanical work which we put into the system, augmented by the fraction of the heat introduced which could be theoretically changed into work, and diminished by the now familiar expression for the loss of work resulting from irreversible processes.

In using Eq. (17.3) to analyze the operation of the process, it must be appreciated that the dependence of ΔF on W_{pump} and Q_n does not mean that we can obtain efficient operation merely by doing work on the apparatus and supplying heat at elevated temperature without reference to their utilization for the ends desired, since energy so supplied may merely be degraded and serve to increase the term $T_0\Delta S_{\text{irr}}$ without leading to increased production. For example, it is to be appreciated that heat introduced at elevated temperature will, in general, be wasted by conduction to the temperature of the surroundings, unless it is supplied for direct utilization as a needed heat of reaction, or can be utilized in some form of heat engine for the production of work.

The causes for irreversible increases in entropy leading to the term $T_0\Delta S_{\text{irr}}$ in Eq. (17.3) will include friction and viscosity, chemical reaction under non-equilibrium conditions, free mixing of separated substances, irreversible heat flow within the apparatus, and heat flow between the temperature of the apparatus and that of the surroundings. In case the process operates at a temperature above that prevailing in the surroundings, as in the fractional distillation of water-alcohol mixtures, the direction of heat leak will be from apparatus to surroundings, and in case the process operates below the temperature of the surroundings, as in the separation of helium from natural gas by fractional condensation, the direction of heat leak will be from surroundings to the apparatus. In both cases, however, in accordance with our method setting up Eq. (13.1), it is to be appreciated that we must include in the computation of

ΔS_{irr} the increase in entropy caused by the free flow of heat to or from the temperature T_0 of the surroundings.

In the study of the separation of helium from natural gas, mentioned in reference 1, special attention was given to irreversible increases of entropy that were present in an already existing process owing to the unnecessary separation of various components of the natural gas which were subsequently allowed to mix freely, and owing to transfer of heat within the apparatus through large temperature intervals. On eliminating as far as possible these sources of inefficiency, it also proved possible to design a process in which the irreversibility resulting from heat leak was reduced, since the general temperature of operation was raised by condensing the natural gas as a combined mixture without separation of its components, except for the small amount of helium which was left uncondensed and drawn off as a gas at the low temperature end of the apparatus.

Numerous other examples of the usefulness of Eq. (17.3) might be considered. In many of them there will be no transfer of heat except by leak at temperature T_0 , and hence the terms involving Q_n will be absent. As a specially interesting application of the equation, we may consider a living organism in an approximately steady state, not involving rapid growth, nor utilization of sunlight by chlorophyll. The equation could then be applied in the form

$$W_{\text{external}} = F_{\text{food}} - F_{\text{excreta}} - T_0\Delta S_{\text{irr}}, \quad (17.4)$$

where gases such as oxygen taken in and carbon dioxide given out must be included in calculating the thermodynamic potentials of food and excreta. This must now complete our illustrations of the possibilities of applying the efficiency equation (13.1) to cyclical and steady-state processes.

PART IV. APPLICATIONS OF FIRST AND SECOND LAW EQUATIONS

18. Viscous Flow

In the immediately preceding part of this article we have applied the efficiency equation (5.1) to several different cyclical or steady-state processes, in order to illustrate the role of irre-

versible entropy production in reducing the efficiency of such processes. The efficiency equation (5.1) was itself derived as a consequence of the first and second law equations (2.1) and (3.1), after appropriate specialization to cyclical or steady-state conditions.

In the present part of the paper, we shall now apply the first and second law equations directly to two selected theoretical problems, in order to illustrate the increased effectiveness of thermodynamics as a theoretical tool which results from expressing the second law by an equality instead of by an inequality. The two theoretical problems have been so chosen that both illustrate the increased effectiveness of the second law when expressed as an equality. However, in one case we shall find that the information provided by the second law equality is already available to us on other grounds, and in the other case that the information so provided is not already available at least in the present state of theoretical knowledge. Hence, the actual importance of being able to express the second law of thermodynamics by an equality can be different in different cases.

The first problem that we wish to consider is that of developing a general theory for the viscous flow of fluids, under conditions where temperature gradients and heat flow as well as fluid motion may play a role. This problem has already been treated by Eckart,³ and our present treatment will involve some repetition which is needed in order to demonstrate the actual contribution of the second law equality to the theory.

In treating the theory of fluid flow we shall regard it as appropriate to employ the mechanical principles of the conservation of mass and of Newton's second law of motion as well as the two laws of thermodynamics. In accordance with these four principles, we may then evidently write for any selected portion of the fluid: as an expression of the *conservation of mass*

$$\frac{d}{dt} \int \rho dV = 0, \quad (18.1)$$

as an expression of Newton's *second law of motion*

$$\frac{d}{dt} \int \rho \mathbf{u} dV = \mathbf{i} \int t_{ij} \mathbf{j} \cdot d\mathbf{A}, \quad (18.2)$$

as an expression of the *first law of thermodynamics*

$$\begin{aligned} \frac{d}{dt} \int \rho \left(\epsilon + \frac{1}{2} u^2 \right) dV = \int \mathbf{q} \cdot d\mathbf{A} \\ + \int u_i t_{ij} \mathbf{j} \cdot d\mathbf{A}, \end{aligned} \quad (18.3)$$

and as an expression of the *second law of thermodynamics*

$$\frac{d}{dt} \int \rho s dV = \int \frac{\mathbf{q}}{T} \cdot d\mathbf{A} + \int \left(\frac{dS}{dt} \right)_{\text{irr}} dV, \quad (18.4)$$

where, for the selected portion of fluid, we relate the rate of change with time of integrals taken over its volume to integrals taken over its boundary surface, and to an integral giving the rate of irreversible entropy production inside the portion of fluid considered, and where for simplicity we do not consider the action of gravity or other external forces. The quantities occurring in these equations are time t , elements of volume dV and of area $d\mathbf{A}$ taken as an inward pointing vector, unit vectors $\mathbf{i}$ and $\mathbf{j}$ taken as parallel to Cartesian coordinate axes x_i , x_j , and—at any point in the fluid—the density ρ , the internal energy per unit mass ϵ , the entropy per unit mass s , the temperature T , the rate of irreversible entropy production per unit volume $(dS/dt)_{\text{irr}}$, the velocity of fluid flow $\mathbf{u}$, the rate of heat flow per unit cross section $\mathbf{q}$, and the components of the stress tensor t_{ij} , with the usual convention that this symbol denotes the force in the direction of the i axis, exerted across unit area perpendicular to the j axis, by fluid lying on the side of the surface corresponding to smaller values of the coordinate x_j . The expressions as written assume the summation convention for dummy indices i and j .

For our purposes, it will now be desirable to re-express these equations in a differential form applicable at any given point in the fluid. This we do with the help of familiar methods, involving the use of Gauss's theorem to replace surface by volume integrals, the reduction in size of the portion of fluid considered to the neighborhood of a point, and the introduction of obvious cancellations. We then readily obtain

as our desired expressions

$$\frac{d\rho}{dt} + \rho \operatorname{div} \mathbf{u} = 0, \quad (18.5)$$

$$\rho \frac{d\mathbf{u}}{dt} = -\frac{\partial t_{ij}}{\partial x_j} \mathbf{i}, \quad (18.6)$$

$$\rho \frac{d}{dT} (\epsilon + \frac{1}{2} u^2) = -\operatorname{div} \mathbf{q} - \frac{\partial}{\partial x_j} (u_i t_{ij}), \quad (18.7)$$

$$\rho \frac{ds}{dt} = -\frac{1}{T} \operatorname{div} \mathbf{q} - \mathbf{q} \cdot \operatorname{grad} \frac{1}{T} + \left(\frac{dS}{dt} \right)_{\text{irr}}. \quad (18.8)$$

We now wish to examine the extent of the information made available to us by Eq. (18.8) which has resulted from our expression of the second law of thermodynamics by an equality instead of by an inequality. For this purpose, in the first place, we note that we can evidently substitute for the rate of change of the entropy density of the fluid, as a consequence of its known dependence on energy and volume, the expression

$$\frac{ds}{dt} = \frac{1}{T} \frac{d\epsilon}{dt} + \frac{p}{T} \frac{dv}{dt}, \quad (18.9)$$

where p is the internal pressure of the fluid and v its specific volume. In the second place, we note that the irreversible production of entropy in the fluid will evidently result from two causes—the dissipation of mechanical work against viscous forces, and the flow of heat from regions of higher to those of lower temperature. Hence, in accordance with our previous equations, (7.3) and (8.4), we may write for the rate of irreversible entropy production per unit volume of the fluid

$$\left(\frac{dS}{dt} \right)_{\text{irr}} = \frac{1}{T} \frac{dF}{dt} + \mathbf{q} \cdot \operatorname{grad} \frac{1}{T}, \quad (18.10)$$

where dF/dt is the work done per unit time and per unit volume against viscous forces, and for this quantity we can evidently take

$$\frac{dF}{dt} = -\frac{\partial}{\partial x_j} (u_i t_{ij}) + u_i \frac{\partial t_{ij}}{\partial x_j} + p \rho \frac{dv}{dt}, \quad (18.11)$$

where the first term gives the total rate at which work is done on unit volume of the fluid, and

the other two terms subtract off the rates at which work is done reversibly against the forces of inertia and of internal pressure.

Substituting Eqs. (18.9–10–11) in (18.8), we now obtain, with the help of obvious cancellations,

$$\rho \frac{d\epsilon}{dt} = -\operatorname{div} \mathbf{q} - t_{ij} \frac{\partial u_i}{\partial x_j}, \quad (18.12)$$

as a new expression for the information provided by the second law equality (18.8). However, we at once see that this expression could also have been obtained, from Newton's second law of motion and the first law of thermodynamics, by taking the dot product of (18.6) with $\mathbf{u}$ and subtracting from (18.7). Hence, in this case, we are led to the conclusion that the second law equality, although it gives us a valid expression, does not give us additional information beyond that already made available by the principles of mechanics and by the principle of the conservation of energy generalized to allow for heat flow. This should not disturb us, however, since it is clear that thermodynamics can be regarded, in general, as providing theoretical methods to which we need take resort only insofar as sufficient information is not available to permit more elementary methods of treatment.

In concluding this discussion of the general theory of viscous flow, it will be of interest to exhibit a set of supplementary equations which, combined with (18.5–6–7), would be sufficient to provide a complete solution for the behavior of the fluid. This set may be taken as

$$\epsilon = \epsilon(\rho, T), \quad (18.13)$$

$$p = p(\rho, T), \quad (18.14)$$

$$\mathbf{q} = -\kappa \operatorname{grad} T, \quad (18.15)$$

$$t_{ii} = p + \frac{2}{3} \eta \operatorname{div} \mathbf{u} - 2 \eta \frac{\partial u_i}{\partial x_i}, \quad (18.16)$$

(not summed over i)

$$t_{ij} = -\eta \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right), \quad (i \neq j) \quad (18.17)$$

where ϵ and p are regarded as known functions of ρ and T , $\mathbf{q}$ is given by our previous expression (8.5) in terms of the coefficient of thermal con-

ductivity κ and of the temperature gradient, and the components of the stress tensor t_{ij} are given by known expressions involving the coefficient of viscosity η .⁸ Paying due regard to the number of scalar quantities that correspond to a given vector quantity, we then see that Eqs. (18.5–6–7) together with (18.13–14–15–16–17) furnish us a total of 19 scalar equations for determining—as a function of position and time—the values of the 19 dependent scalar quantities corresponding to ρ , ϵ , p , T , $\mathbf{u}$, $\mathbf{q}$, and t_{ij} .

This analysis shows once more that the second law equality (18.8), which we did not count in as one of our equations, is not needed in order to secure a quantitative solution of the equations of motion for a viscous fluid. Nevertheless, it is also of interest to remark at this point that the second law of thermodynamics can be regarded as exerting a qualitative influence on the nature of the supplementary equations which can allowably be taken in order to secure a solution, since it is clear that these must at least be of such a character as to make $(dS/dt)_{\text{irr}}$ a positive quantity. Noting, however, the value for $(dS/dt)_{\text{irr}}$ provided by Eqs. (18.10–11), we readily verify that this condition is satisfied by the supplementary Eqs. (18.15–16–17) which we have introduced as expressions for heat flow $\mathbf{q}$ and for stress tensor t_{ij} .

Discussion of the different senses in which temperature has been employed in the development of the foregoing theory of viscous flow will be found at the end of §22.

19. Thermoelectric Effect

We now turn to the consideration of a problem where, at least in the present state of theoretical knowledge, the introduction of the second law of thermodynamics in the form of an equality does assist in providing a solution. This is Kelvin's old problem of the thermodynamic theory of the thermoelectric effect, where it has already been stated by Bridgman (see reference 4) that the appropriate consideration of irreversible entropy production leads to a more satisfactory theoretical treatment than was previously possible.

⁸ See Lamb, *Hydrodynamics* (Dover Publications, New York, 1945), sixth edition, §326.

To apply our method of attack to this problem, let us consider a thermoelectric circuit consisting of two wires, A and B , composed of different metals, with one junction maintained at an upper temperature T and the other at a lower temperature T_0 , and with the rest of the circuit insulated from thermal contact with the surroundings. Let us then consider a steady state of this system in which I is the electric current flowing in the circuit in the direction from A to B at the hotter junction, and in which Q and Q_0 are the amounts of heat absorbed per unit time at the two junctions. In accordance with Eqs. (4.1) and (4.2), applying to steady-state systems, we can then write, as a consequence of the first law of thermodynamics,

$$Q + Q_0 = 0, \quad (19.1)$$

and as a consequence of the second law of thermodynamics,

$$\frac{Q}{T} + \frac{Q_0}{T_0} + \Delta S_{\text{irr}} = 0, \quad (19.2)$$

where ΔS_{irr} is the entropy irreversibly produced in unit time inside the system as a result of the flow of electric current against resistance, and of the flow of heat from regions of higher to those of lower temperature.

In order to obtain useful results from these equations, we must now analyze the quantities which they contain. For this purpose we may begin by considering the flow of heat into and out of the junction at temperature T , and writing the obvious relation

$$Q = IP_{AB}(T) + q_A(T) + q_B(T), \quad (19.3)$$

where $P_{AB}(T)$ is the Peltier heat reversibly absorbed on the passage of unit quantity of electricity from wire A to B at temperature T , and $q_A(T)$ and $q_B(T)$ are the rates of heat flow in the two wires A and B away from the junction at temperature T toward the junction at the lower temperature T_0 . Similarly, considering the flow of heat into and out of the junction at T_0 , we can write

$$Q_0 = -IP_{AB}(T_0) - q_A(T_0) - q_B(T_0), \quad (19.4)$$

where the significance of the symbols will be evident from the foregoing.

Furthermore, as we pass along either of the wires A or B in the direction of T to T_0 , we can relate the increases in heat flow, for each element of length traversed, to the thermal energy irreversibly evolved in that element in accordance with the Joule effect by the flow of electricity against resistance, and to the thermal energy reversibly absorbed or evolved in the element in accordance with the Thomson effect by the flow of electricity through a temperature gradient. This permits us to write

$$dq_A = I^2 dR_A + I\sigma_A dT_A, \quad (19.5)$$

and

$$dq_B = I^2 dR_B - I\sigma_B dT_B, \quad (19.6)$$

where dR_A and dR_B are the resistances of the elements considered, dT_A and dT_B are the changes in temperature on passing through these elements, and σ_A and σ_B are the Thomson coefficients for the two materials. Integrating Eqs. (19.5) and (19.6) for the whole length of the two wires, we can also write

$$q_A(T_0) - q_A(T) = I^2 R_A + I \int_T^{T_0} \sigma_A dT, \quad (19.7)$$

and

$$q_B(T_0) - q_B(T) = I^2 R_B - I \int_T^{T_0} \sigma_B dT. \quad (19.8)$$

Finally, we can evidently compute the rate of irreversible entropy production within these two wires by consideration of the degradation of energy accompanying the Joule heating effect, and by consideration of the irreversible flow of heat from higher to lower temperatures. In accordance with earlier equations (7.4) and (8.4), this then permits us to write

$$\Delta S_{\text{irr}} = \int_T^{T_0} \left[\frac{I^2}{T_A} dR_A - \frac{q_A}{T_A^2} dT_A + \frac{I^2}{T_B} dR_B - \frac{q_B}{T_B^2} dT_B \right],$$

or substituting (19.5) and (19.6)

$$\begin{aligned} \Delta S_{\text{irr}} &= \int_T^{T_0} \left[\frac{dq_A}{T_A} - \frac{I\sigma_A}{T_A} dT_A - \frac{q_A}{T_A^2} dT_A \right. \\ &\quad \left. + \frac{dq_B}{T_B} + \frac{I\sigma_B}{T_B} dT_B - \frac{q_B}{T_B^2} dT_B \right] \\ &= \int_T^{T_0} \left[d\left(\frac{q_A}{T_A}\right) + d\left(\frac{q_B}{T_B}\right) \right. \\ &\quad \left. - \frac{I\sigma_A}{T_A} dT_A + \frac{I\sigma_B}{T_B} dT_B \right] \\ &= \frac{q_A(T_0)}{T_0} - \frac{q_A(T)}{T} + \frac{q_B(T_0)}{T_0} - \frac{q_B(T)}{T} \\ &\quad + I \int_{T_0}^T \frac{\sigma_A - \sigma_B}{T} dT. \quad (19.9) \end{aligned}$$

This then completes the results needed in order to return to a consideration of the consequences of the two laws of thermodynamics.

Combining the first law equation (19.1) with Eqs. (19.3-4-7-8), and denoting the total resistance of the circuit by $R = R_A + R_B$, we readily obtain

$$P_{AB}(T) - P_{AB}(T_0) - IR + \int_{T_0}^T (\sigma_A - \sigma_B) dT = 0,$$

or denoting the electromotive force for the circuit by $E = IR$, and differentiating with respect to the temperature T of the upper junction, we can write

$$\frac{dE}{dT} = \frac{dP_{AB}}{dT} + (\sigma_A - \sigma_B), \quad (19.10)$$

as a consequence of the first law of thermodynamics.

Combining the second law equation (19.2) with Eqs. (19.3-4-9), we readily obtain

$$\frac{P_{AB}(T)}{T} - \frac{P_{AB}(T_0)}{T_0} + \int_{T_0}^T \frac{\sigma_A - \sigma_B}{T} dT = 0,$$

and again differentiating with respect to the temperature T of the upper junction, we can

write

$$\frac{dP_{AB}}{dT} = \frac{P_{AB}}{T} - (\sigma_A - \sigma_B), \quad (19.11)$$

as a consequence of the second law of thermodynamics taken in the form of an equality.

By solving Eqs. (19.10) and (19.11) for Peltier heat and difference in Thomson coefficients, we then obtain the familiar expressions

$$P_{AB} = T \frac{dE}{dT} \quad (19.12)$$

and

$$\sigma_A - \sigma_B = -T \frac{d^2E}{dT^2}, \quad (19.13)$$

in a form suitable for experimental verification with the help of calorimetric measurements.

The foregoing analysis demonstrates the simple and unforced character of the thermodynamic treatment of the thermoelectric effect which is made possible by expressing the second law of thermodynamics in the form of an equality. In the past, doubts have been felt as to the validity of applying thermodynamics to a derivation of thermo-electromotive force, since it was not possible to go simultaneously to a limit where irreversibilities caused by heat flow and ohmic resistance would both vanish. It should be emphasized that the expression of the second law of thermodynamics in the form of an equality gives assurance that we can apply the principles of thermodynamics to systems where irreversible processes are taking place without having to consider the possibility of limiting cases where the irreversibilities would vanish (compare reference footnote 4).

Our analysis also shows, unlike the findings in the previous case of the theory of viscous flow, that the second law equality now provides a necessary part of the information required for the solution of the problem. This is connected with the circumstance that in the theory of viscous flow we could make use of the Newtonian expression (18.6) for the forces acting on the fluid in solving for its motion, while in the present theory of the thermoelectric circuit we do not have a similar explicit expression for the forces acting on the electric fluid. This is in

agreement with the general point of view that the methods of thermodynamics are particularly useful in the absence of knowledge as to the detailed internal behavior of a system.

Discussion of the different senses in which temperature has been employed in the development of the foregoing theory of the thermoelectric effect will be found at the end of §22.

PART V. DISCUSSION OF THE CONCEPT OF TEMPERATURE

20. Temperature in the Case of Equilibrium

In bringing this article to a conclusion it is desirable to make some additional remarks on thermodynamic theory, which have a bearing on our previous discussions and which are needed in obtaining a full understanding of them. In the present section our remarks will be directed to the circumstance that the temperature of a system is a concept which can be unambiguously applied only to systems in states of thermal equilibrium.

The concept of temperature may be introduced into the theory of heat in the following manner. In accordance with empirical facts, it is possible to arrange any set of isolated bodies, which are themselves in states of equilibrium, in a series such that—on establishment of thermal contact—heat will flow from any body at a higher position to any body at a lower position in the series, and thermal equilibrium without flow of heat will ensue for all bodies having the same position in the series. This makes it possible to introduce a qualitative definition of temperature for such bodies by assigning higher or lower temperatures to the bodies in accordance with the eventual direction of thermal flow, and assigning the same temperature to bodies in thermal equilibrium. Employing this qualitative definition of temperature, we can then obtain the important empirical result that the temperature of any system in a condition of equilibrium is definitely determined by its state, since the position of the system in the temperature series is experimentally found to be uniquely determined by the values of any set of independent variables that we choose for specifying the possible states of equilibrium of the system. This now makes it possible to introduce a quantita-

tive definition of temperature, by choosing some given body to act as a "thermometer" and taking the temperature of any system, with which the thermometer comes into thermal equilibrium, as defined in terms of the measured values of the variables determining the state of the thermometer, for example, as given by the volume of a thermometric fluid maintained under constant pressure. The values of temperature given by different kinds of thermometers are of course interrelated and can be reduced to any particular temperature scale that we may wish to select.

The above described method of introducing the concept of temperature undertakes a definition of temperature only for cases of systems in states of equilibrium. The simplicity of definition in such cases is connected with the possibility of then relating the temperature of the system to the values of the relatively small number of variables needed for the specification of equilibrium states. For non-equilibrium conditions, it is in general necessary to specify the values of an infinite number of variables in order to describe the state of a system, and no immediate definition of temperature presents itself for systems in such states. The conclusion that we can expect no unique definition of temperature in the absence of equilibrium will be reinforced if we now consider the experimental determination of temperature by usual methods.

Unambiguous determination of temperature by the accepted methods of thermometry is possible only for systems in thermal equilibrium, since it is only under such circumstances that thermometers of different construction will give consistent measurements. Thermometers of different construction respond with different degrees of sensitivity to the different forms of energy that can, in general, be present inside a system,—associated, for example, with the disordered or coherent motion of various kinds of molecules, atoms, ions, electrons, or other particles, with the presence of electromagnetic radiation of different frequencies, and with different possibilities for chemical reaction. In a state of thermal equilibrium, the densities of the different forms of energy inside a system will have adjusted themselves to equilibrium values, and the readings of different kinds of thermom-

eters will be found to give consistently interrelated values, all of which can be reduced to a single scale of temperature, for example, absolute temperature T on the Kelvin scale. In the absence of thermal equilibrium, however, the densities of different forms of energy will depend essentially on the arbitrary past history of the system, and no consistent relations will be found between the readings of different kinds of thermometers that responds with different sensitivities to different forms of energy. A striking example of the discrepancies between the temperature readings, obtained with different kinds of thermometers in the absence of equilibrium, is furnished by the case of mercury thermometers with reflecting and absorbing bulbs held outdoors in the sunlight, where one thermometer responds primarily to the energy of the air and the other to that of the radiation.

In view of the foregoing we conclude that unique values of temperature can be assigned only in cases of thermal equilibrium and must inquire into the extent of justification that can be offered for the somewhat common use of the concept of temperature in situations where thermal equilibrium does not prevail. In the next section, we shall give special attention to the role of temperature when regarded as providing a driving force for thermal flow, and in the following section we shall consider the role of temperature in the calculation of the entropy transfer accompanying thermal transfer at a finite rate.

21. Temperature in the Case of Thermal Flow

In accordance with the preceding section, it is evident that further consideration is necessary when the concept of temperature is applied to non-equilibrium situations. Under such circumstances some approximation to temperature may be sufficient, or some specific definition appropriate to the particular situation may be needed. As an important example of the application of the concept in non-equilibrium situations, we may consider the relation of temperature differences to flow of heat.

When two isolated bodies, in conditions of thermal equilibrium at different temperatures, are placed in thermal interaction, thermal equilibrium is disturbed, and heat flow takes place

from the body at the originally higher to that at the originally lower temperature. This continues until a new condition of thermal equilibrium is reached with the two bodies at some intermediate temperature which is the same for both. This phenomenon makes it natural to regard temperature difference as providing some kind of driving force for heat flow, and to seek for quantitative relations connecting intensity of heat flow with temperature differences which would hold even during the period of thermal flow. As familiar examples of such quantitative relations, we have the Fourier expression for the flow of heat inside a conducting medium, Newton's law for the cooling of bodies by conduction, and Stefan's law for the cooling of bodies by transfer of radiation.

As a typical example of such quantitative relations, which will illustrate the kinds of problem that arise, we shall take the Fourier expression for internal conduction, as already given by our previous equation (8.5). This equation,

$$\mathbf{q} = -\kappa \text{grad} T, \quad (21.1)$$

connects the rate of heat flow $\mathbf{q}$, per unit time and per unit cross section, inside an isotropic medium, with thermal conductivity κ regarded as a parameter depending on the properties of the medium at the point under consideration, and with the rate of change in temperature, at that point of the medium, as given by the gradient of T . Since this relation is regarded as holding under conditions of thermal flow rather than of thermal equilibrium, we must now make special inquiry into the possibility of a satisfactory determination of the quantity T which it contains.

In making this inquiry, it has to be pointed out at the start that Eq. (21.1) evidently requires the determination of temperature as a sufficiently precise function of time and position to give a good value for the instantaneous gradient, and hence requires the correction of actual thermometer readings for "temporal lag" and "spatial spread." Such corrections can, however, presumably be introduced by obvious methods, for example, by experimentation with smaller and smaller thermometers of the kind chosen. Hence, there appears to be no insuperable theoretical obstacle to the measurement of temperature as a sufficiently precise function of

position and time, provided we have some suitable kind of thermometer to use. This then brings us directly to the fundamental point of our inquiry, since in the absence of thermal equilibrium different kinds of thermometer would not give concordant readings even when corrected for "lag" and "spread." The resolution of this difficulty appears to us to lie along the following lines.

In the first place, it is to be remarked that Eq. (21.1) has in any case merely the status of an empirical law, rather than that of a necessary theoretical principle. Although it agrees with the second law of thermodynamics by making spontaneous flow of heat lead to increase in entropy, as shown by our earlier equation (8.6), it is not derivable from the second law as a necessary relation. In view of this empirical status, it is hence not essential to require precise validity for Eq. (21.1), nor to demand the possibility of precise determination for the quantities which it contains.

In the second place, it is to be pointed out that differences between the readings of different kinds of thermometer will tend toward zero as the degree of disturbance away from thermal equilibrium is reduced. Hence, by reducing the temperature gradient and the rate of heat flow, it is possible that discrepancies between different kinds of temperature measurement might become negligible, and that Eq. (21.1) might approach precise validity as we approach the limit of vanishing heat flow and temperature gradient. Indeed, it appears probable that there are many cases where the equation would have this limiting kind of precise validity and significance.

Finally, even in the case of finite rates of heat flow, it is to be emphasized that Eq. (21.1) often does have at least closely approximate validity when temperature measurements are made using commonly available thermometric methods. Under such circumstances, we can then maintain the usefulness of Eq. (21.1) by introducing a specific definition of temperature in which we prescribe some kind of thermometer for its determination which will make (21.1) approximately valid. For example, if heat transfer is taking place mainly as a consequence of molecular collisions, it is presumable that an appropri-

ate kind of thermometer for the purpose would be one primarily sensitive to molecular collision rather than to radiation.

The foregoing discussion shows the possibility of introducing a specific definition of temperature which proves useful in interpreting the intensity of thermal flow. In the discussions given in the next section, we shall present a possibility for introducing a different specific definition of temperature which proves helpful in interpreting the transfer of entropy by thermal flow. This illustrates the general possibility, in the absence of equilibrium, of introducing special definitions of temperature which prove useful for some particular purpose, as, for example, when we assign different temperatures to matter and radiation in the path of sunlight.

22. Temperature in the Calculation of Entropy Transfer

In accordance with the second law of thermodynamics, the temperature T of a system serves as an integrating factor for heat in the fundamental equation,

$$\Delta S = \int \frac{dQ}{T}, \quad (22.1)$$

which gives the change in the entropy of the system, that accompanies a reversible change in its state. Since this equation is valid only for reversible changes, it applies only to the limiting case of change through a succession of equilibrium states. Hence in computing the result given by (22.1), the temperature T to be used at each stage of the integration is that corresponding to some state of equilibrium of the system. There is, therefore, in this case no difficulty as to the unambiguous determination of the correct values of T to be used, as there would be in the absence of equilibrium.

Equation (22.1) can now be used, however, to investigate, from a more general point of view, the relation between entropy transfer and heat transfer when heat is supplied from a heat reservoir. In the first place, since the equation applies only to reversible processes without any irreversible production of entropy, the increase in entropy of the system as given by (22.1) must be equal to the entropy brought into the system

by the transfer of heat. In the second place, since the heat is transferred reversibly, we can take the temperature T_r of the reservoir from which the heat is supplied as equal to the temperature T of the system itself. Hence, in accordance with (22.1) we can now write

$$S_r = \frac{Q_r}{T_r} \quad (22.2)$$

as an expression for the amount of entropy S_r transferred from a heat reservoir by the transfer of an amount of heat Q_r , under limiting conditions such that the reservoir can be regarded as remaining substantially in a state of equilibrium at temperature T_r during the process of heat transfer.

This new equation (22.2) appreciably increases our understanding of the process of entropy transfer since it evidently gives us a valid expression for the entropy carried into a system by heat flow, under the restriction that the heat is provided from a reservoir substantially in a state of equilibrium, but now without any restriction on the nature of the processes that go on inside the system which may actually take place under non-equilibrium conditions involving irreversible production of entropy inside the system. It is also evident that the equation can be applied when the heat flow between reservoir and system is in either direction, and when more than a single heat reservoir is involved. Hence this equation can be used, in general, to determine the transfer of entropy by thermal flow between a system and its surroundings, whenever the thermal flow can be regarded as from or into heat reservoirs of such a character that they remain substantially at equilibrium at definite temperatures.

Factors which affect the extent to which a heat reservoir is disturbed away from equilibrium include the specific heat and the thermal conductivity of the material filling the reservoir, and the extent of reservoir volume supplying heat to the surface of transmission. As these factors are made larger and larger, for a given rate of heat transfer, thermometer readings throughout the reservoir will become more and more nearly uniform and constant, and the condition of the reservoir will approach nearer and

nearer to that of equilibrium. Thus, in principle, there is the possibility of constructing reservoirs that will transfer heat under conditions approaching what is necessary for the validity of Eq. (22.2). Furthermore, in practice, many situations are encountered where heat transfer actually does take place with reservoirs so nearly in conditions of thermal equilibrium that there is no appreciable uncertainty as to the values of the temperatures T_r which should be substituted into (22.2) in order to secure correct results. Hence Eq. (22.2) has an immediate wide range of applications.

Moreover, there is an important possibility for extending the application of Eq. (22.2) to certain situations where the heat reservoir is not in a condition of thermal equilibrium. Under such circumstances, we cannot make immediate use of Eq. (22.2) to calculate the entropy S_r carried into a system by the heat Q_r , since, as we have seen in §20, different kinds of thermometers will give discrepant temperature readings in the absence of equilibrium, and we shall have no unambiguous value of the temperature T_r of the reservoir to substitute into our equation. In view of this difficulty, however, we may now consider the possibility of replacing the actual reservoir which supplies the heat Q_r to the system under non-equilibrium conditions by an ideal reservoir constructed as described above in such a manner as to supply heat substantially under equilibrium conditions. On making such a replacement, we shall have to find by trial a temperature T_r for the ideal reservoir which will lead to the same rate of heat transfer as from the actual reservoir. Furthermore, we shall have to determine by observation whether the behavior of the system when it receives the heat Q_r from the ideal reservoir is substantially the same as it was when it received heat Q_r from the actual reservoir. It is evident, however, that there will be many situations in which this is the case.

Hence, we now have the important possibility of extending the application of Eq. (22.2) to situations where the heat reservoir is not in a condition of thermal equilibrium, provided we substitute as the value of T_r in the equation the temperature which would be found for an ideal heat reservoir in a condition of equilibrium, which would deliver the same heat to the system and se-

cure the same behavior of the system as in the actual situation. We thus have a further illustration of the general possibility, in the absence of equilibrium, of introducing a special definition of temperature which proves useful for some particular purpose.

We have been interested in making the foregoing analysis of the range of valid application for Eq. (22.2), since the result shows that there is a wide range of circumstances in which we can properly apply our original second law equation (3.1), which we wrote in the form

$$\Delta S = \sum_m S_m + \sum_n \frac{Q_n}{T_n} + \Delta S_{\text{irr}}. \quad (22.3)$$

There will, of course, be cases where the terms on the right-hand side of this equation would not be sufficient to cover all the ways in which the entropy of a system may be increased. As a particular example we have the possible introduction of entropy by irradiation, with light of specified frequencies, but the treatment of this may be left to another occasion.

It is also of interest to consider the bearing of the foregoing discussions on the validity of our previous expressions (8.4), (8.5), and (8.6) for the rate of irreversible production of entropy per unit volume, in a conducting medium,

$$\left(\frac{dS}{dt}\right)_{\text{irr}} = \mathbf{q} \cdot \text{grad} \left(\frac{1}{T}\right), \quad (22.4)$$

for the rate of the thermal flow in an isotropic conducting medium

$$\mathbf{q} = -\kappa \text{grad} T, \quad (22.5)$$

and, by substitution, as a new expression for rate of entropy production,

$$\left(\frac{dS}{dt}\right)_{\text{irr}} = \frac{\kappa}{T^2} [\text{grad} T]^2. \quad (22.6)$$

In accordance with the discussions in the present section, we see that the validity of (22.4) depends on a special definition for T , securing agreement with the temperatures of ideal heat reservoirs, that might be introduced to obtain unaltered conditions of thermal flow in the medium, maintaining equilibrium conditions in the reservoirs. And in accordance with the dis-

cussions of the preceding section, we have seen that the validity of (22.5) depends on a different special definition for T which would make the equation give a good representation of the actual rate of thermal flow. Hence the validity of the final equation (22.6), which is obtained by substituting (22.4) in (22.5), requires agreement between the results given by the two different definitions. It is evident, however, that we can often expect to find sufficient agreement between the two definitions so that Eq. (22.6) will be a useful one.

Finally, it is of interest to consider the bearing of our discussion of temperature on the treatments which we have given in §§18 and 19 to the theories of viscous flow and of the thermoelectric effect. In developing the theory of viscous flow we have treated the temperature of the fluid as a sufficiently well defined and unambiguous function of position so that it could be used in all of the following connections: as a variable determining the state of an element of the fluid, Eqs. (18.13) and (18.14), as the factor to be taken in calculating change in entropy for a reversible change in state, Eq. (18.9), as the

factor to be taken in calculating entropy transfer as related to heat transfer, Eq. (18.8), as the factor to be taken in calculating irreversible entropy production by the dissipation of mechanical energy and by the free flow of heat, Eq. (18.10), and as a variable determining the rate of heat flow, Eq. (18.15). And, in developing the theory of the thermoelectric effect, we have treated the temperature in the wires composing the circuit as a sufficiently well defined and unambiguous function of position so that it could be used: as the factor to be taken in calculating entropy transfer as related to heat transfer, Eq. (19.2), as the factor to be taken in calculating irreversible entropy production by the dissipation of electrical energy and by the free flow of heat, Eq. (19.9), and as a variable the change of which determines the Thomson heat absorbed by the passage of electricity, Eqs. (19.5–6). In view of these different senses in which temperature has been used, it will be necessary to regard the above theories of viscous flow and of the thermoelectric effect as applying under conditions such that discrepancies between these different kinds of temperature can be neglected. It is presumable that this would often be the case when application of these theories is desired.