

PROPERTIES OF STEAM  
AND  
THERMODYNAMIC THEORY  
OF TURBINES

BY  
H. L. CALLENDAR, M.A., LL.D., F.R.S.,

LATE FELLOW OF TRINITY COLLEGE, CAMBRIDGE,  
PROFESSOR OF PHYSICS IN THE IMPERIAL  
COLLEGE OF SCIENCE AND TECHNOLOGY



LONDON  
EDWARD ARNOLD

1920

(All rights reserved)

Callendar  
1920

though Carnot was the first to use it for calculating  $F'(t)$ . Clapeyron was the first to employ the indicator diagram for illustrating the performance of an ideal cycle, and to deduce general expressions for  $F'(t)$ , applicable to all substances, in terms of the partial differential coefficients, which are now generally known as the thermodynamical relations (see Appendix I, § 188).

Kelvin (1848) proposed to base an absolute scale of temperature on Carnot's function, since it was the same for all substances at the same temperature, and endeavoured to deduce the relation between  $F'(t)$  and the scale of the gas-thermometer by means of Regnault's experiments on steam. Joule about the same time inferred from the properties of gases that  $F'(t)$  should be simply  $J/T$ . But this was first clearly explained, in terms of the mechanical theory of heat, by Clausius and Rankine (1850), who showed that  $F'(t)$  should be exactly  $J/T$  for a perfect gas, suitably defined by assuming the work done in isothermal expansion equivalent to the heat absorbed, or the difference of the specific heats independent of the temperature, either of which assumptions would make Carnot's expression  $T \times F'(t)$  constant and equal to the mechanical equivalent  $J$ . But there were large discrepancies between the experimental values of  $F'(t)$  and  $J/T$ , and it remained uncertain how far these were due simply to experimental errors or to systematic deviations of actual gases from the properties assumed in defining the perfect gas. This question was attacked by the porous plug method of Joule and Kelvin, who succeeded in showing that the scale of absolute temperature  $T$ , defined in terms of Carnot's function by the relation  $F'(t) = J/T$ , agreed even more closely than could have been anticipated with the gas-scale, especially in the case of the hydrogen thermometer, which has been adopted by general agreement as giving the practical equivalent of the absolute scale of temperature. In this way the relation between the available work and the temperature limits in the Carnot cycle is reduced to the simplest possible form.

**64. The Entropy Measure of Heat.** It follows from Carnot's principle, as above explained, that, when a quantity of heat energy  $Q$  is supplied to any working substance at a temperature  $T$  in a heat-engine, the maximum quantity of work obtainable in a cycle per degree fall is represented by the product  $Q \times F'(t)$ , which is equal to  $JQ/T$  by the definition of absolute temperature. Expressed in heat units, the proportion of the heat energy con-

vertible into work per degree fall is  $Q/T$ , or the quantity  $dQ$  convertible in a range  $dT$  is  $Q(dT/T)$ , or  $(Q/T)dT$ . By the first law, the heat rejected at  $T - dT$  is  $Q - dQ$ .

In a simple Carnot cycle, no heat is received except at the upper limit of temperature  $T'$ , and no heat is rejected except at the lower limit  $T''$ . We may therefore obtain the result for any finite range  $T'$  to  $T''$  by integrating the relation  $dQ/Q = dT/T$ , between limits  $T'$  and  $T''$ , which gives

$$Q'/T' = Q''/T'' = (Q' - Q'')/(T' - T'') = AW/(T' - T''), \dots (3)$$

where  $Q'$  is the heat received at the higher temperature,  $Q''$  the heat rejected at the lower temperature, and  $AW$  the thermal equivalent  $Q' - Q''$  of the work obtainable in the cycle. This method of integration was, in fact, applied by Carnot, and explained (*loc. cit.*, p. 27) as being equivalent to the employment of a series of engines, each working through an infinitesimal range and receiving the caloric rejected by the engine next above it in the series. But the correct expression for the work obtainable in a Carnot cycle of *finite* range, in terms of heat-energy on the mechanical theory, was first given by Rankine (*Phil. Mag.*, 1851, p. 55).

The thermal equivalent of the work obtainable in a Carnot cycle is seen to be equal to the product of the quantity  $Q'/T'$  (depending only on the heat received and the temperature of reception) and the temperature fall  $T' - T''$ . For a cycle of any form, in which the heat is not all received at one temperature, Rankine showed how to deduce the equivalent of the work obtainable by dividing each elementary quantity of heat  $dQ$  by the temperature of reception  $T$ , multiplying each by the corresponding range of temperature, and summing the results for the cycle. Examples of this method for other cycles are given in Chapter X.

Since the primary object of a heat-engine is to obtain the maximum output of work from heat per degree fall of temperature, it is evident that the quotient  $Q/T$  (or the integral of  $dQ/T$  in the generalised form) is a quantity of great importance in the theory of the heat-engine. Rankine called it the Thermodynamic Function, which is a somewhat vague and inconvenient name. Its properties were more fully investigated by Clausius at a later date, who gave it the name of Entropy, which has been universally adopted.

From many points of view, the entropy  $Q/T$  of a quantity of energy  $Q$  in the form of heat at a temperature  $T$ , may most simply be regarded as being merely a different measure of heat, in terms

of work obtainable per degree fall instead of in terms of total energy. The two measures are equally logical and definite, and are very simply related, but the entropy of a quantity of heat has quite different properties to the energy. The essential difference between the entropy and energy measures of heat is most readily appreciated by analogy with the case of a material fluid. A liquid, like water, is often measured by weight, that is to say, implicitly in terms of the work it is capable of doing per unit fall of level. This method gives a direct measure of quantity, analogous to the entropy measure of heat in terms of work per degree fall of temperature. But we might also measure the total energy possessed by the water in virtue of its elevation, by allowing it to fall to a definite level, and observing the rise of level which it was capable of producing in a known mass by any suitable mechanism. This would be analogous to the measurement of the total energy of a quantity of heat by observing the rise of temperature it was capable of producing in a calorimeter of known thermal capacity. Entropy is sometimes called "heat-weight" on the ground of the first analogy, and is the most appropriate measure of heat *quantity* as distinct from heat *energy*, but there is no simple method of measuring it directly. Thus, when a quantity of heat-energy  $Q$  is allowed to pass from a hot body at a temperature  $T'$  to a calorimeter at a temperature  $T''$ , the gain of *energy* of the calorimeter is equal to the loss of energy of the hot body, by the law of conservation of energy, and is easily measured. But this is not true of the entropy. The gain of entropy  $Q/T''$  of the calorimeter is necessarily *greater* than the loss of entropy  $Q/T'$  of the hot body, because  $T'$  is by hypothesis greater than  $T''$ . If the heat-energy  $Q$  had been supplied to a Carnot engine at  $T'$ , the entropy of the heat rejected at  $T''$  would have been equal to that of the heat supplied, namely  $Q/T'$ ; and the heat-energy rejected would have been reduced by the thermal equivalent of the work utilised, namely  $Q(T' - T'')/T'$ . When the heat  $Q$  is allowed to flow directly from  $T'$  to  $T''$ , without performance of work, the increase of entropy, namely  $Q/T'' - Q/T'$ , is the equivalent of the available work divided by  $T''$ , and is the same as if the work had actually been realised and then converted into heat by friction at the lower temperature.

The properties postulated for caloric on the older theory were similar in most respects to those of entropy, but did not correspond with those of heat measured as energy in a calorimeter. This naturally led to grave difficulties in connection with the theory of gases,

and of heat generated by friction. Fortunately it did not affect the validity of Carnot's reasoning, which, though expressed in the language of the caloric theory, was in the main independent of any assumption as to the nature of heat or the manner in which it was measured. (*Proc. Phys. Soc.* 23, p. 153, 1911.)

Heat is always measured as *energy* in practice, and the corresponding changes of entropy are inferred by dividing each addition of heat in thermal units by the temperature at which it is received. The entropy of a substance in any state is reckoned per unit mass from a standard state selected as the zero of entropy for the substance. The numerical values obtained in this way as representing the entropy of a substance, are independent of the temperature scale and the unit of mass, and are the same in all rational systems of units. The unit of entropy is often called a "Rank," after Rankine, but the name is seldom required, because there is practically only one unit of zero dimensions, so that troublesome questions of conversion or nomenclature do not arise.

**65. Properties of the Entropy.** The most important properties of the entropy for the present purpose are as follows:

The entropy of a body remains constant when no energy in the form of heat is lost or gained, a condition usually implied by the term "adiabatic." It is not altered by the performance of external work in adiabatic expansion or compression, provided that there is no internal friction. If there is any friction between parts of the substance moving with different velocities, or between the body considered and neighbouring bodies, the increase of entropy is the thermal equivalent of the work wasted in friction divided by the absolute temperature.

If there is any interchange of heat between different parts of the body at different temperatures, the effect is always to increase the entropy of the whole. For any direct transfer of heat-energy  $Q$  from a part at a temperature  $T'$  to a part at a lower temperature  $T''$ , the increase of entropy is  $Q/T'' - Q/T'$ , which is necessarily positive.

We have already seen that, in a simple Carnot cycle, the entropy of the heat received  $Q'/T'$  is equal to the entropy of the heat rejected  $Q''/T''$ . The same proposition is true for a cycle of any form, provided that it is reversible. This condition is tacitly assumed for any cycle represented on the indicator diagram, since the state of the working fluid is supposed to be one of equilibrium