

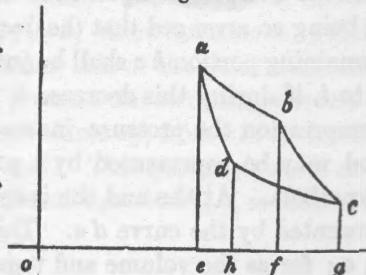
garded as a function of the two others ; the latter will then be the independent variables which determine the condition of the gas\*.

We will now endeavour to ascertain in what manner the quantities which relate to the *amount of heat* depend upon  $v$  and  $t$ .

When any body whatever changes its volume, the change is always accompanied by a mechanical work produced or expended. In most cases, however, it is impossible to determine this with accuracy, because an unknown *interior* work usually goes on at the same time with the *exterior*. To avoid this difficulty, Carnot adopted the ingenious contrivance before alluded to : he allowed the body to undergo various changes, and finally brought it into its primitive state ; hence if by any of the changes *interior* work was produced, this was sure to be exactly nullified by some other change ; and it was certain that the quantity of *exterior* work which remained over and above was the total quantity of work produced. Clapeyron has made this very evident by means of a diagram : we propose following his method with permanent gases in the first instance, introducing, however, some slight modifications rendered necessary by our maxim.

In the annexed figure let  $oe$  represent the volume, and  $ea$  the pressure of the unit-weight of gas when the temperature is  $t$  ; let us suppose the gas to be contained in an expansible bag, with which, however, no exchange of heat is possible. If the gas be permitted to expand, no new heat

Fig. 1.



\* [Clapeyron in his researches generally selected  $v$  and  $p$  for his two independent variables—a choice which accords best with the graphic representation, about to be described, wherein  $v$  and  $p$  constitute the coordinates. I have preferred, however, to consider  $v$  and  $t$  as the independent variables, and to regard  $p$  as a function thereof ; since in the theory of heat the temperature  $t$  is especially important, and at the same time very suitable for determination by direct measurements, accordingly it is ordinarily regarded as a previously known magnitude upon which depend the several other magnitudes which there enter into consideration. For the sake of uniformity I have everywhere abided by this choice of independent variables ; it need scarcely be remarked, however, that occasionally the equations thus established would assume a somewhat simpler form, if instead of  $v$  and  $t$ ,  $v$  and  $p$  or  $t$  and  $p$  were introduced therewith as independent variables.—1864.]

being added, the temperature will fall. To avoid this, let the gas during the expansion be brought into contact with a body A of the temperature  $t$ , from which it shall receive heat sufficient to preserve it constant at the same temperature. While this expansion by constant temperature proceeds, the pressure decreases according to the law of M., and may be represented by the ordinate of a curve  $a\ b$ , which is a portion of an equilateral hyperbola. When the gas has increased in volume from  $o\ e$  to  $o\ f$ , let the body A be taken away, and the expansion allowed to proceed still further without the addition of heat; the temperature will now sink, and the pressure consequently grow less as before. Let the law according to which this proceeds be represented by the curve  $b\ c$ . When the volume of the gas has increased from  $o\ f$  to  $o\ g$ , and its temperature is lowered from  $t$  to  $\tau$ , let a pressure be commenced to bring it back to its original condition. Were the gas left to itself, its temperature would now rise; this, however, must be avoided by bringing it into contact with the body B at the temperature  $\tau$ , to which any excess of heat will be immediately imparted, the gas being thus preserved constantly at  $\tau$ . Let the compression continue till the volume has receded to  $h$ , it being so arranged that the decrease of volume indicated by the remaining portion  $h\ e$  shall be just sufficient to raise the gas from  $\tau$  to  $t$ , if during this decrease it gives out no heat. By the first compression the pressure increases according to the law of M., and may be represented by a portion  $c\ d$  of another equilateral hyperbola. At the end the increase is quicker, and may be represented by the curve  $d\ a$ . This curve must terminate exactly in  $a$ ; for as the volume and temperature at the end of the operation have again attained their original values, this must also be the case with the pressure, which is a function of both. The gas will therefore be found in precisely the same condition as at the commencement.

In seeking to determine the amount of work performed by these alterations, it will be necessary, for the reasons before assigned, to direct our attention to the *exterior* work alone. During the expansion, the gas *produces* a work expressed by the integral of the product of the differential of the volume into the corresponding pressure, which integral is represented geometrically by the quadrilaterals  $e\ a\ b\ f$ , and  $f\ b\ c\ g$ . During the compression,

however, work will be *expended*, which is represented by the quadrilaterals  $g c d h$  and  $h d a e$ . The excess of the former work above the latter is to be regarded as the entire work produced by the alterations, and this is represented by the quadrilateral  $a b c d$ .

If the foregoing process be reversed, we obtain at the conclusion the same quantity  $a b c d$  as the excess of the work *expended* over that *produced*.

In applying the foregoing considerations analytically, we will assume that the various alterations which the gas has undergone have been *infinitely small*. We can then consider the curves before mentioned to be straight lines, as shown in the accompanying figure. In order to determine its superficial content, the quadrilateral  $a b c d$  may be regarded as a parallelogram, for the error in this case can only amount to a differential of the *third* order, while the area itself is a differential of the *second* order. The latter may therefore be expressed by the product  $e f \cdot b k$ , where  $k$  marks the point at which the ordinate  $b f$  cuts the lower side of the parallelogram. The quantity  $b k$  is the increase of pressure due to raising the temperature of the gas, at the constant volume  $o f$ , from  $\tau$  to  $t$ , that is to say, due to the differential  $t - \tau = dt$ . This quantity can be expressed in terms of  $v$  and  $t$  by means of equation (I.), as follows :

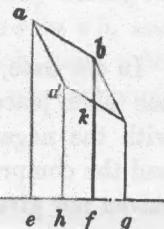
$$dp = \frac{Rdt}{v}.$$

If the increase of volume  $ef$  be denoted by  $d v$ , we obtain the area of the quadrilateral, and with it

$$\text{The work produced} = \frac{R dv dt}{v}. . . . . \quad (1)$$

We must now determine the quantity of heat consumed during those alterations. Let the amount of heat which must be imparted during the transition of the gas in a definite manner from any given state to another, in which its volume is  $v$  and its temperature  $t$ , be called  $Q$ ; and let the changes of volume occurring in the process above described, which are now to be regarded se-

Fig. 2.



the first will be the quantity of heat transferred from K to K', and the second the quantity generated from work.

According to this view the double process appears as a process of the same kind as the two simple ones of which it consists; for the circumstance that the generated heat is not imparted to a third body, but to one of the two between which the transmission of heat takes place, makes no essential difference, because the temperature of the generated heat is arbitrary, and may therefore have the same value as the temperature of one of the two bodies; in which case a third body would be superfluous. Consequently, for the two quantities of heat  $Q$  and  $Q' - Q$ , an equation of the same form as (6) must hold, i. e.

$$(Q' - Q) \cdot f(t') + Q \cdot F(t, t') = 0.$$

Eliminating the magnitude  $Q'$  by means of (7), and dividing by  $Q$ , this equation becomes

$$F(t, t') = f(t') - f(t), \dots \dots \dots \quad (8)$$

so that the temperatures  $t$  and  $t'$  being arbitrary, the function of two temperatures which applies to the second kind of transformation is reduced, in a general manner, to the function of one temperature which applies to the first kind.

For brevity, we will introduce a simpler symbol for the last function, or rather for its reciprocal, inasmuch as the latter will afterwards be shown to be the more convenient of the two. Let us therefore make

$$f(t) = \frac{1}{T}, \dots \dots \dots \quad (9)$$

so that  $T$  is now the unknown function of the temperature involved in the equivalence-values. Further,  $T_1$ ,  $T_2$ , &c. shall represent particular values of this function, corresponding to the temperatures  $t_1$ ,  $t_2$ , &c.

According to this, the second fundamental theorem in the mechanical theory of heat, which in this form might appropriately be called the *theorem of the equivalence of transformations*, may be thus enunciated :

*If two transformations which, without necessitating any other permanent change, can mutually replace one another, be called*

*equivalent, then the generation of the quantity of heat Q of the temperature t from work, has the equivalence-value*

$$\frac{Q}{T},$$

*and the passage of the quantity of heat Q from the temperature t<sub>1</sub> to the temperature t<sub>2</sub>, has the equivalence-value*

$$Q\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

*wherein T is a function of the temperature, independent of the nature of the process by which the transformation is effected.*

If to the last expression we give the form

$$\frac{Q}{T_2} - \frac{Q}{T_1},$$

it is evident that the passage of the quantity of heat Q, from the temperature t<sub>1</sub> to the temperature t<sub>2</sub>, has the same equivalence-value as a double transformation of the first kind, that is to say, the transformation of the quantity Q from heat at the temperature t<sub>1</sub> into work, and from work into heat at the temperature t<sub>2</sub>. A discussion of the question how far this external agreement is based upon the nature of the process itself would be out of place here\*; but at all events, in the mathematical determination of the equivalence-value, every transmission of heat, no matter how effected, can be considered as such a combination of two opposite transformations of the first kind.

By means of this rule, it will be easy to find a mathematical expression for the total value of all the transformations of both kinds, which are included in any cyclical process, however complicated. For instead of examining what part of a given quantity of heat received by a reservoir of heat, during the cyclical process, has arisen from work, and whence the other part has come, every such quantity received may be brought into calculation as if it had been generated by work, and every quantity lost by a reservoir of heat, as if it had been converted into work. Let us assume that the several bodies K<sub>1</sub>, K<sub>2</sub>, K<sub>3</sub>, &c., serving as reservoirs of heat at the temperatures t<sub>1</sub>, t<sub>2</sub>, t<sub>3</sub>, &c., have received during the process the quantities of heat Q<sub>1</sub>, Q<sub>2</sub>, Q<sub>3</sub>, &c., whereby the loss of a quantity of heat will be counted

[\* This subject is discussed in one of the subsequent memoirs.—1864.]

which equation may also be written

$$dQ = d(mr) - \frac{mr}{T} dT + McdT, \quad (55)$$

or still shorter,

$$dQ = Td\left(\frac{mr}{T}\right) + McdT. \quad . . . \quad (56)$$

I will not enter here into the applications of these equations, since they have frequently been discussed in the First and Fifth Memoirs of this collection.

#### 14. All the foregoing considerations had reference to changes

changes the freezing-point very little, and hence the differential coefficient  $\frac{dp}{dT}$  has, in this case, a very great value. The procedure which I adopted in my Note on this subject (p. 82 of this collection) is therefore not quite accurate, since I there also employed, in numerical calculations, the known values of  $c$  and  $h$  which correspond to the specific heats of water and ice at constant pressure. In the Appendix to the Note (p. 89), I have, in fact, already alluded to this circumstance. If we assume, in accordance with the calculations made in that Note, that for an increment of pressure amounting to one atmosphere the freezing-point sinks about  $0^{\circ}00733$ , we must put

$$\frac{dp}{dT} = -\frac{10333}{0.00733}.$$

On bringing this value into combination with the coefficients of expansion of water and of ice at  $0^{\circ}$  in the same manner as before, we obtain, instead of the numbers 1 and 0.48 which represent the specific heats of water and ice at constant pressure, the following values :—

$$c = 1 - 0.05 = 0.95, \\ h = 0.48 + 0.14 = 0.62.$$

Applying these values to the equation

$$\frac{dr}{dT} = c - h + \frac{r}{T},$$

we have, instead of the result,

$$\frac{dr}{dT} = 0.52 + 0.29 = 0.81,$$

given at p. 82, the following somewhat different one :—

$$\frac{dr}{dT} = 0.33 + 0.29 = 0.62.$$

It may, however, be remarked, with reference to the small correction which we have here taken occasion to introduce, that it relates only to an isolated calculation,—in fact to the numerical calculation of an equation, which, as I have stated in the Note, is practically unimportant, and only merits mention for theoretical considerations; the equation itself and the theoretical considerations referring thereto are not affected by this correction.

which occurred in a reversible manner. We will now also take *non-reversible* changes into consideration in order briefly to indicate at least the most important features of their treatment.

In mathematical investigations on non-reversible changes two circumstances, especially, give rise to peculiar determinations of magnitudes. In the first place, the quantities of heat which must be imparted to, or withdrawn from a changeable body are not the same, when these changes occur in a non-reversible manner, as they are when the same changes occur reversibly. In the second place, with each non-reversible change is associated an uncompensated transformation, a knowledge of which is, for certain considerations, of importance.

In order to be able to exhibit the analytical expressions corresponding to these two circumstances, I must in the first place recall a few magnitudes contained in the equations which I have previously established.

One of these is connected with the first fundamental theorem, and is the magnitude  $U$ , contained in equation (I a) and discussed at the beginning of this Memoir; it represents the *thermal and ergonal content*, or the energy of the body. To determine this magnitude, we must apply the equation (I a), which may be thus written,

$$dU = dQ - dw; \dots \dots \dots \dots \quad (57)$$

or, if we conceive it to be integrated, thus :

$$U = U_0 + Q - w. \dots \dots \dots \dots \quad (58)$$

Herein  $U_0$  represents the value of the energy for an arbitrary initial condition of the body,  $Q$  denotes the quantity of heat which must be imparted to the body, and  $w$  the exterior *ergon* which is produced whilst the body passes in any manner from its initial to its present condition. As was before stated, the body can be conducted in an infinite number of ways from one condition to another, even when the changes are to be reversible, and of all these ways we may select that one which is most convenient for the calculation.

The other magnitude to be here noticed is connected with the second fundamental theorem, and is contained in equation (II a).

In fact if, as equation (II a) asserts, the integral  $\int \frac{dQ}{T}$  vanishes

whenever the body, starting from any initial condition, returns thereto after its passage through any other conditions, then the expression  $\frac{dQ}{T}$  under the sign of integration must be the complete differential of a magnitude which depends only on the present existing condition of the body, and not upon the way by which it reached the latter. Denoting this magnitude by S, we can write

$$dS = \frac{dQ}{T}; \quad \dots \dots \dots \quad (59)$$

or, if we conceive this equation to be integrated for any reversible process whereby the body can pass from the selected initial condition to its present one, and denote at the same time by  $S_0$  the value which the magnitude S has in that initial condition,

$$S = S_0 + \int \frac{dQ}{T}. \quad \dots \dots \dots \quad (60)$$

This equation is to be used in the same way for determining S as equation (58) was for defining U.

The physical meaning of the magnitude S has been already discussed in the Sixth Memoir. If in the fundamental equation (II) of the present Memoir, which holds for all changes of condition of the body that occur in a reversible manner, we make a small alteration in the notation, so that the heat taken up by the changing body, instead of the heat given off by it, is reckoned as positive, that equation will assume the form

$$\int \frac{dQ}{T} = \int \frac{dH}{T} + \int dZ. \quad \dots \dots \dots \quad (61)$$

The two integrals on the right are the values for the case under consideration, of two magnitudes first introduced in the Sixth Memoir.

In the first integral, H denotes the heat actually present in the body, which, as I have proved, depends solely on the temperature of the body and not on the arrangement of its parts.

Hence it follows that the expression  $\frac{dH}{T}$  is a complete differential, and consequently that if for the passage of the body from its initial condition to its present one we form the integral  $\int \frac{dH}{T}$ .

we shall thereby obtain a magnitude which is perfectly defined by the present condition of the body, without the necessity of knowing in what manner the transition from one condition to the other took place. For reasons which are stated in the Sixth Memoir, I have called this magnitude the *transformation-value* of the heat present in the body.

It is natural when integrating, to take, for initial condition, that for which  $H=0$ , in other words, to start from the absolute zero of temperature; for this temperature, however, the integral  $\int \frac{dH}{T}$  is infinite, so that to obtain a finite value, we must take an initial condition for which the temperature has a finite value. The integral does not then represent the transformation-value of the entire quantity of heat contained in the body, but only the transformation-value of the excess of heat which the body contains in its present condition over that which it possessed in the initial condition. I have expressed this by calling the integral thus formed *the transformation-value of the body's heat, estimated from a given initial condition* (p. 248). For brevity we will denote this magnitude by  $Y$ .

The magnitude  $Z$  occurring in the second integral I have called the *disgregation* of the body. It depends on the arrangement of the particles of the body, and the measure of an increment of disgregation is the equivalence-value of that transformation from ergon to heat which must take place in order to cancel the increment of disgregation, and thus serve as a substitute for that increment. Accordingly we may say that the disgregation is the transformation-value of the existing arrangement of the particles of the body. Since in determining the disgregation we must proceed from some initial condition of the body, we will assume that the initial condition selected for this purpose is the same as that which was selected for the determination of the transformation-value of the heat actually present in the body.

The sum of the two magnitudes  $Y$  and  $Z$ , just discussed, is the before-mentioned magnitude  $S$ . To show this, let us return to equation (61), and assuming, for the sake of generality, that the initial condition, to which the integrals in this equation refer, is not necessarily the same as the initial condition which

was selected when determining Y and Z, but that the integrals refer to a change which originated in any manner whatever suited to any special investigation, we may then write the integrals on the right of (61) thus :

$$\int \frac{dH}{T} = Y - Y_0 \quad \text{and} \quad \int dZ = Z - Z_0,$$

wherein  $Y_0$  and  $Z_0$  are the values of Y and Z which correspond to the initial condition. By these means equation (61) becomes

$$\int \frac{dQ}{T} = Y + Z - (Y_0 + Z_0). \quad \dots \dots \dots \quad (62)$$

Putting herein

$$Y + Z = S, \quad \dots \dots \dots \quad (63)$$

and in a corresponding manner

$$Y_0 + Z_0 = S_0,$$

we obtain the equation

$$\int \frac{dQ}{T} = S - S_0, \quad \dots \dots \dots \quad (64)$$

which is merely a different form of the equation (60), by which S is determined.

We might call S the *transformational content* of the body, just as we termed the magnitude U its *thermal and ergonal content*. But as I hold it to be better to borrow terms for important magnitudes from the ancient languages, so that they may be adopted unchanged in all modern languages, I propose to call the magnitude S the *entropy* of the body, from the Greek word *τροπή*, *transformation*. I have intentionally formed the word *entropy* so as to be as similar as possible to the word *energy*; for the two magnitudes to be denoted by these words are so nearly allied in their physical meanings, that a certain similarity in designation appears to be desirable.

Before proceeding further, let us collect together, for the sake of reference, the magnitudes which have been discussed in the course of this Memoir, and which have either been introduced into science by the mechanical theory of heat, or have obtained thereby a different meaning. They are six in number, and possess in common the property of being defined by the present condition of the body, without the necessity of our knowing the mode in which the body came into this condition : (1) the

*thermal content*, (2) the *ergonal content*, (3) the sum of the two foregoing, that is to say the thermal and ergonal content, or the *energy*, (4) the *transformation-value of the thermal content*, (5) the *disgregation*, which is to be considered as the transformation-value of the existing arrangement of particles, (6) the sum of the last two, that is to say, the *transformational content*, or the *entropy*.

15. In order to determine the energy and the entropy for particular cases, the several expressions above given for  $dQ$  have to be used in conjunction with the equations (57) and (59), or (58) and (60). I will here, by way of example, treat a few simple cases merely.

Let the body under consideration be homogeneous and of the same temperature throughout, upon which the only active foreign force is a uniform and normal surface-pressure, and let us assume that it can change its volume, with a change of temperature and pressure, without at the same time suffering a partial change of its state of aggregation; then if the weight of the body be taken as unit, we can employ for  $dQ$  the equations (28), (29), and (32) given in Art. 9. In these equations, the specific heat at constant volume, there denoted by  $c$ , and the specific heat at constant pressure, denoted by  $C$ , occur; now, since the latter specific heat is that which is usually directly determined by observation, we will use the equation (29) in which it occurs, namely,

$$dQ = CdT - AT \frac{dv}{dT} dp^*.$$

With respect to the exterior ergon we have, for an infinitesimal change of condition during which the volume increases by  $dv$ , the equation

$$dw = Apdv;$$

and if  $T$  and  $p$  are chosen as independent variables, we can give this equation the form

$$dw = Ap \left( \frac{dv}{dT} dT + \frac{dv}{dp} dp \right).$$

\* I write here simply  $\frac{dv}{dT}$  instead of the symbol  $\left(\frac{dv}{dT}\right)_p$  in (29), because in a case where only  $T$  and  $p$  occur as independent variables, it is manifest that in the differentiation with respect to  $T$ , the other variable  $p$  is supposed constant.