VI. *On the Geometrical Representation of the Expansive Action of Heat, and the Theory of Thermo-dynamic Engines.* *By* William John Macquorn Rankine, *C.E., F.R.SS. Lond. and Edin. &c.*

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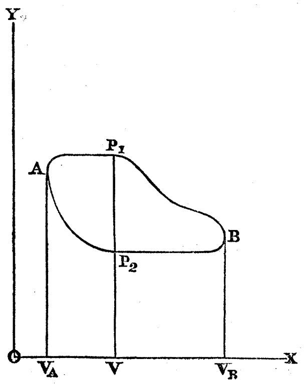
Section I.—INTRODUCTION AND GENERAL THEOREMS.

(Article 1.) THE first application of a geometrical diagram to represent the expansive action of Heat was made by James Watt, when he contrived the well-known Steam-Engine Indicator, subsequently altered and improved by others in various ways. As the diagram described by Watt's Indicator is the type of all diagrams representing the expansive action of heat, its general nature is exhibited in fig. 1.

Let abscissæ, measured along, or parallel to, the axis OX represent the volumes successively assumed by a given mass of an elastic substance, by whose alternate expansion and contraction heat is made to produce motive power; OV_A and OV_B being the least and greatest volumes which the substance is made to assume, and OV any intermediate volume. For brevity's sake, these quantities will be denoted by V_A, V_B, and V, respectively. Then $V_B - V_A$ may represent the space traversed by the piston of an engine during a single stroke.

Fig. 1.



Let ordinates, measured parallel to the axis OY and at right angles to OX, denote the expansive pressures successively exerted by the substance at the volumes denoted by the abscissæ. During the increase of volume from V_A to V_B, the pressure, in order that motive power may be produced, must be, on the whole, greater than during the diminution of volume from V_B to V_A; so that, for instance, the ordinates VP_1 and VP_2, or the symbols P_1 and P_2, may represent the pressures corresponding to a given volume V during the expansion and contraction of the substance respectively.

Then the area of the curvilinear figure, or *Indicator-diagram*, AP_1BP_2A, will represent the motive power, or "Potential Energy," *developed* or *given out* during a complete stroke, or cycle of changes of volume of the elastic substance. The algebraical expression for this area is

$$\int_{V_A}^{V_B} (P_1 - P_2)dV. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.)$$

The practical use of such diagrams, in ascertaining the power and the mode of action of the steam in steam-engines, where the curve AP_1BP_2A is described by a pencil attached to a pressure-gauge, on a card whose motion corresponds with that of the piston, is sufficiently well known.

(2.) It appears that the earliest application of *diagrams of energy* (as they may be called) to prove and illustrate the theoretical principles of the mechanical action of heat, was made either by CARNÔT, or by M. CLAPEYRON in his account of CARNÔT's theory; but the conclusions of those authors were in a great measure vitiated by the assumption of the substantiality of heat.

In the fifth section of a paper on the Mechanical Action of Heat, published in the Transactions of the Royal Society of Edinburgh, vol. xx., a diagram of energy is employed to demonstrate the general law of the economy of heat in thermo-dynamic engines according to the correct principle of the action of such machines, viz. that the area of the diagram represents at once the potential energy or motive power which is developed at each stroke, and the mechanical equivalent of the actual energy, or heat, which permanently disappears.

As the principles of the expansive action of heat are capable of being presented to the mind more clearly by the aid of diagrams of energy than by means of words and algebraical symbols alone, I purpose, in the present paper, to apply those diagrams, partly to the illustration and demonstration of propositions already proved by other means, but chiefly to the solution of new questions, especially those relating to the action of heat in all classes of engines, whether worked by air, or by steam, or by any other material; so as to present, in a systematic form, those theoretical principles which are applicable to all methods of transforming heat to motive power by means of the changes of volume of an elastic substance.

Throughout the whole of this investigation, quantities of heat, and coefficients of specific heat, are expressed, not by units of temperature in a unit of weight of water, but by equivalent quantities of mechanical power, stated in foot-pounds, according to the ratio established by Mr. JOULE's experiments on friction (Phil. Trans. 1850); that is to say,

772 foot-pounds per degree of FAHR., or
1389·6 foot-pounds per Centigrade degree,

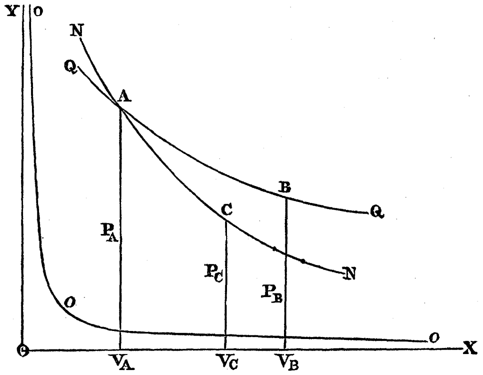
applied to one pound of liquid water at atmospheric temperatures.

(3.) *Of Isothermal Curves, and Curves of No Transmission of Heat.*

A curve described on a diagram of energy, such that its ordinates represent the pressures of a homogeneous substance corresponding to various volumes, while the total *sensible* or *actual heat* present in the body is maintained at a constant value, denoted, for example, by Q, may be called the *Isothermal Curve of Q* for the given substance. (See fig. 2.) Suppose, for instance, that the co-ordinates of the point A, V_A and P_A, represent respectively a volume and a pressure of a given substance, at which the actual heat is Q; and the co-ordinates of the point B, viz. V_B and P_B, another volume and pressure at which the actual heat is the same; then are the points A and B situated on the same isothermal curve QQ.

On the other hand, let the substance be allowed to expand from the volume and pressure V_A, P_A, without receiving or emitting heat; and when it reaches a certain volume, V_C, let the pressure be represented by P_C, which is less than the pressure would have been had the actual heat been maintained constant, because, by expansion, heat is made to disappear. Then C will be a point on a certain curve NN passing through A, which may be called a *Curve of No Transmission.*

Fig. 2.



It is to be understood that, during the process last described, the potential energy developed during the expansion, and which is represented by the area ACV_CV_A, is entirely communicated to external substances; for if any part of it were expended in agitating the particles of the expanding substance, a portion of heat would be reproduced by friction.

If *o o o* be a curve whose ordinates represent the pressures corresponding to various volumes when the substance is absoletely destitute of heat, then this curve, which may be called the *Curve of Absolute Cold,* is at once an isothermal curve and a curve of no transmission.

So far as we yet know, the curve of absolute cold is, for all substances, an asymptote to all the other isothermal curves and curves of no transmission, which approach it and each other indefinitely as the volume of the substance increases without limit.

Note.—The following remarks are intended to render more clear the precise meaning of the term *Total Actual Heat.*

The Total Actual Heat of a given mass of a given substance at a given temperature, is the quantity of Physical Energy present in the mass *in the form of Heat* under the given circumstances.

If, for the purpose of illustrating this definition, we assume the hypothesis that heat consists in molecular revolutions of a particular kind, then the Total Actual Heat of a mass is measured by the mechanical power corresponding to the *vis viva* of those revolutions, and is represented by

$$\frac{1}{2}\Sigma . mv^2,$$

m being the mass of any circulating molecule, and v^2 the mean-square of its velocity.

But the meaning of the term Total Actual Heat may also be illustrated without the aid of any hypothesis.

For this purpose, let us take the ascertained fact of the production of heat by the expenditure of mechanical power in friction, according to the numerical proportion determined by Mr. JOULE; and let E denote the quantity of mechanical power which must be expended in friction, in order to raise the temperature of unity of weight of a given substance from that of absolute privation of heat to a given temperature τ.

During this operation, let the several elements of the external surface of the mass undergo changes of relative position expressed by the variations of quantities denoted generally by p, and let the increase of each such quantity as p be resisted by an externally-applied force such as P.

Then during the elevation of temperature from absolute cold to τ, the energy converted to the potential form in overcoming the external pressures P will be

$$\Sigma.\int \mathrm{P}dp.$$

Also let the internal particles of the mass undergo changes of relative position expressed by the variations of quantities denoted generally by r, and let the increase of each such quantity as r be resisted by an internal molecular force such as R.

Then the energy converted to the potential form in overcoming internal molecular forces will be

$$\Sigma.\int \mathrm{R}dr.$$

Subtracting these quantities of energy converted to the potential form by means of external pressures and internal forces, from the whole power converted into heat by friction in order to raise the temperature of the mass from that of absolute privation of heat to the given temperature τ, we find the following result:—

$$\mathrm{Q}=\mathrm{E}-\Sigma.\int \mathrm{P}dp-\Sigma.\int \mathrm{R}dr;$$

and this remainder is the quantity of energy which *retains the form of heat*, in unity of weight of the given substance at the given temperature; that is to say, the Total Actual Heat.

It is obvious that Total Actual Heat cannot be ascertained directly; first, because the temperature of total privation of heat is unattainable; and secondly, because the molecular forces R are unknown.

It can, however, be determined indirectly from the latent heat of expansion of the substance. For the heat which disappears during the expansion of unity of weight of an elastic substance at constant actual heat from the volume $\mathrm{V_A}$ to the volume $\mathrm{V_B}$, under the constant or variable pressure P, is expressed (as will be shown in the sequel) by

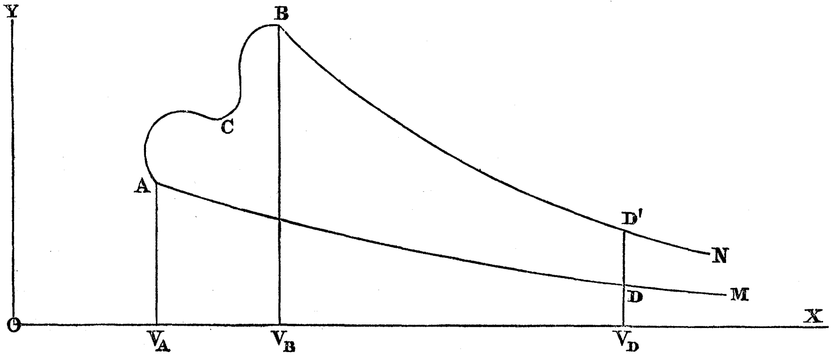
$$\mathrm{Q}.\frac{d}{d\mathrm{Q}}\int_{\mathrm{V_A}}^{\mathrm{V_B}} \mathrm{P}d\mathrm{V};$$

so that from a sufficient number of experiments on the amount of heat transformed to potential energy by the expansion of a given substance, the relations, for that substance, between pressure, volume, and Total Actual Heat, may be determined.

(4.) PROPOSITION I.—THEOREM. *The Mechanical Equivalent of the Heat absorbed or given out by a substance in passing from one given state as to pressure and volume to another given state, through a series of states represented by the co-ordinates of a given curve on a diagram of energy, is represented by the area included between the given curve and two curves of no transmission of heat drawn from its extremities, and indefinitely prolonged in the direction representing increase of volume.*

(Demonstration) (see fig. 3). Let the co-ordinates of any two points, A and B, represent respectively the volumes and pressures of the substance in any two conditions; and let a curve of any figure, ACB, represent, by the co-ordinates of its points, an arbitrary succession of volumes and pressures through which the substance is made to pass, in changing from the condition A to the condition B. From the points A and B respectively, let two curves of no transmission AM, BN, extend indefinitely towards X; then the area referred to in the enunciation is that contained between the given arbitrary curve ACB and the two indefinitely prolonged curves of no transmission; areas above the curve AM being considered as representing heat absorbed by the substance, and those below, heat given out.

Fig. 3.



To fix the ideas, let us in the first place suppose the area MACBN to be situated above AM. After the substance has reached the state B, let it be expanded according to the curve of no transmission BN, until its volume and pressure are represented by the co-ordinates of the point D'. Next, let the volume V_D be maintained constant, while heat is abstracted until the pressure falls so as to be represented by the ordinate of the point D, situated on the curve of no transmission AM. Finally, let the substance be compressed, according to this curve of no transmission, until it recovers its primitive condition A. Then the area ACBD'DA, which represents the whole potential energy developed by the substance during one cycle of operations, represents also the heat which disappears, that is, the difference between the heat absorbed by the substance during the change from A to B, and emitted during the change from D′ to D; for if this were not so, the cycle of operations would alter the amount of energy in the universe, which is impossible.

The further the ordinate $V_D DD'$ is removed in the direction of X, the smaller does the heat emitted during the change from D′ to D become; and consequently, the more nearly does the area ACBD′DA approximate to the equivalent of the heat absorbed during the change from A to B; to which, therefore, the area of the indefinitely-prolonged diagram MACBN is exactly equal. Q.E.D.

It is easy to see how a similar demonstration could have been applied, *mutatis mutandis,* had the area lain below the curve AM. It is evident also, that when this area lies, part above and part below the line AM, the difference between these two parts represents the difference betweeu the heat absorbed and the heat emitted during different parts of the operation.

(5.) *First Corollary.*—THEOREM. *The difference between the whole heat absorbed, and the whole expansive power developed, during the operation represented by any curve, such as* ACB, *on a diagram of energy, depends on the initial and final conditions of the substance alone, and not on the intermediate process.*

(Demonstration.) In fig. 3, draw the ordinates AV_A, BV_B parallel to OY. Then the area $V_A ACBV_B$ represents the expansive power developed during the operation ACB; and it is evident that the difference between this area and the indefinitely-prolonged area MACBN, which represents the heat received by the substance, depends simply on the positions of the points A and B, which denote the initial and final conditions of the substance as to volume and pressure, and not on the form of the curve ACB, which represents the intermediate process. Q.E.D.

To express this result symbolically, it is to be considered, that the excess of the heat or actual energy *received* by the substance above the expansive power or potential energy *given out* and exerted on external bodies, in passing from the condition A to the condition B, is equal to the whole energy *stored up* in the substance during this operation, which consists of two parts, viz.—

Actual energy; being the increase of the actual or sensible heat of the substance in passing from the condition A to the condition B, which is to be represented by this expression,

$$\Delta.Q = Q_B - Q_A;$$

Potential energy; being the power which is stored up in producing changes of molecular arrangement during this process; and which, it appears from the Theorem just proved, must be represented, like the actual energy, by the difference between a function of the volume and pressure corresponding to A, and the analogous function of the volume and pressure corresponding to B; that is to say, by an expression of the form,

$$\Delta S = S_B - S_A.$$

Let $$H_{A,B} = \text{area MACBN}$$

represent the heat received by the substance during the operation ACB, and

$$\int_{V_A}^{V_B} PdV = \text{area } V_A ACBV_B$$

the power or potential energy, given out.

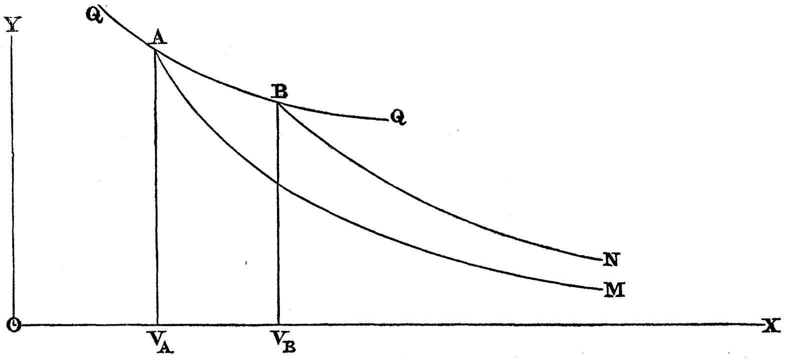
Then the theorem of this article is expressed as follows:—

$$H_{A,B} - \int_{V_A}^{V_B} PdV = Q_B - Q_A + S_B - S_A = \Delta Q + \Delta.S \quad . \quad . \quad . \quad . \quad (2.)$$

being a form of the General Equation of the Expansive Action of Heat, in which the *Potential of Molecular Action*, S, remains to be determined.

(6.) *Second Corollary* (see fig. 4).—The *Latent Heat of Expansion* of a substance, from one given volume V_A to another V_B, for a given amount of actual heat Q; that is to say, the heat which must be absorbed by the substance in expanding from the volume V_A to the volume V_B, in order that the actual heat Q may be maintained constant, is represented geometrically as follows. Let QQ be the isothermal curve of the given actual heat Q on the diagram of energy; A, B two points on this curve, whose co-ordinates represent the two given volumes and the corresponding pressures. Through A and B draw the two curves of no transmission AM, BN, produced indefinitely in the direction of X. Then the area contained between the portion of isothermal curve AB, and the indefinitely-produced curves AM, BN, represents the mechanical equivalent of the latent heat sought, whose symbolical expression is formed from Equation 2 by making $Q_B - Q_A = 0$, and is as follows:—

Fig. 4.

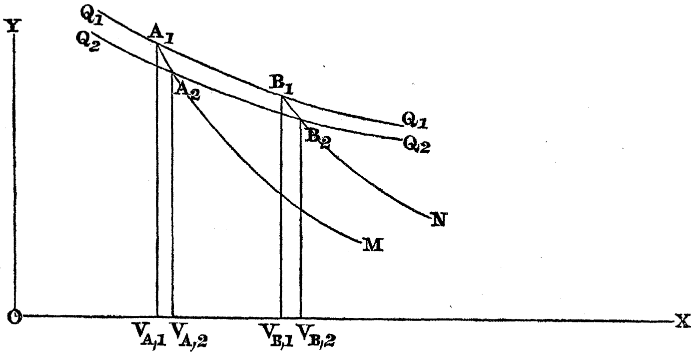


$$H_{A,B} \text{ (for } Q = \text{const.)} = \int_{V_A}^{V_B} PdV + S_B - S_A. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.)$$

SECTION II.—PROPOSITIONS RELATIVE TO HOMOGENEOUS SUBSTANCES.

(7.) PROPOSITION II.—THEOREM. *In fig.* 5, *let* A_1A_2M, B_1B_2N *be any two curves of no transmission, indefinitely extended in the direction of* X, *intersected in the points,* A_1, B_1, A_2, B_2, *by two isothermal curves,* $Q_1A_1B_1Q_1$, $Q_2A_2B_2Q_2$, *which are indefinitely near to each other; that is to say, which correspond to two quantities of actual heat,* Q_1 *and* Q_2, *differing by an indefinitely small quantity* $Q_1-Q_2=\delta Q$.

Fig. 5.



Then the elementary quadrilateral area, $A_1B_1B_2A_2$, *bears to the whole indefinitely-prolonged area* MA_1B_1N, *the same proportion which the indefinitely small difference of actual heat* δQ *bears to the whole actual heat* Q_1; *or*

$$\frac{\text{area } A_1B_1B_2A_2}{\text{area } MA_1B_1N}=\frac{\delta Q}{Q_1}.$$

(Demonstration.) Draw the ordinates A_1V_{A1}, A_2V_{A2}, B_1V_{B1}, B_2V_{B2}. Suppose, in the first place, that δQ is an aliquot part of Q_1, obtained by dividing the latter quantity by a very large integer n, which we are at liberty to increase without limit.

The entire indefinitely-prolonged area MA_1B_1N represents a quantity of heat which is converted into potential energy during the expansion of the substance from V_{A1} to V_{B1}, in consequence of the continued presence of the total actual heat Q_1; for if no heat were present no such conversion would take place. *Mutatis mutandis,* a similar statement may be made respecting the area MA_2B_2N. By increasing without limit the number n and diminishing δQ, we may make the expansion from V_{A2} to V_{B2} as nearly as we please an identical phenomenon with the expansion from V_{A1} to V_{B1}. The quadrilateral $A_1B_1B_2A_2$ represents the diminution of conversion of heat to potential energy, which results from the abstraction of any one whatsoever of the n small equal parts δQ into which the actual heat Q_1 is supposed to be divided, and it therefore represents the effect, in conversion of heat to potential energy, of the presence of any one of those small portions of actual heat. And as all those portions δQ are similar and similarly circumstanced, the effect of the presence of the whole actual heat Q_1 in causing conversion of heat to potential energy, will be simply the sum of the effects of all its small portions, and will bear the same ratio to the effect of one of those small portions, which the whole actual heat bears to the small portion. Thus, by virtue of the general law enunciated below and assumed as an axiom, the theorem is proved when δQ is an aliquot part of Q_1; but δQ is either an aliquot part, or a sum of aliquot parts, or may be indefinitely approximated to by a series of aliquot parts; so that the theorem is universally true. Q.E.D.

The symbolical expression of this theorem is as follows. When the actual heat Q_1, at any given volume, is varied by the indefinitely small quantity δQ, let the pressure vary by the indefinitely small quantity $\frac{dP}{dQ}\delta Q$; then the area of the quadrilateral $A_1B_1B_2A_2$ will be represented by

$$\delta Q.\int_{V_{A,1}}^{V_{B,1}}\frac{dP}{dQ}dV,$$

and consequently, that of the whole figure MA_1B_1N, or the latent heat of expansion from $V_{A,1}$ to $V_{B,1}$, at Q_1, by

$$H_1=Q_1\int_{V_{A1}}^{V_{B1}}\frac{dP}{dQ}dV; \quad \ldots\ldots\ldots\ldots \quad (4.)$$

a result identical with that expressed in the sixth section of a paper published in the Transactions of the Royal Society of Edinburgh, vol. xx.

The demonstration of this theorem is an example of a special application of the following

General Law of the Transformation of Energy.

The effect of the presence, in a substance, of a quantity of Actual Energy, in causing transformation of Energy, is the sum of the effects of all its parts:—
a law first enunciated in a paper read by me to the Philosophical Society of Glasgow on the 5th of January, 1853.

(8.) General Equation of the Expansive Action of Heat.

The two expressions for the Latent Heat of Expansion at constant Actual Heat, given in equations 3 and 4 respectively, being equated, furnish the means of determining the potential energy of molecular action S, so far as it depends on volume, and thus of giving a definite form to the general equation 2.

The two expressions referred to may be thus stated in words:—

I. The heat which disappears in producing a given expansion, while the actual heat present in the substance is maintained constant, is equivalent to the sum of the potential energy given out in the form of expansive power, and the potential energy stored up by means of molecular attractions.

II. It is also equivalent to the potential energy due to the action during the expansion, of a pressure $Q\frac{dP}{dQ}$, at each instant equal to what the pressure would be, if its actual rate of variation with heat at the instant in question were a constant coefficient, expressing the ratio of the whole pressure to the whole actual heat present.

The combination of these principles, expressed symbolically, gives the following result:—

$$H_{A,B}(\text{for } Q=\text{const.})=Q\int_{V_A}^{V_B}\frac{dP}{dQ}dV=\int_{V_A}^{V_B}PdV+S_B-S_A;$$

whence we deduce the following general value for the potential of molecular action:—

$$S=\int\left(Q\frac{dP}{dQ}-P\right)dV+\phi.Q, \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5.)$$

in which $\phi.Q$ denotes some function of the total actual heat not depending on the density of the substance. This value being introduced into equation (2.), produces the following:—

$$\begin{aligned} H_{A,B}-\int_{V_A}^{V_B}PdV&=Q_B-Q_A+S_B-S_A \\ &=Q_B-Q_A+\phi.Q_B-\phi.Q_A+\int_{V_A}^{V_B}\left(Q\frac{dP}{dQ}-P\right)dV=\Psi_B-\Psi_A. \; . \quad (6.) \end{aligned}$$

The symbol $\Psi=Q+S$ is used to denote the sum of the actual energy of heat, and the potential energy of molecular action, present in the substance in any given condition.

The above is the General Equation of the Expansive Action of Heat in a homogeneous substance, and is the symbolical expression of the Geometrical Theorems I. and II. combined.

When the variations of actual heat and of volume become indefinitely small, this equation takes the following differential form:—

$$\left.\begin{aligned} &d.\Psi=d.H-PdV=dQ+d.S=\left(1+\phi'.Q+Q\frac{d^2}{dQ^2}\int PdV\right)dQ+\left(Q\frac{dP}{dQ}-P\right)dV \\ &\text{otherwise} \qquad d.H=\frac{K_V}{\mathfrak{k}}.dQ+Q\frac{dP}{dQ}.dV \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \end{aligned}\right\} (7.)$$

The coefficient of dQ in the above expressions, viz.

$$\frac{K_V}{\mathfrak{k}}=1+\phi'.Q+Q\frac{d^2}{dQ^2}\int PdV, \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8.)$$

is the ratio of the apparent specific heat of the substance at constant volume to its real specific heat; that is, the ratio of the whole heat consumed in producing an indefinitely small increase of actual heat, to the increase of actual heat produced.

These general equations are here deduced independently of any special molecular hypothesis, as they also have been, by a method somewhat different, in the sixth section of a paper previously referred to*. Equations equivalent to the above have also been deduced from the Hypothesis of Molecular Vortices, in the paper already mentioned, and in a paper on the Centrifugal Theory of Elasticity in the same volume.

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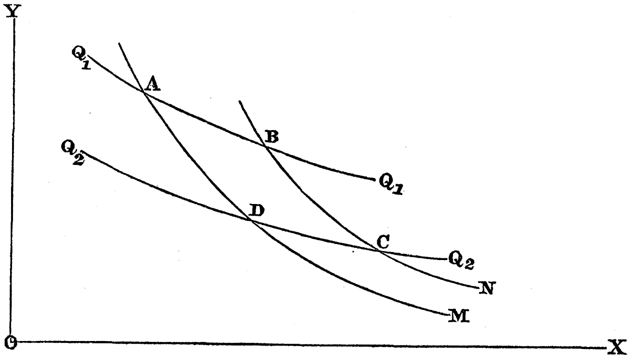
* Trans. Roy. Soc. Edinb. vol. xx.

(9.) *First Corollary from Proposition* II.—THEOREM. *If a succession of isothermal curves corresponding to quantities of heat diminishing by equal small differences* δQ, *be drawn across any pair of curves of no transmission, they will cut off a series of equal small quadrilaterals.*

Second Corollary.—THEOREM. *In fig.* 6, *let* ADM, BCN *be any two curves of no transmission, indefinitely prolonged in the direction of* X, *and let any two isothermal curves* Q_1Q_1, Q_2Q_2, *corresponding respectively to any two quantities of actual heat* Q_1, Q_2, *be drawn across them. Then will the indefinitely-prolonged areas* MABN, MDCN, *bear to each other the simple ratio of the quantities of actual heat* Q_1, Q_2.

Fig. 6.



Or, denoting those areas respectively by H_1, H_2—

$$\frac{H_2}{H_1}=\frac{Q_2}{Q_1}. \qquad (9.)$$

This corollary is the geometrical expression of the law of the maximum efficiency of a perfect thermo-dynamic engine, already investigated by other methods. In fact, the area MABN represents the whole heat expended, or the latent heat of expansion, the actual heat at which heat is received being Q_1; MDCN, the heat lost, or the latent heat of compression, which is carried off by conduction at the actual heat Q_2; and ABCD (being the indicator-diagram of such an engine), the motive power, produced by the permanent disappearance of an equivalent quantity of heat; and the *efficiency* of the engine is expressed by the ratio of the heat converted into motive power to the whole heat expended, viz.—

$$\frac{\mathrm{ABCD}}{\mathrm{MABN}}=\frac{H_1-H_2}{H_1}=\frac{Q_1-Q_2}{Q_1}. \qquad (10.)$$

(10.) *Third Corollary* (*of Thermo-Dynamic Functions*).

If the two curves of no transmission in fig. 6, ADM, BCN, be indefinitely close together, the ratio of the heat consumed in passing from one of those curves to the other, to the actual heat present, will be the same, whatever may be the form and position of the curve indicating the mode of variation of pressure and volume, provided it intersects the two curves of no transmission at a finite angle; because the area contained between this connecting curve and the two indefinitely-prolonged curves of no transmission will differ from an area whose upper boundary is an isothermal curve, by an indefinitely small area of the second order.

To express this symbolically, let

$$\frac{\delta H}{Q}=\delta F$$

be the ratio in question, for a given indefinitely-close pair of curves of no transmission. Let the change from one of these curves to the other be made by means of any indefinitely-small changes of actual heat and of volume, $\delta Q, \delta V$. Then by the general equation 7, the following quantity

$$\delta F=\frac{\delta H}{Q}=\left\{\frac{1+\phi'.Q}{Q}+\frac{d^2}{dQ^2}\int P dV\right\}\delta Q+\frac{dP}{dQ}.\delta V=\frac{K_V}{kQ}.\delta Q+\frac{dP}{dQ}\delta V \quad . \; . \; . \quad (11.)$$

is constant for a given pair of indefinitely-close curves of no transmission, and is, therefore, the complete variation of a function, having a peculiar constant value for each curve of no transmission, represented by the following equation :—

$$F=\int\frac{dH}{Q}=\int\frac{1+\phi'.Q}{Q}dQ+\int\frac{dP}{dQ}dV. \quad . \; . \; . \; . \; . \; . \quad (12.)$$

This function, which I shall call a *Thermo-dynamic function*, has the following properties :—

$$H=\int Q dF \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (13.)$$

is equivalent to the general equation (6.);

$$dF=0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (14.)$$

is the equation common to all curves of no transmission; and

$$F=\text{a given constant}, \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (14\,\text{A.})$$

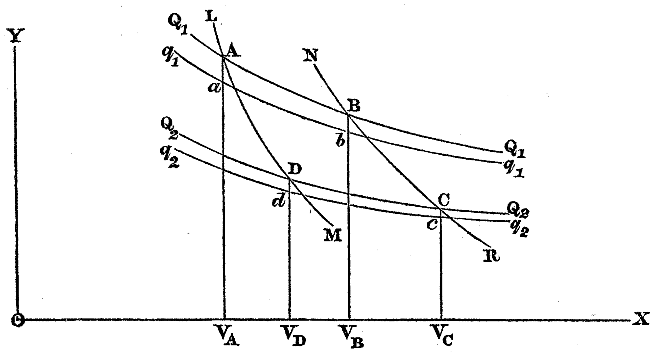
is the equation of a particular curve of no transmission.

(11.) PROPOSITION III.—PROBLEM. *Let it be supposed that for a given substance, the forms of all possible isothermal curves are known, but of only one curve of no transmission; it is required to describe, by the determination of points, another curve of no transmission, passing through a given point, situated anywhere out of the known curve.*

(Solution) (see fig. 7). Let LM be the known curve of no transmission; B the given point. Through B draw an isothermal curve Q_1ABQ_1, cutting LM in A. Q_1 being the quantity of heat to which this curve corresponds, draw, indefinitely near to it, the isothermal curve $q_1\,q_1$, corresponding to the quantity of heat $Q_1-\delta Q$, where δQ is an indefinitely small quantity. Draw any other pair of indefinitely close isothermal curves $Q_2\,Q_2$, $q_2\,q_2$, corresponding to the quantities of heat Q_2, $Q_2-\delta Q$; δQ being the same as before. Let D be the point where the isothermal curve Q_2Q_2 cuts the known curve of no transmission. Draw the ordinates AV_A, BV_B parallel to OY, enclosing, with the isothermal curves of Q_1 and $Q_1-\delta Q$, the small quadrilateral AB*ba*. Draw the ordinate DV_D parallel to OY, intersecting the isothermal curve of $Q_2-\delta Q$

in *d*. Lastly, draw the ordinate CV_C in such a position as to cut off from the space between the isothermal curves of Q_2 and $Q_2-\delta Q$ a quadrilateral DC*cd*, of area equal to the quadrilateral AB*ba*.

Fig. 7.



Then will C, where the last ordinate intersects the isothermal curve of Q_2, approximate indefinitely to the position of a point in the curve of no transmission passing through the given point B, when the variation of actual heat δQ is diminished without limit. And thus may be determined, to as close an approximation as we please, any number of points in the curve of no transmission NBR which passes through any given point B, when any one curve of no transmission LM is known.

(Demonstration.) For when the variation δQ diminishes indefinitely, the curves q_1q_1, q_2q_2, approach indefinitely towards the curves Q_1Q_1, Q_2Q_2 respectively; and the small quadrilaterals bounded endways by the ordinates approximate indefinitely to the small quadrilaterals bounded endways by the curves of no transmission; which latter pair of quadrilaterals are equal, by the first corollary of Proposition II.

The *symbolical expression* of this proposition is as follows:—

Let V_A, V_B, V_C, V_D be the volumes corresponding to the four points of intersection of a pair of isothermal curves with a pair of curves of no transmission; A and B being on the isothermal curve of Q_1, C and D on that of Q_2, A and D on one of the curves of no transmission, B and C on the other: then

$$\left.\begin{array}{l}\displaystyle\int_{V_A}^{V_B}\frac{dP}{dQ}dV \text{ (for } Q=Q_1)=\int_{V_D}^{V_C}\frac{dP}{dQ}dV \text{ (for } Q=Q_2) \\ \text{or} \qquad F_B-F_A=F_C-F_D \text{ . . . .}\end{array}\right\} \text{ . . . (15.)}$$

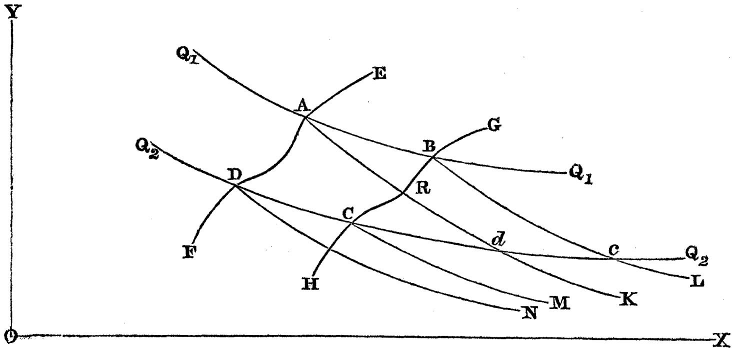
The second form of this equation is in the present case identical, because

$$F_D=F_A;\ F_C=F_B.$$

(12.) PROPOSITION IV.—PROBLEM (see fig. 8). *The forms of all isothermal curves for a given substance being given, let* EF *be a curve of any form, representing an arbitrarily assumed succession of pressures and volumes. It is required to find, by the determination of points, a corresponding curve passing through a given point* B, *such, that* *the quantity of heat absorbed or emitted by the substance, in passing from any given isothermal curve to any other, shall be the same, whether the pressures and volumes be regulated according to the original curve* EF, *or according to the curve passing through the point* B.

(Solution.) The process by which the latter curve is to be deduced from the former is precisely the same with that by which one curve of no transmission is deduced from another, in the last problem.

Fig. 8.



(Demonstration.) Let GBH be the required curve. This curve, and the curve EF, in their relation to each other, may be called *Curves of Equal Transmission.* Through B draw the isothermal curve Q_1Q_1, intersecting the curve EF in A. Draw also any other isothermal curve Q_2Q_2, intersecting EF in D and GH in C. Through A,B,C,D, respectively, draw the four indefinitely-prolonged curves of no transmission, AK, intersecting Q_2Q_2 in *d*, BL, intersecting Q_2Q_2 in *c*, CM, and DN. Conceive the whole space between the isothermal curves Q_1Q_1, Q_2Q_2, to be divided by other isothermal curves, into a series of indefinitely narrow stripes, corresponding to equal indefinitely-small variations of actual heat. Then, by the construction of the solution, the quadrilaterals cut from those stripes by the pair of curves EF, GH are all equal; and so also are the quadrilaterals cut from the stripes by the pair of curves of no transmission, AK, BL. Therefore the area ABCD is equal to the area AB*cd.* The indefinitely-prolonged areas, MCDN, L*cd*K, are evidently equal; therefore, adding this pair of equal areas to the preceding, the pair of indefinitely-prolonged areas LBAK, MCBADN are equal. Subtracting from each of these areas the part common to both, ABR, and adding to each the indefinitely-prolonged area KRCM, we find, finally, that the indefinitely-prolonged areas KADN, LBCM are equal.

But the former of those areas (by Prop. I.) represents the mechanical equivalent of the heat absorbed by the substance in passing from the actual heat Q_2 to the actual heat Q_1 through a series of pressures and volumes represented by the co-ordinates of the curve EF; and the latter, the corresponding quantity for the curve GH; therefore those curves are, with respect to each other, *Curves of Equal Transmission,* which was required

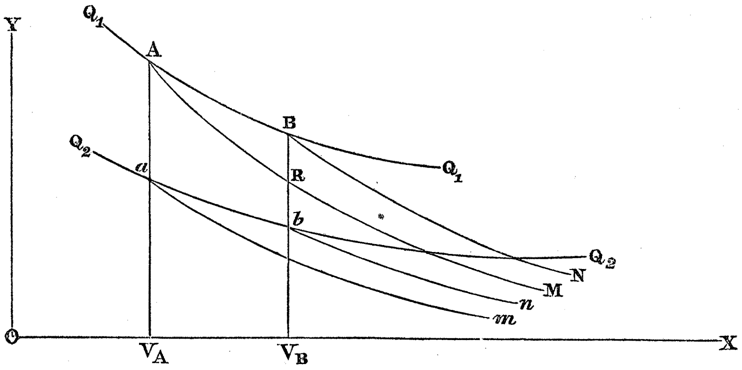
The algebraical expression of this result is that the equation (15.) holds for any pair of curves of equal transmission, as well as for a pair of curves of no transmission; or, in other terms, let F_A, F_B, F_C, F_D be the thermo-dynamic functions for the curves of no transmission passing through the four points where a pair of isothermal curves cut a pair of curves of equal transmission: A, B being on the upper isothermal curve; C, D on the lower; A, D on one curve of equal transmission, B, C on the other: then

$$F_B-F_A=F_C-F_D. \quad \ldots\ldots\ldots\ldots \quad (16.)$$

(13.) Proposition V.—Theorem. *The difference between the quantities of heat absorbed by a substance, in passing from one given amount of actual heat to another, at two different constant volumes, is equal to the difference between the two latent heats of expansion in passing from one of those volumes to the other, at the two different amounts of actual heat respectively, diminished by the corresponding difference between the quantities of expansive power given out.*

(Demonstration) (see fig. 9). Let Q_1Q_1 be the isothermal curve of the higher amount of actual heat; Q_2Q_2 that of the lower. Let V_A, V_B be the two given volumes. Draw the two ordinates $V_A a A$, $V_B b B$, and the four indefinitely-prolonged curves of no transmission AM, am, BN, bn. The quantities of heat absorbed, in passing from the actual heat Q_2 to the actual heat Q_1, at the volumes V_A and V_B, are represented respectively by the indefinitely-prolonged areas MAam, NBbn. Then adding to each of those areas the indefinitely-prolonged area nbBAM (observing that the space below the intersection R is to be treated as negative), we find for their difference

Fig. 9.



$$\mathrm{NB}bn-\mathrm{MA}am=\mathrm{NBAM}-nb\mathrm{BA}am=(\mathrm{NBAM}-nbam)-(V_B\mathrm{BA}V_A-V_B ba V_A);$$

but NBAM and $nbam$ represent the latent heats of expansion from V_A to V_B, at the actual heats Q_1 and Q_2 respectively; and $V_B\mathrm{BA}V_A$ and $V_B ba V_A$ represent the power given out by expansion from V_A to V_B at the actual heats Q_1 and Q_2 respectively; therefore the proposition is proved. Q.E.D.

This proposition, expressed symbolically, is as follows. ΔQ being the difference of actual heat, Q_1-Q_2, let $\Delta(Q+S_A)$ be the heat absorbed in passing from Q_2 to Q_1 at the volume V_A, and $\Delta(Q+S_B)$ the corresponding quantity at the volume V_B; ΔS_A and ΔS_B representing quantities of potential energy stored up in altering molecular arrangement. Then

$$\Delta(S_B-S_A)=\Delta\left(Q\frac{d}{dQ}-1\right)\int_{V_A}^{V_B}PdV. \quad . \quad . \quad . \quad . \quad . \quad (17.)$$

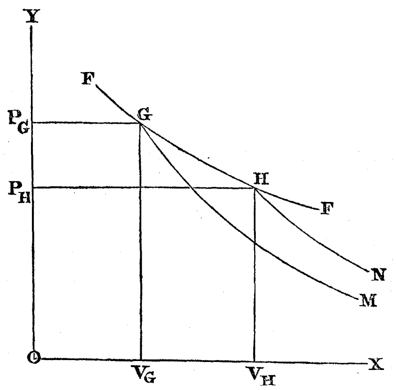
(14.) *Of Curves of Free Expansion.*

In all the preceding propositions, the whole motive power developed by an elastic substance in expanding is supposed to be communicated to external bodies; to a piston, for example, which the substance causes to move, and to overcome the resistance of a machine.

Let us now suppose that as much as possible of the motive power developed by the expansion is expended in agitating the particles of the expanding substance itself, by whose mutual friction it is finally reconverted into heat (as when compressed air escapes freely from a small orifice); and let us examine the properties of the curves which, on a diagram of energy, represent the law of expansion of the substance under these circumstances, and which may be called *Curves of free Expansion.*

(15.) PROPOSITION VI.—THEOREM. *If from two points on a curve of free expansion there be drawn two straight lines perpendicular to and terminating at the axis of ordinates, and also two curves of no transmission, indefinitely prolonged away from the origin of co-ordinates; then the area contained between the curve of free expansion, the two straight lines and the axis of ordinates, will be equal to the area contained between the curve of free expansion, and the two indefinitely-prolonged curves of no transmission.*

Fig. 10.



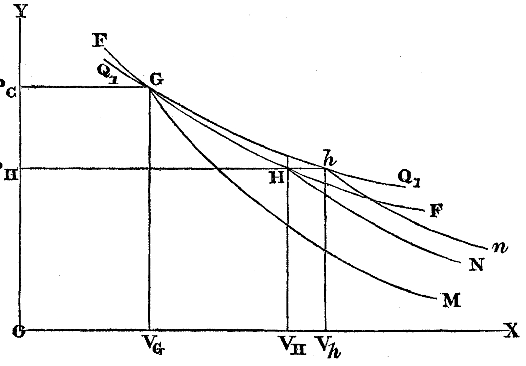
(Demonstration.) Let FF (fig. 10) be a curve of Free Expansion; G, H any two points in it; GV_G, HV_H ordinates; GP_G, HP_H lines perpendicular to OY; GM, HN curves of no transmission, indefinitely prolonged in the direction of X. Then the indefinitely-prolonged area MGHN represents the heat which would have to be communicated to the substance, if the motive power developed were entirely transferred to external bodies. while the area V_GGHV_H represents that motive power The excess of the rectangular area P_HHV_HO above the area P_GGV_GO, is the power necessarily given out by the elastic fluid in passing from a vessel in which the pressure is P_G and volume V_G, to a vessel in which the pressure is P_H and volume V_H. The remainder of the expansive power, represented by the area P_GGHP_H, by the mutual friction of the particles of the expanding substance, is entirely reconverted into heat, and is exactly sufficient (by the definition of the curve of free expansion) to render the communication of heat to the substance unnecessary; from which it follows, that this area is equal to the area MGHN. Q.E.D.

The equation of a curve of free expansion is

$$d(\Psi+\mathrm{PV})=0. \quad \ldots\ldots\ldots\ldots \quad (17\,\mathrm{A.})$$

(16.) *Corollary.*—In fig. 11, the same letters being retained as in the last figure, through G draw an isothermal curve Q_1Q_1, which the line P_HH produced cuts in *h*;

Fig. 11.



and from *h* draw the indefinitely-prolonged curve of no transmission, *hn*. Then because, by the proposition just proved, the areas P_GGHP_H and MGHN are equal, it follows that the indefinitely-prolonged area, MG*hn*, which represents the latent heat of expansion at the constant actual heat Q_1, from the volume V_G to the volume V_h, exceeds P_GGhP_H, by the indefinitely-prolonged area NH*hn*, which represents the heat which the substance would give out, in falling, at the pressure P_H, from the actual heat Q_1 to the actual heat corresponding to the point H on the curve of free expansion passing through G. Subtracting from this area the excess of the rectangle P_HV_h above the rectangle P_GV_G, we obtain the excess of the area MG*hn* above the area V_GGhV_h.

This conclusion may be thus expressed:—Let Q_2 be the actual heat for the point H; $\frac{K_P}{\mathfrak{k}}$ the ratio of specific heat at the constant pressure P_H to real specific heat; then

$$\left.\begin{array}{ll} & \int_{Q_2}^{Q_1}\frac{K_P}{\mathfrak{k}}dQ-P_HV_h+P_GV_G=\left(Q\frac{d}{dQ}-1\right)\int_{V_G}^{V_h}PdV(\text{for }Q=Q_1); \\ \text{otherwise :—} & \int_{Q_2}^{Q_1}\frac{K_P}{\mathfrak{k}}dQ+\int_{P_H}^{P_G}VdP=Q_1(F_h-F_G). \quad \ldots\ldots \end{array}\right\} \quad . \quad (18.)$$

Equation (18.) may be used, either to find points in the curve of free expansion which passes through G, when the isothermal curves and the curves of no transmission are known; or to deduce theoretical results from experiments on the form of curves of free expansion, such as those which have been for some time carried on by Mr. JOULE and Professor WILLIAM THOMSON.

Considered geometrically, these experiments give values of the area NH*hn*.

$$\text{The area } P_GGhP_H=\int_{P_H}^{P_G}VdP$$

is known, in each case, from previous experiments on the properties of the gas employed; and this area, by Proposition VI., is equal to the area MG*h*HN; to which adding the area NH*hn*, ascertained by experiment, we obtain the area MG*hn*, that is, the latent heat of expansion from the volume V_G to the volume V_h, at the constant actual heat Q_1, denoted symbolically by

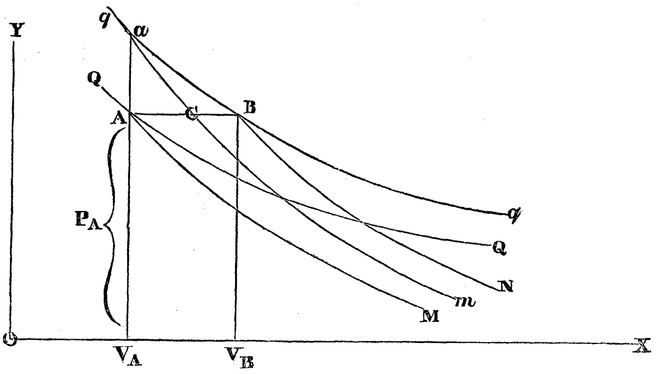
$$H = Q_1 \frac{d}{dQ} \int_{V_G}^{V_h} P dV = Q_1 (F_h - F_G).$$

Now the problem to be solved is of this kind. We know the *differences* of actual heat corresponding to a certain series of isothermal curves for the substance employed; and we have to ascertain the *absolute quantities* of actual heat corresponding to those curves. Of the above expression for the area MG*hn*, therefore, the factor Q_1 is to be determined, while the other factor, being the difference between two thermo-dynamic functions, is known; and the experiments of Messrs. THOMSON and JOULE, by giving the value of the product, enable us to calculate that of the unknown factor, and thence to determine the point on the thermometric scale corresponding to absolute privation of heat.

(17.) PROPOSITION VII.—PROBLEM. *To determine the ratio of the Apparent Specific Heats of a substance at Constant Volume and at Constant Pressure, for a given Pressure and Volume; the isothermal curves and the curves of no transmission being known.*

(Solution.) In fig. 12, let A be the point whose co-ordinates represent the given volume V_A and pressure P_A; QAQ the isothermal curve passing through A; *q q* another isothermal curve, very near to QQ. Through A draw the ordinate V_AA*a* parallel to OY, cutting *qq* in *a*; draw also AB parallel to OX, cutting *qq* in B. From A, *a*, B, draw the three indefinitely-prolonged curves of no transmission AM, *am*, BN.

Fig. 12.



Then the heat absorbed in passing from the actual heat Q to the actual heat *q*, at the constant volume V_A, is represented by the indefinitely-prolonged area MA*am*, while at the constant pressure P_A it is represented by the area MABN. Let the curve *qq* be supposed to approximate indefinitely to QQ. Then will the three-sided area A*a*B diminish indefinitely as compared with the areas between the curves of no transmission AM, *am*, BN; and consequently the area MABN will approximate indefinitely to the sum of the areas MA*am* and *ma*BN; the ultimate ratio of which sum to the area MA*am* is therefore the required ratio of the specific heats. Now *ma*BN, as *qq* approaches QQ, approximates indefinitely to the latent heat of the small expansion V_B-V_A at the actual heat Q, and this small expansion bears ultimately to the increment of pressure P_a-P_A, the ratio of the subtangent of the isothermal curve QQ to its ordinate at the point A.

The symbolical expression of this proposition is as follows:—Let δQ denote the indefinitely small difference of actual heat between the isothermal curves QQ, *qq*; δV the indefinitely small variation of volume V_B-V_A; δP the indefinitely small variation of pressure P_a-P_A; $\frac{K_V}{\mathfrak{k}}\delta Q$, $\frac{K_P}{\mathfrak{k}}\delta Q$ the quantities of heat required to produce the variation δQ, at the constant volume V_A, and at the constant pressure P_A respectively.

Then
$$\delta V=\frac{\delta P}{-\frac{dP}{dV}}=\frac{\frac{dP}{dQ}}{-\frac{dP}{dV}}\cdot\delta Q;$$

$$\left.\begin{aligned}
&\text{and} && \frac{K_P}{\mathfrak{k}}\cdot\delta Q=\frac{K_V}{\mathfrak{k}}\cdot\delta Q+Q\frac{dP}{dQ}\cdot\delta V=\left\{\frac{K_V}{\mathfrak{k}}+\frac{Q\left(\frac{dP}{dQ}\right)^2}{-\frac{dP}{dV}}\right\}\delta Q;\\
&\text{consequently} && \frac{K_P}{K_V}=1+\frac{\mathfrak{k}}{K_V}\cdot\frac{Q\left(\frac{dP}{dQ}\right)^2}{-\frac{dP}{dV}};\ \ldots\ldots
\end{aligned}\right\}\quad\ldots\ (19.)$$

equations agreeing with equation 31 of a paper on the Centrifugal Theory of Elasticity before referred to.

(18.) *First Corollary.*—As the curves AM, *am*, BN approximate indefinitely towards parallelism, and the point *a* towards C, where *am* intersects AB, the ratio of the areas MABN : MA*am*, approximates indefinitely to that of the lines AB : AC, which are ultimately proportional, respectively, to the subtangents of the isothermal curve and the curve of no transmission passing through A. Therefore,

$$\frac{K_P}{K_V}=\frac{\text{Subtangent of Isothermal Curve}}{\text{Subtangent of Curve of No Transmission}}.\quad\ldots\ldots\ (20.)$$

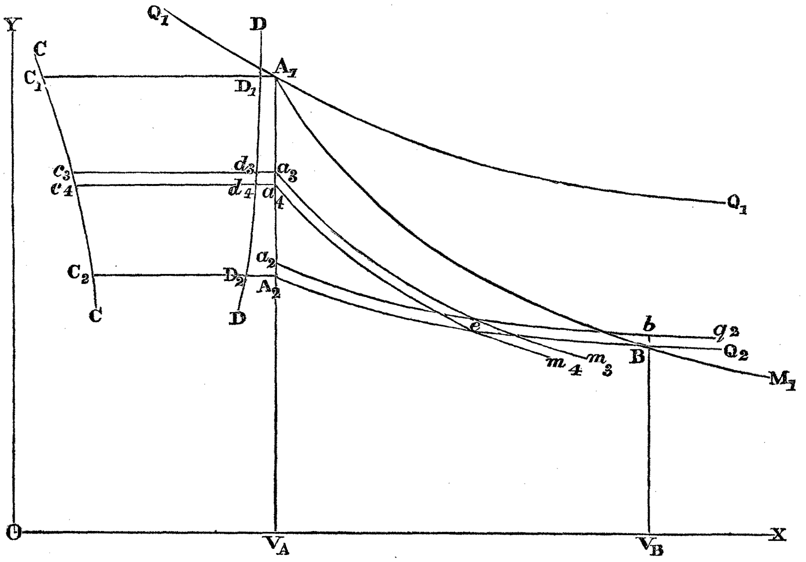
(19.) *Second Corollary.—Velocity of Sound.* The subtangents of different curves at a given point on a diagram of energy being inversely proportional to the increase of pressure produced by a given diminution of volume according to the respective curves, are inversely proportional to the squares of the respective velocities with which waves of condensation and rarefaction will travel when the relations of pressure to volume are expressed by the different curves. Therefore, if there be no sensible transmission of heat between the particles of a fluid during the passage of sound, the square of the velocity of sound must be greater than it would have been had the transmission of heat been instantaneous in the ratio of the subtangent of an isothermal curve to that of a curve of no transmission at the same point, or of the specific heat at constant pressure to the specific heat at constant volume.

This is a geometrical proof of LAPLACE's law for all possible fluids. The same law is deduced from the Hypothesis of Molecular Vortices in the paper before referred to on the Centrifugal Theory of Elasticity.

(20.) PROPOSITION VIII.—PROBLEM. *The isothermal curves for a given substance being known, and the quantities of heat required to produce all variations of actual heat at a given constant volume; it is required to find any number of points in a curve of no transmission passing through a given point in the ordinate corresponding to that volume.*

(Solution). In fig. 13, let V_AA_1 be the given ordinate; Q_1Q_1, A_2Q_2 isothermal curves meeting it in A_1, A_2, respectively; and let it be required, for example, to find the point where the curve of no transmission passing through A_1 intersects the isothermal curve A_2Q_2. On the line $V_AA_2A_1$, as an axis of abscissæ, describe a curve CC, whose ordinates (such as A_2C_2, a_4c_4, &c) are proportional to the specific heat of the substance at the constant volume V_A, and at the degrees of actual heat corresponding to the points where they are erected, divided by the corresponding rate of increase of pressure with actual heat; so that the area of this curve between any two ordinates (*e. g.* the area $a_4c_4c_3a_3$) may represent the mechanical equivalent of the heat absorbed in augmenting the actual heat from the amount corresponding to the lower ordinate to that corresponding to the higher (*e.g.* from the amount corresponding to a_4 to that corresponding to a_3).

Fig. 13.



Very near to the isothermal curve A_2Q_2, draw another isothermal curve a_2q_2, and let the difference of actual heat corresponding to the interval between these curves be δQ. Draw a curve DD, such that the part cut off by it from each ordinate of the curve CC shall bear the same proportion to the whole ordinate which the difference δQ bears to the whole actual heat corresponding to the ordinate; for example, let

$$\overline{A_1C_1} : \overline{A_1D_1} :: Q_1 : \delta Q$$
$$\overline{A_2C_2} : \overline{A_2D_2} :: Q_2 : \delta Q, \text{ \&c.}$$

Then draw an ordinate $V_B Bb$, parallel to OY, cutting off from the space between the isothermal curves A_2Q_2, a_2q_2, a quadrilateral area A_2Bba_2 equal to $A_1D_1D_2A_2$, the area of the curve DD between the ordinates at A_1 and A_2.

Then if the difference δQ be indefinitely diminished, the point B will approximate indefinitely to the intersection required of the isothermal curve A_2Q_2 with the curve of no transmission passing through A_1; and thus may any number of points in this curve of no transmission be found.

(Demonstration.) Let A_1M_1 be the curve of no transmission required. Let a_3c_3, a_4c_4 be any two indefinitely-close ordinates of the curve CC, corresponding to the mean actual heat $Q_{3,4}$. Let a_3m_3, a_4m_4 be curves of no transmission, cutting the curves a_2q_2, A_2Q_2, so as to enclose a small quadrilateral area e. Then by the construction, and Proposition I.,

The area $a_3c_3c_4a_4$=the indefinitely-prolonged area $m_3a_3a_4m_4$;

and by the first corollary of the second proposition and the construction,

$$\frac{\text{the area } e}{m_3a_3a_4m_4}=\frac{\delta Q}{Q_{3,4}}=\frac{\text{area } a_3d_3d_4a_4}{\text{area } a_3c_3c_4a_4}.$$

Therefore the area e=the area $a_3d_3d_4a_4$; but the area $A_1D_1D_2A_2$ is entirely made up of such areas as $a_3d_3d_4a_4$, to each of which there corresponds an equal area such as e; and when the difference δQ is indefinitely diminished the area A_2Bba_2 approximates indefinitely to the sum of all the areas such as e, that is, to equality with the area $A_1D_1D_2A_2$. Q.E.D.

The symbolical expression for this proposition is found as follows:—

$$\text{The area } A_1D_1D_2A_2 \text{ ultimately}=\delta Q.\int_{Q_2}^{Q_1}\frac{K_V}{kQ}.dQ \text{ (for } V=V_A);$$

$$\text{the area } A_2Bba_2 \text{ ultimately}=\delta Q.\int_{V_A}^{V_B}\frac{dP}{dQ}dV \text{ (for } Q=Q_2);$$

divide both sums by δQ and equate the results; then

$$\int_{V_A}^{V_B}\frac{dP}{dQ}dV(\text{for} Q=Q_2)=\int_{Q_2}^{Q_1}\frac{K_V}{kQ}dQ \text{ (for } V=V_A), \quad . \ . \ . \ . \quad (21.)$$

which denotes the equality of two expressions for the difference, F_1-F_2, between the thermo-dynamic functions for the curve of no transmission A_1M, and for that passing through the point A_2.

When the relations between pressure, volume, and heat, for a given substance, are known, the equation (21.) may be transformed into one giving the volume V_B corresponding to the point at which the required curve of no transmission cuts the isothermal curve of Q_2.

Suppose, for instance, that for a perfect gas

$$PV=NQ \text{ sensibly; and } \frac{K_V}{\mathfrak{k}}=1 \text{ sensibly; } \quad . \quad . \quad . \quad (22.)$$

N being a constant (whose value for simple gases and for atmospheric air and carbonic oxide is about 0·41); then the thermo-dynamic function for a perfect gas is sensibly

$$F=\text{hyp. log } Q+N \text{ hyp. log } V; \quad . \quad . \quad . \quad . \quad . \quad . \quad (22\text{ A.})$$

and equation (21.) gives, for the equation of a curve of no transmission,

$$\frac{V_B}{V_A}=\left(\frac{Q_1}{Q_2}\right)^{\frac{1}{N}}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23.)$$

whence

$$\frac{P_B}{P_A}=\left(\frac{V_B}{V_A}\right)^{-1-N}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24.)$$

Equations (23.) and (24.) are forms of the equation of a curve of no transmission for a perfect gas, according to the supposition of MAYER; and are approximately true for a perfect or nearly perfect gas on any supposition.

According to the hypothesis of molecular vortices, the relations between pressure, volume, and actual heat for a perfect gas are expressed by these equations:—

$$PV=NQ+h; \ \frac{K_V}{\mathfrak{k}}=1+\frac{N^2hQ}{(NQ+h)^2}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (25.)$$

where h is a very small constant, which is inversely proportional to the specific gravity of the gas, and whose value, in the notation of papers on the hypothesis in question, is

$$h=N\mathfrak{k}\kappa, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25\text{ A.})$$

κ being the height, on the scale of a perfect gas thermometer, of the point of absolute cold above the absolute zero of gaseous tension. Hence we find, for the thermo-dynamic function of a perfect gas,

$$F=\text{hyp. log } Q-\frac{Nh}{NQ+h}+N \text{ hyp. log } V, \quad . \quad . \quad . \quad . \quad . \quad (26.)$$

and for the equation of a curve of no transmission,

$$\frac{V_B}{V_A}=\left(\frac{Q_1}{Q_2}\right)^{\frac{1}{N}}.e^{\left\{\frac{h}{NQ_2+h}-\frac{h}{NQ_1+h}\right\}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27.)$$

For all practical purposes yet known, these equations may be treated as sensibly agreeing with equation (23.), owing to the smallness of h as compared with NQ.

Section III.—OF THE EFFICIENCY OF THERMO-DYNAMIC ENGINES, WORKED BY THE EXPANSION AND CONDENSATION OF PERMANENT GASES.

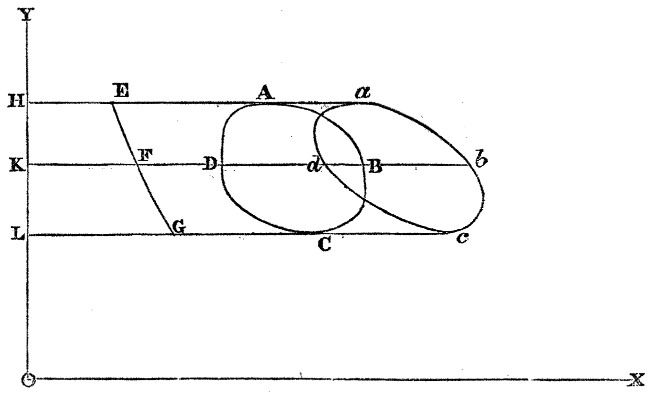
(21.) The *Efficiency* of a Thermo-dynamic Engine is the proportion of the whole heat expended which is converted into motive power; that is to say, the ratio of the motive power developed to the mechanical equivalent of the whole heat consumed.

To determine geometrically the efficiency of a thermo-dynamic engine, it is necessary to know its true indicator-diagram; that is to say, the curve whose co-ordinates represent the successive volumes and pressures which the elastic substance working the engine assumes during a complete revolution. This true indicator-diagram is not necessarily identical in figure with the diagram described by the engine on the indicator-card; for the abscissæ representing volumes in the latter diagram, include not only the volumes assumed by that portion of the elastic substance, which really performs the work by alternately receiving heat while expanding, and emitting heat while contracting, in such a manner as permanently to transform heat into motive power, but also the volumes assumed by that portion of the elastic substance, if any, which acts merely as a *cushion* for transmitting pressure to the piston, undergoing, during each revolution, a series of changes of pressure and volume, and then the same series in an order exactly the reverse of the former order, so as to transform no heat permanently to power.

The thermo-dynamic engines to be considered in the present section, are those in which the elastic substance undergoes no change of condition. We shall in the first place investigate the efficiency of those which work *without* the aid of the contrivance called an "economizer" or "regenerator," and afterwards, those which work *with* the aid of that piece of apparatus.

(22.) Lemma.—Problem. *To determine the true from the apparent indicator-diagram of a Thermo-dynamic Engine; the portion of the elastic substance which acts as a* cushion *being known, and the law of its changes of pressure and volume.*

Fig. 14.



(Solution.) In fig. 14, let *abcd* be the apparent indicator-diagram. Parallel to OX draw $\overline{\mathrm{H}a}$ and $\overline{\mathrm{L}c}$, touching this diagram in a and c respectively; then those lines will be the lines of maximum and minimum pressure. Let $\overline{HE}$ and $\overline{LG}$ be the volumes occupied by the *cushion* at the maximum and minimum pressures respectively: draw the curve EG, such that its co-ordinates shall represent the changes of volume and pressure undergone by the cushion during a revolution of the engine. Let KFdb be any line of equal pressure, intersecting this curve and the apparent indicator-diagram; so that $\overline{Kb}$, $\overline{Kd}$ shall represent the two volumes assumed by the whole elastic body at the pressure $\overline{OK}$, and $\overline{KF}$ the volume of the cushion at the same pressure. On this line take

$$\overline{bB}=\overline{dD}=\overline{KF};$$

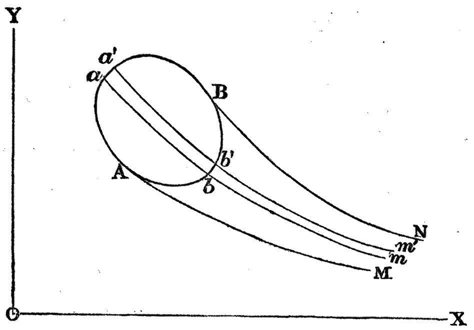
then it is evident that B and D will be two points in the true indicator-diagram; and in the same manner may any number of points be found.

The area of the true diagram ABCD is obviously equal to that of the apparent diagram *abcd.*

(23.) Proposition IX.—Problem. *The true indicator-diagram of a thermo-dynamic engine worked by the expansion and contraction of a substance which does not change its condition, and without a regenerator, being given, it is required to determine the efficiency of the engine.*

(Solution.) In fig. 15, let Aaa' B$b'b$A be the given true indicator-diagram. Draw two curves of no transmission, AM, BN, touching this figure at A and B respectively, and indefinitely produced towards X. Then during the process denoted by the portion Aaa'B of the diagram the elastic substance is receiving heat, and the mechanical equivalent of the total quantity received is represented by the indefinitely-prolonged area MAaa'BN; during the process denoted by the portion B$b'b$A of the diagram, the substance is giving out heat, and the mechanical equivalent of the total heat given out is represented by the indefinitely-prolonged area MAbb'BN; while the difference between those areas, that is, the area of the indicator-diagram itself, represents at once the heat which permanently disappears and the motive power given out. The Efficiency of the engine is the ratio of this last quantity to the total heat received by the elastic substance during a revolution; that is to say, it is denoted by the fraction,

Fig. 15.



$$\frac{\text{area } \mathrm{A}aa'\mathrm{B}b'b\mathrm{A}}{\text{area } \mathrm{MA}aa'\mathrm{BN}}.$$

To express this result symbolically, find the limiting points A and B by combining the equation of the indicator-diagram with the general equation of curves of no transmission, viz.—

$$d\mathrm{F}=0.$$

Then draw two indefinitely-close and indefinitely-prolonged curves of no transmission, *abm*, *a'b'm'*, through any part of the diagram, cutting out of it a quadrilateral stripe, *abb'a'*. Let Q_1 be the mean actual heat corresponding to the upper end *aa'* of this quadrilateral stripe; Q_2, that corresponding to the lower end, *bb'*.

The area of this indefinitely-narrow stripe representing a portion of the heat converted into motive power, is found, according to the principles and notation of the third corollary to Proposition II. and of Proposition III., by multiplying the difference between the actual heats by the difference between the thermo-dynamic functions for the curves of no transmission that bound the stripe, thus:—

$$\delta E=(Q_1-Q_2)\delta F;$$

while the area of the indefinitely-prolonged stripe, *maa'm'*, representing part of the total heat expended, is, according to the same principles,

$$\delta H_1=Q_1\delta F;$$

and that of the indefinitely-prolonged stripe *mbb'm'*, representing part of the heat given out, is

$$\delta H_2=Q_2\delta F.$$

Integrating these expressions we find the following results:—

$$\left.\begin{array}{ll}\text{whole heat expended,} & H_1=\int_{F_A}^{F_B} Q_1 dF; \\ \text{heat given out,} & H_2=\int_{F_A}^{F_B} Q_2 dF; \\ \text{motive power given out,} & E=H_1-H_2=\int_{F_A}^{F_B} (Q_1-Q_2) dF; \\ \text{efficiency,} & \dfrac{E}{H_1}=\dfrac{\int_{F_A}^{F_B} (Q_1-Q_2) dF}{\int_{F_A}^{F_B} Q_1 dF}; \end{array}\right\} \quad \dots\dots \quad (28.)$$

formulæ agreeing with equation (28.) of a paper on the Centrifugal Theory of Elasticity*; it being observed that the symbol F in the last-mentioned paper denotes, not precisely the same quantity which is denoted by it in this paper, and called a thermodynamic function, but the product of the part of that function which depends on the volume, by the real specific heat of the substance.

(24.) *First Corollary. Maximum Efficiency between given limits of Actual Heat.*

When the highest and lowest limits of actual heat at which the engine can work are fixed, it is evident that the greatest possible efficiency of an engine without a regenerator will be attained when the whole reception of heat takes place at the highest limit, and the whole emission at the lowest; so that the true indicator diagram is such a quadrilateral as is shown in fig. 6, and referred to in the second corollary of Proposition II.; bounded above and below by the isothermal curves denoting

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* Trans. Roy. Soc. Edinb. vol. xx.

the limits of actual heat, and, laterally, by any pair of curves of no transmission. The efficiency in this case, as has been already proved in various ways, is represented by

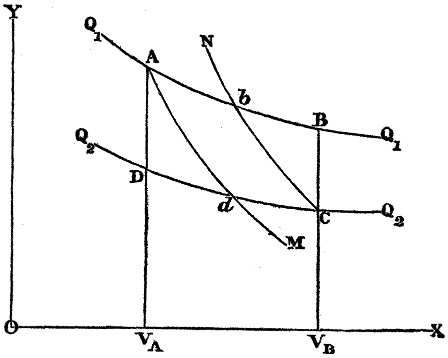
$$\frac{E}{H_1}=\frac{Q_1-Q_2}{Q_1}, \quad \ldots \ldots \ldots \quad (29.)$$

being the maximum efficiency possible between the limits of actual heat, Q_1 and Q_2.

(25.) *Second Corollary.*—PROBLEM. *To draw the diagram of greatest efficiency of a Thermo-dynamic Engine without a Regenerator, when the extent of variation of volume is limited, as well as that of the variation of actual heat.*

(Solution.) In fig. 16, let Q_1Q_1, Q_2Q_2 be the isothermal curves denoting the limits of actual heat; V_A, V_B the limits of volume. Draw the ordinates V_ADA, V_BCB, intersecting the isothermal curves in the points A, B, C, D. Through A and C respectively draw the curves of no transmission, AM cutting Q_2Q_2 in *d*, and CN cutting Q_1Q_1 in *b*. Then will A*b*C*d* be the diagram required. An analogous construction would give the diagram of greatest efficiency when the variations of pressure and of actual heat are limited; as in the Air-Engine proposed by Mr. JOULE.

Fig. 16.



(26.) *Of the use of the Economizer or Regenerator in Thermo-dynamic Engines.*

As the actual heat of the elastic substance which works a Thermo-dynamic Engine requires to be alternately raised and lowered, it is obvious that unless these operations are performed entirely by compression and expansion, without reception or emission of heat (as in the case of maximum efficiency described in the first corollary of Proposition IX.), part, at least, of the heat emitted during the lowering of the actual heat may be stored up, by being communicated to some solid conducting substance, and used again by being communicated back to the elastic substance, when its actual heat is being raised. The apparatus used for this purpose is called an Economizer or Regenerator, and was first invented, about 1816, by the Rev. ROBERT STIRLING. In the Air-Engine proposed by him, it consisted of a sheet-metal plunger surrounded by a wire grating or network; in that of Mr. JAMES STIRLING, it is composed of thin parallel plates of metal or glass through which the air passes longitudinally, and in the engine of Captain ERICSSON, of several sheets of wire gauze.

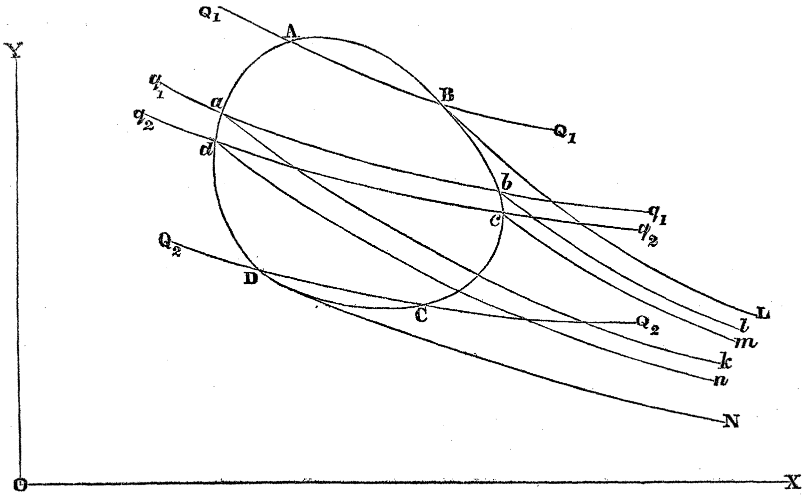
A regenerator may be regarded as consisting of an indefinite number of strata, with which the elastic substance is successively brought into contact; each stratum serving to store up and give out the heat required to produce one particular indefinitely small variation of the actual heat of the working substance.

A *perfect regenerator* is an ideal apparatus of this kind, in which the mass of material is so large, the surface exposed so extensive, and the conducting powers so great, as to enable it to receive and emit heat instantaneously without there being any sensible difference of temperature between any part of the regenerator and the contiguous portion of the working substance ; and from which no appreciable amount of heat is lost by conduction or radiation. In theoretical investigations it is convenient, in the first place, to determine the saving of heat effected by a perfect regenerator, and afterwards to make allowance for the losses arising from the non-fulfilment of the conditions of ideally perfect action; losses which, in the present imperfect state of our knowledge of the laws of the conduction of heat, can be ascertained by direct experiment only *.

(27.) PROPOSITION X.—PROBLEM. *The true indicator-diagram of any thermo-dynamic engine being given, to determine the amount of heat saved by a perfect regenerator.*

(Solution.) Let ABCD (in fig. 17) be the given indicator-diagram. Across it draw any two indefinitely-close isothermal curves; q_1q_1 intersecting it in a, b; and q_2q_2 intersecting it in d, c. To the stripe between those two curves, speaking generally, a certain layer or stratum of the regenerator corresponds, which receives heat from the working substance during the change from b to c, and restores the same amount of heat during the change from d to a. The amount of heat economized by the layer in question is thus found. Through the four points a, b, c, d, draw the indefinitely-prolonged curves of no transmission, ak, bl, cm, dn ; then the smaller of the two indefinitely-prolonged areas, $lbcm$, $kadn$, represents the heat saved by the layer of the regenerator corresponding to the indefinitely-narrow stripe between the isothermal curves q_1q_1 and q_2q_2.

Fig. 17.



Draw two curves of no transmission, BL, DN, touching the diagram ; and through

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* It is true that the problem of the waste of heat in the action of the regenerator is capable of a hypothetical solution by the methods of FOURIER and POISSON ; and I have by these methods obtained formulæ which are curious in a mathematical point of view ; but owing to our ignorance of the absolute values and laws of variation of the coefficients of conductivity contained in these formulæ, they are incapable of being usefully applied ; and I therefore for the present refrain from stating them.

the points of contact, B and D, draw the isothermal curves, Q_1Q_1 cutting the diagram in A and B, and Q_2Q_2 cutting it in C and D. Then because, during the whole of the change from D through A to B, the working substance is receiving heat, and during the whole of the change from B through C to D, emitting heat, the regenerator can have no action above the isothermal curve Q_1Q_1, nor below the isothermal curve Q_2Q_2.

The whole of the diagram between these curves is to be divided by indefinitely-close isothermal curves into stripes like *abcd*; and the saving of heat effected by the layer of the regenerator corresponding to each stripe ascertained in the manner described, when the whole saving may be found by summation or integration.

The symbolical expression of this result is as follows. Let the points of contact, B, D, which limit the action of the regenerator, and the corresponding quantities of actual heat, Q_1, Q_2, be found, as in Proposition IX., by means of the equation $dF=0$.

Then

$$\text{the saving of heat} = \int_{Q_2}^{Q_1} Q\frac{d.F}{dQ}dQ = \int_{Q_2}^{Q_1} \left(\frac{K_V}{\mathfrak{k}} + Q\frac{dP}{dQ}\cdot\frac{d.V}{dQ}\right)dQ \quad . \; . \; . \; . \; . \; . \quad (30.)$$

care being taken, when $\frac{d.F}{dQ}$ has different values for the same value of Q, corresponding respectively to the two sides of the diagram, to choose the smaller in performing the integration.

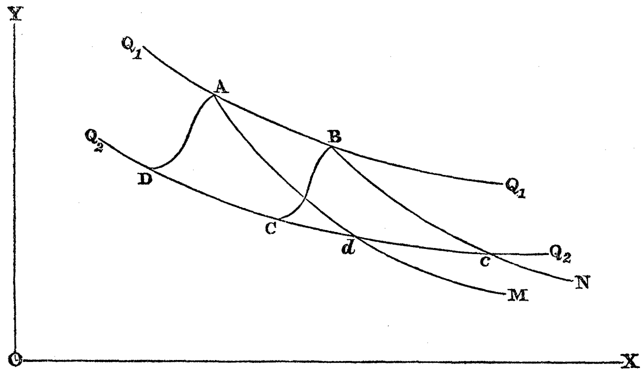
(28.) *Corollary.*—It is evident that the regenerator acts most effectually, when the outlines of the indicator-diagram from A to D, and from B to C, are portions of a pair of curves of *equal transmission* (determined as in Proposition IV.); for then, if the operation of the regenerator is perfect, the changes from B to C and from D to A will be effected without expenditure of heat; the heat transmitted from the working substance to a given stratum of the regenerator, during any part such as *bc*, of the operation BC, being exactly sufficient for the corresponding part, *da*, of the operation DA. In this case $\frac{d.F}{dQ}$ for each value of Q between Q_1 and Q_2, has the same value at either side of the diagram.

In fact, the effect of a perfect regenerator is, to confer upon any pair of curves of *equal transmission* the properties of a pair of curves of *no transmission.*

(29.) Proposition XI.—Theorem. *The greatest efficiency of a thermo-dynamic engine, working between given limits of actual heat, with a perfect regenerator, is equal to the greatest efficiency of a thermo-dynamic engine, working between the same limits of actual heat, without a regenerator.*

(Demonstration.) In fig. 18, let Q_1Q_1, Q_2Q_2 be the isothermal curves denoting the given limits of actual heat. Let AD, BC be a pair of curves of equal transmission of any form. Then by the aid of a perfect regenerator, the whole of the heat given out by the elastic substance during the operation BC may be stored up, and given out again to that substance in such a manner as to be exactly sufficient for the operation DA; so that the whole consumption of heat in one revolution by an engine

Fig. 18.



whose indicator-diagram is ABCD, may be reduced simply to the latent heat of expansion during the operation AB, which is represented by the indefinitely-prolonged area MABN, A*d*M and B*c*N being curves of no transmission. The efficiency of such an engine is represented by

$$\frac{\text{the area ABCD}}{\text{the area MABN}}.$$

Now the maximum efficiency of an engine without a regenerator, working between the same limits of actual heat, is represented by

$$\frac{\text{the area AB}cd}{\text{the area MABN}}=\frac{Q_1-Q_2}{Q_1};$$

and from the mode of construction of curves of equal transmission, described in Proposition IV., it is evident that

$$\text{the area ABCD}=\text{the area AB}cd;$$

hence the maximum efficiencies, working between the given limits of actual heat, Q_1 and Q_2, are equal, with or without a perfect regenerator. Q.E.D.

(30.) *Advantage of a Regenerator.*

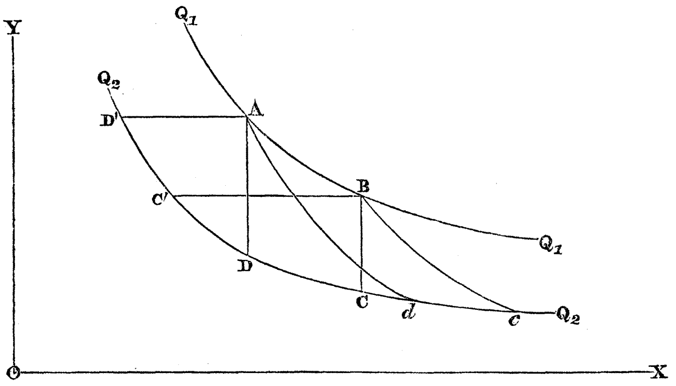
It appears from this theorem that the advantage of a regenerator is, not to increase the maximum efficiency of a thermo-dynamic engine between given limits of actual heat, but to enable that amount of efficiency to be attained with a less amount of expansion, and consequently with a smaller engine.

Suppose, for instance, that to represent the isothermal curves, and the curves of no transmission, for a gaseous substance, we adopt the approximate equations already given in article 20, viz.—

$$\left.\begin{array}{l}\text{for the isothermal curve of Q, PV=NQ;}\\ \text{for a curve of no transmission } \frac{V_2}{V_1}=\left(\frac{Q_2}{Q_1}\right)^{-\frac{1}{N}}=\left(\frac{P_2}{P_1}\right)^{\frac{-1}{1+N}};\end{array}\right\}\quad\ldots\quad(31.)$$

and let us compare the forms of the indicator-diagrams without and with a regenerator, for a perfect air-engine, working between given limits as to actual heat, defined by the isothermal curves Q_1Q_1, Q_2Q_2 in fig 19.

Fig. 19.



The amount of expansion at the higher limit of heat being arbitrary, let us suppose it to be from the volume V_A to the volume V_B, corresponding respectively to the points A and B, and to be the same in all cases, whether with or without a regenerator.

The engine being without a regenerator, the diagram corresponding to the maximum efficiency has but one form, viz. AB*cd*, where B*c*, A*d* are curves of no transmission. Hence, in this case, there must be an additional expansion, from the volume V_B to the volume

$$V_c = V_B \cdot \left(\frac{Q_1}{Q_2}\right)^{\frac{1}{N}}, \quad \ldots \ldots \ldots \ldots \quad (32.)$$

for the purpose merely of lowering the actual heat of the air without loss of heat; and the engine must be made large enough to admit of this expansion, otherwise heat will be wasted.

On the other hand, if the engine be provided with a perfect regenerator, any pair of curves of equal transmission passing through A and B will complete a diagram of maximum efficiency. The property of a pair of these curves being, as shown in Proposition IV., that the difference of their thermo-dynamic functions,

$$\Delta F \left(= \int \frac{dP}{dQ} dV \text{ when Q is constant} \right),$$

is the same for every value of Q, it follows, that for a gas, according to the approximate equation (23.), the property of a pair of curves of equal transmission is, that the volumes corresponding to the intersections of the two curves by the same isothermal curve, are in a ratio which is the same for every isothermal curve. Thus let V_a, V_b be such a pair of volumes, then this equation

$$\frac{V_b}{V_a} = \frac{V_B}{V_A} \quad \ldots \ldots \ldots \ldots \quad (33.)$$

defines a pair of curves of equal transmission. From this and from equation (31.), it follows, that for such a pair of curves

$$\frac{P_b}{P_a}=\frac{P_B}{P_A}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34.)$$

If one of the curves, or lines, of equal transmission is a straight line of equal volumes, that is, an ordinate AD parallel to OY, then the other is an ordinate BC, parallel to OY also. Then ABCD is the diagram of maximum efficiency for an air-engine with a perfect regenerator, when the air traverses the regenerator without alteration of volume; and by adopting this diagram, the additional expansion from V_B to V_c is dispensed with.

If one of the curves, or lines, of equal transmission is a straight line of equal pressures AD′ parallel to OX, then the other also is a straight line of equal pressures BC′. The diagram thus formed, ABC′D′, is suitable, when the air, as in ERICSSON's engine, has to traverse the regenerator without change of pressure.

It must be observed, that no finite mass, or extent of conducting surface, will enable a regenerator to act with the ideal perfection assumed in Propositions X. and XI., and their corollaries.

Owing to the want of a general investigation of the theory of the action of the regenerator based on true principles, those who have hitherto written respecting it have either exaggerated its advantages or unduly depreciated them. From this remark, however, must be excepted a calculation of the expenditure of heat in Captain ERICSSON's engine, by Professor BARNARD of the University of Alabama*.

(31.) *General Remarks on the preceding Propositions.*

The eleven preceding propositions, with their corollaries, are the geometrical representation of the theory of the mutual transformation of heat and motive power, by means of the changes of volume of a homogeneous elastic substance which does not change its condition. All these propositions are virtually comprehended in the first two, of which, perhaps, the most simple enunciations are the following :—

I. The mechanical equivalent of the heat absorbed or given out by a substance in passing from one given state as to pressure and volume to another given state, through a series of states represented by the co-ordinates of a given curve on a diagram of energy, is represented by the area included between the given curve and two curves of no transmission of heat drawn from its extremities, and indefinitely prolonged in the direction representing increase of volume.

II. If across any pair of curves of no transmission on a diagram of energy there be drawn any series of isothermal curves at intervals corresponding to equal differences of actual heat, the series of quadrilateral areas thus cut off from the space between the curves of no transmission will be all equal to each other.

These two propositions are the necessary consequences of the definitions of iso-

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* Silliman's Journal, September 1853.

thermal curves and curves of no transmission on a diagram of energy, and are the geometrical representation of the application to the particular case of heat and expansive power, of two axioms respecting Energy in the abstract, viz.—

I. The sum of Energy in the Universe is unalterable.

II. The effect, in causing Transformation of Energy, of the whole quantity of Actual Energy present in a substance, is the sum of the effects of all its parts.

The application of these Axioms to Heat and Expansive Power virtually involves the following Definition of Expansive Heat:—

Expansive Heat is a species of Actual Energy, the presence of which in a substance affects, and in general increases, its tendency to expand.

And this definition, arrived at by induction from experiment and observation, is the foundation of the theory of the expansive action of heat.

SECTION IV.—OF TEMPERATURE, THE MECHANICAL HYPOTHESIS OF MOLECULAR VORTICES, AND THE NUMERICAL COMPUTATION OF THE EFFICIENCY OF AIR-ENGINES.

(32.) In order to apply the propositions of the preceding articles to existing substances, besides experimental data sufficient for the determination, direct or indirect, of the isothermal curves and curves of no transmission, it is necessary also to know the relation, for the substance in question, between the quantity of heat actually present in it under any circumstances, and its *Temperature*; a quantity measured by the product of the pressure, volume, and specific gravity of a mass of perfect gas, when in such a condition that it has no tendency to communicate heat to, or to abstract heat from, the substance whose temperature is ascertained.

The nature of the relation between heat and temperature has been discussed in investigations already published, as a consequence deducible from a hypothesis respecting the molecular constitution of matter, with the aid of data supplied by the experiments of Messrs. THOMSON and JOULE and of M. REGNAULT. Nevertheless it seems to me desirable to add here a few words respecting the grounds, independent of direct experiment, for adopting the hypothesis of molecular vortices as a probable conjecture, the extent to which, by the aid of this hypothesis, the results of experiment were anticipated, and its use, in conjunction with the results of experiment, as a means of arriving at a knowledge of the true law of the relation between temperatures and total quantities of heat.

To introduce a hypothesis into the theory of a class of phenomena, is to suppose that class of phenomena to be, in some way not obvious to the senses, constituted of some other class of phenomena with whose laws we are more familiar. In thus framing a hypothesis, we are guided by some analogy between the laws of the two classes of phenomena: we conclude, from this analogy of laws, that the phenomena themselves are probably alike. This act of the mind is the converse of the process of ordinary physical reasoning; in which, perceiving that phenomena are alike, we conclude that their laws are analogous. The results, however, of the latter process of reasoning may be certainly true, while those of the former can never be more than probable; for how complete soever the analogy between the laws of two classes of phenomena may be, there will always remain a possibility of the phenomena themselves being unlike. A hypothesis, therefore, is incapable of absolute proof; but the agreement of its results with those of experiment may give it a high degree of probability.

The laws of the transmission of radiant heat are analogous to those of the propagation of a transverse oscillatory movement. The laws of thermometric heat are analogous to those of motion, inasmuch as both are convertible into mechanical effect; and motion, especially that of eddies in liquids and gases, is directly convertible into heat by friction. If, guided by these analogies, we assume as a probable hypothesis that heat consists in some kind of molecular motion, we must suppose that thermometric heat is such a molecular motion as will cause bodies to tend to expand; that is to say, a motion productive of centrifugal force. Thus we are led to the hypothesis of Molecular Vortices.

This hypothesis, besides the principles already enunciated, of the mutual transformation of heat and motive power in homogeneous substances, leads to the following special conclusion respecting the

RELATION BETWEEN TEMPERATURE AND ACTUAL HEAT:—

When the temperature of a substance, as measured by a perfect-gas thermometer, rises by equal increments, the actual heat present in the substance rises also by equal increments:—

a principle expressed symbolically by the equation

$$Q=\mathfrak{k}(\tau-\kappa), \qquad (35.)$$

where Q is the actual heat in unity of weight of a substance, τ its temperature, measured from the absolute zero of gaseous tension, κ the temperature of absolute cold, measured from the same point, and $\mathfrak{k}$ the real specific heat of the substance, expressed in terms of motive power*.

The enunciation of this law was originally an anticipation of the results of experiment; for when it appeared, no experimental data existed by which its soundness could be tested.

Since then, however, one confirmation of this law has been afforded by the experiments of M. REGNAULT, showing that the specific heat of atmospheric air is sensibly constant at all temperatures and at all densities throughout a very great range; and another, by the experiments of Messrs. JOULE and THOMSON referred to in Proposition VI., on the thermic phenomena of gases rushing through small apertures, which not only verify the theoretical principle, but afford the means of computing approximately the position κ of the point of absolute cold on the thermometric scale.

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* The hypothesis of MAYER amounts to supposing that $\kappa=0$, or that the zero of gaseous tension coincides with the point of absolute cold.

According to this relation between temperature and heat, every isothermal curve on a diagram of energy is also a curve of equal temperature. The isothermal curve, for example, corresponding to a constant quantity of actual heat, Q, corresponds also to a constant absolute temperature,

$$\tau = \frac{Q}{\mathfrak{k}} + \varkappa. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (36.)$$

The curve of absolute cold is that of the absolute temperature $\varkappa$.

Any series of isothermal curves at intervals corresponding to equal differences of heat, correspond to a series of equidistant temperatures.

Hence we deduce

Proposition XII.—Theorem. *Everything that has been predicated, in the propositions of the preceding articles, of the mutual proportions of quantities of actual heat and their differences, may be predicated also of the mutual proportions of temperatures as measured from the point of absolute cold, and their differences.*

The symbolical expression of this theorem is, that in all the equations of the preceding sections, we may make the following substitutions :—

$$\frac{Q_2}{Q_1} = \frac{\tau_2 - \varkappa}{\tau_1 - \varkappa}; \quad \frac{(\Delta, \delta, \text{ or } d)Q}{Q} = \frac{(\Delta, \delta, \text{ or } d)\tau}{\tau - \varkappa}. \quad . \quad . \quad . \quad . \qquad (36\text{ A.})$$

This theorem is not, like those which have preceded it, the consequence of a set of definitions. It is a law known by induction from experiment, aided by a hypothesis or conjecture with the results of which those of experiment have been found to agree.

It is true that the theorem itself might have been stated in the form of a definition of degrees of temperature ; but then induction from experiment would still have been required, to prove that temperature, as measured in the usual way, agrees with the definition.

By substituting symbols according to the above theorem, and making

$$\varphi.Q = f.\tau,$$

the general equation of the expansive action of heat is made to take the following form :—

$$\Delta.\Psi = \Delta.H - \int P dV = \Delta Q + \Delta.S = \mathfrak{k}.\Delta\tau + \Delta f.\tau + \int\left\{(\tau - \varkappa)\frac{dP}{d\tau} - P\right\}.dV, \quad . \qquad (37.)$$

which agrees with the equation deduced directly from the hypothesis of molecular vortices, if we admit that

$$\left.\begin{array}{ll} & f.\tau = \mathfrak{k}N\varkappa\left(\text{hyp. log } \tau + \frac{\varkappa}{\tau}\right) \\ \text{and consequently} & f'.\tau = \mathfrak{k}N.\left(\frac{\varkappa}{\tau} - \frac{\varkappa^2}{\tau^2}\right). \quad . \quad . \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (37\text{ A.})$$

The differential form of equation (37.) is

$$d.\Psi = d.H - PdV = dQ + d.S = K_V d\tau + \left\{(\tau - \varkappa)\frac{dP}{d\tau} - P\right\}dV, \quad . \quad . \quad . \qquad (38.)$$

where $$K_V=\mathfrak{k}+f'.\tau+(\tau-\varkappa)\int\frac{d^2P}{d\tau^2}.dV.$$

The expression for the Thermo-dynamic function denoted by F takes the form

$$F=\int\frac{1+\frac{1}{\mathfrak{k}}.f'.\tau}{\tau-\varkappa}.d\tau+\frac{1}{\mathfrak{k}}\int\frac{dP}{d\tau}.dV; \quad \ldots\ldots\ldots \quad (39.)$$

but a more convenient thermo-dynamic function, bearing the same relation to temperature as reckoned from the point of absolute cold, which the function F does to actual heat, is formed by multiplying the latter by the real specific heat $\mathfrak{k}$, thus :—

$$\Phi=\mathfrak{k}F=\int\frac{\mathfrak{k}+f'.\tau}{\tau-\varkappa}d\tau+\int\frac{dP}{d\tau}dV, \quad \ldots\ldots\ldots \quad (40.)$$

which, being introduced into the general equation, transforms it to

$$\Delta.\Psi=\int(\tau-\varkappa)d\Phi-\int PdV. \quad \ldots\ldots\ldots \quad (40\text{ A.})$$

(33.) *Of the Numerical Computation of the Efficiency of Air-Engines, with or without a perfect Regenerator.*

The relation between temperature and heat being known, the preceding propositions can be applied to determine the efficiency, and other circumstances relative to the working of Thermo-dynamic engines. To exemplify this application of the theory, let the substance working the engine be atmospheric air, and let the real indicator-diagram be such as to develope the maximum efficiency between two given absolute temperatures τ_1 and τ_2, being a quadrilateral, as in fig. 19, of which two sides are portions of the isothermal curves of those temperatures, and the other two, portions of a pair of curves of equal transmission, of such a form as may be best suited to the easy working of the engine. Should these curves be curves of no transmission, a regenerator may be dispensed with. In every other case a regenerator is necessary, to prevent waste of heat; and for the present its action will be assumed to be perfect, as the loss which occurs from its imperfect action cannot be ascertained except by direct experiment.

In this investigation it is unnecessary to use formulæ of minute accuracy; and for practical purposes, those will be found sufficient which treat air as a perfect gas, whose thermometric zero of pressure coincides with the point of absolute cold, viz.—

$$\left.\begin{array}{l}272°\tfrac{1}{2}\text{ Centigrade, or}\\ 490°\tfrac{1}{2}\text{ Fahrenheit,}\end{array}\right\}\text{below melting ice};*$$

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* This estimate of the position of the point of absolute cold is to be considered as merely approximate, recent experiments and calculations having shown that it may possibly be too high by about 1½° Centigrade. It is, however, sufficiently correct for all practical purposes.—W. J. M. R., June 1854.

whose real specific heat is equal to its specific heat at constant volume, being

$$\mathfrak{k}=\mathrm{K_V}=\begin{cases}234{\cdot}6 \text{ feet of fall per Centigrade degree, or}\\ 130{\cdot}3 \text{ feet of fall per degree of Fahrenheit;}\end{cases}$$

whose specific heat at constant pressure (as determined by M. Regnault) is 0·238 × the specific heat of liquid water, or

$$\mathrm{K_P}=\begin{cases}330{\cdot}8 \text{ feet of fall per Centigrade degree, or}\\ 183{\cdot}8 \text{ feet of fall per degree of Fahrenheit;}\end{cases}$$

the ratio of these two quantities being

$$\frac{\mathrm{K_P}}{\mathrm{K_V}}=1+\mathrm{N}=1{\cdot}41,$$

as calculated from the velocity of sound.

The volume occupied by an avoirdupois pound of air, at the temperature of melting ice, under the pressure of one pound on the square foot, as calculated from the experiments of M. Regnault, is

$$\mathrm{P_0V_0}=26214{\cdot}4 \text{ cubic feet.}$$

This represents also the length in feet of a column of air of uniform density and sectional area, whose weight is equal to its elastic pressure on the area of its section at the temperature of melting ice.

It will be found convenient, in expressing the temperature, as measured from the point of absolute cold, to make the following substitution:—

$$\tau-\varkappa=\mathrm{T}+\mathrm{T_0}, \quad \ldots\ldots\ldots \quad (41.)$$

where T represents the temperature as measured on the ordinary scale from the temperature of melting ice, and T_0 the height of the temperature of melting ice above the point of absolute cold, as already stated.

Then we have

$$\mathrm{N}\mathfrak{k}=\frac{\mathrm{P_0V_0}}{\mathrm{T_0}}. \quad \ldots\ldots\ldots \quad (41\ \text{A.})$$

According to these data, the equation of the isothermal curve of air for any temperature T is

$$\mathrm{PV}=\mathrm{P_0V_0}.\frac{\mathrm{T}+\mathrm{T_0}}{\mathrm{T_0}}=\mathrm{N}\mathfrak{k}(\mathrm{T}+\mathrm{T_0}). \quad \ldots\ldots \quad (42.)$$

The thermo-dynamic functions are—

$$\left.\begin{array}{l}\text{for quantities of actual heat,}\quad \mathrm{F}=\text{hyp. log Q}+\text{N hyp. log V};\\ \text{for temperatures,}\quad \Phi=\mathfrak{k}\mathrm{F}+\text{constant}=\mathrm{K_V}\{\text{hyp. log }(\mathrm{T}+\mathrm{T_0})+\text{N hyp. log V}\}\\ \qquad =\mathrm{K_V}\ \text{hyp. log }(\mathrm{T}+\mathrm{T_0})+\frac{\mathrm{P_0V_0}}{\mathrm{T_0}}.\text{hyp. log V};\end{array}\right\}\ (42\ \text{A.})$$

consequently the equation of any curve of no transmission is

$$\left.\begin{array}{c}\Phi=\text{constant; otherwise}\\ (T+T_0).V^N=\text{const.; or } P.V^{1+N}=\text{const.; or}\\ (T+T_0).P^{-\frac{N}{1+N}}=\text{constant;}\end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (43.)$$

in which $N=0{\cdot}41$, $1+N=1{\cdot}41$, $\frac{N}{1+N}=0{\cdot}2908$.

The maximum possible efficiency between any two temperatures T_1 and T_2 is given by the universal formula,

$$\frac{E}{H_1}=\frac{H_1-H_2}{H_1}=\frac{T_1-T_2}{T_1+T_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (44.)$$

The latent heat of expansion of unity of weight of air at a given constant temperature T_1, from the volume V_A to the volume V_B, is sensibly equivalent simply to the expansive power developed, being given by the following formula :—

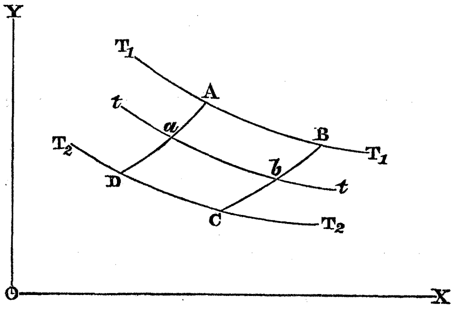
$$H_1=(T_1+T_0).(\Phi_B-\Phi_A)=P_0V_0.\frac{T_1+T_0}{T_0}.\text{hyp. log}\,\frac{V_B}{V_A}=\int_{V_A}^{V_B}PdV. \quad . \quad . \quad (45.)$$

Let V_a and V_b be the volumes corresponding to the points at which any isothermal curve intersects a given pair of curves of no transmission, or of equal transmission; then the ratio of these volumes,

$$\frac{V_b}{V_a}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (46.)$$

is constant for every such pair of points on the given pair of curves; because the difference of the thermo-dynamic functions, which is proportional to the logarithm of this ratio, is constant.

Fig. 19 A.



Hence, if in fig. 19 A, two isothermal curves, T_1T_1, T_2T_2, be the upper and lower boundaries of an indicator-diagram of maximum energy for an air-engine, A*a*D an arbitrary curve bounding the diagram at one side, and B the other limit of the expansion at the higher temperature; the fourth boundary, being a curve of equal transmission to A*a*D, may be described by this construction; draw any isothermal curve *tt* cutting A*a*D in *a*, and make

$$V_A:V_B::V_a:V_b, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47.)$$

then will *b* be a point in the curve sought, B*b*C.

Suppose, for example, that the form assumed for A*a*D is a hyperbola, concave towards OY, and having the following equation,—

$$P_a = \frac{\alpha}{\beta - V_a}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47 \text{ A.})$$

in which α and β are two arbitrary constants; and let the ratio $\frac{V_B}{V_A} = r$.

Then must the curve B*b*C be another hyperbola concave towards OY, having for its equation

$$P_b = \frac{\alpha}{r\beta - V_b}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47 \text{ B.})$$

The total expenditure of heat, per pound of air per stroke, in a perfect air-engine, is the latent heat of expansion from V_A to V_B, given by equation (45.).

The heat to be abstracted by refrigeration is the latent heat of compression from V_C to V_D; and is found by substituting in the same equation, the lower temperature T_2 for the higher temperature T_1.

The indicated work, per pound of air per stroke, being the difference between those two quantities, is found by multiplying the range of temperature by the difference of the thermo-dynamic functions Φ for the curves AD, BC, or by multiplying the latent heat of expansion by the efficiency, and has the following value:—

$$E = H_1 - H_2 = (T_1 - T_2).(\Phi_B - \Phi_A) = P_0V_0.\frac{T_1 - T_2}{T_0}.\text{hyp. log}\,\frac{V_B}{V_A}. \quad . \quad . \quad . \quad (48.)$$

The heat alternately stored up and given out by the regenerator (supposing it to work perfectly) is to be computed as follows. Let the arbitrary manner in which volume is made to vary with temperature, on either of the curves D*a*A, C*b*B, be expressed by an equation

$$V = \Psi.T,$$

then the thermo-dynamic function Φ takes the form

$$\Phi = K_V\,\text{hyp. log}\,(T + T_0) + \frac{P_0V_0}{T_0}\,\text{hyp. log}\,\Psi.T\,;$$

and the total heat stored up and given out, per pound of air per stroke, is

$$\int_{T_2}^{T_1}(T + T_0)\frac{d.\Phi}{dT}dT = K_V(T_1 - T_2) + \frac{P_0V_0}{T_0}\int_{T_2}^{T_1}\frac{(T + T_0)\Psi'.T}{\Psi.T}dT. \quad . \quad . \quad . \quad . \quad (49.)$$

For example, if, as before,

$$P_a = \frac{\alpha}{\beta - V_a}$$

be the equation of the curve DA, then

$$V_a = \frac{\beta(T + T_0)}{T + T_0\left(1 + \frac{\alpha}{P_0V_0}\right)},$$

and the heat stored up, per pound of air per stroke, is

$$K_V(T_1-T_2)+\alpha.\text{hyp. log}\left\{\frac{T_1+T_0\left(1+\frac{\alpha}{P_0V_0}\right)}{T_2+T_0\left(1+\frac{\alpha}{P_0V_0}\right)}\right\} \quad . \quad . \quad . \quad . \quad . \quad (49\text{ A.})$$

(33 A.) *Numerical Examples.*

To illustrate the use of these formulæ, let us take the following example:—

Temperature of receiving heat, $T_1=343^{\circ}\cdot 3$ Centigrade.

$T_1+T_0=615^{\circ}\cdot 8$ Centigrade.

Temperature of emitting heat, $T_2=\ 35^{\circ}\cdot 4$ Centigrade.

$T_2+T_0=307^{\circ}\cdot 9$ Centigrade.

Ratio of Effective Expansion, $\frac{V_B}{V_A}=\frac{V_C}{V_D}=\frac{P_A}{P_B}=\frac{P_D}{P_C}=\frac{3}{2}$.

From these data are computed the following results:—

Maximum Efficiency,—

$$\frac{307^{\circ}\cdot 9}{615^{\circ}\cdot 8}=\frac{1}{2}.$$

Heat expended, or latent heat of expansion,—

$H_1=P_0V_0\times\frac{615.8}{272\cdot 5}\times\text{hyp. log}\frac{3}{2}=24020$ foot-pounds per pound of working air per stroke.

Heat abstracted by refrigeration,—

$H_2=P_0V_0\times\frac{307\cdot 9}{272\cdot 5}\times\text{hyp. log}\frac{3}{2}=12010$ foot-pounds per pound of working air per stroke.

Work performed,—

$H_1-H_2=P_0V_0\times\frac{307\cdot 9}{272\cdot 5}\times\text{hyp. log}\frac{3}{2}=12010$ foot-pounds per pound of working air per stroke.

To exemplify the computation of the heat stored by a perfect regenerator, let it be supposed, in the first place, that the indicator-diagram resembles ABC′D′ in fig. 19, where the curves of equal transmission are represented by a pair of lines of constant pressure. Then the heat to be stored is

$K_P(T_1-T_2)=101{,}800$ foot-pounds per pound of working air per stroke.

Secondly, let the diagram resemble ABCD in fig. 19, where the curves of equal transmission are represented by a pair of lines of constant volume. Then the heat to be stored is

$K_V(T_1-T_2)=72{,}233$ foot-pounds per pound of working air per stroke.

Thirdly, let the curves of equal transmission, as in a recent example, be hyperbolas, concave towards OY, and let the arbitrary constant α have the following value,—

$\alpha=P_0V_0=26214\cdot 4$ foot-pounds;

then the heat to be stored, according to equation (49 A.), is

$$72{,}233+26214{\cdot}4\times\text{hyp. log}\,\frac{888{\cdot}3}{580{\cdot}4}=72{,}233+11{,}157$$

$$=83{,}390 \text{ foot-pounds per pound of working air per stroke.}$$

The large proportions borne by these quantities to the whole heat expended, show the importance of efficient action in the regenerator to economy of fuel. The quantity of heat to be stored, however, becomes smaller, as the curves of equal transmission approach those of no transmission, for which it is null. The additional expansion requisite in this last case is found by the following computation,—

$$\frac{V_C}{V_B}=\frac{V_D}{V_A}=\left(\frac{T_1+T_0}{T_2+T_0}\right)^{\frac{1}{N}}=2^{\frac{1}{0{\cdot}41}}=5{\cdot}423,$$

the result of which shows the great additional bulk of engine required, in order to obtain the maximum efficiency without a regenerator.

Supposing one pound of coal, by its combustion, to be capable of communicating heat to the air working in an engine corresponding with the above example, to an amount equivalent to

6,000,000 foot-pounds

(an amount which would evaporate about 7 lbs. of water), the maximum theoretical duty of one pound of such coal in such an engine, without waste of heat or power, would be

3,000,000 foot-pounds,

corresponding to

$\frac{3{,}000{,}000}{12{,}010}=249$ strokes of a pound of working air, with the effective expansion $\frac{3}{2}$.

The deductions to be made from this result in practice must of course be determined by experience.

Section V.—PROPOSITIONS RELATIVE TO A HETEROGENEOUS MASS, OR AGGREGATE, ESPECIALLY IN VAPOUR-ENGINES.

(34.) The Heterogeneous Mass to which the present investigation refers, is to be understood to mean an Aggregate of portions of different ingredients, in which each ingredient occupies a space, or a number of spaces, of sensible magnitude.

The results arrived at are not applicable to mixtures in which there is a complete mutual diffusion of the molecules of the ingredients, so that every space of appreciable magnitude contains every ingredient in a fixed proportion. A mixture of this kind, when the relations between its pressure, volume, heat, and temperature are known, may be treated, so far as regards the expansive action of heat, as a homogeneous substance.

The ingredients of an aggregate are heterogeneous with respect to the expansive action of heat, when either their specific heats, or their volumes for unity of weight at a given pressure and temperature, or both these classes of quantities, are different.

Hence a portion of a liquid, and a portion of its vapour, enclosed in the same vessel, though chemically identical and mutually transformable, are heterogeneous, and are to be treated as an aggregate, with respect to the expansive action of heat.

M. CLAUSIUS and Professor WILLIAM THOMSON have applied their formulæ to the aggregate composed of a liquid and its vapour, and have pointed out certain relations which must exist between the pressure and density of a liquid and its vapour, and the latent heat of evaporation.

I shall now apply the geometrical method of this paper to the theory of the expansive action of heat in an aggregate, especially that consisting of a liquid and its vapour. The total volumes are, for the present, supposed not to be large enough to exhibit any appreciable differences of pressure due to gravitation.

(35.) PROPOSITION XIII.—THEOREM. *In an aggregate in equilibrio, the pressure of each ingredient must be the same ; and the quantity of heat in unity of weight of each ingredient must be inversely proportional to its real specific heat ; that is to say, the temperature must be equal.*

The following is the symbolical expression of this theorem, with certain conclusions to which it leads.

Let $\tau-\varkappa$ be the common temperature of the ingredients, as measured from the point of absolute cold ;

P their common pressure ,

n_1, n_2, n_3, &c. their proportions by weight, in unity of weight of the aggregate ;

v_1, v_2, v_3, &c. the respective volumes of unity of weight of the several ingredients ;

V the volume of unity of weight of the aggregate ;

q_1, q_2, q_3, &c. the respective quantities of actual heat in unity of weight of the several ingredients ;

$\mathfrak{k}_1, \mathfrak{k}_2, \mathfrak{k}_3$, &c. their respective real specific heats ;

Q the quantity of heat in unity of weight of the aggregate ;

Φ a thermo-dynamic function for the aggregate.

Then these quantities are connected by the following equations :—

$$\Sigma.n=1. \qquad (50.)$$

$$\mathrm{V}=\Sigma.nv. \qquad (51.)$$

$$\tau-\varkappa=\frac{q_1}{\mathfrak{k}_1}=\frac{q_2}{\mathfrak{k}_2}=\frac{q_3}{\mathfrak{k}_3}=\text{ \&c.} \qquad (52.)$$

$$\mathrm{Q}=\Sigma.nq=(\tau-\varkappa).\Sigma.n\mathfrak{k}. \qquad (53.)$$

$$\Phi=\int\frac{\Sigma.n(\mathfrak{k}+f'.\tau)}{\tau-\varkappa}.d\tau+\int\frac{d\mathrm{P}}{d\tau}.d\mathrm{V}. \qquad (54.)$$

It is evident that all these equations hold whether the proportions of the ingredients n_1, &c. are constant, as in an aggregate of chemically distinct substances, or variable, as in the aggregate of a liquid and its vapour.

Let δH be the heat which disappears in consequence of a small expansion of the aggregate at constant temperature represented by

$$\delta V = \Sigma . \delta u, \quad \ldots \ldots \ldots \quad (55.)$$

δu representing any one of the parts arising from the changes undergone by the different ingredients, of which the whole expansion of the aggregate, δV, is made up. Then

$$\delta H = \Sigma \left\{ (\tau - \varkappa) \frac{dP}{d\tau} . \delta u \right\}; \quad \ldots \ldots \ldots \quad (56.)$$

but the pressure P is the same for every ingredient, as well as the temperature; therefore the factor $(\tau - \varkappa) \frac{dP}{d\tau}$ is the same for every ingredient, and consequently for the whole aggregate; that is to say,

$$\delta H = (\tau - \varkappa) \frac{dP}{d\tau} . \delta V = (\tau - \varkappa) \delta \Phi. \quad \ldots \ldots \quad (57.)$$

This equation shows, that the relation of *temperature* to the mutual transformation of heat and expansive power is the same in an aggregate as in a homogeneous substance.

Consequently, if we define *Isothermal Curves* for an Aggregate to be *Curves of Constant Temperature,* we arrive at the following conclusion :—

PROPOSITION XIV.—THEOREM. *Isothermal curves on the diagram of energy of an Aggregate, have the same properties, with reference to the mutual transformation of Heat and Expansive Power, with those on the diagram of energy of a homogeneous substance.*

It is unnecessary to enunciate separately a similar proposition for curves of no transmission; for the demonstration of Proposition I., on which all their properties depend, is evidently applicable to an aggregate constituted in any manner.

Hence it appears, that if the isothermal curves for an aggregate be drawn according to the above definition, all the propositions proved in this paper respecting homogeneous substances become true of the aggregate.

(36.) PROPOSITION XV.—THEOREM. *Every Isothermal line for an aggregate of a liquid and its vapour, is a straight line of equal pressure, from the volume corresponding to complete liquefaction to the volume corresponding to complete evaporation.*

This is a fact known by experiment. The Theorem is equivalent to a statement, that the pressure of a liquid and its vapour in contact with each other, is a function of the temperature only.

Corollary.—THEOREM. *At any given temperature, the volume of an aggregate of liquid and vapour is arbitrary between and up to the limits of total liquefaction and total evaporation.*

To express this symbolically, let P be the pressure of an aggregate of liquid and vapour corresponding to the absolute temperature τ; and, unity of weight being the quantity of the aggregate under consideration, let v be the volume corresponding to complete liquefaction, v' that corresponding to complete evaporation, and V the actual volume at any time; let n be the proportion of liquid, and $1-n$ that of vapour, corresponding to the aggregate volume V; then

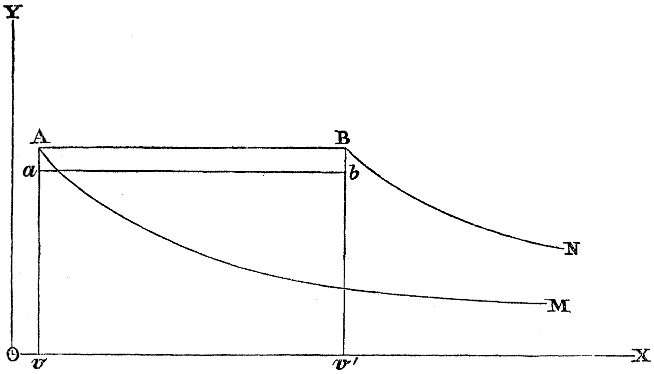
$$V=nv+(1-n)v', \quad \ldots \ldots \ldots \quad (58.)$$

and V may have any value not less than v nor greater than v', while P and τ remain constant; the proportion of liquid, n, being regulated according to the foregoing equation.

(37.) PROPOSITION XVI.—PROBLEM. *The density of a liquid and of its vapour, when in contact at a given temperature, being given, and the isothermal lines of the aggregate; it is required to determine the latent heat of evaporation of unity of weight of the fluid.*

(Solution.) The densities of the liquid and of its vapour, are respectively the reciprocals of the volumes of total liquefaction and total evaporation of unity of weight, above-mentioned. In fig. 20, let the abscissæ Ov, Ov' represent these volumes, and the equal ordinates, vA, v'B, the pressure corresponding to the given temperature; so that AB parallel to OX is the isothermal line of the aggregate for that temperature. Suppose two curves of no transmission, AM, BN, to be drawn from A and B respectively, and indefinitely prolonged towards X; then the indefinitely-prolonged area MABN represents the mechanical equivalent of the latent heat sought; and this area is to be computed in the following manner. Draw a second isothermal line ab indefinitely near to AB, at an interval corresponding to the indefinitely-small difference of temperature $d\tau$; then, ultimately,

Fig. 20.



$$d\tau : \tau-\kappa :: \text{area } ABba : \text{area } MABN;$$

or, symbolically,

$$L=\text{latent heat of evaporation}=(\tau-\kappa)\frac{dP}{d\tau}(v'-v). \quad \ldots \quad (59.)$$

This is simply the application of Propositions I. and II. to the aggregate of a liquid and its vapour, *mutatis mutandis*.

(*Remarks.*)—The existence of a necessary relation between the density, pressure, and temperature of a vapour and its liquid in contact, and the latent heat of evaporation, was first shown by CARNÔT. If for $\tau-\kappa$ in the preceding equation be substituted, according to Professor THOMSON's notation, $\frac{J}{\mu}$, J being "JOULE's equivalent" and μ "CARNÔT's function," the equation is transformed into that deduced by Messrs. CLAUSIUS and THOMSON from the combination of CARNÔT's theory with the law of the mechanical convertibility of heat.

(38.) *Corollary.*—The volume occupied by unity of weight of vapour at saturation may be computed from its latent heat of evaporation by means of the inverse formula,—

$$v'-v=\frac{L}{(\tau-\kappa)\frac{dP}{d\tau}}; \quad \ldots\ldots\ldots\ldots \quad (60.)$$

the latent heat, L, being of course always stated in units of motive power.

The want of satisfactory experiments on the density of vapours of any kind, has hitherto prevented the use of the direct formula (59.).

It is otherwise, however, with the inverse formula (60.), at all events in the case of steam; for, so far as we are yet able to judge, the experiments of M. REGNAULT have determined the latent heat of evaporation of water with accuracy throughout a long range of temperature.

M. CLAUSIUS, applying to those experimental data a formula founded on the supposition of MAYER (that is to say, similar to the above, with the exception that κ is supposed$=0$), has calculated the densities of steam at certain temperatures, so as to show how much they exceed the densities calculated from the pressures and temperatures, on the supposition that steam is a perfect gas. From these calculations he concludes, that either the supposition of MAYER is erroneous, or steam deviates very much, at high densities, from the condition of a perfect gas.

In the following table, the value of κ is supposed to be $2^{\circ}\cdot 1$ Centigrade; and use has been made of the formula for calculating the pressure of steam and other vapours at saturation, first published in the Edinburgh New Philosophical Journal for July 1849, viz.—

$$\log P=\alpha-\frac{\beta}{\tau}-\frac{\gamma}{\tau^2}. \quad \ldots\ldots\ldots\ldots \quad (61.)$$

This table exhibits, side by side, the volume in cubic feet occupied by one pound avoirdupois of steam, at every twentieth Centigrade degree from -20° to $+260^{\circ}$ (that is, from -4° to $+500^{\circ}$ Fahrenheit):—first, as extracted from a table for computing the power of steam-engines, in the Transactions of the Royal Society of Edinburgh, vol. xx., which was calculated on the supposition that steam is a perfect gas; and secondly, as computed by equation (60.) from the latent heat of steam as determined by M. REGNAULT. The excess of the former quantity above the latter is also given in each case, with its ratio to the second value of the volume.

For convenience' sake, a column is added containing the pressures of steam corresponding to the temperatures in the table, in pounds per square foot.

Table of Computed Volumes of 1 lb. avoirdupois of Steam.

Temperature.		Volume supposed a Perfect Gas.	Volume computed from Latent Heat.	Difference.	Ratio of difference to lesser value of volume.	Pressure.
Fahrenheit.	Centigrade.					
Deg.	Deg.	Cubic feet.	Cubic feet.	Cubic feet.		lb. per square foot.
− 4	−20	15757	15718	39	0·0025	2·4799
+32	0	3390·4	3377·2	13·2	0·0039	12·431
68	+20	936·81	934·50	2·31	0·0025	48·265
104	40	314·88	313·56	1·32	0·0042	153·34
140	60	123·65	122·63	1·02	0·0083	415·33
176	80	55·05	54·19	0·86	0·0158	988·67
212	100	27·166	26·478	0·688	0·0260	2116·4
248	120	14·596	14·076	0·520	0·0369	4149·3
284	140	8·420	8·004	0·416	0·0502	7557·0
320	160	5·158	4·838	0·320	0·0661	12931
356	180	3·326	3·071	0·255	0·0830	20979
392	200	2·241	2·033	0·208	0·1023	32512
428	220	1·568	1·396	0·172	0·1232	48425
464	240	1·134	0·990	0·144	0·1455	69680
500	260	0·843	0·722	0·121	0·1676	97275
Col. (1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)

The fourth column of this table could easily be extended and filled up, so as to replace the column of volumes of steam for every fifth Centigrade degree in the table previously published; but it would be unadvisable to do so at present, for the following reasons:—

First, the value of the constant κ is still uncertain*.

Secondly, the results of M. Regnault's direct experiments, on the density of steam and other vapours, may soon be expected to appear.

Thirdly, it is possible that the values of the latent heat of evaporation of water, as deduced from M. Regnault's experiments, may still have to undergo some correction; because, according to the theoretical definition of the latent heat of evaporation, the liquid is supposed to be under the pressure of an atmosphere of its own vapour, which atmosphere, as it increases in bulk, performs work of some kind, such as lifting a piston; whereas, in M. Regnault's experiments, the water is pressed by an atmosphere of mingled steam and air, whose united pressure is that corresponding to the temperature of internal ebullition of the water; so that the pressure of the steam alone on the surface of the water, which regulates the superficial evaporation, may be less than the maximum pressure corresponding to the temperature of ebullition; and this steam, moreover, has no mechanical work to perform except to propel itself along the passage leading to the calorimeter, and to agitate the water in the latter vessel. Under these circumstances, it is possible, though by no means certain, that the latent

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* It is probable that κ may be found to be inappreciably small; in which case, the numbers in column (4.) will have to be diminished to an extent varying from $\frac{1}{150}$th to $\frac{1}{300}$th of their amount.

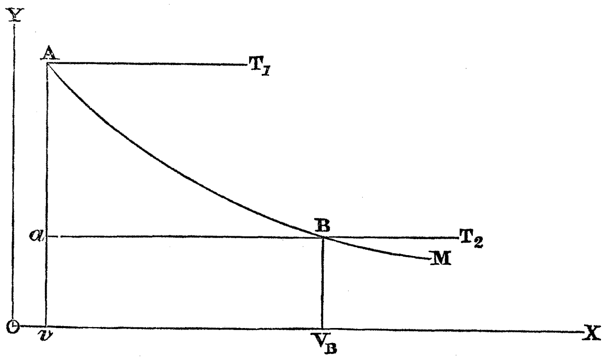
heat of evaporation of water, as deduced from M. Regnault's experiments, may be somewhat smaller than that which corresponds to the theoretical definition, especially at high pressures ; and a doubt arises as to the precise applicability of the formulæ (59.) and (60.) to those experimental results, which cannot be solved except by direct experiments on the density of steam.

Notwithstanding this doubt, however, the preceding table must be regarded as adding a reason to those already known, for believing that saturated steam of high density deviates considerably from the laws of the perfectly gaseous condition*.

(39.) Proposition XVII.—Problem. *The isothermal lines for a liquid and its vapour, and the apparent specific heat of the liquid at all temperatures being given, and the expansion of the liquid by heat being treated as inappreciably small:—to determine a curve of no transmission for the aggregate, passing through a given point on the ordinate whose distance from the origin approximately represents the volume of the liquid.*

(Solution.) In fig. 21, let Ov represent the volume of the liquid, assumed to be approximately constant for all temperatures under consideration ; let vA be an ordinate parallel to OY, and let the heat consumed by the liquid in passing from the temperature corresponding to any point on this ordinate to that corresponding to any other point, be known ; let the isothermal lines for the aggregate of liquid and vapour, all of which are straight lines of equal pressure parallel to OX, such as AT$_1$, aBT$_2$, be known. Then to draw a curve of no transmission through any point A on the ordinate vA, the same process must be followed as in Proposition VIII.

Fig. 21.



To apply to this case the symbolical representation of Proposition VIII., viz. equation (21.), let τ_1 be the absolute temperature corresponding to the point A (that is, to the isothermal line AT$_1$) ; τ_2 that corresponding to any lower isothermal line aBT$_2$; V$_B$ the volume of the aggregate of liquid and vapour, corresponding to the point B

---

* Evidence in favour of this opinion is afforded by the experiments recorded by Mr. C. W. Siemens (Civil Engineer and Architect's Journal). A remarkable cause, however, of uncertainty in all such experiments, has lately been investigated by Professor Magnus (Poggendorff's Annalen, 1853, No. 8), viz. a power which solid bodies have of condensing, by attraction on their surfaces, appreciable quantities of gases.

where the curve sought, AM, intersects the latter isothermal line; K_L the apparent specific heat of the liquid;—then making the proper substitutions of the symbols of temperature for those of heat, and observing that the operation

$$\int_{V_A}^{V_B} dV$$

is in this case equivalent to multiplication by V_B-v, we have

$$\Delta\Phi=\frac{dP}{d\tau}(V_B-v)(\text{for } \tau=\tau_2)=\int_{\tau_2}^{\tau_1}\frac{K_L}{\tau-\kappa}d\tau, \quad . \quad . \quad . \quad . \quad . \quad . \quad (62.)$$

being an equation between two expressions for the difference between the thermodynamic functions Φ for the curve AB, and for that which passes through a.

If the specific heat of the liquid is approximately constant, this equation becomes

$$\Delta\Phi=\frac{dP}{d\tau}(V_B-v)(\text{for } \tau=\tau_2)=K_L \text{ hyp. log} \frac{\tau_1-\kappa}{\tau_2-\kappa}. \quad . \quad . \quad . \quad . \quad . \quad (63.)$$

(40.) *Corollary*.—PROBLEM. *The same data being given as in the preceding problem, and the expansion of the liquid by heat neglected, a mass of liquid, having been raised from the absolute temperature τ_2 to the absolute temperature τ_1, is supposed to be allowed to evaporate partially, under pressure, without receiving or emitting heat, until its temperature falls again to τ_2, at which temperature it is liquefied under constant pressure by refrigeration: it is required to find the power developed.*

(Solution.) The power developed is represented by the area of the three-sided diagram of energy in fig. 21, ABa; that is to say, by

$$\int_{\tau_2}^{\tau_1}(V-v)\frac{dP}{d\tau}.d\tau=\iint_{\tau_2}^{\tau_1}\frac{K_L}{\tau-\kappa}d\tau^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (64.)$$

which, if K_L is nearly constant, becomes

$$K_L\int_{\tau_2}^{\tau_1}\text{hyp. log}\frac{\tau_1-\kappa}{\tau-\kappa}.d\tau=K_L\left\{(\tau_1-\kappa)-(\tau_2-\kappa).\left(1+\text{hyp. log}\frac{\tau_1-\kappa}{\tau_2-\kappa}\right)\right\}. \quad . \quad (65.)$$

(41.) *Numerical Example.*

Let one pound avoirdupois of water be raised, in the liquid state, from $T_2=40°$ Centigrade, to $T_1=140°$ Centigrade. Then

$$\tau_1-\kappa=T_1+T_0=140°+272\tfrac{1}{2}°=412\tfrac{1}{2}° \text{ Centigrade.}$$

$$\tau_2-\kappa=T_2+T_0=\ 40°+272\tfrac{1}{2}°=312\tfrac{1}{2}° \text{ Centigrade.}$$

The mean apparent specific heat of liquid water between those temperatures is

$K_L=K_W$ (or JOULE's equivalent) $\times$ 1·006 = 1398 feet per Centigrade degree;

consequently the heat expended is equivalent to 139,800 foot-pounds.

The other numerical data are,—

$\frac{dP}{d\tau}$ at 40° Centigrade $=8{\cdot}2075$ lbs. per square foot, per Centigrade degree;

$v=$mean volume of 1 lb. of liquid water $=0{\cdot}017$ cubic foot, nearly.

Let it be required to find, in the first place, V_B, the volume to which the water must be allowed to expand by partial evaporation under pressure, in order that its temperature may fall to 40° Centigrade; and secondly, how much power will be developed in all, after the water has been totally reliquefied by refrigeration at constant pressure, at the temperature of 40°.

First, by the equation (63.),

$$\Delta\Phi=\frac{dP}{d\tau}(V_B-v)=1398\times\text{hyp. log}\,\frac{412\frac{1}{2}}{312\frac{1}{2}}=402{\cdot}624\,;$$

$$\text{divide by }\frac{dP}{d\tau}=8{\cdot}2075\,;\ \text{ then } V_B-v=49{\cdot}055 \text{ cubic feet.}$$

$$\text{add } v=\ \ 0{\cdot}017$$

Aggregate volume of water and steam at 40°, $V_B=49{\cdot}072$ cubic feet.

As the volume of one pound of steam at 40° Centigrade, according to the fourth column of the table in article (38.), is 313·56 cubic feet, it appears from this calculation that somewhat less than one-sixth of the water will evaporate.

Secondly, it appears, from equation (65.), that after the water has been restored to the liquid state by refrigeration at 40° Centigrade, the whole power developed, that is to say, the area AB*a*, will be

$$1398\text{ foot-pounds}\times\left\{412^{\circ}{\cdot}5-312^{\circ}{\cdot}5\left(1+\text{hyp. log}\,\frac{412{\cdot}5}{312{\cdot}5}\right)\right\}$$

$$=1398\text{ ft. lb.}\times10^{\circ}\text{ Centigrade}=13{,}980\text{ ft. lb.},$$

or one-tenth of the equivalent of the heat expended. The other nine-tenths constitute the heat abstracted during the reliquefaction at 40° Centigrade.

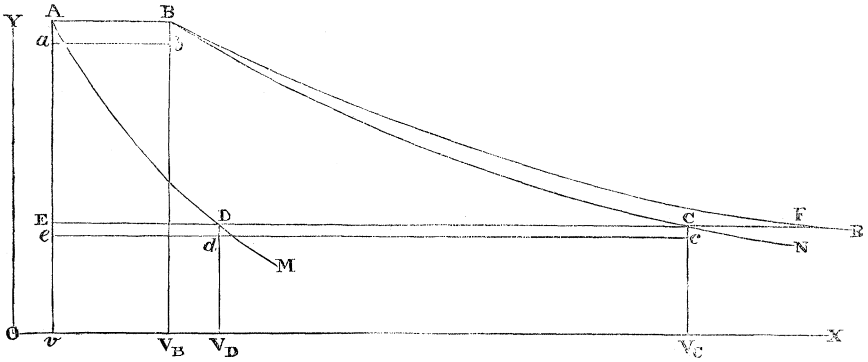
This calculation further shows, that in order that one pound of water and steam at 40° C. may be raised to 140° C. solely by compressing it into the liquid state, it must occupy at the commencement of the operation the volume $V_B=49{\cdot}072$ cubic feet; and that the power expended in the compression will be as follows:—

	Foot-pounds.
Area of the curvilinear triangle AB*a*, fig. 21, as already calculated	13,980
Area of the rectangle $aBV_Bv=P_2\,(V_B-v)=$	7,522
Total	21,502

(42.) PROPOSITION XVIII.—PROBLEM. *Having the same data as in the last proposition, it is required to draw a curve of no transmission through any point on the diagram of energy for the aggregate of a liquid and its vapour.*

(Solution.) In fig. 22, through the given point B draw the straight isothermal line AB corresponding to the absolute temperature τ_1, and cutting the ordinate corresponding to the volume of total liquefaction in A. Through A, according to the last proposition, draw the curve of no transmission, ADM. Let EDC be any other isothermal line, corresponding to the absolute temperature τ_2, and cutting the curve AM in D. Draw isothermal lines *ab*, *edc* at indefinitely small distances from AB, EDC respectively, corresponding to the same indefinitely small difference of temperature $\delta\tau$. Draw the ordinates $V_D dD$, $V_B bB$; then draw the ordinate $V_C cC$ at such a distance from $V_D dD$, that the indefinitely small rectangles DC*cd*, AB*ba* shall be equal. Then as the difference $\delta\tau$ is indefinitely diminished, C approximates indefinitely to a point on the required curve of no transmission, BN.

Fig. 22.



This is Proposition III. applied to aggregates, *mutatis mutandis.*

The symbolical representation of this proposition is as follows:—let P_1 and P_2 be the pressures of the aggregate of liquid and vapour corresponding respectively to the temperatures τ_1 and τ_2; then the following expressions for the difference between the thermo-dynamic functions Φ of the curves AM, BN are equal,

$$\Delta\Phi=\frac{dP_2}{d\tau}(V_C-V_D)=\frac{dP_1}{d\tau}(V_B-v) \qquad (66.)$$

(43.) *Corollary.* (*Absolute Maximum Efficiency of Vapour-Engines.*)

If the volume V_B be that corresponding to complete evaporation at the temperature τ_1, that is to say, if

$$V_B=v',$$

then the curve BCN will represent the mode of expansion under pressure, of vapour of saturation in working an engine, and will be defined by the equation

$$V_C-V_D=\frac{\frac{dP_1}{d\tau}(v'-v)}{\frac{dP_2}{d\tau}} \qquad (67.)$$

If in this equation be substituted the value of $v'-v$ in terms of the latent heat of evaporation at the higher temperature, given by equation (60.), it becomes

$$V_C-V_D=\frac{L_1}{(\tau_1-\varkappa)\frac{dP_2}{d\tau}}. \quad \dots\dots\dots \quad (68.)$$

In this case the diagram ABCD, fig. 22, is evidently that of a vapour-engine working with the absolute maximum of efficiency between the absolute temperatures τ_1 and τ_2. The heat expended at each single stroke, per unit of weight of fluid, is the latent heat of evaporation at the higher temperature, or L_1; the area of the diagram is given by the following equation,

$$E=(\tau_1-\tau_2)\Delta\Phi=\frac{\tau_1-\tau_2}{\tau_1-\varkappa}.L_1. \quad \dots\dots \quad (69.)$$

This is the mechanical power developed at each single stroke by a unit of weight of the substance employed. The efficiency is represented by

$$\frac{E}{L_1}=\frac{\tau_1-\tau_2}{\tau_1-\varkappa}, \quad \dots\dots\dots\dots \quad (70.)$$

being the expression for the maximum efficiency of thermo-dynamic engines in general.

The conditions of obtaining this efficiency are the following :—

First; that the elevation of temperature from τ_2 to τ_1, during the operation represented by the curve DA on the diagram, shall be produced entirely by compression. The volume at which this heating by compression must commence is given, according to Proposition XVII., by the following equation :—

$$V_D= v+\frac{1}{\frac{dP_2}{d\tau}}.K_L \text{ hyp. log } \frac{\tau_1-\varkappa}{\tau_2-\varkappa}. \quad \dots\dots \quad (71.)$$

Secondly; that the expansive working of the vapour shall be carried on until the temperature falls, by expansion alone, to its lower limit; that is to say, until the volume reaches the following value, obtained by adding together equations (68.) and (71.) :—

$$V_C=v+\frac{1}{\frac{dP_2}{d\tau}}.\left\{K_L \text{ hyp. log } \frac{\tau_1-\varkappa}{\tau_2-\varkappa}+\frac{L_1}{\tau_1-\varkappa}\right\}. \quad \dots\dots \quad (72.)$$

(44.) *Numerical example.*

To exemplify this numerically, let the same data be employed as in article (41.), the substance working being one pound avoirdupois of water. These data, with some additional data deduced from them, are given in the following table :—

	At upper limit of Actual Heat.	At lower limit of Actual Heat.
Temperature in Centigrade Degrees:—		
Above melting ice (T)	140°	40°
Above zero of gaseous tension (τ) . . .	414·6	314·6
Above absolute cold ($\tau-\kappa$)	412·5	312·5
Pressure in pounds per square foot (P)	7557	153·34
,, ,, per square inch	52·5	1·065
Initial Volume of saturated steam, $V_B = v'_1$ = . .	8·004 cubic feet per pound.	
Latent Heat of Evaporation:—		
In degrees, applied to one pound of liquid water	509°·1 Centigrade.	
In foot-pounds (L_1)	707,445·36.	

From these data are deduced the following results:—

Absolute Maximum Efficiency; $\frac{100}{412\cdot5} = 0\cdot2424$.

Duty of one pound of water; being the area of the diagram ABCD	171,484·75 ft. lb.
Volume at which the compression must commence; calculated as in art. (41.) . .	V_D = 49·1 cubic feet per pound.
Volume to which the Expansion must be carried; calculated by equation (72.) . .	V_C = 258·1 cubic feet per pound.
Ratio of Expansion	$= \frac{V_C}{V_B} = \frac{258\cdot1}{8\cdot004} = 32\cdot25$.

(45.) *Liquefaction of Vapour by Expansion under Pressure.*

In fig. 22, let the abscissæ of the curve BFR indicate the volumes corresponding to complete evaporation at the pressures denoted by its ordinates. For most known fluids, a curve of no transmission BCN, drawn from any point B of the curve of complete evaporation in the direction of X, falls within that curve; so that by expansion of saturated vapour under pressure, a portion in most cases will be liquefied.

To ascertain whether this will take place in any particular case, and to what extent, equation (60.), which gives the volume of unity of weight of saturated vapour at the temperature τ_2, is to be compared with equation (72.), which gives the volume at the same temperature of unity of weight of an aggregate of liquid and vapour, which has expanded under pressure from a state of complete evaporation at the temperature τ_1. The difference between the volumes given by these equations is as follows (neglecting, as usual, the expansibility in the liquid state):—

$$v'_2 - V_C = \frac{1}{\frac{dP_2}{d\tau}} \cdot \left\{ \frac{L_2}{\tau_2-\kappa} - \frac{L_1}{\tau_1-\kappa} - K_L . \text{hyp. log} \frac{\tau_1-\kappa}{\tau_2-\kappa} \right\} . \quad . \quad . \quad . \quad . \qquad (73.)$$

That this quantity is almost always positive appears from the following considerations. The latent heat of evaporation L is in general capable of being represented approximately by an expression of this form :

$$L = a - b(\tau - \varkappa). \quad \ldots \ldots \ldots \ldots \quad (74.)$$

(For water, $a = 796°$ Centigr. $\times K_W = 1{,}106{,}122$ ft. lb.; $b = 0{\cdot}695 \times K_W = 965{\cdot}772$ ft. lb. per Centigrade degree.)

Hence the second factor in equation (73.) is nearly equal to

$$\frac{a(\tau_1 - \tau_2)}{(\tau_1 - \varkappa).(\tau_2 - \varkappa)} - K_L . \text{hyp. log} \frac{\tau_1 - \varkappa}{\tau_2 - \varkappa}. \quad \ldots \ldots \ldots \quad (75.)$$

Now

$$\text{hyp. log} \frac{\tau_1 - \varkappa}{\tau_2 - \varkappa} < \frac{\tau_1 - \tau_2}{\tau_2 - \varkappa}.$$

Therefore the expression (75.) is positive so long as

$$\frac{a}{\tau_1 - \varkappa} \text{ exceeds } K_L, \text{ the specific heat of the liquid.} \quad \ldots \quad (75\text{ A.})$$

For Water, this condition is fulfilled for all temperatures lower than 523½° Centigrade (at which $\tau_1 - \varkappa = 796°$ Centigrade) ; and there is reason to believe that it is fulfilled also for other fluids at those temperatures at which their vapours can be used for any practical purpose.

To determine the proportion of the fluid which is liquefied by a given expansion under pressure, we have the following formula, deduced from equation (58.) :—

$$n = \frac{v'_2 - V_C}{v'_2 - v}. \quad \ldots \ldots \ldots \ldots \ldots \quad (76.)$$

As a numerical example, we may take the case of art. (44.), where saturated steam at 140° Centigrade is supposed to be expanded under pressure until its temperature falls to 40° Centigrade. The volume of one pound of water and steam at the end of the expansion has already been found to be

$$V_C = 258{\cdot}1 \text{ cubic feet.}$$

While, according to the table in article (38.), the volume of a pound of steam at that temperature is

$$v'_2 = 313{\cdot}56 \text{ cubic feet.}$$

Consequently the fraction liquefied by the expansion is

$$n = \frac{313{\cdot}56 - 258{\cdot}1}{313{\cdot}56 - 0{\cdot}016} = \frac{55{\cdot}46}{313{\cdot}544} = 0{\cdot}177.$$

This conclusion was arrived at contemporaneously and independently, by M. CLAUSIUS and myself, about four years since. Its accuracy was subsequently called in question, chiefly on the ground of experiments, which show that steam, after being expanded by being " wire-drawn," that is to say, by being allowed to escape through a narrow orifice, is super-heated, or at a higher temperature than that of liquefaction at the reduced pressure. Soon afterwards, however, Professor WILLIAM THOMSON proved that those experiments are not relevant against the conclusion in question, by showing the difference between the *free expansion* of an elastic fluid, in which all the power due to the expansion is expended in agitating the particles of the fluid, and is reconverted into heat, and the expansion of the same fluid *under a pressure equal to its own elasticity*, when the power developed is all communicated to external bodies, such, for example, as the piston of an engine.

The free expansion of a vapour will be considered in the sequel.

(46.) *Efficiency of a Vapour-Engine without heating by compression.*

The numerical example of article (44.) sufficiently illustrates the fact, that the strict fulfilment of the condition specified in article (43.), as necessary to the attainment of the absolute maximum of efficiency of a vapour-engine, is impossible in practice.

Let us consider, in the first place, the effect of dispensing with the process DA, during which the fluid is supposed to have its high temperature restored solely by compression.

The effect of this modification is evidently, to add to the heat expended, that which is necessary to elevate the temperature of the liquid from τ_2 to τ_1, and to add to the power developed an amount represented by the area ADE, fig. 22.

To express this symbolically, we have—

The Latent Heat of Evaporation at τ_1, as before . .	L_1	
The additional heat expended (K_L being the *mean specific heat* of the liquid between τ_1 and τ_2) . . .	$K_L(\tau_1-\tau_2)$	
Total heat expended . .	$L_1+K_L(\tau_1-\tau_2)$	. (77.)

Then for the power developed, we have

the area ABCD, as in article (43.), $=\frac{\tau_1-\tau_2}{\tau_1-\varkappa}.L_1$,

the area ADE, as in Article (40), equation (65.),

$$=K_L\left\{(\tau_1-\varkappa)-(\tau_2-\varkappa)\left(1+\text{hyp. log}\frac{\tau_1-\varkappa}{\tau_2-\varkappa}\right)\right\}$$

the sum of which quantities is the total power developed. . . . . (78.)

The efficiency may be expressed in the following form :—

$$\frac{\text{Power developed}}{\text{Heat expended}}=\frac{\tau_1-\tau_2}{\tau_1-\varkappa}-\frac{K_L(\tau_2-\varkappa)\left\{\text{hyp. log}\,\frac{\tau_1-\varkappa}{\tau_2-\varkappa}-\frac{\tau_1-\tau_2}{\tau_1-\varkappa}\right\}}{L_1+K_L(\tau_1-\tau_2)}, \quad . \ . \ . \ . \ . \quad (79.)$$

an equation which shows at once how far the efficiency falls short of the absolute maximum.

For a numerical example, the same data may be taken as in articles (41.) and (44.). Then the heat expended, per pound of steam, is thus made up :—

	Foot-pounds.
Latent Heat of Evaporation, as in art. (44.)	707,445·36
Heat required to raise the water 100° C., as in article (41.) .	139,800·00
Total heat expended, per lb. of water . . .	847,245·36

The power developed consists of,—

	Foot-pounds.
The area ABCD, as in article (44.)	171,484·75
The area ADE, as in article (41.)	13,980·00
Total power developed, per lb. of water . .	185,464·75

Efficiency, $\frac{185,484 \cdot 75}{847,245 \cdot 36}$	$\doteq$ 0·2189
Absolute maximum efficiency, as in art. (44.)	0·2424
Loss of efficiency by omitting the heating by compression	0·0235

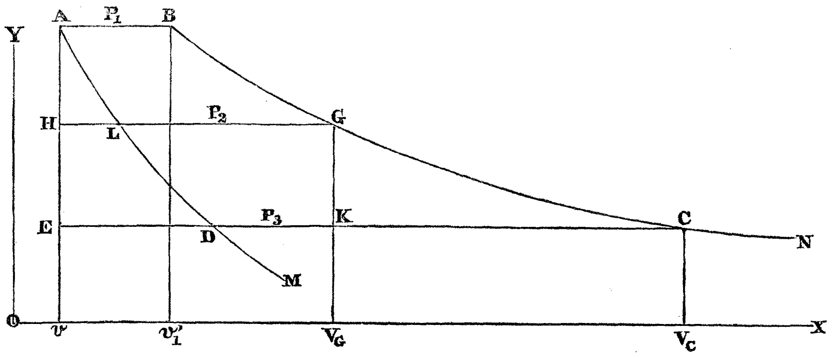
or about one-tenth part of the absolute maximum.

(47.) *Efficiency of a Vapour-Engine with incomplete expansion.*

It is in general impossible in practice to continue the expansion of the vapour down to the temperature of final liquefaction; and from this cause a further loss of efficiency is incurred.

Let it be supposed, for example, that while the pressure of evaporation P_1 corresponds to the line AB in fig. 23, and the pressure of liquefaction, P_3, to the line EDC, the pressure at which the expansion terminates, P_2, corresponds to an intermediate line HLG. Let vA, v'_1B, as before, be the ordinates corresponding to complete liquefaction, and to complete evaporation, at the pressure P_1.

Fig. 23.



Draw, as before, the curves of no transmission AM, BN, cutting HLG in L and G, and EDC in D and C; draw also the ordinate V_GKG, cutting EDC in K.

Then the expansion terminates at the volume V_G, and ABGKE is the indicator-diagram of the engine.

To find the power represented by this diagram, the area ALH is to be found as in article (40.), the area ABGL as in article (43.), and the rectangle HGKE by multiplying its breadth $V_G - v$ (found as in article (43.)) by its height HE, which is the excess of the pressure at the end of the expansion, P_2, above the pressure of final liquefaction, P_3.

Hence we have the following formula for the indicated power developed, per unit of weight of fluid evaporated.

$$\left.\begin{array}{l} \mathrm{E}=\text{area ABGKE}=\mathrm{K_L}\left\{(\tau_1-\varkappa)-(\tau_2-\varkappa)\left(1+\text{hyp. log}\,\frac{\tau_1-\varkappa}{\tau_2-\varkappa}\right)\right\}+\mathrm{L_1}.\frac{\tau_1-\tau_2}{\tau_1-\varkappa} \\ +(\mathrm{P_2}-\mathrm{P_3})\frac{1}{\frac{d\mathrm{P_2}}{d\tau}}\left\{\frac{\mathrm{L_1}}{\tau_1-\varkappa}+\mathrm{K_L}\,\text{hyp. log}\,\frac{\tau_1-\varkappa}{\tau_2-\varkappa}\right\}.\quad .\quad .\quad .\quad . \end{array}\right\}. \quad (80.)$$

The heat expended is of course $\mathrm{L_1}+\mathrm{K_L}(\tau_1-\tau_3)$.

To illustrate this numerically, let the fluid be water; let the temperature of evaporation be 140° Centigrade, and that of liquefaction 40°, as in the previous examples; and let the expansion terminate when the pressure has fallen to 100° Centigrade.

The numerical data in this case are the following:—

	1. During the evaporation.	2. At the end of the expansion.	3. During the final liquefaction.
Temperature in Centigrade degrees:—			
Above melting ice	140°	100°	40°
Above zero of gaseous tension, $\tau=$.	414·6	374·6	314·6
Above absolute cold, $\tau-\varkappa$	412·5	372·5	312·5
Pressure, in lb. per square foot, $\mathrm{P}=$ . .	7557	2116·4	153·34
Pressure, in lb. per square inch	52·5	14·7	1·065
$\frac{d\mathrm{P}}{d\tau}$ in lb. per sq. foot per Centigr. deg. . .	214·16	75·617	8·2075
Initial Volume of steam in cubic feet per lb.	8·004		
Latent Heat of Evaporation, $\mathrm{L_1}$, in foot-pounds per pound of steam . . .	707,445·36		
Total heat expended, in foot-pounds per lb. of steam	847,245·36		

Mean specific heat of liquid water—	
Between 40° and 140° C.	1398 feet of fall.
Between 100° and 140° C.	1409 feet of fall.

Applying equation (80.) to these data, we obtain the following results:—

	Foot-pounds
Area ALH	2,818
Area ABGL	68,601
Area HGKE $=(\mathrm{P_2}-\mathrm{P_3}).(\mathrm{V_G}-v)=$ 1963 lbs. per square foot × 24·58 cubic feet	=48,250
Total power developed by 1 lb. of water evaporated	119,669

	Foot-pounds.
Efficiency $= \frac{119,669}{847,245}$	$=0{\cdot}1413$
Efficiency computed in the last article	0·2189
Difference=loss of Efficiency by incomplete expansion .	0·0776

Ratio of Expansion $\frac{V_G}{v'} = \frac{24{\cdot}60}{8{\cdot}004} = 3{\cdot}07$ nearly.

If the power of the same engine be now computed by the tables and formulæ published in the 20th volume of the Transactions of the Royal Society of Edinburgh, which were calculated on the supposition that steam is sensibly a perfect gas, the following results are obtained:—

Ratio of expansion, $\frac{24{\cdot}60}{8{\cdot}4204} = 2{\cdot}921 = s$ in tables.

	Foot-pounds.
"Action at full pressure" (P_1V_1 in tables)	63,633
"Coefficient of Gross Action" (Z in tables) for the expansion 2·921	1·98
Gross Action (P_1V_1Z)	125,993 ft. lb.
Deduct for back-pressure of liquefaction $P_3V_G = 153{\cdot}34 \times 24{\cdot}6$.	3,772 ft. lb.
Power developed per pound of steam . .	122,221 ft. lb.

This result is too large by about one forty-seventh part; a difference to be ascribed chiefly to the error of treating steam as a perfect gas. This difference, however, is not of material consequence in computing theoretically the power of a steam-engine, being less than the amount of error usually to be expected in such calculations.

(48.) My object in entering thus minutely into the theory of the efficiency of vapour-engines is, not so much to provide new formulæ for practical use, as to illustrate the details of the mechanical action of heat under varied and complicated circumstances, and to show with precision the nature and influence of the circumstances which prevent the production, by steam-engines, of the absolute maximum of efficiency corresponding to the temperatures between which they work.

To illustrate the results of these calculations with respect to the consumption of coal, let it be assumed, as in article (33.), that each pound of coal consumed in the furnace communicates to the water, or air, or other elastic substance which performs the work, an amount of heat equivalent to 6,000,000 foot-pounds, which corresponds to a power of evaporating, in round numbers, about seven times its weight of water. Then the following calculation shows the theoretical indicated duty of one pound of such coal, when the limits of working temperature are 140° and 40° Centigrade, at the absolute maximum of theoretical efficiency, and at the reduced efficiency computed in the preceding article, on the supposition that the expansive working ceases at the atmospheric pressure.

	Efficiency.		Effect per pound of coal in foot-pounds.	
Absolute Theoretical Maximum, being the same for every perfect Thermo-dynamic Engine working between the same limits of temperature, $\frac{140^\circ-40^\circ}{140^\circ+272\frac{1}{2}^\circ}$	....	0·2424	....	1,454,400
Deductions:—				
For raising the temperature of the feed-water from 40° to 140° Centigrade..	0·0235	....	141,000	
For stopping the expansive working at 3·07 times the initial volume instead of 32 times	0·0776	....	465,600	
		0·1011		606,600
Reduced Efficiency and Effect	....	0·1413	....	847,800

The last of these quantities corresponds to a consumption of about 2·34 lbs. of coal per indicated horse-power per hour.

The conditions of the preceding investigation are very nearly fulfilled in steam-engines with valves and steam-passages so large, and a velocity of piston so moderate, that the pressure in the cylinder during the admission of the steam is nearly the same with that in the boiler.

In many steam-engines, however, the steam is more or less "wire-drawn"; that is to say, it has to rush through the passages with a velocity, to produce which there is required a considerable excess of pressure in the boiler above that in the cylinder. The power developed during the expansion of the steam from the pressure in the boiler to that in the cylinder is not altogether lost; for, as already stated in article (45.), it is expended in agitating the particles of the steam, and is ultimately converted into heat by friction, so that the steam begins its action on the piston in a super-heated state; and both its initial pressure and its expansive action are greater than those of steam of saturation of the same density. The numerical relations of the temperature, pressure, and density of super-heated steam are not yet known with sufficient precision to constitute the groundwork of a system of exact formulæ representing its action. Some general theorems, however, will be proved in the sequel, respecting super-heated vapours, which may be found useful when the necessary experimental data have been obtained.

Calculation and experiment concur to prove, that in Cornish single-acting engines, the initial pressure of the steam in the cylinders is very much less than the maximum pressure in the boilers; generally, indeed, less than one-half*. It is doubtful, however, whether this arises altogether from wire-drawing in the steam-passages and valves; for when it is considered, that in such engines, even at their greatest speed, the steam-valve remains shut during nearly the whole of each stroke, being opened during a small portion of the stroke only, it may be regarded as probable, that the

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* See Mr. Pole's work on the Cornish Engine, and article 36 of a paper on the Mechanical Action of Heat, Trans. Roy. Soc. Edinb. vol. xx.

sudden opening of this valve causes a temporary reduction of temperature and pressure in the boiler itself.

(49.) *Composite Vapour-Engines.*

The Steam-and-Ether Engine of M. du Trembley is an example of what may be called a *Composite Vapour-Engine*, in which two fluids are employed, a less and a more volatile; the heat given out during the liquefaction of the less volatile fluid serving to evaporate the more volatile fluid, which works an auxiliary engine, and is liquefied in its turn by refrigeration.

Let the efficiency of the engine worked by the less volatile fluid be expressed in the form

$$1-\frac{1}{n};$$

so that $\frac{1}{n}$ is the fraction of the whole heat expended which is given out to the more volatile fluid. Let the efficiency of the engine worked by the more volatile fluid be

$$1-\frac{1}{n'};$$

then the efficiency of the combined engines will be

$$1-\frac{1}{nn'}. \quad \ldots\ldots\ldots\ldots \quad (81.)$$

If both the engines are perfect thermo-dynamic engines, let τ_1 be the absolute temperature at which the first fluid is evaporated; τ_2 that at which it is condensed, and the second fluid evaporated; and τ_3 that at which the second fluid is condensed; then,

$$1-\frac{1}{n}=1-\frac{\tau_2-\kappa}{\tau_1-\kappa}; \quad 1-\frac{1}{n'}=1-\frac{\tau_3-\kappa}{\tau_2-\kappa}; \quad 1-\frac{1}{nn'}=1-\frac{\tau_3-\kappa}{\tau_1-\kappa}; \quad \ldots \quad (81\text{ A.})$$

being equal to the theoretical maximum efficiency of a simple thermo-dynamic engine working between the limits of temperature τ_1 and τ_3.

Composite Vapour-Engines, therefore, have the same theoretical maximum efficiency with simple vapour-engines, and other engines moved by heat, working between the same temperatures; but they may, nevertheless, enable the same efficiency to be obtained with smaller engines.

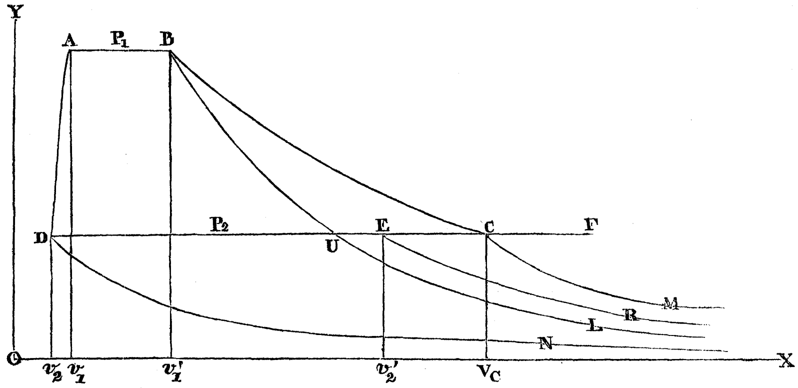
(50.) *Curves of Free Expansion for Nascent Vapour.*

By *Nascent Vapour* is to be understood, that which is in the act of rising from a mass of liquid. If this vapour be at once conducted to a condenser, without performing any work, and there liquefied at a temperature lower than that at which it was evaporated, its expansion, from the pressure of evaporation down to the pressure of liquefaction, will take place according to a law defined by a curve analogous in some respects, but not in all, to the curve of free expansion for a homogeneous substance referred to in Proposition VI. To determine theoretically the form of this curve, it is necessary to know the properties of the isothermal curves and curves of no transmission for the fluid in question in the gaseous state, when above the temperature of saturation for its pressure. Having these data, we can solve numerically the following problem :—

PROPOSITION XIX.—PROBLEM. *To draw the curve of Free Expansion for vapour nascent under a given pressure.*

(Solution.) In fig. 24, let AB, parallel to OX, be the isothermal line of an aggregate of liquid and vapour at the pressure of evaporation P_1 corresponding to the temperature τ_1: let Av_1, Bv'_1 be ordinates parallel to OY; so that v_1 is the volume of unity of weight of the liquid at this temperature, and v'_1 that of unity of weight of the vapour, at saturation. Let DF be a line drawn parallel to OX, at a distance representing any lower pressure P_2 corresponding to the temperature τ_2. It is required to find the point where the curve of free expansion drawn from B intersects DF.

Fig. 24.



Let v_2 be the volume of unity of weight of the liquid at the lower pressure and temperature, v_2D an ordinate parallel to OY, and DA a curve representing the law of expansion of the liquid as the pressure and temperature increase. Draw the curves of no transmission DN, BL indefinitely prolonged towards X; ascertain the indefinitely-prolonged area LBADN; draw a curve of no transmission MC, cutting DF in C, such that the indefinitely-prolonged area MCDN shall be equal to the indefinitely-prolonged area LBADN; then will C be the point required, where the curve of free expansion BC intersects the line DF.

(Demonstration.) Unity of weight of the fluid being raised in the liquid state from the temperature τ_2 and corresponding pressure P_2 to the temperature τ_1 and corresponding pressure P_1; then evaporated completely at the latter pressure and temperature; then expanded without performing work, until it falls to the original pressure P_2; then cooled at this pressure till it returns to the original temperature τ_2, at which it is finally liquefied;—the area ABCD represents the expansive power developed during this cycle of operations, which, as no work is performed, must be wholly expended in agitating the fluid, and reproducing, by friction, the heat consumed by the free expansion represented by the curve BC; which heat is measured by the indefinitely-prolonged area MCBL; which area is therefore equal to the area ABCD.

Subtracting from each of these equal areas the common area BUC, and adding to each of the equal remainders the indefinitely prolonged area LUDN, we form the areas MCDN, LBADN; which are consequently equal. Q.E.D.

(51.) *Of the Total Heat of Evaporation.*

The symbolical expression of the preceding proposition is formed in the following manner. The area LBADN represents the *total heat of evaporation, at* the temperature τ_1, *from* the temperature τ_2, and is composed of two parts, as follows:—

$$\text{LBADN}=\int_{\tau_2}^{\tau_1}\text{K}_\text{L}d\tau+\text{L}_1, \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (82.)$$

of which the first is the heat necessary to raise the liquid, whose specific heat is K_L, from τ_2 to τ_1, and the second is the latent heat of evaporation at τ_1.

Let v'_2 be the volume of unity of weight of the vapour at the pressure P_2 and temperature of saturation τ_2; draw the ordinate $v'_2\text{E}$, meeting DF in E, through which point draw the indefinitely-prolonged curve of no transmission ER: then is the area MCDN divided into two parts, as follows:—

$$\text{MCDN}=\text{MCER}+\text{REDN}=\int_{\tau_2}^{\tau_\text{C}}\text{K}_\text{P}d\tau+\text{L}_2, \quad . \; . \; . \; . \quad (83.)$$

in which equation τ_C denotes the temperature corresponding to the point C on the curve of free expansion, and K_P the specific heat of the vapour, at the constant pressure P_2 when above the temperature of saturation; so that the first term represents the heat abstracted in lowering the temperature of the vapour from τ_C to the temperature of saturation τ_2, at the constant pressure P_2; and the second term, the latent heat of evaporation at τ_2, abstracted during the liquefaction.

By equating the formulæ (82.) and (83.), the following equation is obtained:—

$$\int_{\tau_2}^{\tau_1}\text{K}_\text{L}d\tau+\text{L}_1-\text{L}_2=\int_{\tau_2}^{\tau_\text{C}}\text{K}_\text{P}d\tau, \quad . \; . \; . \; . \; . \; . \; . \; . \quad (84.)$$

which is the symbolical solution of Proposition XIX., and shows a relation between the total heat of evaporation of a fluid, the free expansion of its vapour, and the specific heat of that vapour at constant pressure.

(52.) *Approximate Law for a Vapour which is a perfect gas.*

If the vapour of the fluid in question be a perfect gas, and of very great volume as compared with the fluid in the liquid state, the curve BC will be nearly a hyperbola, and will nearly coincide with the isothermal curve of the higher temperature τ_1, to which, consequently, τ_C will be nearly equal; and the following equation will be approximately true:

$$\int_{\tau_2}^{\tau_1}\text{K}_\text{L}d\tau+\text{L}_1-\text{L}_2=\int_{\tau_2}^{\tau_1}\text{K}_\text{P}d\tau, \quad . \; . \; . \; . \; . \; . \; . \; . \quad (85.)$$

which, when the difference between the higher and lower temperatures diminishes indefinitely, is reduced to the following :—

$$K_L + \frac{dL}{d\tau} = K_P, \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (86.)$$

that is to say :—

Corollary.—Theorem. *When a vapour is a Perfect Gas, and very bulky as compared with its liquid, the rate of increase of the total heat of evaporation with temperature is nearly equal to the specific heat of the vapour at constant pressure.*

This was demonstrated by a different process, in a paper read to the Royal Society of Edinburgh in 1850. It has not yet been ascertained, however, whether any vapour at saturation approaches sufficiently near to the condition of perfect gas to render the theorem applicable.

(53.) *Concluding Remarks.*

In conclusion, it may be observed, that the Theory of the Expansive Action of Heat embodied in the propositions of this paper contains but one principle of hypothetical origin; viz. Proposition XII., according to which the actual heat present in a substance is simply proportional to its temperature, measured from a certain point of absolute cold, and multiplied by a specific constant; and that although existing experimental data may not be adequate to verify this principle precisely, they are still sufficient to prove, that it is near enough to the truth for all purposes connected with Thermodynamic Engines, and to afford a strong probability that it is an exact physical law.