THERMODYNAMICS.

BY PROFESSOR DE VOLSON WOOD.

(Continued from page 140.)

This rate, then, involves the imperfection of the gas. We will attempt a more general explanation. The higher an imperfect fluid is heated at a constant volume, the more nearly will it approach to the condition of a perfect gas. Thus, in the equation before given

$$p v = R \tau - \frac{a}{v} - \frac{a}{v \tau} - \text{etc.}$$

the larger τ is, the more nearly does $p v = R \tau$; and, conversely, the less τ is the more imperfect is the fluid, and p increases less for a given increase of τ than if it were a perfect gas. Hence, between τ small and τ large, p must increase more rapidly for an imperfect than for a perfect fluid. This granted, it follows that the rate $\frac{dp}{d\tau}$, or $\frac{dp}{dQ}$, is greater for an imperfect than for a perfect fluid, other conditions being the same, as already shown by the equation above. This being the virtual increase of the pressure for one degree of temperature, and the rate being maintained constant at the temperature τ by the absorption of heat, and since all the heat absorbed must have Q units of heat and is transmuted into work at that heat, the virtual pressure during the expansion dv will be Q times the above rate, or

$$Q \frac{dp}{dQ} = \tau \frac{dp}{d\tau},$$

hence, the total work, both external and internal, for the isothermal expansion dv will be

$$dW = \tau \frac{dp}{d\tau} dv$$

and for an isothermal expansion from v_1 to v_2 ,

$$W = \int_{v_2}^{v_1} \tau \frac{dp}{d\tau} dv = \tau \int_{v_2}^{v_1} \frac{dp}{d\tau} dv. \quad (11)$$

So much for the analysis and the symbolic representation of the

second law. As we have made no reference, thus far, to that law, the question may be asked: What is its use? Why not dispense with it? There is an advantage in stating the fundamental principles of a science in the form of laws. They are like the foundation-stones of an edifice, they show on what the structure rests. Subjects may be developed in accordance with fundamental principles without statements of formal laws. Newton's three laws of motion have served, and continue to serve, a good purpose in the development of mechanics. The science of thermodynamics is developed by some writers without a reference to a second law, or even the formal statement of any laws. The first law is an expression of the equivalence of heat and work. The second law is an expression for the total work deduced from the external during an isothermal expansion. Let the point be emphasized that the kinetic energy—the heat energy—of a pound of a fluid, or of any given mass of it, depends directly upon its absolute temperature, so that if the latter be maintained constant during a change of volume, the heat-energy will be constant. This can be proved directly for perfect gases, and is believed to be true for imperfect ones, at least in a constant state of aggregation.

We now examine the wording and the meaning of Rankine's second law, as quoted in the early part of this paper. This is the law that Maxwell pronounced "inscrutable." Rankine made several statements of this law, including symbolic expressions of it, but they do not all cover the same ground. Some intensify one point and some another, but they do not antagonize each other, and must be considered as containing a common principle, and if any one of the statements does not cover all the principles necessary for the establishment of the analysis, it must be considered defective or incomplete; otherwise there would be several different laws all claiming to be the second. Rankine expressly states that these several statements are intended to be essentially the same.

According to the symbolic expression already investigated above, the law must contain the idea of isothermal expansion. Certainly, the law contains no such statement explicitly, and if found there at all, it must be in the words "causing work to be performed;" and in order that these words shall convey this idea, it must be considered that neither the substance nor the heat in the substance does the work, but that it is merely an agent for

transmitting the heat from the source to the working-piston, or to some other potential form. But there is no intimation that there is a source of heat, and since this is a necessity, it must be inferred on account of the conditions of the problem; and the temperature of the source must be at least as high as that of the substance. The principle contained in this last statement is sometimes referred to as the second law, viz.: "that heat cannot of itself pass from a body of a lower temperature to one of a higher;" but most writers, especially Rankine and Thomson, consider this as an axiom, and make the second law include a measurable quantity. A source of heat, then, is a necessity, and must be understood in Rankine's second law; or, we might say, as before stated, that the fact of a constant temperature must be admitted, for otherwise the law does not furnish a foundation for the analysis. It will be admitted that the interpretation we have given of this part of the law is somewhat forced; that naturally the words will not convey the idea which we have imputed to them; and that it may be questionable whether they should be so understood; but if not, then the statement of the law is incomplete in this particular. Either the "scope" of the words must be very large, or more words are needed. Rankine, in one of his original papers, supplied the necessary words in a sentence which is so clearly and fully expressed that we copy it, italicizing a part of it:

"Let us conceive that unity of weight of any substance occupying the bulk V under the pressure P , and possessing the absolute quantity of thermometric heat, whose mechanical equivalent is Q , undergoes the indefinitely small increase of volume dV ; and let us investigate how much heat becomes latent, or is converted into expansive power during this process, *the thermometric heat being maintained constant, so that the heat which disappears must be supplied from some external source.*"—(*Misc. Sc. Papers*, p. 311.)

If the "disappearance of heat" in the quotation near the beginning of this article is the same as "*the heat which disappears*" in this last quotation, as it ought to be, we see no good reason for retaining the words "of this" in the former quotation. To retain them, only compels a forced and awkward repetition.

The italicized words contain a principle which should be included in the second law, if it is to furnish a complete foundation for the symbolic expression. Next, consider the expression, "The

total actual heat." This is simply the heat which remains in the body as heat; it is not the heat absorbed by the body, for such heat may have been expended in doing external work, in which case it is no longer heat, none of it being retained as heat; or some of it may have been expended in effecting molecular changes of some kind, called internal work, in which case so much of the heat disappearing in this potential form is no longer heat, although its effect remains in the body. All the heat absorbed by the body remaining after deducting all that has been changed to potential energy is "actual heat" or "total actual heat," it is sensible or thermometric heat. The law states: "If the total actual heat of a homogeneous and uniformly hot substance be conceived to be divided into any number of equal parts," etc. The divisions here mentioned may be conceived as produced in two distinct ways, first, by dividing the substance into equal parts, which, in the case of a uniformly hot, homogeneous substance, will divide the heat into the same number of equal parts, and each part will have the same temperature, and secondly, by conceiving the heat in the entire substance to be produced by equal increments beginning with zero heat. There is nothing in the nature of the case, nor in the language of the author, up to this point, that compels the acceptance of one of these modes of division to the exclusion of the other, and hence the one which will furnish the clearest explanation of the solution sought, will naturally be accepted. For this reason, we conceive that the heat is divided by dividing the mass of the substance. For the sake of greater definiteness, conceive that the substance is in an ordinary steam cylinder, and that it is divided into an indefinite number of prisms having their basis against the piston at one end and the head at the other. The heat of the substance being Q , the amount in each small prism will be dQ , when the prisms are indefinitely small, and the number of such prisms will be

$$\frac{Q}{dQ};$$

and the amount of work which each can do by expanding an amount $d v$, the thermometric heat, Q , being maintained constant, will be

$$\frac{d p}{d Q} d Q d v,$$

and since all those parts are not only equal but altogether alike in nature and similarly circumstanced, their effects must be equal, therefore the entire energy must be the effect of one of the parts multiplied by the number of parts, or

$$\frac{Q}{d} \frac{Q}{Q} \times \frac{d p}{d Q} d Q d v = Q \frac{d p}{d Q} d v,$$

which is the symbolic expression of the second law. It may be noticed that this process is slightly different from that in the text, for there the factor $d Q$ is integrated, while here it is cancelled in the operation of multiplying, but the results are the same. The fact is, we have here followed the precise process, amounting to nearly a literal quotation, of the author in his original paper, read January 5, 1853 (*Misc. Sc. Papers*, p. 204).

As to the other mode of division, that by increments of heat, it will lead to the same result by a deduction from the former by making the increments of heat, $d Q$, the same in value as the heat in one of the small prisms. It needs no argument to show that this is possible, and hence, numerically, the value of the last expression will not be changed by this mode of division. But as an independent proposition, it raises this vital question—does an element of heat, $d Q$, low down in the scale, say, for instance, at $\frac{1}{4} Q$, cause the same work as the last $d Q$ when the heat becomes Q , and if not, how can it be said that “the effect of each of those parts in causing work to be performed is equal?” This mode of division gives a scale of temperature, and so we repeat the question in this form: Is it plain that an increment of heat, $d \tau$, will cause the same work to be performed by a pound of gas when the temperature is $\frac{1}{4} \tau$, as when it is τ ? It can easily be shown to be true for perfect gases in which increments of pressure vary directly as the increments of temperature, and in which also the total work is external, but can it be asserted as equally true for imperfect gases? Before we complete this discussion, these questions will be definitely answered and the obscurity, if any, in regard to the proper mode of dividing the heat into equal parts, will be removed.

As a consequence of the relation between the sensible heat and temperature, we have directly

$$\frac{d Q}{Q} = \frac{d \tau}{\tau},$$

thus reducing the former expression to

$$\tau \frac{d p}{d \tau} d v$$

The last expression has been established in a variety of ways. M. Clausius, Thomson and Joule first considered it in the form

$$\varphi(\tau) \frac{d p}{d \tau} d v,$$

in which $\varphi(\tau)$ was an unknown function, to be determined by experiment, and it was so determined by Joule and Thomson, as recorded in Thomson's *Mathematical and Physical Papers*. M. Mayer assumed it to be simply the absolute temperature itself; while Rankine, from his hypothesis of molecular vortices, deduced the form,

$$\varphi(\tau) = \tau - x,$$

x being the absolute temperature on the perfect gas-thermometer corresponding to the total privation of heat, whose value is very small—at first found to be about 2.1° C.—but after the experiments of Thomson and Joule, with the porous plug, it was found that the error resulting from considering $x = 0$ would be less than those resulting from the errors of observation, since which it has been considered as zero, and we have

$$\varphi(\tau) = \tau,$$

and to this expression Thomson has given the name "Carnot's function." Knowing this result, as Rankine did when he wrote his *Manual*, he assumed it, and so greatly abbreviated the investigation. In regard to expression $Q = k \tau$, Rankine remarks, at the close of his celebrated paper "On the Geometrical Representation of the Expansive Action of Heat," (*Trans. Roy. Soc.*, 1854; *Misc. Sc. Papers*, p. 409,) that it is a hypothetical principle, "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 law." This conclusion has been verified in many ways within the ranges of temperatures used in ordinary practice.

Rankine gives two other statements of the second law in the *Manual*, one expressed in regard to absolute temperature graphi-

cally expressed, the symbolic expression of which, $\tau \frac{d p}{d \tau} d v$, is the one most frequently used; the other, a functional relation, which results in the same value as that just given. In his other writings, are several other statements; for instance, in the *Engineer*, of June 28, 1867, is the following:

"If the substance which does the work in a perfect heat-engine receives all the heat expended at one fixed temperature, and gives out all the heat which remains unconverted into work at a lower fixed temperature, the fraction of the whole heat expended, which is converted into external work, is expressed by dividing the difference between those temperatures by the higher of them, reckoned from the absolute zero. Now this is, in fact, the second law of thermodynamics expressed in other words." (See also *Misc. Sc. Papers*, p. 436.)

Yes! exclaims the student, "in other words" this statement is explicit and easily understood, but one does not recognize it as the equivalent of that in the *Manual*. This is a mere ratio, *that* the measure of a quantity; *this* is the fraction of the whole heat converted into external work, *that* a measure of both external and internal. The statement includes isothermal expansion, and, taken as a whole, may be made the basis of an analysis for producing the expression $\tau \frac{d p}{d \tau} d v$. This is the principle used by Clausius, Thomson, and other writers, for deducing the symbolic expression; and it is probable, if not certain, that Rankine had this operation in mind when he wrote the various expressions for the second law.

Again, in the same article referred to above, is another expression, as follows: "That law (the second) is capable of being expressed in a variety of forms, expressed in different words, although virtually equivalent to each other. The most convenient form for the present purpose appears to be the following:

To find the whole work, internal and external, multiply the absolute temperature at which the change of dimensions takes place, by the rate per degree at which the external work is varied by a small variation of the temperature."

This is explicit, but with the exception of the first eight words, it is merely substituting words for the algebraic expression

$$\tau \frac{d^2 U}{d\tau} = \tau \frac{dp dv}{d\tau} = \tau \frac{dp}{d\tau} dv.$$

Isothermal expansion is asserted in the words, "the absolute temperature *at* which the change of dimensions takes place." The change takes place *at* a constant temperature. Here, the author explicitly states that the work done during isothermal expansion includes the internal work, and the same fact may be inferred from other parts of his writings. According to the last quotation, it follows that any statement of principles, which is sufficient for the establishment of the expression $\tau \frac{dp}{d\tau} dv$ may be considered as the second law. Laws forming the foundation of a science should be simple, explicit, avoiding ambiguity, and complete in their assertions. The one we are considering does not conform to these conditions, and is at best only a remote suggestion of a physical operation. We propose to amplify it, so as to make it include all the principles necessary for the establishment of the symbolic expression, using substantially the language of the author as found in different parts of his writings, as follows:

SECOND LAW.—*If work is done by the expansion of a homogeneous and uniformly hot substance, the thermometric heat being maintained constant by a supply from an external source, and the total actual heat be conceived to be divided into any number of indefinitely small parts, each of the parts being not only equal, but altogether alike and similarly circumstanced, their effects in causing work to be performed will be equal; the total work performed being the external and internal during the expansion.*

I would substitute for all these, and other expressions, a principle common to all of them, and common also to the corresponding principles in the writings of Thomson and Clausius, as follows:

SECOND LAW.—*The work, both external and internal, done during the expansion of a substance at constant temperature, equals the heat absorbed.*

When thus stated, the analyst is free to choose his own method of determining the heat absorbed during isothermal expansion, and when found, the law states that it equals the work done during the absorption. One way of determining the heat absorbed is as follows:

Let a substance capable of indefinite expansion, whose initial volume is $o v_1 = v_1$, *Fig. 2*, and pressure $v_1 A = p$, expand at constant temperature τ , from $o v_1$ to $o v_2 = v_2$; then will the locus AB of the upper ends of the ordinates representing pressures, be an isothermal line. Through A pass the adiabatic MA , and through B the adiabatic BN , then if the adiabatics be indefinitely extended, they will be asymptotes to ox , and the indefinitely extended area $MABN$ will be the heat absorbed during the expansion from v_1 to v_2 . To find this area, conceive it to be intersected by isothermals differing from each other by $d\tau$, then will the number of strips be $\frac{\tau}{d\tau}$. The area of these strips will equal each other. To prove this, we use Thomson's absolute scale of temperatures. Conceive that the substance after expanding to B expands without transmission of heat until the temperature falls $d\tau$, the pressure will fall until

it reaches the consecutive isothermal fe ; then compress the substance along fe isothermally, during which operation heat will be rejected by the substance, the amount of rejection being represented by the area $Me f N$, then compress the substance without transmission of heat adiabatically along eA to A . The resultant work will be represented by the area $ABfe$, and this also represents the heat which disappears by this operation.

Now, if when B is reached, the expansion be prolonged adiabatically until the temperature falls $2d\tau$, the pressure will fall until it reaches the second isothermal, then compress along the second isothermal until MA is reached, then compress adiabatically to A . Since no heat is lost along the adiabatics, but all that is lost is along the isothermals, twice the heat will have been abstracted in the second as in the first operation, and the area of the

two strips will be twice that of the upper one. Proceeding in this manner we show that all the strips are equal, so that the area of any one multiplied by the entire number, will give the entire area $MA B N$. In the case of perfect gases, it is easy to find the area of any one of the strips, for the equation to the adiabatics are known, but generally, it is easiest to find the area of the topmost strip, where p and v are known. At any point a in $A b$ draw the vertical $a d$ to the next isothermal, and construct the vanishing parallelogram $a d e b$; its area will be $d p d v$, and the area

$$A B f e = \int_{v_1}^{v_2} d p d v.$$

But this cannot be integrated since $d p$ is variable, decreasing from A to B . But, for any assigned value of v , p is a function of τ only, and since $d \tau$ is constant from A to B , we express $d p$ as a function of τ . This, according to the calculus, may be expressed thus:

$$\frac{d p}{d \tau} d \tau$$

and our expression becomes

$$A B f e = d \tau \int_{v_1}^{v_2} \frac{d p}{d \tau} d v$$

where $d \tau$ is placed outside the integral, since it is constant. If $\frac{d p}{d \tau}$ contains τ , the integration may be performed, because τ is also constant from A to B , or from v_1 to v_2 . To illustrate, the differential of the most general form of the equation for imperfect gases, already given in equation (6), is

$$\frac{d p}{d \tau} = \frac{R}{v} + \frac{a}{v^2 \tau^2} + \frac{2 a_2}{v^2 \tau^3} + \text{etc.},$$

which contains τ , but since that and $d \tau$ are to be constant from A to B , the integral may be performed, giving

$$A b f e = d \tau \left[R \log \frac{v_2}{v_1} + \left(\frac{2 a_1}{\tau^2} + \frac{4 a_2}{\tau^3} + \text{etc.} \right) \left(\frac{1}{v_1} - \frac{1}{v_2} \right) \right].$$

Observing that the area of each strip equals that of $A b f e$, and that the number of strips is $\frac{\tau}{d \tau}$, we find the area

$$M A B N = \frac{\tau}{d\tau} d\tau \int_{v_1}^{v_2} \frac{dp}{d\tau} dv = \tau \int_{v_1}^{v_2} \frac{dp}{d\tau} dv,$$

which is an expression for the total heat absorbed during the isothermal expansion, and hence equals the total work done.

It remains to be determined whether Thomson's absolute scale can be measured by a thermometer constructed of actual materials.

This scale would be represented by a perfect gas-thermometer, for all the work done by a perfect gas expanding isothermally will be external. Thomson and Joule made a series of delicate experiments upon air, known as the experiments with a "porous plug," to determine if air could be considered as a perfect gas when used as a thermometer, and it was found that the errors resulting therefrom were not greater than the errors resulting from direct observation, so that τ may be considered as the absolute temperature measured with an air-thermometer, and a good mercurial-thermometer agrees sufficiently well with the air-thermometer to be used in ordinary practice.

In the light of this solution, it may be asked: Is it not the heat absorbed during expansion that is to be divided into equal parts? While it is certain that it is so divided, it is equally certain that it is not the heat to which Rankine referred, when he said: "Let unity of weight of the substance possessing the actual heat Q . . . Conceive Q to be divided, etc." It is not the source of heat, nor the heat absorbed that is, fundamentally, divided into equal parts; but the heat of the working substance. We are explicit on this point, because we find that such an eminent author as Prof. Cotterell appears to have fallen into an error on these points. We quote from page 111, of his work on *The Steam Engine*, as follows:

"Let us now imagine the temperature T_1 of the hot body, or source of heat, to be divided into n equal parts, and let us imagine a quantity of heat, Q , to flow from that body to a second body, the temperature of which is $T_1 \left(1 - \frac{1}{n}\right)$, then our results show that a quantity, $\frac{Q}{n}$, of mechanical work is capable of being produced, and that, consequently, if such conversion be effected, the quantity $\frac{n-1}{n} Q$ will pass into the second body. Now, imagine

a third body, the temperature of which is $T_1 \left(1 - \frac{2}{n}\right)$, and let this heat pass from the second body to the third body; then the heat capable of being turned into work, is

$$\frac{n-1}{n} Q \cdot \frac{T_1}{T_1 \left(1 - \frac{1}{n}\right)} = \frac{Q}{n}$$

as before. This process may be continued indefinitely, and we thus see that—*If the temperature of a source of heat be divided into any number of equal parts, then the effect of each of these parts, in causing work to be performed, is the same.*"

Here the temperature—not the actual heat—is imagined to be divided; also, the source of heat is divided, not the heat of the working substance; also, Q is the quantity of heat imagined to flow from the source, while in Rankine's analysis, Q is the actual heat of the working substance. It is not clear what the division of the source into equal parts has to do with this analysis. This quantity, Q , is independent of the amount in the source, and also of that in the working substance; and it is assumed that this amount flows from the source to the second body, but that only an amount $\frac{n-1}{n} Q$ flows into the second body. The conclusion is also unfortunate, at least in form, for it reads as if the equal temperatures caused work to be performed, instead of equal heats. This attempt to explain Rankine's second law is, to say the least, not a success. The assertion that equal quantities of heat will do equal quantities of work, is nothing more than the first law.

In the case of a perfect gas, Rankine's operation of the second law, may be thus: Let one pound of the substance possessing the actual heat Q be conceived to be divided into n equal parts. While the substance possesses the actual heat Q , let it expand against a resistance doing work while its heat is maintained at Q by a supply from an external source, and after it has expanded by enlarging the vessel an amount $v_2 - v_1$, *Fig. 2*, let it be brought back in any manner to its original state of volume v_1 and heat Q ; its pressure will then also be the initial, or p_1 . Now, let $\frac{1}{n}$ th of Q be abstracted from the substance at the constant volume v_1 , the

pressure will fall to $(1 - n) p_1$, after which let the substance be again expanded at the constant heat $\left(1 - \frac{1}{n}\right) Q$, the same amount, $v_2 - v_1$, as before. Repeat the operation, by expanding it, the same amount, as before, from v_1 to v_2 , at the heat $\left(1 - \frac{2}{n}\right) Q$, and so on. Then will the difference between the works done during the successive expansions be equal. It is in this sense that "the effects of the equal parts in causing work to be performed are equal." The operation may be represented geometrically by dividing the space $v_1 A B v_2$ into n strips by isothermal lines extending from $v_1 A$ to $v_2 B$. This divides the external work $v_1 A B v_2$ into equal parts, and since, in a perfect gas all the work will be external, the division accomplishes the purpose sought. The actual heat absorbed, $M A B N$, will also be divided into the same number of equal parts by the same isothermals.

But when the fluid is imperfect, this process will not divide the external work into equal parts, and much less afford any measure of the internal work, for the internal work is a function of the volume as well as of the temperature, as shown by the equation preceding (6). To illustrate the case for imperfect fluids, conceive successive isothermals drawn as before starting on the ordinate $v_1 A$, but extended to the right to the adiabatic $B N$, then will the successive strips between the adiabatics be equal. For the area $M A B N$ represents heat—not work—and it will be divided into successive equal increments of heat. As the heat falls in temperature, the strips become longer and narrower, their areas remaining constant. It is this complex operation that is involved in the expression, "the effects of the equal parts in causing work to be performed are equal." The operation is known as Carnot's cycle, and we are thus brought to Thomson's Prop. II, and Clausius's mode of analysis. This solution admits of but one mode of division of the actual heat Q ; that of a division according to a thermometric scale from zero to Q , and is unquestionably the mode of division intended by the author. It is not a division of the substance in which each part would have the original temperature of the substance, but one in which the temperature of the entire substance is reduced by the abstraction of equal quantities of heat from the substance. The equal parts of heat do no work, but are

indices of the grade of the heat doing the work. All of the heat doing the work must be of the grade Q , but to find the work which the heat absorbed can do, we conceive it to be worked in a perfect reversible engine, first at the grade Q , next at the grade $Q - dQ$, third at the grade $Q - 2dQ$, and so on, as already described, in which neither the beginnings nor endings of the works are arbitrary, but are limited by one pair of adiabatics. The phrase, "causing work to be performed," is not even suggestive of the manner according to which the work is to be done. Carnot's cycle is fundamental. Although Rankine deduced it from an independent hypothesis, yet had his analysis conflicted with this principle, the hypothesis and not the principle would have suffered.

We have thus established definitely the essential, and, we believe, the correct, meaning contained in the paragraph quoted at the beginning of this article.

(To be continued.)

ALUMINIUM AND ITS ALLOYS; WITH EXPERIMENTAL INVESTIGATIONS.

BY EDWARD D. SELF, Stevens Institute of Technology.*

Should we assume the existence of a metal superior in valuable properties to iron, and predict its entrance into the arts as a far more useful servant to man, even the remote possibility of such an event would be an interesting subject for discussion.

When, however, we can with truth point to the presence of such a metal in immeasurable quantities, it is indeed remarkable that in this age of progress such a wonderful substance should be so generally regarded simply as a chemical curiosity—the result of an interesting experiment.

This universally distributed metal, though now disguised, excels iron in lightness, is nearly equal to it in strength, does not rust or corrode by acid vapors and, what is more striking, is the third in respect to abundance of the constituents of the earth's crust.

This metal for which the arts have long waited, is aluminium, or "silver made from clay."

* Graduation Theses, 1886.