

ART. V.—ON CARNOT'S CYCLE IN THERMODYNAMICS.—BY PROF. J. G. MACGREGOR.

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The object of this paper, which is pedagogic rather than scientific, is to point out and remove a defect in the proofs usually given of the universality of the results obtained in Thermodynamics by the consideration of Carnot's Cycle of Operations.

From the Second Law of Thermodynamics it is proven that a Heat Engine has the greatest efficiency possible, provided, (1) it is reversible, and (2) when worked directly (*i. e.*, so as to do external work), its "working substance" absorbs heat when at a high temperature, and emits heat when at a low temperature. The second of these two conditions is not generally specified in so many words by writers on Thermodynamics; but the argument by which the efficiency of the reversible heat engine is shewn to be the greatest possible always assumes that the heat engine referred to is one of the kind specified above.

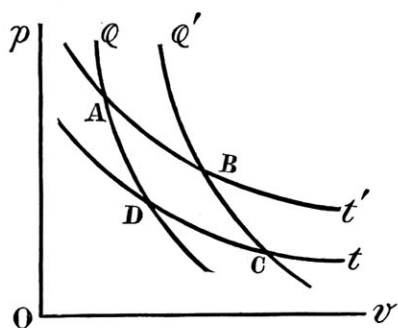
It is next pointed out that a substance subjected by the aid of Carnot's Ideal Heat Engine to what is known as Carnot's Cycle of Operations, in such a way that the cycle is reversible, constitutes a heat engine fulfilling both the above conditions. It follows that its efficiency is the greatest possible, and is independent of the nature of the working substance; and a result is thus reached which is of extreme importance, because of its perfect generality.

The defect referred to above is in the proof that any substance whatever subjected to Carnot's Cycle, in such a manner that it does external work, absorbs heat when at a high temperature and emits heat when at a low temperature. All writers* on Thermodynamics known to me, prove, not that this is true of any substance whatever, but only that it is true of one or two

* I do not refer here to writers on air and steam engines, who rightly enough restrict themselves to a study of Carnot's Cycle as applied to gases and saturated vapours.

classes of substances, usually gases and substances partly in the liquid state and partly in the state of saturated vapour. And they either assume it to be true of all other classes of substances without any farther statement or state that it may be shewn to be so. These other substances, however, including simple substances which contract as their temperature rises and mixtures of substances in the solid and liquid state, some of which contract while others expand on liquefaction, differ in their thermal properties in so marked a manner from both gases and saturated vapours, that it would seem to be necessary before applying to them the results of the study of Carnot's Cycle, to prove that they too when subjected to that cycle, so as to do external work, absorb heat when at a high temperature and emit heat when at a low temperature.

To shew how different the proofs are for substances of different kinds, I give them for all kinds, including those ordinarily given in works on Thermodynamics. In all cases I assume the operations of the cycle to be applied directly, i. e., so that the working substance does external work. As the conditions of reversibility may be fulfilled equally well by all substances, it will follow that when so subjected to the operations of the cycle that work is done on the working substance by the external forces, heat is absorbed by the working substance when at a low temperature and emitted by it when at a high temperature.



Let the variation of the physical state of a body when subjected to Carnot's cycle be represented in the usual way on the Indicator diagram, by the line ABCDA, ϕ and ϕ' being the two adiabats or isentropics, and t and t' the two isothermals, of which portions are described by the indicating point during the cycle. Let ϕ , ϕ' , stand also for the entropy of the isentropics, and t t' for the temperatures of the isothermals.

In the case of an ordinary substance which expands with rise of temperature at constant pressure, t' is obviously a higher isothermal than t , and ϕ' a higher isentropic than ϕ . Hence, during the operation A B heat is absorbed, the substance being at a high temperature, and during the operation C D heat is emitted, the substance being at a low temperature.

In the case of a substance which contracts with rise of temperature at constant pressure, t is a higher temperature than t' . For as a greater volume corresponds to a lower temperature, a straight line drawn in the direction of Ov (the axis of volumes) must meet successively isothermals of lower and lower temperature. Also in this case, ϕ is a higher isentropic than ϕ' . For, in order that such a substance may be made to expand at constant pressure, heat must be taken from it; and therefore a straight line drawn in the direction Ov must meet successively adiabatics of lower and lower entropy. It follows that in the case of substances which contract with rise of temperature, heat is emitted during the operation AB, and absorbed during the operation CD; but in this case the temperature during the operation AB is low, and that during CD is high.

In the case of a substance consisting of a mixture of a liquid and its vapour, AB and DC are straight lines, parallel to the axis of volumes. Since the saturation pressures of all vapours increase with the temperature, t' is a higher temperature than t . And since evaporation at constant pressure invariably increases the volume of a substance and involves absorption of heat, ϕ' is a higher isentropic than ϕ . Hence, in this case, heat is absorbed during AB when the working substance is at a high temperature, and emitted during CD when it is at a low temperature.

In the case of a working substance which is partly in the solid and partly in the liquid state, and which contracts on liquefaction, AB and DC are straight lines, parallel to the line of volumes. For the absorption of heat at constant pressure diminishes the volume. It follows from this consideration also that ϕ is a higher isentropic than ϕ' , for it cuts a line parallel to Ov at a point nearer Op than ϕ' does. As the working substance in this case is always at the melting point, t' and t are

the melting points at higher and lower pressures respectively. Now it may be proved by the aid of the First Law of Thermodynamics alone that the melting point of a substance which contracts on liquefying must lower as the pressure rises. It was so proved originally by Professor James Thomson.* Hence, in this case, t is a higher temperature than t' . It follows that in this case heat is emitted during the operation AB when the temperature of the working substance is low, and absorbed during CD when its temperature is high.

In the case of a working substance which is partly in the solid and partly in the liquid state and which expands on liquefaction, A B and D C will again be straight lines parallel to O v. In this case, however, since absorption of heat at constant pressure means increase of volume ϕ' is a higher isentropic than ϕ . Also, it may be proved by the aid of the First Law of Thermodynamics alone by an argument similar to that of Prof. James Thomson, referred to above, that in this case the melting point rises as the pressure increases, and therefore that t' is a higher temperature than t . Hence, in this case, heat is absorbed during A B when the temperature is high and emitted during C D when the temperature is low.

Hence, in the case of all kinds of working substances, Carnot's Cycle when carried out so that work is done against external forces, involves absorption of heat when the substance is at a high temperature and emission of heat when at a low temperature.

And the differences in the above arguments by which this result is reached in the case of different kinds of substances seem to shew that it is not sufficient to prove it for one and then assume it for all, but that it should be proved for all before being regarded as universally applicable.

* Trans. Roy. Soc., Edin., Jan. 2, 1849; Sir Wm. Thomson's Mathematical and Physical Papers, Vol. I, p. 156.