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MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

An Experimental Investigation of the Thermodynamical Properties of Super-Heated Steam. On the Cooling of Saturated Steam by Free Expansion

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PHILOSOPHICAL TRANSACTIONS.

I. *An Experimental Investigation of the Thermodynamical Properties of Superheated Steam.—On the Cooling of Saturated Steam by Free Expansion.*

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Contents.

Section I.—*Introduction.*

In a paper on the "Dryness of Saturated Steam and the Condition of Steam Gas," read before the Manchester Literary and Philosophical Society on November 3, 1896, by Professor Osborne Reynolds, F.R.S., the following passage occurs, "The whole theory of the properties of steam, as at present accepted, and all the steam tables are founded on the experiments of REGNAULT on the total heat of evaporation, so that if any other definition is given of saturated steam than that which results from boiling the water under constant pressure after it has been drained of entangled water by gravitation, these properties and tables will not apply." In the same paper Professor REYNOLDS describes a method of experimenting in which it is sought to determine whether, by sufficient wiredrawing of saturated steam at a known initial pressure and temperature, the steam could be finally brought into the condition of steam gas.

Having undertaken the experimental verification of the conclusions given in Professor REYNOLDS'S paper, the author begs to point out the significance of the above extract in relation to any work which may be done in this subject, and to remark that it governs the methods and principles which have been adopted in the research, the results of which it is the object of this paper to describe.

The method given by Professor REYNOLDS is briefly as follows. If saturated steam be wiredrawn by passage through a small orifice from one chamber in which the pressure can be kept constant to another in which the pressure can be adjusted to have any lower value required, the steam in the second chamber will become superheated, and at first the temperature will fall, but if the pressure can be so far reduced in the second chamber that the amount of superheat contained by the steam is sufficient to render it perfectly gaseous, the temperature will be then unaffected by any further reduction in the pressure in the second chamber. Whether this "perfect gas" condition can be reached, by wiredrawing saturated steam from pressures up to 200 lbs. per square inch, is the question which it is the primary object of the present research to decide.

Before proceeding, however, very closely into the research, an examination of the theory of such wiredrawing experiments will reveal a point which would require definite settlement before the method described above could be adopted. In reducing the results of any wiredrawing experiments it would be necessary to know, or to possess some knowledge of, the precise law of flow which the steam obeys during its passage through the orifice. The usual theory adopted assumes that this law is the adiabatic one for saturated steam, but whether adiabatic flow is ever obtained in actual wiredrawing experiments is as yet undecided, and will, as mentioned above, require definite settlement.

Hence the author was recommended by Professor REYNOLDS to preface the research by an independent investigation into the laws governing the flow of steam through orifices of different natures. If it could be shown that the law of flow was never truly adiabatic, then the results of any wiredrawing experiments would not be capable of easy or accurate reduction to yield the thermodynamical properties which superheated steam possesses, but if such flow could be shown under certain circumstances to be adiabatic, then under these conditions the reductions would be both easy and direct.

The results of this preliminary inquiry, which are described in a paper* ("On the Law of Flow of Saturated Steam through Small Orifices"), recently presented to the Royal Society by the author, show clearly that adiabatic flow of saturated steam through an orifice occurs when the orifice is drilled in a piece of plate glass, under which circumstances the theory of the subject can be easily and directly applied to the experimental results.

Since the research is directly based on the experimental results of REGNAULT, it is necessary to at once accept as a definition of dry saturated steam that condition of steam which is obtained by draining from wet steam any entangled moisture, though it must be understood that as yet this condition has not been shown to be unique for any particular temperature and pressure of saturation, a point which can only be settled by experiment.

SECTION II.—*Short Theory.*

The account of the theory here given is that given by Professor REYNOLDS in the paper above quoted. Let p_1 be the pressure, T_1^1 the temperature, u_1 the velocity, and S_1 the dryness fraction of the steam before passing the orifice, and let the same letters with suffix 2 denote corresponding quantities after passing the orifice. Also let H_1 be the mechanical equivalent of the total heat of evaporation at pressure p_1, and $H_1 - h_1$, the equivalent of the latent heat at the same pressure per lb. of dry saturated steam as determined from REGNAULT'S steam tables. Let H_2 and $H_2 - h_2$ be corresponding quantities at the pressure p_2, and let H_J denote the equivalent of any heat received from external sources. Let T_2 be the temperature of saturated steam at the pressure p_2, a quantity to be determined from tables.

The total energy per lb. of fluid before passing the orifice is therefore

$$S_1(H_1 - h_1) + h_1 + \frac{u_1^2}{2g} + H_J,$$

and after passing the orifice the same quantity is

$$S_2(H_2 - h_2) + h_2 + \frac{u_2^2}{2g} + K(T_2^1 - T_2),$$

where K is the mean specific heat at constant pressure between the temperatures T_2 and T_2^1. Since the energy of motion developed in the orifice is entirely returned as heat, by the law of conservation of energy we may equate the two quantities here found, and we get

$$S_1(H_1 - h_1) + h_1 + \frac{u_1^2}{2g} + H_J = S_2(H_2 - h_2) + h_2 + \frac{u_2^2}{2g} + K(T_2^1 - T_2) \quad (1).$$

Now in this equation if S_2 is not equal to unity we must have $T_2^1 = T_2$, and in this case we should have

$$S_1(H_1 - h_1) + h_1 + \frac{u_1^2}{2g} + H_J = S_2(H_2 - h_2) + h_2 + \frac{u_2^2}{2g} \quad . \quad . \quad (2),$$

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* Not printed, but preserved for reference in the archives of the Society.

or, if S_2 is equal to unity, in which case the steam becomes superheated, we have

$$S_1(H_1 - h_1) + h_1 + \frac{u_1^2}{2g} + H_J = H_2 + \frac{u_2^2}{2g} + K(T_2^1 - T_2) \quad . \quad . \quad . \quad (3).$$

Further, if we make u_1 and u_2 small enough to be neglected, and ensure that $H_J = 0$, we get instead of (2) and (3) the equations

$$S_1(H_1 - h_1) + h_1 = S_2(H_2 - h_2) + h_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4),$$

when S_2 is not equal to unity, and

$$S_1(H_1 - h_1) + h_1 = H_2 + K(T_2^1 - T_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (5),$$

when S_2 is equal to unity.

The second of these two equations is the one used in wiredrawing experiments in which it is sought to determine the initial dryness of the steam, for this purpose a value of K being assumed, which is usually REGNAULT'S determination of the mean specific heat at constant pressure (atmospheric) from 248° to 428° F. approximately.

Now from previous experiments made with superheated steam there appears to be good reason for thinking that when the steam is superheated to a considerable degree its condition approximates to that of a perfect gas. If in any wiredrawing experiments, such as those here described, the amount of superheating in the wiredrawn steam is sufficient to bring it to the gaseous condition, the temperature of the wiredrawn steam will suffer no further diminution, however much the wiredrawing be increased by lowering the pressure below the orifice. If such a condition could be experimentally obtained, it would be then easily possible to obtain the value K_p of the specific heat at constant pressure of steam gas. But RANKINE has proved* that if H_2^1 be the total heat of gasification of steam gas at temperature T_2^1 from any temperature T_0 at which saturated steam is sensibly a perfect gas, the operation being performed under constant pressure, then

$$H_2^1 = H_0 + K_p\,(T_2^1 - T_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6),$$

where H_0 is the latent heat of evaporation of saturated steam at the temperature T_0.

RANKINE assumed that saturated steam at 32° F. was sensibly a perfect gas, in which case the formula takes the form

$$H_2^1 = 1091{\cdot}7 + K_p(T_2^1 - 32) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7).$$

The formula may, however, be put in the more general form

$$H_2^1 = A + BT_2^1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8),$$

the constants A and B being obtained from any two experiments in each of which the perfectly gaseous condition is obtained by wiredrawing steam having a known total heat H_2^1 in its initial saturated condition.

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* 'The Steam Engine,' p. 330.

SECTION III.—*Preliminary Experiments.*

After completing the experiments on the quantities of steam discharged from an orifice, as described in the paper before referred to, at Professor REYNOLDS'S advice, I made some experiments on the temperatures of the wiredrawn steam, using for this purpose a thermo-electric junction inserted in the steam, and a second similar junction in the same circuit immersed in an oil bath, the temperature in which (given by a thermometer) may be adjusted to have any required value, both junctions being in circuit with a galvanometer. The remainder of the apparatus was unaltered. When both junctions are at the same temperature no deflection of the galvanometer needle will be observed, and hence the temperature in the oil could be adjusted to that in the steam.

The object of these experiments was to observe to what extent the results would be affected by radiation.

The results obtained were very useful in this direction. The amount of lagging of the channel containing the wiredrawn steam was altered in different experiments made under the same initial conditions of pressure and temperature above the orifice, the comparison of the results showing that radiation affects the results to a very great degree, even with a fair amount of lagging.

The fall of temperature in the wiredrawn steam in any experiment was almost proportional to the difference of pressure, a result which is in accord with those of later experiments.

The results of these preliminary experiments showed clearly that before any accurate work could be done on the temperatures, the effect of radiation must be eliminated, and in the construction of the apparatus as finally used (see Section V.) the manner in which this was effected will be described.

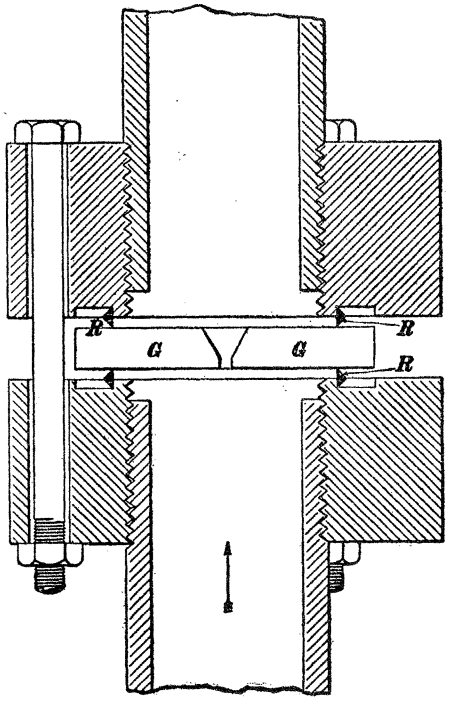
SECTION IV.—*Nature of Orifice used.*

In the paper on the "Flow of Saturated Steam" it is shown that steam flowing through a circular orifice in a glass plate expanded according to the adiabatic law. As a glass plate would also diminish materially the passage of heat by conduction from one side to the other of the orifice, it has many advantages over other materials for wiredrawing experiments in which the difference of temperature on the two sides of the orifice may be considerable, sometimes amounting to 70° F. in the following experiments.

The orifice used was a circular one of about $\frac{1}{16}$ inch diameter drilled in a piece of plate glass $\frac{1}{4}$ inch thick. This orifice plate O, is fixed between two cast-iron flanges, F and F, figure 3, the joints being made by copper rings; the flanges are connected by three bolts $\frac{3}{16}$ inch in diameter, passing through holes in the flanges $\frac{1}{4}$ inch diameter, thus preventing any material transfer of heat through the fastenings from the saturated steam to the wiredrawn steam.

The use of glass, however, increased the experimental difficulties considerably, for it often happened that the orifice plate would break during the heating of the apparatus, necessitating its removal and the insertion of a fresh plate before the experiment could be proceeded with. In the later experiments, made with great differences of pressure, the area exposed to this difference of pressure had to be reduced considerably for the plate to bear the combined differences of pressure and temperature. A full-size sectional view of the orifice plate and fastenings is shown in fig. 1.

Fig. 1.

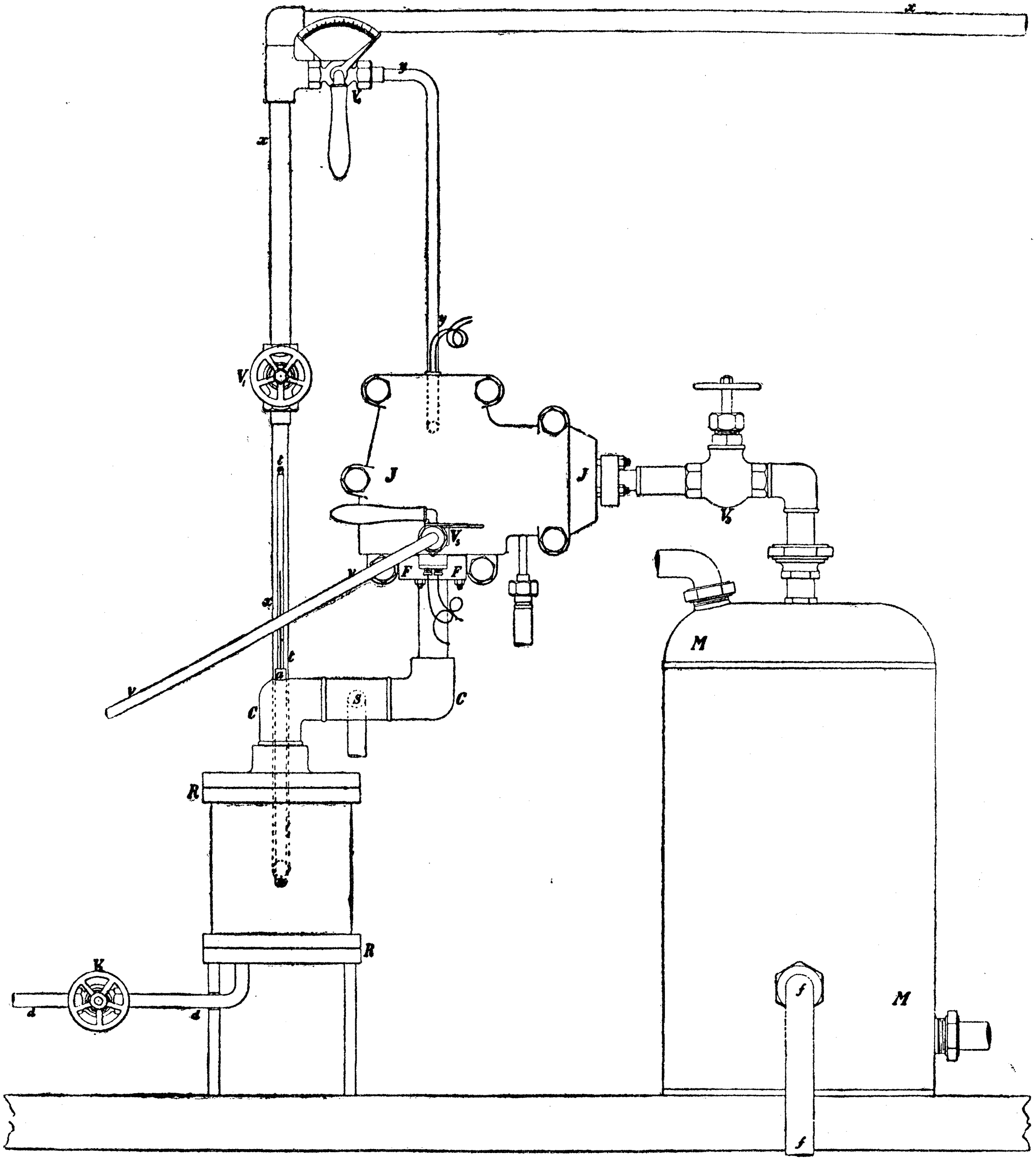


GG, glass plate.
RR, copper rings.

SECTION V.—*Description of Apparatus.*

A front view of the main portion of the apparatus is shown in fig. 2, RR being a vertical cylinder, forming a reservoir in which the steam is received through the pipe *xx* from the boiler. This reservoir or steam chest is of about 86 cubic inches capacity, and is provided with a drain pipe *dd*; the steam enters about the middle of its length, and the temperature in the chest is observed on a thermometer *tt*, standing in a tube *aa*, containing oil. The steam from this chamber flows upwards through the channel CC, leading from the centre of the upper cover to the orifice, the plate containing which is just hidden by the steam jacket JJ, to be presently described. The portion of the channel enclosed by the steam jacket is shown in section in fig. 3, O being the orifice plate. The steam after passing the orifice proceeds to the condenser MM, in fig. 3, and from thence by the pipe *ff* to an air vessel connected to an air pump (neither of which are shown in the figure).

Fig. 2.



The pressure in the chest RR is regulated by the valves V_1 in the admission

Fig. 3.

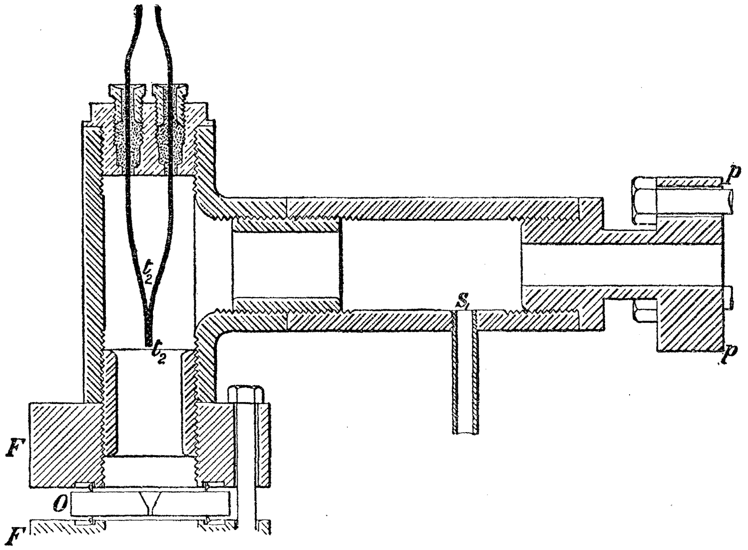
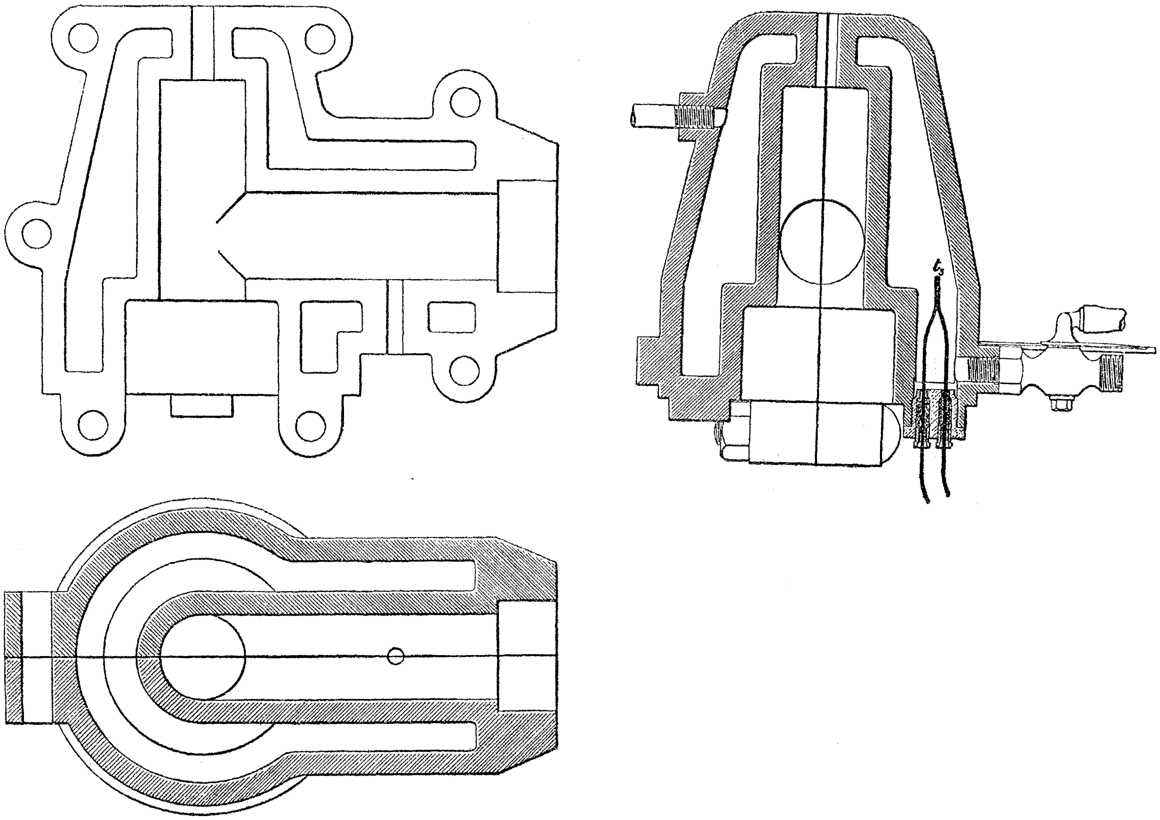


Fig. 4.



pipe and V_2 in the drain pipe, and its value is read by means of a pressure gauge, the siphon from which enters the channel CC at S. The pressure p_2 in the steam after passing the orifice is regulated by the valve V_3; but as the pressure below this valve is the same as that in the air vessel below the condenser, by sufficiently reducing this pressure in the air vessel by means of the air pump, it is possible to maintain any value of p_2, ranging from 2 or 3 lbs. absolute to p_1, the pressure in the chest RR.

The steam jacket to cover the channel containing the wiredrawn steam is shown in fig. 4. It was constructed so as to completely surround the channel leading from the orifice to a distance of about 8 inches from the orifice.

The portion of the channel surrounded by the jacket is separated from the other parts of the channel by the orifice plate O at one end, and by a ring of cork or asbestos at the other end *pp*, fig. 3. It consists of two sections at right angles to each other, a thermo-junction t_2t_2 entering at the elbow, and the siphon of a pressure gauge for registering the pressure p_2 entering at S_1.

The steam jacket is supported by the channel it surrounds, and is itself a complete and enclosed vessel; it was made of cast iron, its thickness $\frac{3}{8}$ inch throughout, and was made in two halves, so that it could be removed, if required, without disturbing the remainder of the apparatus. These two halves are bolted together, the joints being made by rings of copper. The jacket steam was drawn from the pipe *xx* (fig. 2) coming from the boiler, by the branch pipe *yy*, and a small flow of steam was kept up through the drain pipe *vv* from the jacket. The temperature in the jacket was regulated to any desired value by altering the pressure of the steam in the jacket by the valves V_4 and V_5 in the admission pipe *yy* and drain pipe *vv* respectively.

The idea of constructing a steam cosie,* which should be entirely independent of the steam channel it surrounds, was due to Professor REYNOLDS, and the author is indebted to Mr. FOSTER, the chief assistant in the laboratory, for valuable aid in its construction.

Such, then, is the apparatus as finally used in the experiments. Its arrangement was, however, not altogether a simple matter of preconceived design, but was the outcome of continued adaptability and enlargement to meet the necessities and difficulties as they arose.

The source of steam supply when initial pressures up to 50 lbs. per square inch were used was a large Lancashire boiler used for heating purposes. When higher initial pressures were required, the author obtained permission from Professor REYNOLDS to use the locomotive boiler used in connection with the experimental engines in the Whitworth Engineering Laboratory of the Owens College, Manchester, and the author must express his indebtedness to the assistant, Mr. J. HALL, for the excellent manner in which the boiler pressure was kept constant during the long experiments.

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* Used by REGNAULT in his latent heat experiments.

SECTION VI.—*On the Methods of Determining the Pressures and Temperatures.*

Into the reservoir RR a tube of brass *aa*, closed at the bottom, penetrates, as shown in fig. 2. This tube contains oil, and in it a thermometer is placed; the length of this thermometer immersed in oil being a matter of importance, it was sought to keep the amount of oil in the tube as constant as possible during the experiments.

The pressure of the steam before entering the orifice was observed on a Bourdon pressure gauge, the siphon from which enters the steam channel at S, between the reservoir and the orifice.

The pressure of the wiredrawn steam was observed, during the experiments with steam from the Lancashire boiler, by a mercury pressure gauge, and afterwards by a second Bourdon pressure gauge, the siphon from which passed through the jacket surrounding the channel, and entered the channel at S_1, fig. 3.

The temperature of the wiredrawn steam was determined by inserting a thermo-junction of iron and copper into the steam channel, as at t_2t_2, fig. 3, the wires passed out of the channel through two small glands in a brass plug, the joints being made with asbestos, which also formed the insulator for the wires. A second similar thermo-junction in circuit with the first is placed in an oil bath, the temperature in which could be adjusted to any required degree, the oil being stirred by two screw blades, worked by a small water motor. In this bath a thermometer was fixed, and the equality of temperature between the junction in the oil and the junction in the steam was shown by a galvanometer with mirror and scale. The ends of the copper wires from the two junctions dipped into two small mercury cups, and the ends of two copper wires from the galvanometer were dipped into these cups, completing the circuit. If any difference of temperature existed between the junctions, the galvanometer needle would be deflected, and by diminishing these deflections by altering the temperature of the oil bath, the final equality of temperatures between the thermo-junctions in the steam and oil was determined.

The difference of temperature between the steam in the jacket and the wiredrawn steam was observed by having a thermo-junction similar to that in the wiredrawn steam placed in the steam jacket at t_3, fig. 4; a second similar junction was placed in the oil bath mentioned above.

These two junctions could now be brought into circuit with the galvanometer in a precisely similar manner to the other pair of junctions in the oil bath and the wiredrawn steam, as described already. When the oil bath temperature has been adjusted to equality with that of the wiredrawn steam, the galvanometer was immediately brought into circuit with the junctions in the oil and the steam jacket; any deflection of the galvanometer needle would now be proportional to the difference of temperature between the oil and the steam in the jacket, and therefore to the difference in the temperatures of the wiredrawn steam and the steam in the jacket.

The use of thermo-electric junctions to determine the temperature of the wiredrawn steam was suggested to the author by Professor Reynolds. The direct determination of the temperature by the insertion of the thermometer in the steam would have increased the difficulty of obtaining correct temperature readings considerably, on account of the many corrections necessary.

Section VII.—*Method of Experiment.*

It was found necessary in beginning an experiment to warm the apparatus gently, as the orifice plate frequently cracked with sudden heating. When sufficient steam was passing through the apparatus and the required pressures attained, the admission valve was fixed sufficiently wide open to allow the maximum quantity of steam per minute required during the experiment to flow through it, and at the same time allow a sufficiency for drainage.

The pressure in the steam reservoir was then kept constant during the experiment by opening or closing the valve in the drain pipe according to the quantity required through the orifice. The opening in the valve V_3 beyond the orifice was then fixed so as to give any desired constant pressure to the wiredrawn steam; the temperature of the oil bath was then raised to equality with that of the wiredrawn steam, and the temperature in the steam jacket adjusted to equality with that in the oil bath by a few observations with the galvanometer. It was then necessary to wait for about 2 hours before a steady condition could be obtained; during this period the temperature of the wiredrawn steam would rise slowly, causing the temperatures in the oil bath and in the steam jacket to be continually readjusted.

After about 3 hours from the commencement of the experiment, the temperatures became sufficiently steady to allow readings to be taken. Observations of the temperatures in the steam reservoir and in the oil bath, and of the pressure below the orifice, are then taken as often as possible, intervals of 2 to 5 minutes elapsing between successive readings, the mean of successive readings taken over a period of from 15 to 30 minutes being taken as the correct reading, as shown in Table I.

The method of taking a reading is as follows:—The pressure being steady on either side of the orifice, the oil in the bath, which is kept at a slightly different temperature from that of the steam, is heated or cooled slowly, as required, during which period the galvanometer is brought several times into circuit with the junction in the steam, until the deflection of the needle ultimately vanishes. When this point is reached the temperature is noted on the oil bath thermometer; immediately this is read the galvanometer is brought into circuit with the junction in the steam jacket, and any deflection of the needle noted. These are entered along with the temperature in the reservoir and the pressure below the orifice in the following table, the column headed R—S giving the reading R before circuiting, and S the deflected reading; if R—S is positive, the steam in the jacket is hotter than the wiredrawn steam, and *vice versâ*.

TABLE I.—Experiment 19.

Thursday, April 21st, 1898.

Boiler pressure about 33 lbs. by gauge.
Pressure in steam chest about 23·4 lbs. by gauge.

Time.	Temp. in Oil T_2	Pressure p_2	Mean T_2	Mean p_2	Initial Temp. T_1	R—S		Remarks.
10.15 a.m.								Pressure in steam chest 20 lbs.
10.40 ,,								Bad leak. Steam shut off and orifice plate moved.
10.53 ,,								Pressure in steam chest 22 lbs.
11.0 ,,								Steady pressures.
1.33 p.m.	248·2	8·5			263·5	6·8	7·0	Boiler pressure 33 lbs. by gauge.
41 ,,	248·8	8·4			263·5	6·2	6·0	
47 ,,	249·0	8·5			263·6	6·2	6·3	
52 ,,	249·7	8·3			263·4	6·0	6·1	
54½ ,,	249·9	8·3			263·5	6·0	6·0	
57 ,,	249·8	8·3	249·83	8·21	263·5	6·0	6·0	
59½ ,,	249·9	8·2			263·5	5·9	5·9	
2.3 ,,	249·9	8·2			263·5	5·9	6·0	
5½ ,,	249·8	8·2			263·5	5·8	5·8	
8½ ,,	249·8	8·2			263·6	5·8	5·8	
12 ,,	249·8	8·2			263·5	5·8	5·8	
15 ,,	249·8	8·2			263·5	5·9	5·9	
16 p.m.								p_2 altered.
28 ,,	254·2	17·0			263·5	5·8	5·7	
32 ,,	254·2	17·0			263·5	5·9	5·8	
41 ,,	254·4	17·1	254·4	17·05	263·6	5·8	5·7	Boiler pressure 33 lbs.
45 ,,	254·4	17·1			263·5	5·8	5·8	
47½ ,,	254·4	17·1			263·5	5·7	5·7	
50 ,,	254·4	17·0			263·7	5·7	5·6	
52½ ,,	254·4	17·0			263·5	5·6	5·6	
55 ,,	254·4	17·0			263 5	5·6	5·6	
56 p.m.								
3.22 ,,	247·0	1·8			263·5	6·0	6·0	
25½ ,,	247·0	1·7			263·5	6·0	6·0	
29 ,,	246·8	1·7			263·5	5·8	6·0	
32 ,,	246·5	1·7			263·5	5·8	5·7	
35 ,,	246·4	1·7			263·6	5·8	5·7	
38 ,,	246·1	1·6	246·13	1·64	263·5	5·8	5·7	
40½ ,,	246·1	1·7			263·4	5·5	5·4	
43 ,,	246·1	1·7			263·5	5·4	5·3	
45½ ,,	246·2	1·7			263·5	5·4	5·4	
47½ ,,	246·2	1·6			263·6	5·2	5·2	
50 ,,	246·1	1·6			263·6	5·4	5·4	
53 ,,	246·1	1·6			263·5	5·3	5·3	

Barometric height.	Time.	Temperature of air.
30·164	1·58	62·0°
30·160	2·53	62·5
30·153	3·51	62·5

TABLE II.

Boiler pressure.	Atmospheric pressure.	Pressure in chest.	T_1.	p_2 (by gauge).	T_2.	Corrections for			Corrected values of		
						T_1.	p_2.	T_2.	T_1.	p_2.	T_2.
33 lbs. by gauges	14·84	23·4 by gauge.	263·5	8·21	249·83	$-2·0$	$-1·55$	0·7	Mean	21·5	250·5
			263·55	17·05	254·4		$-1·6$	0·6	361·5	30·3	255·0
			263·5	1·64	246·13		$-1·2$	0·7		15·3	246·8

In the lower of these tables is given the corrections and the corrected values of the mean temperatures and pressures drawn from the fourth and fifth columns in the first table.

An experiment usually lasts from 6 to 8 hours, during which time three to six mean values of T_2 for different values of p_2 will be found for any initial pressure and temperature in the reservoir.

SECTION VIII.—*The Correction of the Pressure Gauges.*

The Bourdon pressure gauges used during the experiments were corrected by means of a Bailey pressure gauge testing machine. In this machine the gauge is subjected to hydraulic pressure, obtained by placing as many weights as required upon a ram. The machine itself was subjected to examination by checking all the weights used, and also the sectional area of the ram; in this way the pressure per square inch produced by placing any weight upon the ram could be directly calculated. A further test was also made for small loads by the use of a mercury column to balance the pressure produced by the dead load on the ram.

The pressure gauges when tested showed the usual discrepancies of such gauges, but in tests made at various times during the research, the amount of the corrections was very closely determined. Especially was this the case with the pressure gauge used above the orifice, as it was by this gauge that the thermometers were corrected, and it is improbable that the error in the gauge when finally corrected could exceed 0·1 lb. per square inch in any part of the scale.

SECTION IX.—*The Correction of the Thermometers.*

Before proceeding to describe the method of correcting the thermometers used, it is necessary to repeat, as stated in the first part of this paper, that the research is based on REGNAULT'S determinations of the relations between the pressure, temperature, and total heat of evaporation of saturated steam, and hence the definition of temperature assumed for the purposes of this paper is that saturated steam under a certain pressure has a fixed temperature given by REGNAULT'S tabulated results.

The method of correction to be described was adopted since it removed the necessity of correcting the thermometers for the length of stems in the oil, and also any error which may arise from any of the junctions not finally attaining the same temperature of the steam or oil in which they are immersed. This method was to correct the thermometers in position in the apparatus, using the thermo-junctions, and without making any alterations except to substitute for the orifice plate another plate containing a large hole, which would not in any degree wiredraw the steam, so that saturated steam at a known pressure would occupy the whole of the channel and the steam chest; the outflow of steam, or the velocity of steam through the apparatus, could then be regulated by the valve on the low pressure side of the orifice. The pressure gauge relied upon to denote the pressure in the steam was the one used to give the pressure in the reservoir, its readings having been corrected as already described.

The operation of correcting the thermometers was then proceeded with as in an ordinary experiment, the only difference being that now the steam is always saturated in the apparatus.

Experiments were conducted on six days with this object, and from the results of these experiments the necessary corrections for both thermometers were obtained throughout the range of temperature required.

Hence it will be seen that the thermometers were used merely as instruments to effect a comparison of two temperatures, one of which was the temperature of saturated steam under a known pressure, and the other the temperature in the wiredrawn steam, so that the basis of the whole method has been reduced to a comparison between the temperatures of the wiredrawn steam and of saturated steam under known pressures when flowing with approximately the same velocity through the same portions of the apparatus.

SECTION X.—*Results of Experiments.*

The experiments on this subject were commenced in January, 1897, the earlier ones being chiefly devoted to determining the precautions necessary, and the best form of apparatus to use (see Section II.). These experiments showed that the chief source of error was the radiation of heat from the channel containing the wiredrawn steam, this being remedied by the construction of a steam jacket.

The apparatus as finally used, and as described in Section IV., was ready for experiments in November, 1897, and as often as circumstances permitted experiments were made until July, 1898. The first experiments made, however, gave results of very little value, since it was proved that sufficient time had not been allowed for the steady condition of pressure and temperature to become established before taking observations, and henceforward particular attention was given during any experiment to obtaining a few temperature results at pressures covering a wide range of pressure ratio.

Among the many sources of experimental error encountered was one which for some time affected to a great extent the observations taken at very low pressures below the orifice, and which caused a great deal of trouble during the experiments. Thus, when observations at low pressures were being taken and continual pumping required to maintain those pressures, the temperature of the superheated steam could not be obtained with any degree of consistency.

The cause of this inconsistency appeared to be connected with the amount of pumping necessary, and in later experiments, where the low pressures could be maintained with little or no pumping for about half an hour, it was found that consistent readings could be obtained, and only readings obtained under these conditions are accepted and find place in the table of results given below.

The corrected results of twenty-eight experiments made with saturated steam at temperatures varying from 240° to 380° F. are given in the accompanying Table III., T_1 and p_1 being the initial temperature and pressure respectively of the saturated steam before wiredrawing, p_1 being taken from REGNAULT'S steam tables, and T_2 the temperature of the wiredrawn steam corresponding to the pressure p_2.

TABLE III.

No. of experiment.	p_1.	T_1.	p_2.	T_2.	Total heat of the steam from 32° F. in B.T.U.s.
1	24·9	239·8	16·5	232·35	1155·08
			8·9	226·4	
			5·05	224·4	
			8·9	226·75	
			18·1	232·65	
2	24·9	239·8	15·3	232·05	1155·08
			4·2	224·4	
			9·8	227·65	
			4·2	224·2	
			19·5	234·15	
3	24·9	239·8	19·3	234·55	1155·08
			4·6	224·2	
			18·6	233·25	

TABLE III. (continued).

No. of experiment.	p_1.	T_1.	p_2.	T_2.	Total heat of the steam from 32° F. in B.T.U.s.
4	52·5	284·0	27·9	268·7	1168·56
			15·6	261·5	
			3·4	254·35	
5	52·5	284·0	21·5	264·5	1168·56
			33·8	271·45	
			7·8	256·45	
			17·9	262·75	
6	52·5	284·0	17·2	262·4	1168·56
			36·6	272·9	
			5·05	256·1	
7	52·5	284·0	36·45	272·15	1168·56
			22·0	264·7	
			7·5	256·2	
8	36·8	262·0	18·1	248·9	1161·85
			34·1	256·75	
			6·4	240·8	
			25·3	252·3	
9	36·8	262·0	28·65	254·65	1161·85
			34·0	257·6	
			5·6	240·7	
			10·2	243·85	
10	66·2	298·9	54·8	290·1	1173·1
			19·95	272·15	
			28·5	277·2	
11	66·2	298·9	27·05	276·05	1173·1
			45·5	285·2	
			56·3	291·4	
			33·8	279·5	
			15·85	270·4	
			6·9	265·2	
12	66·2	298·9	18·2	271·95	1173·1
			38·6	282·15	
			6·9	265·3	
			7·1	265·5	
			4·5	264·5	
13	66·2	298·9	24·45	274·35	1173·1
			41·05	283·35	
			49·55	287·45	
			31·1	277·9	
			15·65	269·8	
14	66·2	298·9	15·2	270·2	1173·1
			49·65	287·4	
			58·3	291·05	
			15·85	270·5	

TABLE III. (continued).

No. of experiment.	p_1.	T_1.	p_2.	T_2.	Total heat of the steam from 32° F. in B.T.U.s.
15	126·55	345·05	32·7 63·7 91·1 71·35	302·9 316·3 328·1 319·05	1187·18
16	126·7	345·15	48·15 81·1 23·2 15·15	309·15 323·85 298·9 295·1	1187·21
17	126·85	345·25	69·8 96·8 32·2 17·2	319·2 329·6 303·1 296·3	1187·24
18	66·1	298·8	22·15	274·05	1173·07
19	36·7	261·5	21·5 30·3 15·3	250·5 255·0 246·8	1161·7
20	36·7	261·5	20·7	250·2	1161·7
21	36·7	261·5	25·75 33·15 30·05 15·8 6·9	252·5 256·6 254·25 246·2 241·7	1161·7
22	24·8	239·2	16·2 18·4 20·45 21·9 3·9	232·2 233·25 234·45 235·25 224·6	1154·9
23	24·8	239·2	16·4 7·6 4·6 2·45	232·15 226·2 223·3 222·4	1154·9
24	24·8	239·2	17·95 3·35	232·9 223·6	1154·9
25	195·25	379·55	71·95 111·5 151·4	337·05 350·85 363·3	1197·7
26	195·3	379·55	91·5 131·75 182·2	344·05 357·03 373·9	1197·7
27	195·3	379·55	111·65 48·2	350·75 326·9	1197·7
28	195·15	379·5	71·8 52·15 30·4 14·95	337·0 328·2 318·3 311·6	1197·69

SECTION XI.—*On the Effect of Altering the Condition of the Steam below the Orifice.*

The preliminary experiments and those numbered 1 to 10 in Table III. were made with steam from a Lancashire boiler. The steam was withdrawn upwards from this boiler through a channel consisting of $\frac{3}{8}$-inch unlagged steam piping, which passed 2·5 feet vertically, then 64 feet horizontally, and finally 9·7 feet downwards to the steam chest. This great length of piping ensured a great amount of wetness in the steam when received in the steam chest. In the later experiments the steam was taken from a locomotive boiler much nearer the apparatus, the length of the connecting pipe ($\frac{3}{4}$-inch steam piping) being 39 feet. In Experiments 19 to 24 this connecting pipe was well lagged with rough felting, as was also the steam chest; but, comparing the results of Experiments 19 to 21 with those of Experiments 8 and 9, which were made under the same initial conditions, or the results of Experiments 22 to 24 with those of Experiments 1, 2, and 3, it is shown very clearly that, though the condition of the steam in the steam chest when received from the boiler is very different in the two cases, no apparent difference is obtained in the condition of the wiredrawn steam.

The same point is also made clear by comparing the results of Experiments 15, 16, and 17. Experiment 15 was made with the channel from the boiler to the steam chest unlagged, the other two being made with the channel well lagged.

In Experiment 18, an attempt was made to alter, if possible, the initial dryness of the steam by working the injector for about 20 minutes during the experiment. This may have the effect of sending over more priming water by creating a stir in the boiler and also of introducing a little air into the boiler. A difference of 0·2° F. was all that was obtained, this being less than the error of experiment. The results of this Experiment 18, in which the steam pipe from the boiler and the steam chest were well lagged, show no apparent difference from those of Experiments 10—14, during which both the pipe and the steam chest were unlagged.

As a further experiment on the same point, the author tried to find in Experiment 20 the effect of altering the boiler pressure, the pressure in the steam chest being kept constant as usual. In this experiment, $p_1 = 23{\cdot}4$ lbs. by gauge, or 36·7 lbs. per sq. inch absolute, and $p_2 = 20{\cdot}7$ lbs. The boiler pressure during the first part of the experiment was 60 lbs. by gauge, and during the latter part 90 lbs., thus increasing the amount of wiredrawing between the boiler and the steam chest considerably. The mean temperature of the wiredrawn steam was found to be the same both before and after the alteration in the boiler pressure.

This experiment was then continued to observe what effect an alteration in the amount of drainage of steam over and above the water from the steam chest had upon the temperature readings. Keeping p_1 and p_2 the same as above, it was found that by almost closing the drain pipe valve so that only a very small quantity of steam passed with the water from the steam chest, the temperature of the wiredrawn steam became lower by nearly 0·35° in about 10 minutes, and remained at this lower value so long as the drainage was thus restricted. This decrease of temperature was clearly noticeable, and, though its amount was relatively small compared with the increase of wetness in the steam in the steam chest, its existence seemed to impair in a slight degree the deduction that the condition of the steam was always the same just before entering the orifice.

There is, however, one point to notice which has not previously been mentioned, and which was suggested to the author by Professor REYNOLDS as accounting for this peculiar difference observed in the temperature of the wiredrawn steam; the water in the boiler is certainly not free from air, and even a small quantity of air in the steam entering the steam pipe with the steam, owing to the fact that a large quantity of steam leaving the boiler is condensed in the pipe and steam chest, would, if the actual steam drained away is very small, represent a much greater percentage of air entering the orifice with the steam than in the steam leaving the boiler. With good drainage of steam and water from the steam chest, this percentage of air would be very much smaller and most of it would be carried away through the drain pipe on account of its slightly greater density.

In any case, however, this maximum difference of temperature in the wiredrawn steam is scarcely sufficient, considering the good drainage usually allowed from the steam chest in the experiments and the general accuracy to which the results attained, to justify the conclusion that the conditions of the steam just before passing the orifice was ever materially altered.

An examination of all the results of experiments with steam of different conditions of wetness in the steam chest certainly shows that by withdrawing steam upwards from a steam chest containing wet steam, and allowing the moisture to separate by gravitation, the steam can always be obtained in the same condition as to dryness, and it is to these results that the author looks for experimental justification for taking the total heat of the steam before entering the orifice, to be given by tables deduced from the results of REGNAULT'S experiments on the total heat of evaporation of saturated steam.

SECTION XII.—*On the Energy of Motion of the Steam at places where the Temperatures and Pressures are observed.*

Among the many causes which influence the results of experiments on the wiredrawing of steam, the energy of motion of the fluid at the places at which the temperatures and pressures are taken is perhaps the chief. As will be seen in the figure, the thermo-junction by which the temperature of the wiredrawn steam is ascertained, is about 2 inches from the orifice in a narrow channel, and it is to these temperature readings that we must look for the maximum effect of this energy of motion. In the experiments the quantities through the orifice were always relatively small—the orifice being a small one.

In the first place, before making this point the subject of direct experiment, we may remark that the maximum quantities of steam per minute in any two experiments under the same initial conditions were not the same on account of the gradual closing of the orifice by fine particles of dust.

Thus Experiment 18, made under the same initial conditions as regards pressure and temperature to Experiments 10—14, gave results which were not different from those of the latter experiments, though the quantity of steam, when a maximum, in Experiment 18 was only 1 lb. in 40 minutes, while in Experiments 10—14 the maximum quantity would sometimes reach 1 lb. in 8 minutes, which would occur when the orifice was clean as in Experiment 13.

Similar variations in quantity and, therefore, in the energy of motion of the steam occurred in other experiments under the same initial conditions in which, again, no difference could be detected.

The results obtained, therefore, would indicate that the effect of energy of motion on the readings taken was too small to be noticed. To put the matter to a more severe test, however, an orifice of more than three times the sectional area of the one previously used was employed to repeat experiments at low initial steam pressures.

In the first experiment made with this orifice, the quantity of steam through the apparatus was so great that drops of water were carried through the orifice, being the water from the steam condensed just before the orifice was reached. No definite results could, therefore, be obtained as the condition of the wiredrawn steam seldom left the saturated state. The maximum quantity of steam used in this experiment was 1 lb. in 2·1 minutes, the initial temperature being 303° F.

The initial pressure was therefore reduced in the next experiment made with the same orifice. The initial temperature was 262·5°, the quantity of steam used per minute being at least three times greater than that in Experiments 19—21, the initial temperature in these experiments being 261·5°. The experiment gave four temperature readings which, when plotted, showed a mean deviation from the curve drawn through the results of 19—21 of 1·2° F.; as, however, the initial temperature was 1° higher, the difference is not sufficient to show definitely any marked effect of increasing the energy of motion of the steam at least threefold.

As, however, the velocity of the steam was raised in these experiments up to the point at which bubbles of water were carried through the orifice, it is impossible to put a greater test on the apparatus to find the effect of the energy of motion of the fluid on the temperature and pressure readings.

The energy of motion of the steam, after wiredrawing, at the place where the thermo-junction is placed to register its temperature, can also be approximately calculated, and, for present purposes, it will be sufficient to take the actual reading in the experiments at which this energy of motion will probably be greatest. On examination of the pressures and quantities of steam through the orifice per minute, it appears that the reading at the pressure 14·95 lbs. in Experiment 28 will most probably feel the effects of this energy of motion to the greatest extent.

Taking now the sectional area of the channel, using the maximum rate of discharge of the steam in this experiment (1 lb. in 4·8 minutes), and making an approximation to the density of steam at a pressure 14·95 lbs. per square inch and temperature 311·6° F., the velocity of the steam at the place where the thermo-junction is placed works out at 41·6 feet per second. The energy of motion per lb. of steam at that velocity is 54·1 work units or 0·07 B.T.U. Taking the specific heat of superheated steam as 0·5, the fall of temperature due to this energy of motion is 0·14° F., which is much less than the experimental error, and, as this will be probably the maximum fall, being very much less than this for by far the greater part of the readings taken, it will not be necessary to make any corrections upon this head.

The effect of the velocity of the steam on the observed pressure may also be approximately calculated; but, taking the maximum quantities, the loss of pressure due to this cause never exceeded 0·1 lb. on the sq. inch, and, as it is usually very much less than this, we need not take this loss into account.

SECTION XIII.—*On the Position of the Thermo-junction in the Steam.*

After Experiment 27 had been made, a second thermo-junction was inserted in the channel on the low pressure side of the orifice, the junction being placed in the horizontal portion of the channel, about 3½ inches from the orifice. The wires from this junction passed out of the channel between the two flanges at the end *pp*, fig. 3, of that portion covered by the steam jacket. Another similar junction in the same circuit was placed in the oil bath, and the galvanometer was brought into the circuit by the same process as with the previous circuit, viz., by dipping the ends of the wires into mercury cups into which the ends of the wires from the galvanometer can be dipped. By this means either the old circuit or the new one can be brought into the galvanometer circuit. As the above alteration includes the making of an entirely new circuit, which is differently placed in the apparatus to the old one, small differences may exist between the readings given by the two circuits. Hence in any experiment made with the aid of the new circuit the thermometric observations should be corrected by again comparing the temperatures found with those of saturated steam under known pressures, using this same circuit to effect the comparison. An experiment was then made with the new circuit in position, with the object of ascertaining whether the superheated steam had different temperatures in different parts of the channel. The observations taken during this experiment showed a mean increase on those of previous experiments made under the same initial conditions of 1·2° F., the rate of fall of temperature with pressure in the wiredrawn steam being the same as that indicated in previous experiments.

This result appeared very interesting, and appeared to lead to something which may have affected the results considerably, all that is necessary to know now being that the comparison of temperatures given by this circuit is the same as that by the previous one.

To effect this comparison an experiment was made with saturated steam under known pressures flowing through the apparatus, the orifice plate having been removed for this purpose in precisely the same way as described in correcting the thermometers. When the conditions were steady, each of the two circuits from the junctions in the steam were brought in turn into circuit with the galvanometer. The mean of the actual readings on the thermometer in the oil bath given by the two circuits were 248·05° by the new circuit and 246·95° by the old one, and again 248·0° by the new circuit, the difference being about 1·1° F.

Thus it appears that when the results given by the new circuit are corrected in the same manner as were those with the previous circuit, the corrected results do not differ by an amount so great as the natural error of experiment, and above all it is shown that experiments made with the junction immersed in the steam in the horizontal portion of the channel, and therefore not in a position directly opposite the orifice, as is the case with the old junction, would give results which within the limits of experimental accuracy do not differ from those already obtained with the old circuit.

In the last experiment made (No. 28), since the temperatures were here very high, and the flow of steam very great, after the completion of the experiment with the aid of the old circuit, the new circuit was brought into play to see if this same difference existed at higher temperatures. The actual readings taken with the old circuit at the pressure 15·75 lbs. being 310·25°, and with the new circuit 311·3°, the difference being 1·05°, which is practically the same as that found to exist between the observations given by the two junctions at lower temperatures. Hence, as has been shown, the same results would have been obtained had either of the two positions in the steam channel been initially chosen to plan the thermo-junction.

SECTION XIV.—*On the Transference of Heat across the Orifice Plate.*

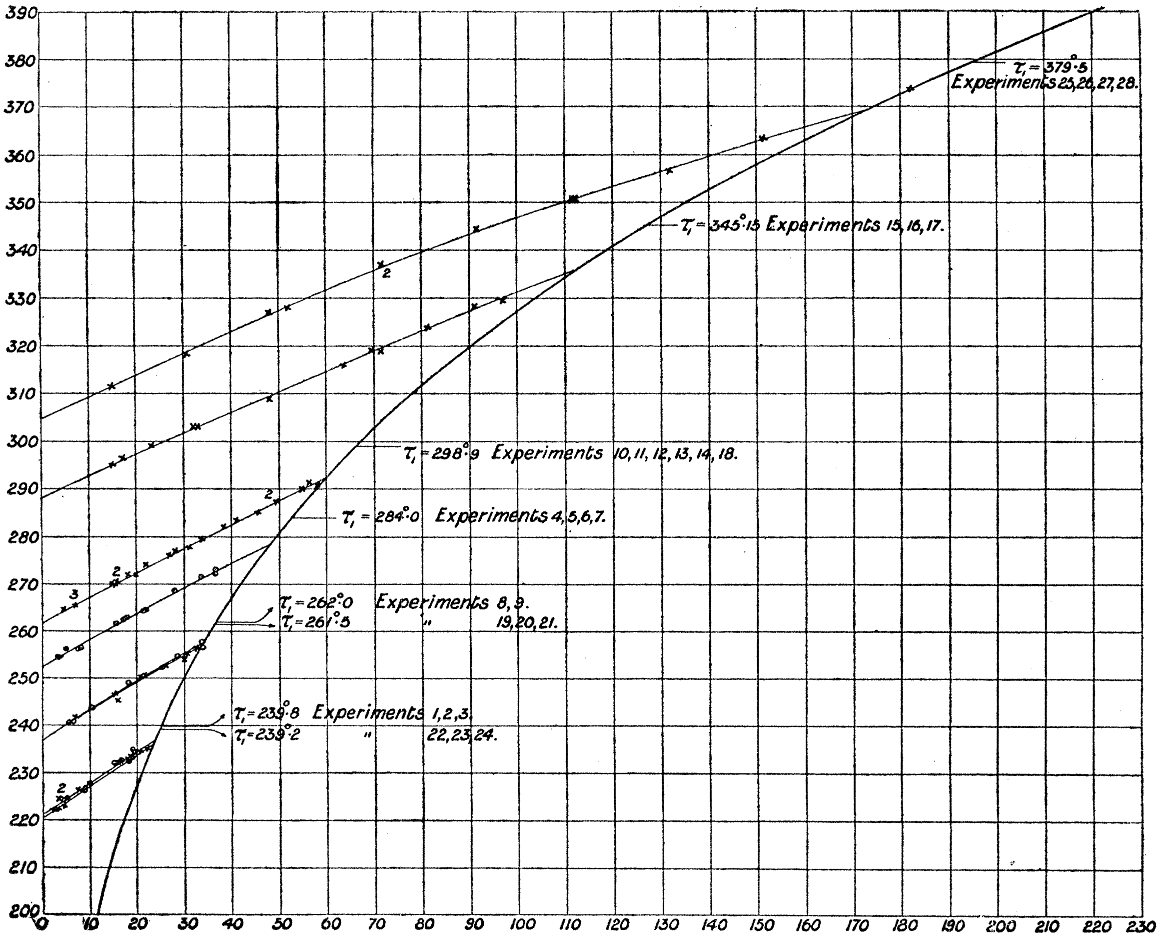
In the experiments made with high initial temperatures the difference of temperature on the two sides of the orifice plate sometimes amounted to over 50°, and if only a small quantity of steam is flowing through the channel the heat transferred from one side to the other of the orifice may become relatively very important.

In order to calculate the maximum difference of temperature caused by this transference, the author took an hypothetical case in which the difference of temperature on the two sides of the orifice plate was 50° F., and the quantity of steam 1 lb. in 12 minutes, the effect of this combination of circumstances being greater than any actually experienced in the experiments. Thus the quantity of heat conducted through a glass plate $\frac{1}{4}$ inch thick and of sectional area 1·11 sq. inches, with a difference of temperature of 50° F. on its faces, would be about 0·037 B.T.U. per minute, and taking the specific heat of the superheated steam as 0·5 and the quantity of steam 1 lb. in 12 minutes, the rise of temperature of the wiredrawn steam is calculated to be nearly 0·9° F. As in actual experiments the difference of temperature due to this transference of heat by conduction will be much less than this, no attempt has been made to correct the actual results for these differences.

SECTION XV.—*Reduction of the Observations.*

The performance of any of the experiments here described will give a series of relations between the pressure and temperature of the wiredrawn steam for a particular initial condition of the steam as regards its pressure and temperature. If now these results be plotted on a diagram with pressures for abscissæ and temperatures as ordinates, we get a series of points as shown in Diagram 5. On this diagram the initial condition of the steam in any experiment is shown on the

Diagram 5.



saturation curve, the number of the experiment being also indicated. When the experiment was made with steam from the large Lancashire boiler, the points representing the p—t relations observed are indicated by small circles.

Suppose now that through the points thus obtained a series of curves be drawn to represent the law of cooling from any initial condition. It will be found that if a mean curve be drawn through all the points obtained by using steam in a given initial condition, it will also be a mean curve for the points obtained from any single experiment at the same initial pressure and temperature. The relative accuracy which the experiments attain is clearly shown by the diagram, the greatest distance from any point representing the p—t relation in any experiment to the mean curve through the points obtained in all experiments under the same initial conditions being little, if any, greater than the expected error of experiment under that particular p—t relation.

The use of these curves will facilitate the deductions from the experiments of the actual law of cooling of the steam and of the variation of the specific heat at constant pressure with both pressure and temperature.

SECTION XVI.—*Summary of Results.*

The first point of importance brought out by the experiments is that so far as they have been carried the steam never became what is known as a perfect gas. For had such a condition been arrived at, the curve representing the pressure—temperature relation in the steam in that condition would have become parallel to the axis of pressures, as the cooling would then have practically vanished.

Coming now to consider any one of the mean curves drawn on Diagram 5, it may be at once remarked that the portions of the curve which are of the greatest interest were the hardest to obtain. For instance, when the difference in the two pressures causing the flow through the orifice was very small, only a relatively small quantity of steam passed through the orifice, which considerably increased the difficulty of obtaining accurate temperature readings in the wiredrawn steam near the saturated condition. Those results, however, which have been obtained and plotted in Diagram 5 show clearly that the actual fall of temperature with pressure is most accurately represented by a curve which commences at the point on the saturation curve representing the initial saturated condition of the steam before wiredrawing, proceeding for a short distance along the saturation curve, and then branching off from this at an apparently definite angle, proceeding in a regular curve of small curvature.

The fact that for a short distance the curve approximately coincides with the saturation curve is very important, as it appears to show that even after the steam has been relieved of suspended moisture by a process of drainage, the law of pressure and temperature in the steam follows the law of saturation very closely till saturation is exhausted, when the steam suddenly follows the law of gases. It should be remembered, however, that in the actual experiments the wetness of the steam in the steam chest from which the steam supply is taken was altered as much as possible in different experiments under the same initial pressures and temperatures, but it was not found possible to affect the apparent dryness of the steam just before entering the orifice by an amount which came within the limits of observation, it being here noted that if the dryness fraction of the steam before entering the orifice had been altered by so little as 0·06 per cent. (the temperature of saturation being 284° F.), a difference of 1° F. would have been observed in the temperature of the wiredrawn steam, a quantity which would at once have been observed.

The experiments, therefore, indicate that even after relieving the steam of moisture by gravitation, there is still an effect as if a small quantity of moisture were present in the steam.

The curve representing the pressure temperature relation in the steam wiredrawn from a definite initial condition coincides for a short distance with the curve representing the law of saturation in Diagram 5, and the length of the coincident portions varies with the initial temperature of the steam, the approximate fall of temperature during the coincidence of the curves being represented by the following table :—

Initial temperature of saturation.	Fall of temperature before the gaseous condition is established.
239·2° F.	2·8° F.
239·8	2·8
261·5	4·7
262·0	4·7
284·0	5·5
298·9	6·6
345·15	9·15
379·5	10·5

Taking the first row in this table, it would appear that saturated steam wiredrawn down till it first becomes gaseous at 236·4° possesses a total heat of gasification under constant pressure identical with the total heat of evaporation of dry saturated steam at 239·2°, and, further, that dry saturated steam at 236·4° is not steam gas, but possesses what is equivalent to a dryness fraction of 99·91 per cent. In a similar manner dry saturated steam (as defined at the commencement of this paper) at 369° F. would apparently have a dryness fraction of 99·63 per cent. to bring it to steam gas.

Proceeding now to examine the lower ends of these curves of free expansion, it will be noticed that the curvature of the curves is very small and regular, even to pressures of 2·5 lbs. per square inch absolute. If now these curves be continued to the zero pressure line as curves of the same curvature throughout (which may or may not represent the true law of cooling at pressures below those obtained in the experiments), the values of the specific heat at constant pressure deduced by taking the temperatures given by the intersection of these curves of free expansion with the zero pressure line show a continual increase with the temperature, which again requires careful consideration, for if steam at ordinary temperatures (under 400° F.) is ever sensibly a perfect gas, it will be so at very low pressures, and it has been assumed by RANKINE that at a pressure of 0·085 lb. per square inch and temperature 32° F. saturated steam is a perfect gas, but in a perfect gas the specific heat at constant pressure is independent of the temperature, so that if steam at very low pressures is a perfect gas, the values of the specific heat at constant pressure given by the various intersections of these curves of known constant total heats with the line of zero pressures should be the same for all temperatures. Hence, either the curves as drawn at pressures below those attained in the experiments are very far from representing the true law of cooling or steam even when indefinitely rarefied at ordinary temperatures is never even approximately a perfect gas.

The latter deduction would appear to be the most correct as no indication of any change in the curvature of the curves of free expansion is found even at low pressures of $2\frac{1}{2}$ lbs. per square inch, and the change of curvature would have to be very sudden and very great in order to create anything like a constant value of the specific heat at constant pressure, an examination of the sort of curve required showing such changes to be very unreasonable.

To find the variation in the value of the specific heat at constant pressure with temperature, the curves of free expansion on Diagram 5 are used, the intersections of the curves with any line of constant pressure giving a series of temperatures between each pair of which the mean specific heat of the steam may be found in the following manner. If H_1 be the total heat of evaporation of saturated steam which, when freely expanded to a pressure p, will be at a temperature T_1, and H_2 the total heat of steam, which, when expanded freely to the same pressure p, will be at a temperature T_2, the value of the specific heat at pressure p between temperatures T_1 and T_2 is

$$\frac{H_1 - H_2}{T_1 - T_2}$$

for, by equation 5, page 4, if we wiredraw dry steam ($S = 1$) from a saturated condition having a total heat of evaporation H_1 to a temperature T_1 and pressure p, at which the temperature of saturation is T_3 and total heat of evaporation H_3, we have

$$H_1 = H_3 + K(T_1 - T_3).$$

Similarly by wiredrawing from a saturated condition represented by a total heat H_2 to a temperature T_2 at the same pressure p, we have

$$H_2 = H_3 + K(T_2 - T_3),$$

and hence by subtraction

$$K = \frac{H_1 - H_2}{T_1 - T_2},$$

K now being the mean specific heat at constant pressure between temperatures T_2 and T_1.

This formula, which is easily applied to the experimental results just given, is, however, not quite so accurate as its deduction from the general theory would lead one to suppose, for it has been shown by HIRN that by neglecting to take account of the energy existing in the liquid water at the temperature from which the total heat of evaporation is measured, in this case 32° F., an error is introduced which may under certain conditions become appreciable, and hence the formula just quoted will be discarded in favour of the more complete expression given by HIRN in his 'Théorie Mécanique de la Chaleur' (Tome I., 3^{me} édition, Paris, 1875, p. 434), viz.

$$K_p = \frac{H_1 - H_2 + \frac{0{\cdot}016}{774}(P_1 - P_2)}{T_1 - T_2},$$

where the 0·016 in the numerator is the volume in cubic feet of 1 lb. of liquid water, 0·774 being JOULE's equivalent, P_1 and P_2 being the pressures from which the wire-drawing takes place, and the remainder, as in the previous formula, for K.

By the aid of this formula the values of the mean specific heat at constant pressure have been calculated for various pressures and between certain temperatures, the results being tabulated in the following Table IV.

TABLE IV.

Pressure, lbs. per sq. inch.	Temperatures between which the specific heat is taken.		Difference of temperature, $T_1 - T_2$.	$H_1 - H_2 + \frac{0{\cdot}016}{774}(P_1 - P_2)$.	Mean specific heat.
5	224·1	240·3	16·2	6·8216	0·4211
	240·3	255·4	15·1	6·8331	0·4525
	255·4	264·6	9·2	4·5853	0·4984
10	227·5	243·5	16·0	6·8216	0·4263
	243·5	258·1	14·6	6·8331	0·4680
	258·1	267·2	9·1	4·5853	0·5039
14·7	230·7	246·5	15·8	6·8216	0·4317
	246·5	260·8	14·3	6·8331	0·4778
	260·8	269·7	8·9	4·5853	0·5152
	269·7	295·0	25·3	14·286	0·5646
	295·0	311·5	16·5	10·696	0·6482
20	234·3	249·5	15·2	6·8216	0·4488
	249·5	263·8	14·3	6·8331	0·4778
	263·8	272·5	8·7	4·5853	0·5270
	272·5	297·4	24·9	14·286	0·5737
	297·4	313·8	16·4	10·696	0·6522

TABLE IV. (continued).

Pressure, lbs. per sq. inch.	Temperatures between which the specific heat is taken.		Difference of temperature, $T_1 - T_2$.	$H_1 - H_2 + \frac{0·016}{774}(P_1 - P_2)$.	Mean specific heat.
25	252·3	266·6	14·3	6·8331	0·4778
	266·6	275·0	8·4	4·5853	0·5459
	275·0	299·6	24·6	14·286	0·5807
	299·6	316·2	16·6	10·696	0·6443
30	255·0	269·3	14·3	6·8331	0·4778
	269·3	277·6	8·3	4·5853	0·5524
	277·6	301·8	24·2	14·286	0·5903
	301·8	318·4	16·6	10·696	0·6443
35	271·9	280·1	8·2	4·5853	0·5592
	280·1	304·0	23·9	14·286	0·5977
	304·0	320·7	16·7	10·696	0·6405
40	274·4	282·6	8·2	4·5853	0·5592
	282·6	306·2	23·6	14·286	0·6053
	306·2	323·0	16·8	10·696	0·6367
45	277·0	385·1	8·1	4·5853	0·5661
	285·1	308·4	23·3	14·286	0·6131
	308·4	325·4	17·0	10·696	0·6292
50	287·6	310·5	22·9	14·286	0·6238
	310·5	327·5	17·0	10·696	0·6292
55	290·2	312·7	22·5	14·286	0·6349
	312·7	329·7	17·0	10·696	0·6292
60	314·8	331·8	17·0	10·696	0·6292
65	317·0	333·9	16·9	10·696	0·6329
70	319·0	335·9	16·9	10·696	0·6329
75	321·2	337·9	16·7	10·696	0·6405
80	323·3	339·7	16·4	10·696	0·6522
85	325·4	341·6	16·2	10·696	0·6602

That a large variation in the value of the specific heat takes place with temperature is clearly shown in the last column of this table; its variation with pressure is not, however, quite so evident. To enable a simple comparison to be made, certain figures are taken from the above table which show the values of the mean specific heats under different pressures but near the same temperature. These are placed in the following Table V., and the comparison this table affords shows very clearly that if there is any variation in the value of the specific heat at constant pressure with pressure it must be very small, especially when viewed in comparison with the variation with temperature as shown by the previous table.

TABLE V.

Temperatures between which mean specific heat is taken.		Mean temperature.	Pressure, lbs. per sq. inch.	Mean value of the specific heats.
255·4	264·6	260·0	5	0·4984
252·3	266·6	259·45	25	0·4778
258·1	267·2	262·65	10	0·5039
255·0	269·3	262·15	30	0·4778
269·7	295·0	282 35	14·7	0·5646
272·5	297·4	284·95	20	0·5737
277·0	285·1	281·05	45	0·5661
295·0	311·5	303·25	14·7	0·6482
297·4	313·8	305·6	20	0·6522
290·2	312·7	301·45	55	0·6349

Hence as regards the values of the specific heat under constant pressure of superheated steam the results of the experiments show that a very large variation in its value occurs with temperature, but its value is practically independent of the pressure.

We see therefore that since the "perfect gas" condition is never obtained in the steam in the experiments, it is impossible to calculate the constants in equation 8, p. 4, or to in any way use RANKINE'S formula 7 for the total heat of gasification of steam anywhere within the limits of pressure and temperature used in these experiments.

SECTION XVII.—*Added October* 4, 1899.

Comparison with previous experiments.

It has been suggested to the author that a comparison of the experimental results with those of previous experimenters would be of interest, and for the sake of comparison, HIRN'S experimental results have been taken, as no others have been made which enable even a small comparison to be made. It may be remarked, however, that experiments such as those by PARENTY,[*] or by PEABODY and KUHNHARDT,[†] though not undertaken with the same object as in the present ones, emphasise the difficulty of obtaining accurate results in this class of experiments. As regards the high values which have been obtained for the value of the specific heat under constant pressure in superheated steam in the present experiments, though in view of REGNAULT'S experimental result of 0·4805 for the mean specific heat between 248° F. and 430° F. they seem highly improbable, there is no direct evidence that a very large variation in its value does not occur, what evidence exists tending in fact to show that very large variations do actually occur; thus, DELAROCHE and BERARD[‡] found that $K_P = 0{\cdot}847$, while recently the value 0·38 has been calculated for the

[*] 'Ann. de Chimie et de Physique', 7me série, tome xii., 1897.

[†] 'Proceedings American Society of Mech. Engineers,' 1890.

[‡] *Vide* ZUENER'S 'La Chaleur,' p. 422.

mean specific heat at atmospheric pressure between 212° and 260° F., the data for the calculations being obtained from REGNAULT'S experimental results.* ZUENER† has also calculated the value 0·568 = K_P by assuming a certain law of expansion to hold in the superheated steam.

The experiments of HIRN, however, afford under atmospheric pressure only a direct comparison with those of the present research, as from the temperatures he obtained by wiredrawing saturated steam from certain initial pressures to atmospheric pressure it is possible to calculate by his formula quoted above the values of the specific heat at atmospheric pressure between certain temperatures. The results have been tabulated in Table VI., in which are also given the results of the present experiments. This table is certainly very interesting, as it shows most clearly that a larger variation exists in the value of K_P as deduced from HIRN'S experiments than the variation deduced from the present experiments.

TABLE VI.—On the values of the Specific Heat K_P at atmospheric pressure as deduced from HIRN'S experimental results and as calculated from the present experiments.

Results calculated from HIRN'S experimental figures.

Temperatures between which the specific heat is taken.		Mean specific heat K_P.
239·0	263·12	0·3048
263·12	271·4	0·6742
271·4	279·9	0·5362
279·9	287·06	0·5428
287·06	291·38	0·7874
291·38	296·6	0·5839
296·6	301·23	0·5977
301·23	306·5	0·9258
306·5	312·04	0·8028
312·04	314·06	0·9577
314·06	316·04	0·9309

Present Experiments.

Temperatures between which the mean specific heat is taken.		Mean specific heat K_P.
230·7	246·5	0·4317
246·5	260·8	0·4778
260·8	269·7	0·5152
269·7	295·0	0·5646
295·0	311·5	0·6482

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* MACFARLANE GRAY, 'Trans. Inst. Naval Arch.,' 1889.

† ZUENER'S 'La Chaleur,' p. 441.

As will be seen from the last column in this table, the values of K_P deduced from HIRN'S experiments are very inconsistent with one another, a careful examination of them showing, however, that as a rule the variations of K_P shown by HIRN'S results is greater than that deduced from the present experiments, and further that HIRN'S results show a distinctly higher value for K_P under atmospheric pressure and about 300° F.

SECTION XVIII.—*Added October* 4, 1899.

On the Cooling Effects observed in the Wiredrawn Steam.

It will be seen on Diagram 5 that the fall of temperature along a line of free expansion is not exactly proportional to the difference of pressure, the lines of free expansion being slightly convex upwards.

Again, in the experiments of JOULE and THOMSON on the cooling effects observed by wiredrawing different gases through a porous plug, it was observed that the cooling effect was almost proportional to the inverse square of the absolute temperature. To observe how far this was true for steam, there were obtained from Diagram 5 various values of the cooling effect $\delta\theta/\delta p$, or, as we will in future call it, C, and by plotting the logarithms of these values of C and of the absolute temperatures T, it appeared that C varied approximately as $(1/T)^{3 \cdot 8}$, the index 3·8 being very different to the value 2 obtained by JOULE and THOMSON.

SECTION XIX.—*On certain Thermodynamical Relations existing between the Cooling Effect, the Specific Heat* K_P, *and Density of Superheated Wiredrawn Steam.*

It early suggested itself to the author that some simple relation existed between the variations in the value of K_P with pressure and temperature, and an examination showed that the cooling effect $C(= \delta\theta/\delta p)$ was connected to K_P in the following relation

$$\frac{\partial}{\partial p}(K_P) = - \frac{\partial}{\partial T}(CK_P) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\alpha),$$

showing that the variation in the value of K_P with the pressure is equal to, but of opposite sign, to the variation with temperature of the product of K_P with the cooling effect. This formula may be deduced in the following manner. From THOMSON'S formula* for the cooling effect produced by wiredrawing, we have

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{v + CK_P}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\beta),$$

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* TAIT'S 'Heat,' (1892), p. 340.

where T is the absolute temperature and v the specific volume of the wiredrawn gas or vapour, and by differentiation we obtain

$$\frac{d^2v}{dT^2} = \frac{1}{T}\frac{\partial}{\partial T}(CK_P) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\gamma),$$

but by RANKINE'S* formula for the specific heat

$$K_P = \text{constant} - T\int_0^P \frac{d^2v}{dT^2}\,dp\,;$$

we obtain by differentiation

$$\left(\frac{\partial K_P}{\partial p}\right)_T = -T\frac{d^2v}{dT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\delta).$$

Hence by comparing γ and δ we have the relation (α). The simplest method of deducing the formula is by considering a small parallelogram on the $p-t$ diagram, bounded by lines of free expansion and lines of constant pressure.

We have therefore a very simple formula for checking the experimental results just obtained, for if K_P does not vary with the pressure as is indicated by Table V., then the product CK_P must be independent of the temperature at any particular pressure. In order to obtain the values of K_P at temperatures for which the cooling effect is shown on Diagram 5, constant pressure curves were drawn on a diagram having for abscissæ absolute temperatures and for ordinates the values $H_1 + \frac{0{\cdot}016}{774}P_1$, as explained on p. 27, H_1 being the total heat of evaporation of the steam before wiredrawing from a pressure P_1 and 0·016 representing the specific volume of water at 32° F., the slopes of these curves giving the values of the specific heat under constant pressure at any particular temperature and for the particular pressure at which the curve is drawn. In this manner the results given in the Table VII. were obtained and the necessary calculations made.

From the fifth column of this table it will be seen that the product CK_P is practically independent of the temperature, and from the sixth column that it is also independent of the pressure, *i.e.*, CK_P is constant between pressures of from 10 to 50 lbs. per square inch, and between temperatures of 227·5° and 327·5° F.

The mean value of CK_P throughout this range of pressure and temperature is 0·2819. Outside this range of pressure it is impossible to give very accurate results, but as no great and distinct variations actually appear, it would seem that the constancy of CK_P could be accepted beyond this range of pressure and temperature.

The fact that the product CK_P is practically constant is of very great importance, as it will simplify many deductions from expressions in which CK_P only occurs as a product.

For example, formula B just quoted gives a relation between v, T, C, and K_P

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* RANKINE'S 'Steam Engine,' p. 317.

TABLE VII.

Pressure, lbs. per sq. inch.	Temperature.	Cooling effect, C.	Specific heat, K_P.	Product, CK_P.	Mean product, CK_P.
10	227·5	0·690	0·400	0·2760	0·2789
	243·5	0·646	0·447	0·2888	
	258·1	0·568	0·488	0·2772	
	267·2	0·524	0·520	0·2725	
	292·8	0·460	0·609	0·2801	
14·7	230·7	0·664	0·404	0·2683	0·2838
	246·5	0·604	0·465	0·2809	
	260·8	0·570	0·512	0·2918	
	269·7	0·524	0·527	0·2761	
	295·0	0·456	0·613	0·2795	
	311·5	0·450	0·680	0·3060	
20	234·3	0·654	0·432	0·2825	0·2837
	249·5	0·582	0·477	0·2776	
	263·8	0·554	0·512	0·2836	
	272·5	0·516	0·541	0·2792	
	297·4	0·450	0·621	0·2794	
	313·8	0·450	0·666	0·2997	
30	255·0	0·550	0·479	0·2634	0·2787
	269·3	0·524	0·522	0·2735	
	277·6	0·508	0·555	0·2819	
	301·8	0·444	0·621	0·2757	
	318·4	0·450	0·664	0·2988	
40	274·4	0·508	0·551	0·2799	0·2832
	282·6	0·500	0·588	0·2940	
	306·2	0·440	0·621	0·2732	
	323·0	0·438	0·652	0·2856	
50	287·6	0·496	0·606	0·3006	0·2821
	310·5	0·432	0·623	0·2691	
	327·5	0·430	0·650	0·2795	

which, since CK_P may be taken as constant, is capable of direct integration. Thus we have

$$\left(\frac{dv}{dT}\right)_P = \frac{v + CK_P}{T}.$$

Hence, integrating under constant pressure we get from

$$\frac{dv}{v + CK_P} = \frac{dT}{T}$$

the result

$$\frac{v + CK_P}{T} = \text{constant for any particular pressure.}$$

This expression

$$\frac{v + CK_P}{T} = A \text{ (say)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\epsilon),$$

may be used in a simple manner to determine the specific volume v in superheated steam at any temperature and pressure, the value of A for this particular pressure being calculated from known data of the saturated condition.

It would appear, however, from Section XVI., p. 25, that the maximum volume which steam can occupy at the temperature of saturation under a certain pressure is not that given in the usual steam tables for the volume of dry saturated steam under that pressure and temperature, as the dry saturated steam used in the experiments does not become superheated with the slightest amount of wiredrawing. A correction, which is usually very small, could be found for the specific volume of the dry saturated steam as obtained from tables, to bring it to the specific volume of steam when a maximum at the temperature and pressure of saturation considered, *i.e.*, when no further increase of volume can occur at that pressure without superheating. Thus, taking an actual example, it is shown on p. 25 that at 236·4° the maximum amount of heat the steam can contain at this temperature of saturation without becoming superheated is equal to the total heat of evaporation of the steam at 239·2° F. as given by the steam tables, *i.e.*, the latent heat required to create the maximum volume at 236·4° F. is greater than that required to bring the steam to the dry saturated condition by the amount

$$0{\cdot}305\,(239{\cdot}2 - 236{\cdot}4) \text{ or } 0{\cdot}854 \text{ B.T.U.},$$

and hence the ratio of the specific volume of dry saturated steam to the maximum volume obtainable under the same conditions of pressure and temperature is $= \frac{949{\cdot}52}{950{\cdot}374}$, 949·52 being the latent heat of evaporation in B.T.U.s of steam at 236·4, for, according to RANKINE's formula for calculating the specific volumes of saturated steam, the volume is proportional to the latent heat.

The maximum volume being obtained in this manner by substituting it in the equation

$$\frac{v + \mathrm{CK_P}}{\mathrm{T}} = \mathrm{A},$$

it is possible to find A, and hence to find v for any other temperature T under the same pressure, the units of $\mathrm{CK_P}$ being altered as required.

By calculations of the preceding nature the volumes have been obtained of superheated steam at various pressures, and at temperatures which enable a direct comparison with HIRN's experimental results to be made. These experiments of HIRN on the densities of superheated steam do not give very consistent results among themselves, but they are the only ones as yet made which cover such a range of pressure and temperature as is the case in the present research, and hence are the only ones with which a comparison can be made. The experiments of FAIRBAIRN and TATE,* however, furnish us with direct evidence that a very large expansion of

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* 'Phil. Trans.,' 1860–2, "On the Law of Expansion of Superheated Steam."

volume takes place between the temperature of saturation and a degree or two above this temperature, and it is probable that this sudden expansion is due to the same cause as that for which the calculation has been made on p. 34, and referred to on pp. 24 and 25, namely, that the volume of dry saturated steam as given in the usual steam tables is not the maximum volume which can exist at that particular temperature of saturation.

The experimental results given by Hirn are placed in the accompanying Table VIII. as affording the only means of comparison as yet obtainable. An examination of this table will show that no great difference exists between the calculated results and those obtained by Hirn, though the constancy of CK_P has been assumed beyond the temperatures obtained in the experiments.

Table VIII.—On the Densities of Superheated Steam.*

Pressure in atmos.	Value of A in formula (ϵ).	Temperature.	Calculated sp. volume.	Hirn's volume.†	Percentage difference.
1	0·04154	212·0	26·43†	26·43‡	
		245·3	27·82	27·84	−0·07
		285·8	29·51	29·64	−0·44
		299·3	30·07	29·95	+0·40
		323·6	31·07	30·91	+0·51
		392·0	33·92	33·32	+1·77
		401·0	34·29	34·28	+0·03
		475·7	37·39	36·66	+1·95
2·25	0·019337	392·0	14·98	14·73	+1·68
3	0·014944	392·0	11·232	11·165	+0·60
3·5	0·013018	384·8	9·495	9·466	+0·30
		393·8	9·613	9·668	−0·57
		437·0	10·175	10·188	−0·13
		475·7	10·679	10·531	+1·39
4	0·011592	329·0	7·642	7·724	−1·07
		392·0	8·373	8·362	+0·13
		437·0	8·894	8·634	+2·92
		475·7	9·343	9·214	+1·38
5	0·009593	320·0	5·977	6·020	−0·72
		392·0	6·668	6·558	+1·65
		401·0	6·754	6·632	+1·81

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[*] In these calculations, the value of J used has been taken as 774, a number recently adopted by Professor Perry (in 'The Steam Engine'), and more in accordance with recent researches than the number 778.

[†] Perry, 'Steam Engine,' p. 577.

[‡] Volume of 1 lb. of dry saturated steam in cu. feet as given in steam tables.

It may be remarked here that the formula (α), viz.

$$\frac{\partial}{\partial p}(\mathrm{K_P}) = -\frac{\partial}{\partial \mathrm{T}}(\mathrm{CK_P})$$

furnishes us with the direct consequence that in any gas or vapour in which the specific heat $\mathrm{K_P}$ is independent of the pressure the product of $\mathrm{K_P}$ and the cooling effect C must be independent of the temperature, and, as applied to the present case of superheated steam, we have here that $\frac{\partial}{\partial \mathrm{T}}(\mathrm{CK_P}) = 0$ and $\frac{\partial}{\partial p}(\mathrm{K_P}) = 0$ directly from the experimental results, and, hence, satisfying relation (α) identically.

Further, in any gas or vapour in which the specific heat $\mathrm{K_P}$ is independent of the pressure, and REGNAULT has proved this to be the case for many important gases, it follows from equation (α) that the product $\mathrm{CK_P}$ shall also be independent of the temperature in that particular gas or vapour, and hence the equation (β) for the cooling effect, viz.

$$\left(\frac{dv}{d\mathrm{T}}\right)_{\mathrm{P}} = \frac{v + \mathrm{CK_P}}{\mathrm{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\beta)$$

is immediately integrable in the form

$$\frac{v + \mathrm{CK_P}}{\mathrm{T}} = f(p),$$

where f denotes some at present undetermined function. If we assume that at very high temperatures all gases become approximately "perfect" ones, as was done by RANKINE for steam, though the point is at present open to question, the form of the function f is easily determined by comparison with the equation for perfect gases

$$pv = \mathrm{RT},$$

R being a constant for each particular gas, and we get for the actual equation connecting the pressure, volume, and temperature in any gas

$$p\,(v + \mathrm{CK_P}) = \mathrm{RT}.$$

The form of this equation is identical with one deduced by JOULE and THOMSON,* but it is here noticed in its connection with the actual condition of things in a gas in which $\mathrm{K_P}$ is independent of the pressure, and which approximates under high temperatures to a perfect gas. We have, however, no evidence to show whether the latter condition is true for superheated steam or not, but the last equation is certainly not true for steam, as, from the data already found, simple calculations may be made showing that R is not a constant but a function of the pressure.

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* 'Phil. Trans.,' 1862, p. 588, "On the Thermal Effects of Fluids in Motion."