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An Experimental Study of the Enthalpy of Steam

G. S. Callendar and Alfred Egerton

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AN EXPERIMENTAL STUDY OF THE ENTHALPY OF STEAM

By G. S. CALLENDAR and Sir ALFRED EGERTON*, F.R.S.

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CONTENTS

The measurements on the total heat† of steam by the condenser method carried out between the years 1931 and 1940 are described. The apparatus was adapted from that used for the measurement of the saturation pressure of steam (Egerton & Callendar 1932). Part I deals with the investigation of the sources of error, particularly the heat-loss correction, as a result of which the modifications in the apparatus described in part II were made. The final measurements, amounting to about 400, range from 10 to 225 Kg/cm² and from 200 to 600 °C, at intervals of about 25 Kg/cm² and 25 °C. The smoothed results are also given in bars, and are considered to lie within about 1 part in 1500 of the true values.

* Sir Alfred Egerton died on 7 September 1959.

† The expression 'total heat' has been used throughout this paper so as to conform with the reports made at the time the experimental work was carried out but, to be consistent with present nomenclature, the word 'enthalpy' has been substituted in the title.

1. Introduction

Owing to renewed interest in the properties of steam, the work which was carried out some time ago (1931–40) is now presented.

The apparatus employed was developed from that designed and used by H. L. Callendar, F.R.S., in his work on the total heat of steam by the condenser method. The present authors modified the apparatus and used this flow method first for the determination of the saturation pressure of steam in the range 170 to 374 °C, paying particular attention to the accurate determination of temperature and pressure (Egerton & Callendar 1932). Agreement was very satisfactory with the values which were being obtained by a statical method at the National Bureau of Standards about the same time (Osborne, Stimson & Fiock 1934) and also at Massachusetts Institute of Technology (Smith, Keyes & Gerry 1934). The work then proceeded towards its main aim, the accurate determination of the total heat of steam up to 225 Kg/cm^2 and 600 °C.

Various alterations to the apparatus were made in the course of the work so as to study and overcome some of the sources of error. As it proceeded, the results, in considerable detail, were issued in a series of 'Technical Reports' to the British Electrical and Allied Industries Research Association, who were supporting the investigation:

1. Ref. J/T 79. An investigation of the errors of determination of the total heat of steam by the condenser method. Part I. (January 1933.)
2. Ref. J/T 83. (Supplement.) The total heat of steam at 10 Kg/cm^2, 200 to 500 °C. (August 1934.)
3. Ref. J/T 83. Investigation of the total heat of steam by the condenser method. Part II. Final measurements up to 150 Kg/cm^2. (November 1934.)
4. Ref. J/T 99. Investigation of the total heat of steam by the condenser method. Part III. Further measurements to 175 Kg/cm^2. (March 1936.)
5. Ref. J/T 115. Investigation of the total heat of steam by the condenser method. Part IV. Experiments with the new high-temperature apparatus and extension of the measurements above 200 Kg/cm^2 and 500 °C. (January 1939.)
6. Ref. J/T 130. Investigation of the total heat of steam by the condenser method. Part V. Experiments in the upper regions of pressure and temperature. (July 1941.)

The measurements which had been made up to 1938 were used as the basis on which to smooth and compute the revised and extended edition of the *(1939) Callendar steam tables* by G. S. Callendar & A. C. Egerton, and also the *1939 Heat-entropy diagram for steam* (British Electrical and Allied Industries Research Association, 1939). It was intended to present the measurements within a consistent thermodynamic framework and in relation to other measurements on the properties of steam, but the work had to be abandoned in the war and was not resumed, neither was it published other than in a restricted way through the above-mentioned reports. The experimental work had been taken nearly as far as was needed at that time by engineers using steam. The only other current experimental work on the *direct* measurement of the total heat of steam by the condenser method was that of Havliček & Miškowský (1936).

In this recount of the work, an indication is given of the many points to which attention had to be paid, but only the main results will be recorded. No attempt has been made to re-evaluate the measurements: it is perhaps not quite the time to do so until present experimental investigations have been further advanced. The work is presented in the sequence in which it was carried out. For this reason, it is divided into two parts. Part I deals with the measurements made up to June 1935 in the original apparatus, and part II with those up to June 1940 in the redesigned apparatus. The part I measurements helped to establish the skeleton tables agreed at the International Steam Table Conference in New York, September 1934, but the part II measurements supersede and extend those in part I. The studies described in part I led to the improvements in the apparatus used for the part II measurements, to their greater range and slightly better accuracy. The results in the final table (part II) are those obtained with the improved apparatus. A final table of results is given transposed into the units which are now adopted (1958), otherwise the work is presented in the units employed when the work was carried out (see p. 147).

PART I

2. The apparatus

The apparatus used in the saturation pressure measurements has been described previously (Egerton & Callendar 1932); for diagrams see figures 1 to 5 therein, pp. 149–51. It consisted of a system for the supply of pure air-freed water, a large positive-action feed pump, an electrically heated boiler, a superheater, a pressure pocket with re-entrant tube in which to place the thermometer for the measurement of the steam temperature, a throttle tube and a double-surface jacketed condenser (figure 1). The boiler was a bundle of Monel metal tubes in series through which the water was pumped; the current was passed through the metal from one end to the other; the bundle was placed inside a 6 in. diameter steam pipe.

The condenser method of determining the total heat of steam (H) involves measuring the temperature and pressure of the steam at a certain position in the 'pressure pocket' after its generation in the boiler and passage through the superheater. The steam is then expanded through a throttle (which is a fine hole in a disk of steel) into the double-surface condenser and the rise in temperature of the cooling water is measured.

$$H = (m_2/m_1)\,(t_1-t_2)\,S_1+S_2 t_3,$$

where m_2/m_1 is the ratio of the mass of the cooling water to that of the condensed steam; (t_1-t_2) is the rise in temperature of the cooling water; S_1 is the mean specific heat of the cooling water between t_1 and t_2; and S_2 is the mean specific heat of water between 0 and t_3 °C, the final temperature of the condensate.

The apparatus briefly described above was modified in several respects at the outset of the work, but later, as a result of the experimental investigations described in part I, the superheater, pressure pocket, etc., were redesigned and constructed in special alloy steels to withstand higher pressures and temperatures (see part II).

At the outset, it was realized that little improvement in H. L. Callendar's measurements on total heat would be got without some essential modifications of the apparatus. Most important was the means of measuring the mass of the condensed steam over a short time interval. Previous measurements had been an average over a 20 min period during which it was not possible to maintain steady pressure and temperature. An accurate means of catching the condensed steam over a carefully timed short interval was therefore devised. A knife edge mounted between two funnels was moved across the jet of water sprayed into a thin sheet. The moment of passage back and forth was timed. A Cambridge Instrument Co. time marker, with phonic wheel and tuning fork, recorded and timed the events on a long paper strip. The same method on a larger scale was employed for measuring the mass flow of the cooling water (figure 2). Nowadays, the timing would be done differently, but not necessarily more effectively.

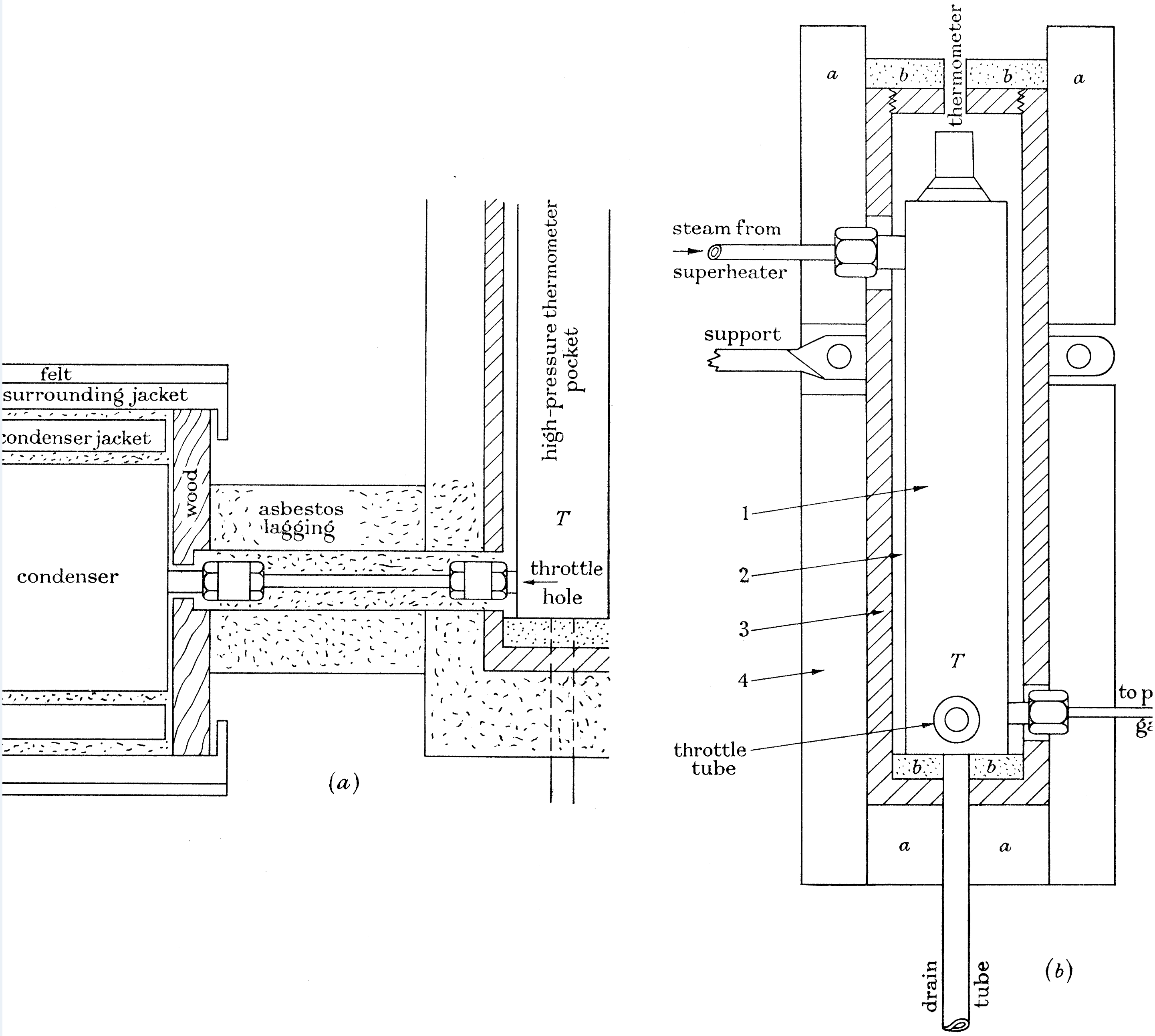

FIGURE 1. (Half full size.) (*a*) Throttle tube showing heat insulation. (*b*) Side view showing heat insulation of high-pressure thermometer pocket. 1, Pocket; 2, $\frac{1}{4}$ in. closed space; 3, $\frac{3}{8}$ in. aluminium jacket; 4, 1 in. asbestos lagging. Lagging materials used: *a*, asbestos; *b*, uralite. Mean temperature measuring point is shown at *T*.

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It was the ratio of the mass of cooling water to that of the condensed steam that mattered and it had to be determined to an accuracy of about 1/5000. The flow of the condensate was of the order of 5 g/s, and an experiment lasted about 2 min, so the start and stop had to be

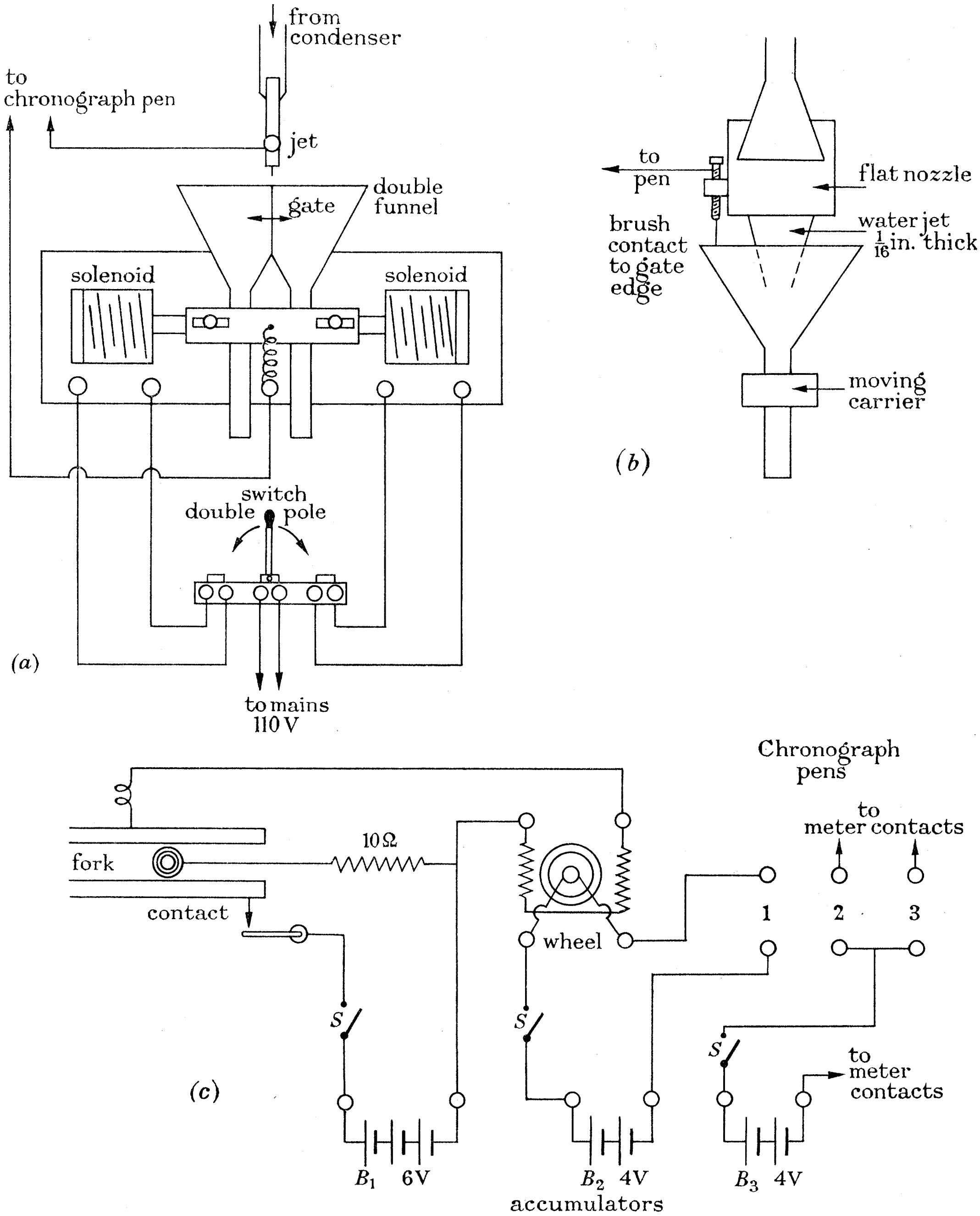

FIGURE 2. (*a*) Front view of switch over gate for metering water. (*b*) Side view of meter jet and funnel. (*c*) Wiring of chronograph.

measured to 0·02 s, and there must be less loss than 0·05 g. The funnel and knife edge or 'gate' was opened electrically. Means were devised for accurate measurement of the strip marks, for providing constant head of condensate and cooling water, for collecting residual traces of water in the funnels, for correcting for evaporation and for weighing with precision.

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(An empirical relation was used for the evaporation correction

$$L = 1{\cdot}45 P_v f^{-\frac{1}{3}} 10^{-5},$$

where P_v is the pressure in mm of water vapour, and f is flow in g/s. The constant, 1·45, was suitable for normal temperature and dryness ($t = 20°$, and $t - t_{\text{wet}} = 5°$), but experiments were made to allow for other conditions. The required correction to the weight of condensate (W) was given by $W(L' - L'')$, where L' is the evaporation at the condensate gate and L'' at the cooling-water gate. A table of $L' - L''$ for various flow and temperatures was prepared.)

By these and other means, the accuracy required was achieved and marked improvement over any previous direct measurements of total heat was obtained.

The double-surface condenser by which the steam was condensed in the narrow space between copper walls cooled on both sides by water was found particularly effective (see figure 4, Egerton & Callendar 1932). The cooling water entered the outer portion of the condenser and picked up any heat that would otherwise be lost from the outgoing water. The difference in temperature was measured by resistance thermometers, the circuit being so arranged that it was given by a single galvanometer reading. A water jacket inside which the lagged condenser was placed provided uniform external conditions. This jacket was fed by water independently to the condenser, but the mass and ingoing and outgoing water temperature could be measured when required.

The apparatus took at least an hour or two to attain a steady state before measurements could be made, but it was possible to get a set of four or more satisfactory observations at a certain temperature and pressure in a day. In the first report, there were about 180 measurements recorded, and full details were given. The aim initially was to attack the various sources of error, particularly the correction for heat loss. As the work proceeded accuracy improved. A shortened description of this attack will first be given.

3. Experimental: preliminary investigation of the errors of measurement

(a) *Changes in the temperature of the condenser cooling water*

Small rapid fluctuations in this temperature can affect the value of the total heat, for the ‘rise’ measurement (difference in temperature of the ingoing and outgoing cooling water) might not correspond exactly to the average true rise over the time of the measurement (2 min). Many experiments were done in order to observe the extent of these fluctuations and their effect on the ‘rise’; the major fluctuation was found to have a period of about a minute. The cooling water was taken from a large tank about 15 ft. above the plant, through a large well-lagged pipe. A mixer was devised consisting of a 15 cm pipe with a number of holes equally spaced along its length immersed in a small cylindrical lagged vessel with a capacity of one minute’s water supply. The water is thus drawn equally from each part of a temperature fluctuation. Before this installation, the maximum change in temperature observed was 0·12 °C during 1 min; afterwards, it was only 0·015 °C. Longer period changes in the water temperature were too small to affect the value of the total heat, as the time of measurement was so short (they only corresponded to about 0·001 °C/min at 32 g/s flow). For a 'rise' temperature of 50 °C, the error from temperature fluctuation of the cooling water was reduced to ±0·01 °C.

(*b*) *Rate of flow of cooling water*

Provided precautions against any small air bubbles which might collect were taken, the very small changes in the steady rate of flow over the short time of the experiment were not found to introduce appreciable error.

(*c*) *Changes in the condensate flow*

This was found to be an appreciable source of error. It was important that the area in the condenser where the steam condensed should not vary so as to cause any surges in the flow of condensate. This was found to happen sometimes at small steam flows and high temperatures. It was avoided by allowing the condensation to occur against a slight back pressure produced by a column of mercury. With 20 cm of water head to the condensate jet, the fluctuation in head in 3 s was ±0·7 cm without the back-pressure arrangement, but with the latter it was only ±0·1 cm. The error which could be 0·5 g in the weight of the condensate (equivalent to 3·7 cal/g on the total heat) was thereby nearly eliminated. The change in the specific heat of water due to the back pressure is negligible. In the subsequent total heat measurements, using the back pressure, the mean deviation of the total heat was improved from ±1·00 to ±0·22 cal/g.

At high temperatures there may be slight reaction of the steam on the metal parts giving rise to hydrogen; no bubbles of gas were, however, detected, and errors due to chemical action must be exceedingly small, as experiments at different flow rates confirmed. The water was frequently tested for purity.

The three-throw hydraulic pump was operated off the Physics Laboratory battery constant-voltage supply and gave a very regular feed of the air-freed distilled water. It was run at a few revolutions per minute through a double reduction gear. Normally the pump was powered by the spare batteries which had no other load at the time. Above 200 atm, the leak rate at the pump increased, but the leak did not change at constant pressure; at one stage of the work the pump had to be dismantled for renewal of the cup leathers.

The boiler was heated from the mains supply and therefore subject to voltage fluctuation. This was one of the chief reasons for cutting down the time of observation. Three or four measurements could often be obtained without a fluctuation of voltage: if fluctuation occurred, it showed on the dead-weight pressure-gauge spring balance and could be checked by adjustment of the boiler current regulator. The fluctuations, although causing waste of time, had no significant effect on the mean values of total heat from the sets of observations, because if any doubt arose from this cause, the set of observations would be discarded and repeated at the same temperature and pressure.

Owing to the great heat capacity of the superheater, the steam temperature remained very steady over the short period of an observation, but it was essential to provide a small amount of superheat to the steam leaving the boiler, to prevent water drops reaching the superheater and causing unsteady pressure. For the same reason, it was necessary to lag thoroughly the pipe leading to the superheater.

(*d*) *Measurement of the temperature*

Throughout the research, stress was laid on accuracy of the temperature measurements. In the work on the saturation pressure (Egerton & Callendar 1932), a compensated resistance in series with the 'zero' resistance thermometer was placed on one side of the bridge, with the coils of the bridge and the other thermometers on the other side, so that the increase in resistance with rising temperature substituted coils of the bridge which were removed from the circuit. This 'substitution' method was limited by the range of the compensating resistance and was not so suitable for the work on the total heat. Instead, the thermometer was placed in the opposite side of the bridge to the coils, the zero thermometer being in series with the coils. This 'opposition' circuit rendered necessary an exact determination of the fixed ratio arms of the bridge, which was found to be 0·999443 in close agreement with the value recorded by H. L. Callendar. Since the opposition circuit resistance changes with temperature and as temperatures up to 600 °C had to be measured, it was necessary to determine carefully the relation between the galvanometer deflexion and resistance, as each coil was brought into circuit, particularly over the range used in the measurement of the cooling water rise. The comparisons were made by immersion of the thermometers in melting paraffin wax, which gave a steady and convenient temperature within the range of the 'rise' temperature. The error of the galvanometer deflexion determinations for each box coil was estimated to be only about 0·001 °C. The total 'rise' temperature was obtained from the mean of five readings of the galvanometer at intervals of 20 s during the total heat measurement. The maximum variation was about ±0·025 °C and the mean observational error about ±0·005 °C. Errors due to 'zero' change of the thermometers were never more than ±0·01 °C.

The error in the determination of the steam temperature (t_s) was ±0·04 °C, but the effect of this error on the value of the total heat was quite small (0·02 cal/g), except near saturation where dH/dt is large, in which case special precautions were taken to observe t_s to ±0·02 °C.

(*e*) *Measurement of pressure*

The pressure was measured as described in the paper on the saturation pressures (1932). A spring balance and dial were used instead of the steel yard, as an accuracy greater than ±1 Lb./in.^{2} (0·07 Kg/cm^2) was not needed. The pressure was set at will and remained steady, during an experiment, with an accuracy of ±0·03 Kg/cm^2 (equivalent to 0·05 cal/g on the total heat).

(*f*) *The correction for heat loss*

The main difficulty in achieving accurate determination of the total heat of steam by the condenser method is the measurement of the correction for heat loss. The steam temperature was measured, within a certain region of the 'pressure pocket', and the steam then passed through the throttle into the condenser (see figure 1). Although the passage was well lagged, the steam had opportunity to lose some heat to the surroundings before being condensed. The metal of the throttle tube could also conduct heat into the condenser, and this may not all have come from the steam which was subject to the measurement. Although the sources of error were small, nevertheless they exist and were not easy to avoid by compensating (with electric heating) or by insulation.

The 'heat loss', which is a net effect since it includes some gain, was determined by measurements made at different rates of flow of the steam. The thermal balance for flow through a throttle is given by

$$E_1+p_1V_1+\tfrac{1}{2}u_1^2 = E_2+p_2V_2+\tfrac{1}{2}u_2^2+Q+W,$$

where $E_1+p_1V_1 = H_1$, the total heat and $\frac{1}{2}u_1^2$ is the kinetic energy for unit mass of steam before throttling, similarly for the quantities with suffix 2 after throttling; Q is the 'heat loss' per unit mass of steam and the work done, W, is zero. (In the experiments to be referred to, the flow was about 4 g/s and the velocity in the annulus of the pocket was about 230 cm/s, so that the kinetic energy contributed only about 0·003 cal/s, which is a negligible part of the total heat.)

If Q, the heat loss, is assumed independent (within limits) of the mass flow,

$$Q = (mm'/[m-m'])\,(H-H'),$$

where H and H' are the total heats observed at two rates of flow, m and m', In all the early part of the work, the heat loss correction, Q, was determined by measuring the total heat at two rates of flow, usually one double the other. Later in the first part of the investigation an attempt was made to test the assumption of the constancy of Q by measurements over a range of flow rates and by exploring the temperature gradients, etc. The information so gained led to the design of the steam-jacketed pocket used in part II, by which the heat-loss correction was diminished in magnitude, although it was still necessary to determine it by experiments at different steam-flow rates. Even with the earlier pocket, the magnitude of the heat-loss correction was only about 2 cal/g at 300 °C and 4·5 cal/g at 500 °C, and only amounts therefore to not more than about 0·5% of the total heat. It has to be determined, however, with as much accuracy as possible; to within 5% if the total heat is to be accurate to 0·2 cal/g.

Part of the heat loss occurred through the lagging surrounding the thermometer pocket and was conveyed away by radiation and convection, part was conducted away by the drain cock and pipe leading to the pressure balance, part was lost from the surface of the lagging surrounding the throttle tube. The condenser gained some heat by conduction along this tube and some heat reached the jacket surrounding the condenser* by radiation and convection (the latter was found not to be sufficient to affect the 'rise' temperature of the cooling water). The net effect was Q', the heat loss per second, and if m g of steam flow per second, $Q'/m = Q$.

Measurements were made of the heat conducted to the condenser by heating the steam pocket to 400 °C electrically, using both Monel metal and german silver connecting tubes, lagged and unlagged. Under steam flow, the mean temperature of the tube was higher and the heat loss from these metal tubes would be greater, but there would also be a 'cooling effect' due to expansion of the steam after passing the throttle. The conditions were therefore not really similar; nevertheless, the measurements helped to ascertain the extent of the heat loss from the various parts of the apparatus. Draughts and any alteration to the lagging affected the heat loss, and special precautions had to be taken to minimize these.

* The heat received by the condenser water jacket was shown to come mainly from the condenser end-plate and from outside sources. When the cooling water flows were large and the condenser 'rise' temperature small, the loss to the jacket would have been smaller.

(In the later measurements of part I, an external water jacket was placed outside the lagging of the throttle tube as well as outside the condenser, so that radiation would occur to a surface at constant temperature.) This part of the investigation showed that the 'heat loss' Q' at 28·12 Kg/cm² and 400 °C was composed of:

heat lost to condenser jacket	−1·0
heat gained by condenser from throttle tube and surroundings	+1·5
heat lost from pressure pocket	−7·9
heat lost from steel drain tube	−1·3
heat lost to copper pressure pipe	−4·5
total heat loss	−13·2 cal/s.

(In the later experiments, series D and E, the heat loss was found to be somewhat lower, −12·5.)

The average dispersion of all the values of Q' from the mean curve was only 0·7 cal/s, and the maximum deviation 2·4 cal/s. From this particular set of ten measurements of Q' at 400 °C, the error of the value 12·5 cal/s was about ±0·4. (This rate of loss corresponded to a correction for heat loss Q' of about 3 cal/g on the value of the total heat, which is about 770 cal/g at 28 Kg/cm².)

4. Preliminary assessment of the sources of error

During the years 1931 and 1932, about 172 measurements of total heat were made in the range 28 to 29 Kg/cm² and temperatures from 235 to 500 °C in several sets of measurements, in order to investigate the sources of error:

series A	19 measurements	October 1931
series B	55 measurements	November, December 1931
series C	33 measurements	December 1931, January 1932
series D	50 measurements	April, May 1932
series E	15 measurements	November 1932.

The curve (for series D and E, figure 3) representing the heat loss was established mainly on the results of the last two series, particularly on those at 400 °C. Since the mean departure from the curve was only about 1 cal/s (equivalent to only about ±0·1 cal/g on the total heat), the determination of the total heat was considered to be well within the accuracy desired.

After correcting for heat loss and for specific heat of cooling water and condensate (in accordance with the then recently determined values obtained by Osborne, Stimson & Fiock (1930), the values in series D and E of the total heat at 28·12 Kg/cm² (400 Lb./in.²) only varied from the values in the then most recent tables (Mollier 1932), based on P.V.T. and specific heat measurements, as follows:

	250 °C	300 °C	350 °C	400 °C	450 °C	500 °C
H_0	684·5	715·9	744·8	772·2	799·6	82·63
$H_0 - H_M$	−0·4	−0·6	−0·3	−0·5	−0·1	0·0

It was considered at this stage of the investigation that the method was giving reliable values and, as a result of a number of special experiments, the assessment of the effect of the various sources of error shown in table 1 was made.

The possible error was thus estimated to be about $\pm 1{\cdot}0$ cal/g. The distribution amongst the various sources of error according to their effect on the accuracy of the total heat measurement was estimated to be as follows, at this early stage of the investigation:

steam temperature	1·2%
steam pressure	2·5
'rise' temperature	28
condensate weight	32
cooling water weight	3·2
specific heat correction (water)	6·3
temperature (t_3)	2·0
heat-loss correction	25

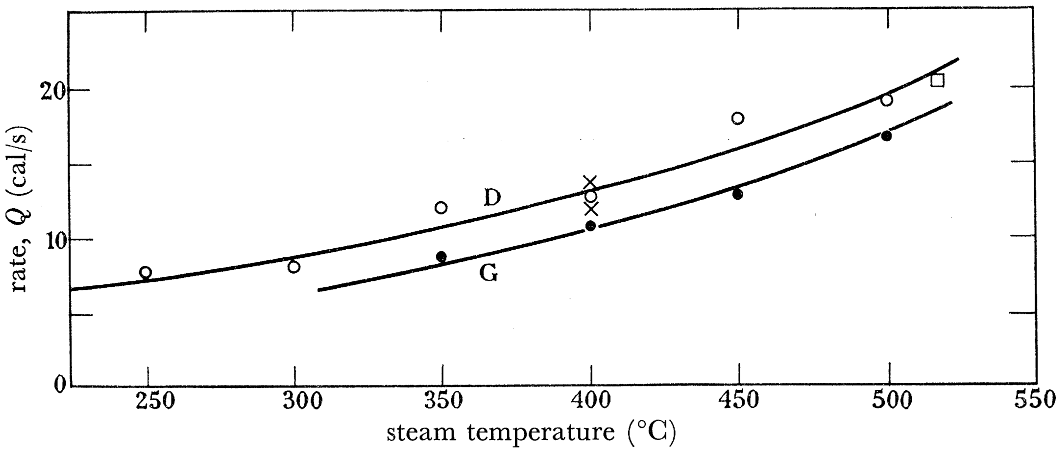

FIGURE 3. Heat-loss curve. Observed values: ○, April–May 1932, series D; □, June 1932, 50 Kg/cm²; ×, November 1932, series E, F. New conditions: ●, March 1933, series G. Number of observations at different temperatures:

°C ...	250	300	350	400	450	500	515
	8	7	5	24	9	8	6

TABLE 1

(*a*) The 'rise' temperature

variation of cooling-water temperature	±0·015 °C
thermometric errors (calibration, etc.)	±0·01 °C
mean observational error	±0·005 °C
	±0·03 °C

(*b*) Condensate/cooling water ratio

correction to weights	±0·02 g
evaporation correction	±0·02 g
measurement of the strip (for time of experiment)	±0·05 g
inaccuracy of weighings	±0·04 g
inaccuracy of setting of contacts	±0·04 g
uneven flow	±0·05 g
	±0·25 g on weight of condensate
	±0·50 g on weight of cooling water

(*c*) Steam, pressure and temperature

pressure	±0·07 Kg/cm²
temperature (t_3, condensate water)	±0·01 °C
temperature of steam	±0·02 °C

The average dispersion from a mean value of 39 of the later total heat determinations in the first series of measurements amounted to $\pm 0{\cdot}41$ cal/g and the probable error of the mean was $\pm 0{\cdot}15$ cal/g.

In relation to subsequent work with the same apparatus (reported in JT/83), these estimates were possibly rather on the optimistic side, particularly in regard to the heat-loss correction.

5. The measurements and further studies with the same apparatus

After we had thus explored the accuracy which might be expected, the next two B.E. & A.I.R.A. reports and supplement dealt with the measurements made in the range 10 to 175 Kg/cm^2 at temperatures up to 500 °C, carried out between 1933 and 1936. All along, further studies were made of the heat loss and other corrections, and small improvements were introduced. A shortened version of these will be given, but reference to the reports would need to be made for an account in more detail.

Neglecting the first three sets of measurements already mentioned, over 500 separate measurements of total heat were accumulated. The error was reduced not only by the number of observations, but by the gradual improvement in the technique gained in dealing with the sources of error. The eventual smoothed results were considered to represent the true total heat of steam throughout the range to within 1 part in 1500.

(a) *Mixing of the condenser cooling water*

Trials had shown that the cooling water near the walls which received heat from the condensed steam might not be always sufficiently mixed with the rest of the cooling water by the time that the water reached the outlet pocket, the hotter water tending to creep up around the thermometer tube. The trouble was found during some experiments at high cooling water flow and low steam flow at a point (100 Kg/cm^2) used for reference. A search was made for the error; the mercury thermometers (at the condensate outlet, etc.) were recalibrated, the fundamental intervals of the 'rise' thermometers were checked, the resistance box coils and connexions were retested, the immersion depth of the resistance thermometer, the weights on the pressure gauge, the timing of the 'gates', leakage in the condenser, temperature gradient changes in the steam pocket, the clean state of the pressure pocket, etc., were all examined, and none of these was found to be a source of the slightly abnormal value of the total heat at the reference point, which was half a calorie too high. Eventually the cause was found to be the faulty mixing of the cooling water and a series of measurements (L), 54 in all, were made to establish the extent of the error.

Two thermometer pockets were used at the cooling water outlet separated by a short length of well-lagged pipe, the loss of heat from which could be determined accurately; the error due to lack of mixing could be found from the difference in the two temperatures observed. It was shown that the trouble had arisen from a slight alteration in the position of the thermometer in the cooling water outlet in the K_2 series of measurements, and it was eliminated by raising the thermometer slightly in the outlet pocket and by introducing baffles. A thorough investigation was made of the possible error which might have resulted from lack of good mixing in the earlier measurements, but it was shown that they had not been subject to the error; which only occurred with large cooling-water flows. Provided the 'rise' temperature was kept nearly constant, reliable values were being obtained.

The error cropped up again later (in series N (1934)). One of the measurements at the 400 °C check point had led to a value of the total heat 0·6 cal/g higher than expected. It was traced to derangement of the baffles. A reverse spiral baffle was substituted and normal values were again obtained. The reverse spiral improved the accuracy of the temperature readings as the following figures indicate:

	with baffles 50/M/3/400	with spiral 50/O/3/400
number of observations	11	6
number of 'rise' readings	55	30
departure from mean	±0·017 °C	±0·0095 °C

(*b*) *Cooling-water temperature*

The temperature of the cooling water was not found to be an appreciable source of error. The measurements in the summer months were as reliable as those in winter, as the values obtained at the check points showed (table 2). Incidentally, they helped to show that the National Bureau of Standards values for the heat content of water were consistent in the range t_1 to t_2. The mean condenser temperature above that of the cold cooling water (ΔC) varied little, although the cooling water (t_1) varied considerably in temperature.

TABLE 2

series	steam flow (g/s)	cooling water, t_1 (°C)	cooling water, t_2 (°C)	condensate temperature, t_3 (°C)	ΔC (°C)	H (obs.) (cal/g)
D	3·916	20·5	64·5	45·1	34·3	739·7
E	3·791	7·7	55·1	32·0	35·8	739·6
F	3·750	9·0	51·4	30·7	32·0	739·5
G	4·027	11·0	56·8	35·2	35·0	739·6
I	2·922	20·6	63·9	42·1	32·4	739·6
J	3·577	18·8	62·4	43·3	34·0	739·6
K	3·655	15·6	60·8	40·6	35·1	739·6

The heat due to the kinetic energy of the cooling water obtained from the loss of head was estimated to be less than 0·05 cal/g on the value of the total heat for a larger than usual flow, and was therefore negligible.

(*c*) *Summary of the series of measurements*

Series D included in the first B.E. & A.I.R.A. report was completed in July 1932. 267 measurements in 9 series followed and were completed by April 1934. Then came series N (54 measurements), including the measurements at 10 Kg/cm², and finally the O series (73 measurements), ending in 1935. When alterations were made, there was some disturbance of the lagging of the pocket.

(*d*) *Measurements at* 10 Kg/cm²

The supplement to J/T 83 dealt with the measurements made during the winter of 1933 and the hot summer months of 1934 at the low pressure of 10 Kg/cm². Experience with the plant was needed to obtain a steady flow of steam and condensate at these low pressures; surging was apt to be set up in the condenser. The back pressure on the condensate was increased to $\frac{1}{4}$ atm, the boiler current and voltage was carefully regulated, and the number of single observations for each point was increased. A very small correction was applied for the rise in cooling-water temperature during an observation. If the cold water was rising at the rate of 0·01 °C/min, it would cause an error of $-0{\cdot}0025$ °C in the observed 'rise' temperature, equivalent to $-0{\cdot}04$ cal/g on H. The maximum correction occurred for the set at 250 °C and amounted to $+0{\cdot}02$ cal/g on the value of H.

TABLE 3

date	series	pressure (Kg/cm^2)	number of observations	changes made
Nov. 1932	E	28	15	thermometer fitted to lagging of pocket
		100	6	water jacket fitted
Dec. 1933–Feb. 1934	F	75	16	thermometer rechecked
		100		
Mar. 1933	G	75	17	new tube on thermometer and resoldering of leads to no. 5 thermometer; mean position of thermometer lower by 2 mm; new thermocouples fitted to jacket of pocket
		75	15	
May 1933	H	125	18	closer temperature setting (to reduce $\Delta H/\Delta T$ correction)
July 1933	I	100	11	resistance thermometer inserted in 'lagging' of steam pocket
		50	21	
Aug.–Oct. 1933	J	100	21	electrically heated aluminium jacket fitted
		50		
Nov., Dec. 1933	K	various	20	thermometer rechecked
	K	150	15	
	K_2	50	21	pocket cleaned internally; lagging replaced
Feb., Mar. 1934	L	100	43	study of cooling water mixing; thermometer at condenser outlet raised slightly
		50		
Apr., May 1934	M	50	18	baffles used for mixing; adjustment of water meters and solenoids
June, July 1934	N	10	58	—
Nov. 1934–July 1935	O	50	30	spiral mixer used
		25	9	
		100	9	
		150	10	
		175	7	
Apr. 1935		50 (nr. satn.)	8	—

TABLE 4

temperature (°C) ...	200	250	300	350	400	450	500
H_s (smoothed) (cal/g)	674·8	701·7	727·7	753·3	778·9	804·4	830·0
$H_0 - H_s$ (cal/g)	+0·04	0·02	0·08	−0·34	+0·10	−0·07	0
number of observations	4	7	8	9	13	4	5
difference from Mollier table (1932)	+1·0	+1·0	+0·9	+0·9	+0·7	+0·7	+0·8

Special care was taken over the determination of this 10 Kg/cm^2 point, because the existing steam table values were more likely to be nearer true values than at higher pressures. The values were all a little lower (from $\frac{1}{2}$ to 3 cal) than the values obtained from steam tables at that time (Mollier 1932; Knoblauch, Raisch, Hausen & Koch 1932; Keenan 1930; Callendar 1931), none of which were in really good agreement. The measured values here given at the 10 Kg/cm^2 point were considered to be correct within $\frac{1}{2}$ cal/g (table 4).

The values at 400 °C afford an example of the agreement in the results which were being obtained at this period of the work.

date	series	number of observations	flow (g/s)	t_1 (°C)	H (cal/g)
7 Nov. 1933	K	4	2·754	11·2	779·06
11 June 1934	M	4	2·946	19·3	779·09
21 June 1934	M_2	5	3·106	19·9	778·87

(*e*) *The correction for the specific heat of water, etc.*

Osborne *et al.* (1930) published preliminary measurements of the total heat of water determined at the National Bureau of Standards, and the most recent values kindly supplied by Dr Osborne were used to substitute for S_1 and S_2 in the equation for the total heat of steam.

A very small correction had to be applied because the Bureau of Standards measurements referred to the total heat of water (h) under its own saturation pressure, whereas for this work the pressure was the barometric pressure:

range (°C)	ΔH_1^P correction (abs. J)
0–50	0·012
0–60	0·019
0–70	0·031
0–80	0·047

(S_1 referred to tap water, S_2 to pure water (see p. 135) but the impurities in the former were not likely to change the specific heat by more than 1 part in 10 000.) A table was prepared giving the mean specific heat between t_1 and t_2 for use in evaluating the total heat of steam from the observations made.

The total heat was presented in I.T. calories, which calorie was defined at the International Steam Table Conference in 1929 as $\frac{1}{86}$ of an international kilowatt hour, then 4·1877 absolute joules. One international watt was then 1·00039 absolute watts and 1 calorie was taken as 4·186 absolute joules, though defined as the amount of heat required to raise the temperature of 1 g of water from 14·5 to 15·5 °C international scale of temperature. (The value of dh/dt from the Bureau of Standards results at 15 °C was only 4·181 international joules per gram (see part II).) The value adopted for the international watt for the purpose of the International Steam Table Conference (1934) was 1·0003 absolute watts.

In order to correct the values observed at a given observed temperature and pressure to an even value, the Mollier tables were used to give the slopes dH/dP and dH/dT. The correction did not lead to an error of more than $\pm 0·02$ cal/g. Where C_P (Mollier) departs from C_P (observed), as at 100 Kg/cm² and 400 °C, the derivative was modified to correspond to the observed value.

(*f*) *The heat-loss correction: further examination*

Examination of the heat-loss correction was the main matter at issue throughout the measurements described in this part, ultimately leading to a redesign of the pressure pocket and redetermination of the total heats (see part II). Nevertheless, provided the heat-loss correction was being obtained experimentally over a suitable range of steam-flow rates, the values of total heat being obtained in the older apparatus were reliable up to about 500 °C (see p. 162). The following paragraphs summarize the investigations which were made on the heat-loss correction.

(i) *Water jacket.* A water jacket was placed around the lower part of the pocket in the heat-loss region for the measurements in set G and thereafter, so as to maintain a uniform condition of temperature of the surroundings to which heat would be radiated. The rate of heat loss before this addition was affected somewhat by the difference between summer and winter conditions and local draughts. Its effect is noticeable in the decrease in heat loss and the improvement in dispersion of the results.

temperature (°C)	series D without jacket (cal/s)	series G with jacket (cal/s)
350	$10{\cdot}5 \pm 1{\cdot}67$	$8{\cdot}2 \pm 0{\cdot}70$
400	$13{\cdot}0 \pm 1{\cdot}30$	$10{\cdot}7 \pm 0{\cdot}52$
450	$16{\cdot}0 \pm 1{\cdot}31$	$13{\cdot}6 \pm 0{\cdot}55$
500	$19{\cdot}0 \pm 1{\cdot}31$	$16{\cdot}7 \pm 0{\cdot}43$

(The drop in heat loss was not chiefly due to the jacket, but mainly to a difference in lagging of the pocket and throttle tube.)

(ii) *Steam pressure.* The effect of steam pressure on the heat loss (corrected to the same heat-loss surface temperature of each flow) was found to be slight:

$$100\ \text{Kg/cm}^2 \text{ and } 400\ °\text{C, heat loss } 11{\cdot}13 \pm 0{\cdot}53\ \text{cal/s}$$
$$28\ \text{Kg/cm}^2 \text{ and } 400\ °\text{C, heat loss } 11{\cdot}05 \pm 0{\cdot}62\ \text{cal/s.}$$

(iii) *Electrically heated jacket.* For the J set of measurements, an aluminium jacket ($\frac{3}{8}$ in. in thickness) was fitted round the pressure pocket with a $\frac{1}{4}$ in. air space between. The jacket was heated electrically, and insulated outside with 1 in. of steam-pipe lagging. This outside jacket made it possible to maintain the outside temperature at about the same temperature as the steam, thereby countering the heat loss from the pocket. The effect of conduction in the metal parts would, however, not be the same as when not using the jacket. Without the jacket, on reducing steam flows, the temperature gradients across the wall of the pocket would become greater, and these in turn would alter the heat conduction along the wall. With the jacket, the heat-loss correction could not be eliminated, but it was hoped to make its determination at different flows more reliable.

By means of a resistance thermometer inserted between the jacket and the pocket, it was possible to study the temperature gradients. The change in surface temperature of the pocket with change of flow (mC_p) was found to be $(\mathrm{d}\Delta t_p/\mathrm{d}mC_p) = (0{\cdot}02t/(mC_p)^2)$, where $\Delta t_p =$ steam temperature (t) minus the jacket inside-surface temperature. (A decrease of mC_p from 3 to 2 would cause a change of only $-0{\cdot}02$ cal/g in the value of the total heat.) It was thus possible to correct the values of the total heat found at various flow rates to the same heat-loss surface temperature. There appeared to be no significant change of heat loss with change of steam flow when the temperature gradients in the pressure pocket were small, other than that due to change in surface temperature. Values were obtained by this method agreeing with the values found in the normal way at different flows, but it was not found that it led to increased accuracy, because it was more difficult to obtain steady conditions. It was useful in tracing the source of heat loss and in examining the effect of flow, but the normal method using two or more rates of flow was more reliable.

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Examples of the results with and without using the jacket (corrected for equal surface temperature) can be quoted:

	50 Kg/cm² 450 °C	100 Kg/cm² 400 °C
with jacket	790·87 cal/g	739·6 cal/g
mean by normal method	791·25 cal/g	739·6 cal/g

(iv) *Position of thermometer in pressure pocket.* In a heat-loss determination, it is the heat-content change between the position where the temperature is recorded and the one where the heat content is measured which has to be found. Consequently, another method of checking the change of heat loss with steam temperature was to measure the temperature gradient in the pressure pocket at a variety of steam temperatures and flows by altering the position of the thermometer in its pocket. If G was the temperature gradient along the pocket, $G = aq/mC_p$, was a found to be 0·105, where q is the loss of heat per centimetre. This indicated that the mean heat drop, per cm, was about one-tenth the total heat loss. Two-thirds of the heat loss was accounted for by loss from the pocket, and about one-third by loss from the various pipes.

The steam temperature was not measured at a precise point, but over the length of the resistance thermometer spiral. None the less the observed temperature corresponded to a certain position, not necessarily half-way along the thermometer. Furthermore, the Monel metal tube in which the thermometer was inserted would not be exactly at the temperature of the steam passing it, for it would radiate to the slightly cooler wall of the pocket, only the inner surface of which is in contact with the steam; that part of the tube surrounding the thermometer spiral is also receiving heat by conduction down the tube from steam which has not yet lost heat higher up. It was shown, however, that this gain by conduction was insufficient to affect the heat-loss correction. It was also shown that the position where the temperature (t_r) could be taken as the recorded temperature was at approximately the same position at various flows in relation to the normal position of the thermometer in its Monel metal tube. This position was, in fact, slightly lower than the end of this tube. It was concluded that if the heat loss remained constant with flow rate, then the heat loss referred to the recorded temperature within the error of the observations of the temperature.

(v) *Determination of the correction by measurements at different flow rates.* The many observations indicated that the heat-loss correction could be determined by measurements at different rates of flow. Whether the measurements were at two flow rates one, about half the other, or whether at three or four different rates, the heat-loss correction gave results within the errors of measurement. Any changes of value could be traced to alterations in the lagging or other disturbance. The results of the determinations in series D and G can be compared (the figures in parentheses give the number of individual measurements):

temperature (°C) ...	250	300	350	400	450	500
series D	6·5 (8)	8·3 (7)	—	13·0 (9)	—	19·0 (8) cal/s
series G	—	—	8·2 (6)	—	13·6 (7)	16·7 (11) cal/s

The jacket and alterations to the lagging were the cause of the lower loss in series G. The equation which best fitted the results for the G series was $6{\cdot}7t^2\,10^{-5}$; t being the temperature °C (see figure 3).

The following heat-loss determinations were made at 400 °C (table 5). They did not all agree, because there were slight alterations to the lagging and other changes; particularly after the second series.

TABLE 5

	P (Kg/cm²)	approx. flows (g/s)	number of experiments	Q' (cal/s)
D	28	4, 2	9	12·67
E_1	28	3, 1·5	8	12·80
E_2	28	4, 1·5	7	11·05
E_3	100	4, 1·5	6	11·13
G	75	4, 2	8	10·31
I	100	4, 3	7	11·03
K	100	4, 2	8	10·10
M	50	multi	14	11·70

The accepted values for Q' cal/s became:

TABLE 6

series	300 °C	400 °C	500 °C	heat loss rate (cal/s)
D	8·3	13·0	19·0	$6{\cdot}7t^2\ 10^{-5}+2{\cdot}3$
E_2 to G	6·0	10·7	16·7	$6{\cdot}7t^2\ 10^{-5}$
H to K	6·3	11·2	17·2	$7{\cdot}0t^2\ 10^{-5}$
M, O		11·5		$7{\cdot}0t^2\ 10^{-5}$

Attempts made to estimate the heat transfer coefficient (h cal s^{-1} cm^{-2} °C^{-1}) to the walls of the pocket in relation to the heat flow of the steam and the radiation from the re-entrant thermometer tube did not accord well with the measurements which had indicated independence of steam flow rate. The convection constant $K = h/(mC_P)^{0{\cdot}8} = 0{\cdot}003$ obtained from Nusselt's measurements in tubes 2 cm diameter at pressures up to 10 Kg/cm² was evidently too small a value to be used for the narrow passages and high pressures in the steam pocket (measurements in narrow channels have indicated a larger constant). There was doubt as to the value for the emissivity of the Monel metal of the thermometer tube and of the radiant transfer from the steam, so the final estimate of the heat transfer coefficient was not very accurate, although it did show that this pressure pocket was not suited for measurements at very small flows and suggested that, in a new design, the pocket-wall temperature gradient should be avoided by jacketing. Such a design would not eliminate the residual conduction effects and the influence that the cooling due to the expansion of the steam at the throttle would have on these, so measurements at different flow rates would still be necessary, but uncertainties due to the heat-loss correction would be reduced.

TABLE 7

series	date	number of observations	H_0 (cal/g)		heat loss rate (cal/s)
D	July 1932	4	739·66	±0·09	13·0
E	Dec. 1932	3	739·58	±0·01	11·2
F	Feb. 1933	3	739·34	−0·23	11·2
G	Mar. 1933	4	739·64	+0·04	11·2
I	June 1933	3	739·61	+0·07	11·2
J	June 1933	4	739·61	+0·04	11·2
K	Oct. 1933	4	739·56	−0·01	11·2
		25	739·57		

(g) *Check-point determinations*

It was desirable to have points at which the value of the total heat could be accepted as 'standard'. The 100 Kg/cm², 400 °C point was the choice, as frequent measurements had been made at this point and it was in the middle of the range of temperature and pressure. The values of table 7 refer to this check point.

Table 8 summarizes the determinations at various check points.

TABLE 8

P (Kg/cm²)	T (°C)	series	number of observations	p.e.	Q (cal/g)	H (cal/g)
10	400	K, N	13	±0·09	3·93	779·00
25	400	D, E, K	20	±0·15	3·75	773·00
50	400	D, I, M, O	38	±0·09	3·86	762·64
75	450	F, G, K	14	±0·09	3·78	782·78
100	400	D, E, F, G, I, J, K	25	±0·10	3·17	739·60
150	350	K, O	6	±0·18	2·77	747·11
			116			

(Q = heat loss correction (see p. 141); p.e. = probable error of the whole set of observations.)
13 values in series O at 50 Kg/cm² and 400 °C gave 762·64 ± 0·28 cal/g.

(*h*) *Further consideration of the errors*

A preliminary estimate of errors was given at the outset (see p. 142). The further studies made gave general confirmation of the estimate, namely a probable accuracy of 1/1500 (i.e. about 0·5 cal in the mid range).

The average dispersion from the mean value of the five or six measurements in the following series was as given in table 9.

TABLE 9

series	P (Kg/cm²)	T (°C)	number of observations	average dispersion
F	75	400	5	±0·33 cal/g
G	75	500	6	±0·36
	75	500	5	±0·17
H	125	400	5	±0·33
K	75	450	6	±0·15
I	50	450	5	±0·13

For all the observed values, series E to M, the mean of the dispersion was 0·33 cal/g.

The observed probable error (not greater than ±0·2 cal/g) of the mean of a set of total heat measurements at any one temperature and pressure does not include errors in the thermometer constants (±0·2 cal/g), weight standardization (±0·04/g), evaporation correction (±0·04/g), meter timing (±0·07/g), heat-loss correction (±0·25/g), and correction to even temperature and pressure (±0·05/g). These could amount to a total error of about 0·6 cal/g, but these errors do not operate together.

6. Results of measurements of the total heat of steam (before alteration of the apparatus)

(*a*) *Measurements in the superheat region*

The values of H_0 (cal/g) in table 10 summarize the results of the measurements made using the original pressure pocket. These values are smoothed values, but values obtained from the actual measurements are mostly within 0·1 to 0·2 cal/g of the smoothed value at each temperature and pressure point, except for two points at 25 Kg/cm², 275 °C and 325 °C, where the difference amounts to 0·4 cal/g.

Some of these measurements were available at the time of the 1934 International Steam Table Conference in New York. The values were appreciably lower than previous steam-table data. The measurements of Havliček & Miškowský (1936), the volume measurements at the Massachusetts Institute (Keyes, Smith & Gerry 1936), and the values for saturation

Table 10

T(°C) \ P(Kg/cm²)	10	25	50	75	100	125	150
200	674·8	—	—	—	—	—	—
250	701·7	687·5	—	—	—	—	—
275	714·7	703·3	678·7	—	—	—	—
300	727·7	717·7	698·5	672·8	—	—	—
325	740·5	731·9	716·4	697·2	671·8	—	—
350	753·3	745·7	732·7	717·4	698·9	676·2	647·1
375	766·1	759·4	747·9	735·1	720·7	—	—
400	778·9	773·0	762·6	751·6	739·7	726·4	711·7
425	791·7	786·5	777·1	767·6	757·6	—	—
450	804·4	799·8	791·4	782·8	774·0	764·6	754·8
500	830·1	826·5	819·6	812·7	805·7	798·8	791·8

Table 11. The departure of Havliček's calculated total heats (submitted 1934) from E and C (mean observed values) in cal/g

T(°C) \ P (Kg/cm²)	25	50	100	150
250	+0·7	—	—	—
300	+0·6	+0·5	—	—
350	+0·7	+0	+0·5	−1·4
400	+0·4	+0·5	+0·5	+0·8
450	+0·2	+0·5	+0·5	+0·4
500	−0·2	+0·2	+0·3	−0·5

conditions obtained at the National Bureau of Standards (Osborne *et al.*) fitted fairly well on the whole. The values adopted at the Conference were within the agreed tolerance and not outside the maximum estimated error of the measured values. The latter were consistently from 0·2 to 0·6 cal/g smaller. It was decided that the British direct measurements of total heat should be continued and carried to the highest temperatures possible.

The values (smoothed) obtained by Havliček by a direct method (sent to the authors privately in 1934) agreed well within their error ($\frac{1}{350}$) with the present measurements (table 11).

The values of total heat computed from the volume measurements by Keyes *et al.* then available varied from 1·6 to 0·5 cal/g higher than the Egerton & Callendar measurements over the range of the experiments.

(*b*) *Some measurements near saturation*

A few experiments were made at points near the saturation temperature at 150 Kg/cm² and at 50 Kg/cm², during the K and O series of measurements. The pressure pocket was not very suitable for such measurements, because condensation on the wall is liable to occur when the temperature is less than 7 °C from the saturation point.

Steam temperatures had to be accurately measured and the superheater carefully regulated. The values at 150 Kg/cm² below 2·5 °C superheat were not likely to have been accurate. Measurements at 50 Kg/cm² were difficult to obtain, but table 13 gives four results each the mean values of twelve measurements, and were probably more reliable than most steam-table values at that time.

Table 12

(Pressure, 150 Kg/cm².)

T (°C)	superheat (°C)	H_0 (cal/g)
350·58	9·49	647·1
345·82	4·67	635·1
343·33	2·51	631·3
342·27	1·48	628·2
341·96	1·01	628·6
341·10	0·23	623·1
340·80	0·67	626·7

I.S.T.C. (1934) value at saturation, 340·85 °C, 625·0 cal/g.

Table 13

(Pressure, 50 Kg/cm².)

T (°C)	superheat (°C)	H_0 (cal/g)
265·70	3·12	669·67
268·88	5·97	$671{\cdot}6_5$
276·14	13·30	$678{\cdot}7_2$
280·00	17·30	$683{\cdot}3_4$

Saturation temperature, 262·68 °C.

A few other points near saturation were amongst the measurements made (table 14).

Table 14

series	T (°C)	P (Kg/cm²)	superheat (°C)	H_0 (cal/g)
D	300	75	10·8	673·0
D	315	100	5·5	659·1
H	330	125	3·7	646·0
K	350	150	9·4	647·1

PART II

The previous work, described in part I, led to redesigning the high-pressure thermometer pocket and the superheater, and adding a special reducing valve.

7. The apparatus

The objects of the changes made in the apparatus were to diminish the heat-loss correction and to render possible measurements at higher temperatures.

(a) *The pressure pocket*

Some of the steam entering the pocket was used to jacket the remainder of the steam which passed on to the condenser and on which the measurements were made. Heat loss from the measured part of the steam was thus diminished, and under control. The material, F.D.P. alloy (an 18:8 nickel:chromium steel), used for the construction of the pocket by

Metro-Vick Electrical Co. Ltd was found to withstand attack by the steam at the higher temperatures. (See figure 4 giving sketch and scale drawing.) A steel tube *A* passed down the centre of the pocket and housed the thermometer. It was securely welded into the top of the

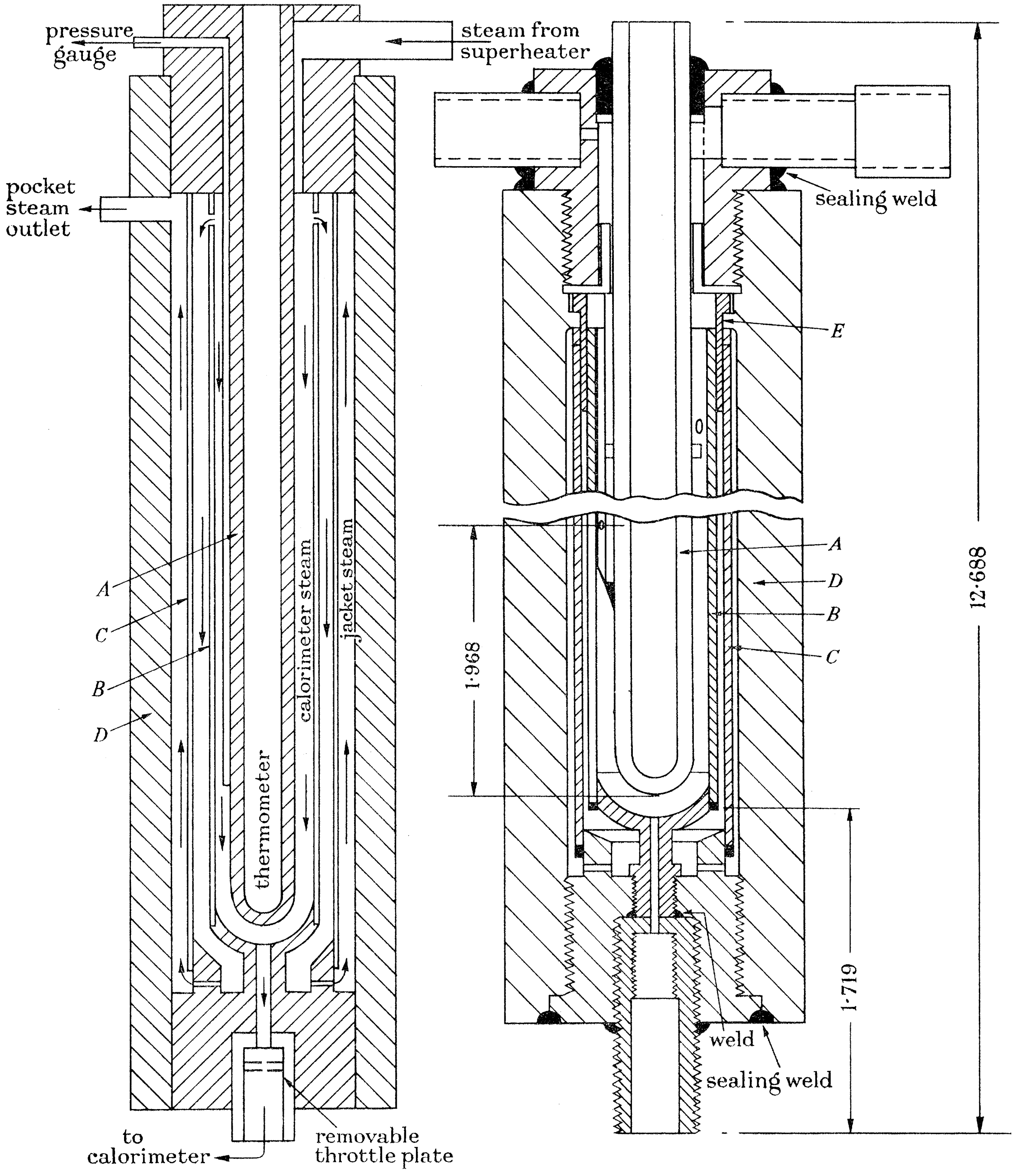

FIGURE 4. Double-shield thermometer pocket for high-pressure steam. (Dimensions in inches.)

pocket; its lower end was clear of the bottom to allow space for the passage of steam This tube was surrounded by two concentric cylindrical metal tubes, *B* and *C*, with a space (3·2 mm) between each. Outside the larger of these tubes was the wall of the pocket *D*, $\frac{1}{4}$ in. thick. A ring *E* served to separate the two tubes *B* and *C*.

The steam from the superheater entered at the top, and divided into two portions, one

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of which travelled down past the thermometer tube to the throttle holder and then to the calorimeter, where its heat content was measured. The other portion, moving in the same direction, passed down the pocket between the two concentric tubes (B and C) and then, changing direction, upwards between the outer surface of C and the wall of the pocket. The exit was near the top. Here it passed through a release valve capable of fine adjustment to within $\pm 0{\cdot}01$ g/s. This double jacket of steam thus surrounded the tube through which the measured steam was passed. The two concentric tubes carrying the jacket steam were free to expand independently of the thicker outer wall; the inner tube was attached

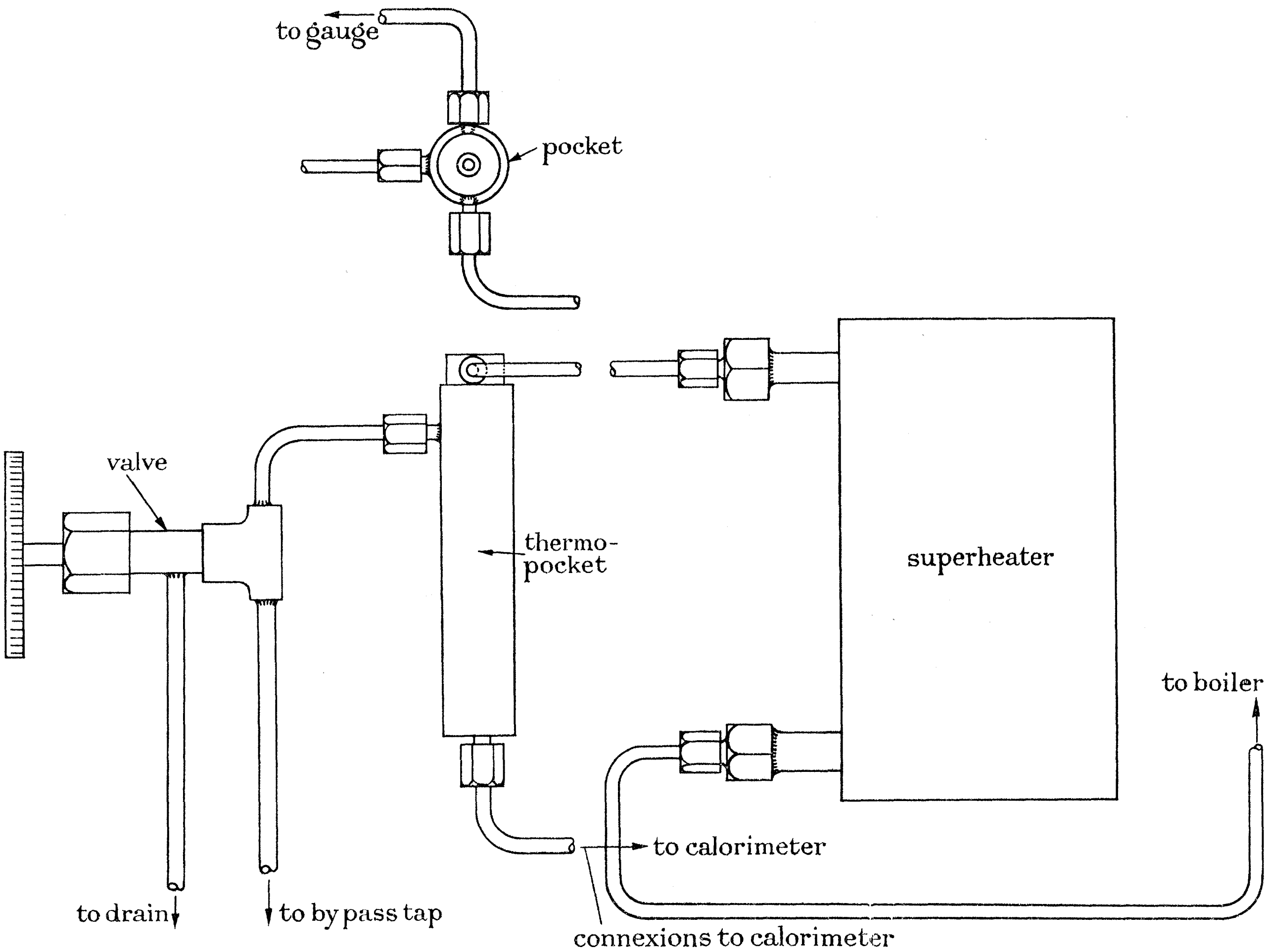

FIGURE 5. General arrangement of high-temperature section of apparatus.

at the bottom and the outer tube at the top. The pressure was measured by connexion with the pressure gauge and balance through a tube which entered at the top of the pocket and had its open end level with the midpoint of the thermometer. The throttle plates were carried in an easily detachable holder at the base of the pocket. The pocket and connecting tubes were completely encased in 2 in. asbestos lagging made so that it could be replaced without alteration. (For general arrangement of apparatus, see figure 5.)

At temperatures from 300 to 600 °C with F.D.P. alloy, no trouble was experienced up to a pressure of 100 Kg/cm^2, but above 500 °C there was a little trouble at high pressures from choking at the throttle with a slight deposit making it more difficult to obtain steady conditions.

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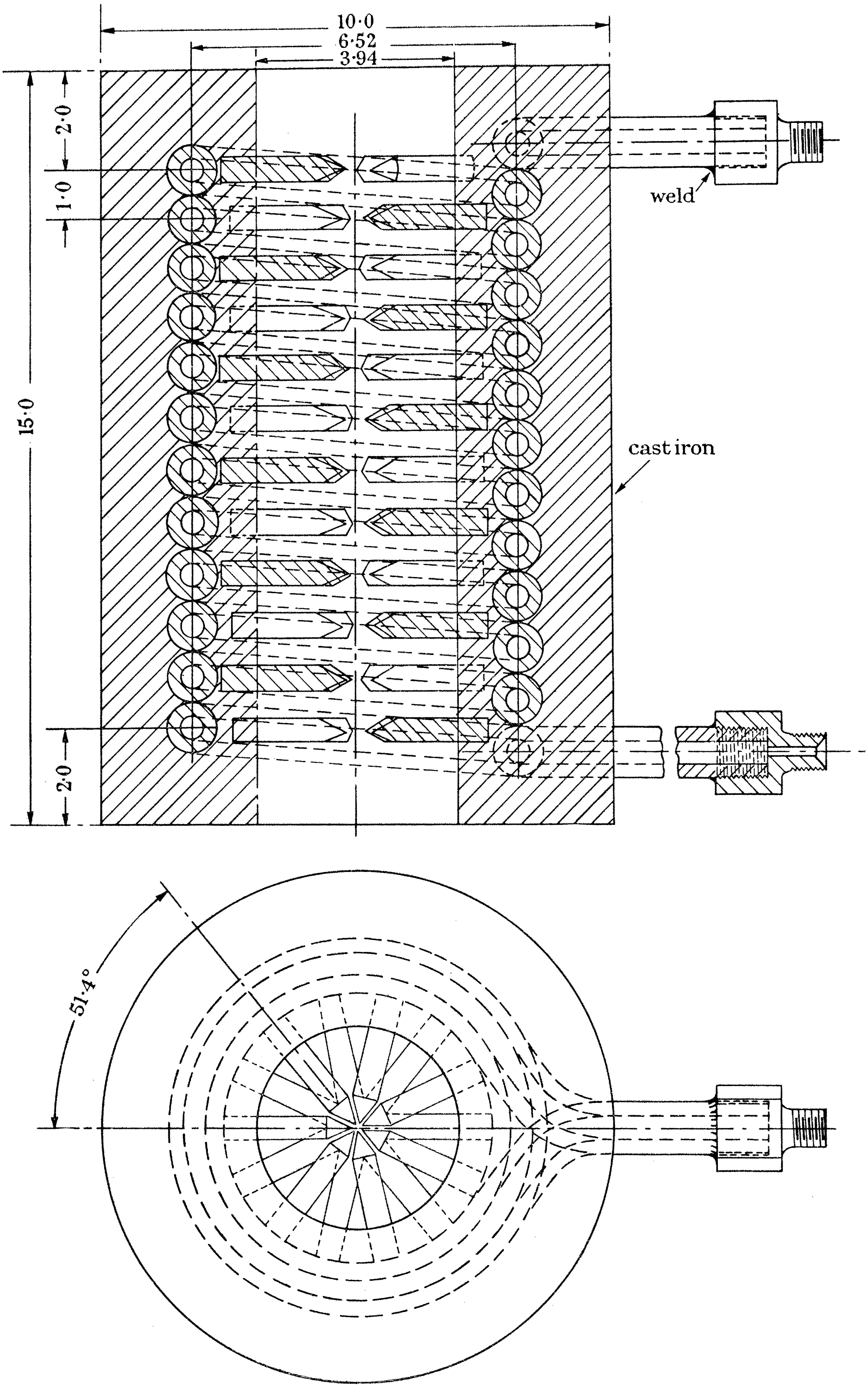

FIGURE 6. The superheater. (Dimensions in inches).

(*b*) *The superheater*

The former superheater could not provide sufficient heat to supply steam at 600 °C, and above 400 °C the superheater coil tended to be attacked by the steam, causing blockage at the throttle.

A new superheater (see figure 6) was designed. It was estimated that 1600 cal/s had to be transferred in order to superheat steam at 5 Kg/cm^2 to 620 °C. The superheater coil was constructed from F.D.P. alloy. The superheater was heated both by gas and by an electrical winding. It was lagged efficiently. There were special arrangements for careful regulation of the heat supply. The temperature of the steam responded more quickly than the old superheater to alterations in the energy supply. Gas heating was generally found sufficient. The figures in table 15 gave the times taken to reach steam temperature, with a normal flow of 3·5 g/s at 280 °C feed from the boiler.

TABLE 15

steam temperature (°C)	time starting from cold (min)	rate of heating (°C/min)
20	—	—
450	135	—
500	167	2·0
550	205	1·0
575	230	0·7
600	270	0·4
610	295	0·3

The efficiency was found to be approximately 48 % at 600 °C for a flow of 4 g/s. The heat required to give 100 °C of superheat at 200 Kg/cm^2 was three times greater than at 50 Kg/cm^2.

The Monel metal boiler was not allowed to function above 380 °C, as the metal becomes weaker, and only one tube burst during the life of the apparatus.

(*c*) *Reducing valve* (see figure 7)

The body of the valve was constructed of stainless steel, the valve spindle of special Twoscore steel (Brown Bailey) and the T piece of F.D.P. alloy. The stuffing-box nut was of rustless iron and special asbestos packing was used in the box. The wheel of the spindle was graduated and the flow of steam could be finely adjusted. Above about 450 °C seizure of joints could occur unless previously treated with Aquadag. The reducing valve could adjust the jacket steam to $\pm 0{\cdot}01$ g/s, and so provide a constant heat flow, which could be measured by weighing the condensed steam.

(*d*) *Further details*

A Smith's No. 2 Difference Bridge (Cambridge Instrument Co.) was used in this part of the work. It was placed in a large, lagged box, so that the temperature remained nearly constant and the fall of temperature by night did not affect the bridge; dry air, freed from sulphur dioxide, was supplied to the box. The necessary checks and calibrations of resistance box coils and resistance thermometers were made from time to time during the period of the measurements. A slight regular change occurred in the constants for the thermometer used for measurement of the steam temperature, owing to long exposure at high temperatures. The value of δ decreased gradually from 0·0001520 to 0·0001513. The resistance was repeatedly checked at the sulphur point. The constants of the 'rise' thermometers remained unchanged. Special care was taken over the barometer readings. A very small creep in the value of the box coils occurred.

At the high pressures, the dead-weight gauge was only placed in connexion with the pocket for the minimum of time whilst the readings were taken, so as to avoid oil leak.

Much the same procedure governed the conduct of the experiments as was used with the old apparatus; the only additional measurement was that of the mass of the jacket steam.

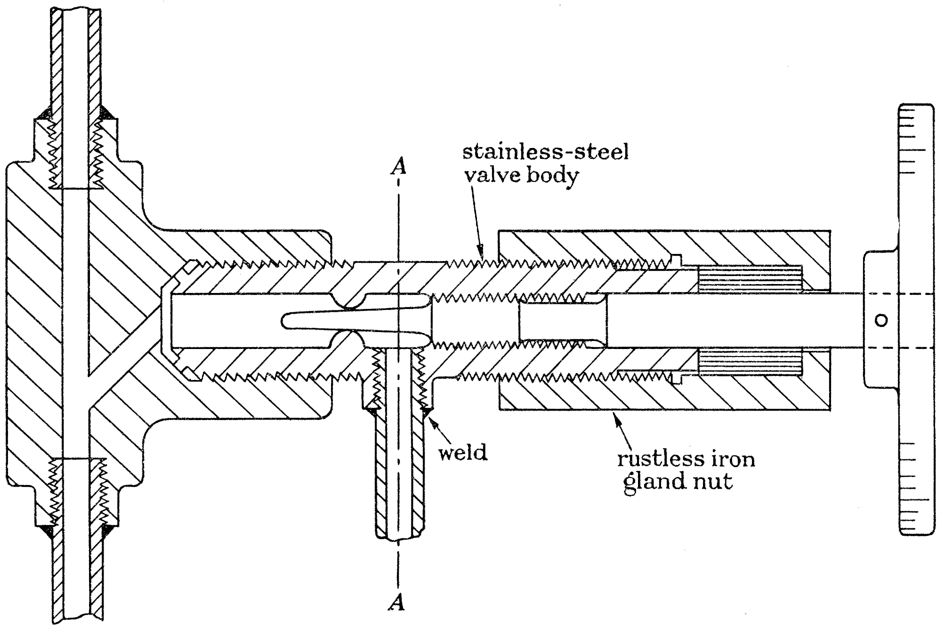

Figure 7. Jacket steam valve.

8. Experimental

(a) *The heat loss*

The new pocket was designed to reduce the heat loss from the steam passing the thermometer, following the investigations described in part I. The steam passes to the throttle at a temperature very close to that observed on the thermometer, it then suddenly expands and the temperature drops rapidly if the steam is near the saturation temperature or at very high pressures. The expanded steam therefore tends to pick up some heat from the short steel tube by which it is guided into the condenser, and this tube receives heat from the steel walls of the pocket. There was thus both a cooling effect and a heat gain by conduction; the measurement of the net effect was determined by experiments at different flow rates and it includes heat loss from the calorimeter, heat gain along the steel tube to the calorimeter and heat loss from the lagging. In the new apparatus, the direct measurement of the total heat of the steam was less affected by these sources of inaccuracy than previously. The heat loss from the pocket became very small and the sign of the correction could change.

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The 'cooling effect' is $(H_0 - H_P)/S_0$, where H_P is the total heat at pressure P, and H_0 that at 1 atm at the same steam temperature, S_0 being the specific heat of steam at 1 atm pressure. (The steam remained superheated after throttling under all conditions quoted in this work. Some additional measurements were however made at high pressures near to saturation.) Heat changes due to differences in eddy motion of the steam were too small to affect the total heat measured.

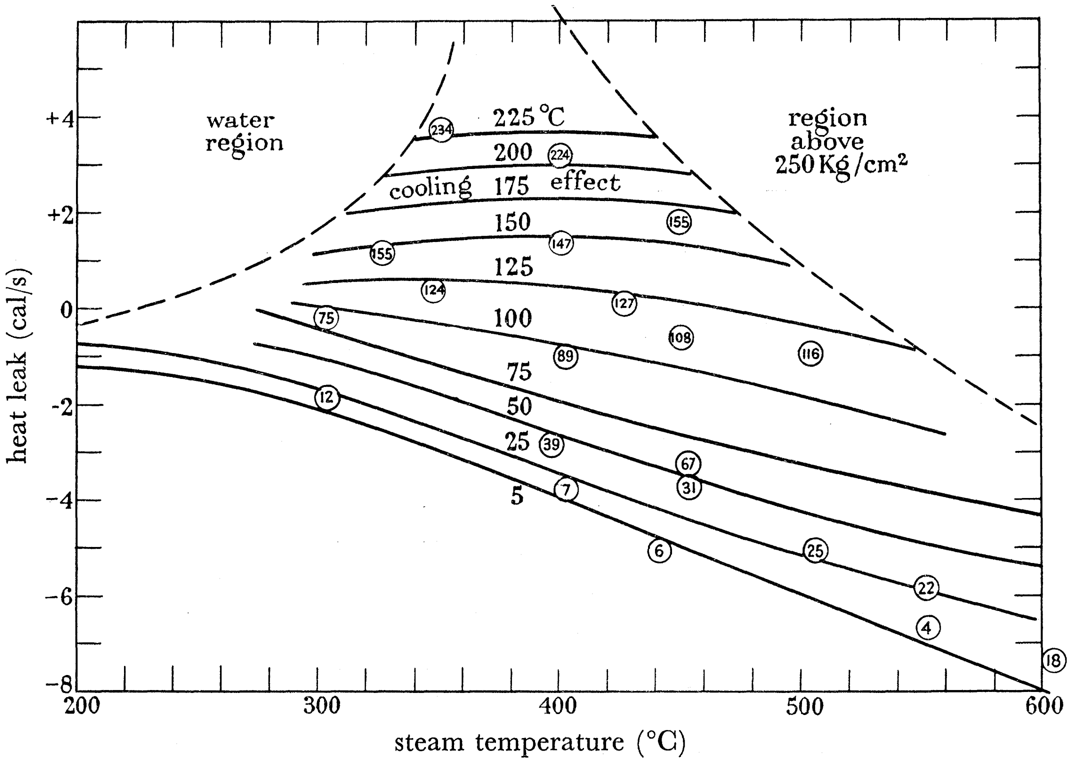

FIGURE 8. Heat-leak chart: lines of constant cooling effect. Observed points with cooling effect in circles.

The curves (figure 8) connecting the heat-loss correction with the cooling effect (°C) showed that there was an increase in heat loss with steam temperature but, as the cooling effect became greater at higher pressures, the correction became approximately independent of temperature; that is, the heat gain by conduction increased with temperature at about the same rate as the external loss.

Table 16 gives the results of experiments at various flow rates to determine the heat loss or heat 'leak' in cal/s at 400 °C in the new apparatus.

The 'mean curve' was established from measurements at different steam-flow rates, made at other temperatures as well as at 400 °C. The following measurements of the heat-loss correction in cal/s refer to those at 50 and 200 Kg/cm²:

T (°C) ...	300	400	450	500	550	600
P (Kg/cm²)						
50	0	−2·9	−3·7	−5·1	−5·9	−7·3
100	—	+3·1	+1·8	−1·0	—	—

Curves of the measured heat 'leak' at various temperatures and pressures against the cooling effect were drawn for each 50 °C, from which table 17 was prepared and used for correcting the observed values of the total heat. The correction factor is thus supported not by a single measurement at the relevant temperature and pressure, but by the results accumulated.

TABLE 16

(Temperature, 400 °C)

P (Kg/cm²) ...	10	50	100	150	200	225
cooling effect (°C)	7	39	89	147	224	270
heat 'leak' (cal/s)	−4·0	−3·0	−1·0	+1·5	+3·1	+3·0
heat leak (cal/s) (from the mean curve)	−4·0	−3·0	−1·2	+1·5	+3·1	+3·5
number of observations	13	17	12	11	8	11

TABLE 17. HEAT LOSS CORRECTION FACTOR OR HEAT 'LEAK'

cooling effect (°C)	steam temperature (°C)											
	200	275	300	325	350	375	400	425	450	500	550	600
0 to 10	−1·2	−1·7	−2·1	−2·5	−3·0	−3·5	−4·0	−4·5	−5·0	−6·0	−7·0	−8·0
10 to 20	−1·0	−1·5	−1·9	−2·3	−2·8	−3·3	−3·8	−4·3	−4·7	−5·5	−6·5	−7·4
20 to 30	−0·8	−1·3	−1·7	−2·0	−2·5	−3·0	−3·5	−3·9	−4·3	−5·1	−6·0	−7·0
30 to 40		−1·0	−1·5	−1·8	−2·2	−2·7	−3·2	−3·6	−4·0	−4·8	−5·7	−6·6
40 to 50		−0·8	−1·3	−1·5	−2·0	−2·5	−3·0	−3·4	−3·7	−4·5	−5·4	−6·3
50 to 60		−0·5	−1·1	−1·3	−1·7	−2·2	−2·7	−3·1	−3·4	−4·2	−5·1	−6·0
60 to 70		−0·3	−0·8	−1·0	−1·5	−1·9	−2·3	−2·7	−3·1	−3·8	−4·7	
70 to 80		−0·1	−0·5	−0·8	−1·2	−1·5	−1·9	−2·3	−2·7	−3·3	−4·1	
80 to 90		+0·1	−0·3	−0·5	−0·8	−1·1	−1·5	−1·8	−2·2	−2·8	−3·5	
90 to 100		+0·3	−0·1	−0·3	−0·5	−0·7	−1·0	−1·3	−1·6	−2·2	−2·9	
100 to 110			0	0	−0·1	−0·3	−0·5	−0·7	−1·0	−1·6	−2·3	
110 to 120			+0·2	+0·2	+0·2	+0·1	0	−0·2	−0·5	−1·0	−1·7	
120 to 130			+0·5	+0·5	+0·5	+0·5	+0·5	+0·2	0	−0·5		
130 to 140			+0·7	+0·8	+0·9	+0·9	+1·0	+0·8	+0·6	0		
140 to 150				+1·0	+1·3	+1·4	+1·4	+1·3	+1·2	+0·7		
150 to 160	water region			+1·2	+1·6	+1·8	+1·8	+1·8	+1·7	+1·4	above 250	
160 to 180				+1·8	+2·0	+2·1	+2·1	+2·1	+2·0	+1·9	Kg/cm²	
180 to 200					+2·5	+2·5	+2·5	+2·5	+2·5			
200 to 220					+3·0	+3·0	+3·0	+3·5	+3·0			
220 to 240					+3·6	+3·5	+3·5					
240 to 260					+4·0	+4·0	+4·0					

Tests were made to determine the effect of changing the flow of steam through the double jacket of the new steam pocket:

(Steam at 50 Kg/cm² and 400 °C)

measured steam flow (g/s)	jacket steam flow (g/s)	jacket heat flow (cal s^{-1} °C^{-1})	H (observed, uncorrected for heat loss)
2·494	2·465	1·43	762·27
2·513	1·745	1·01	762·32
2·485	0·350	0·49	762·00

A heat flow through the jacket of 1 cal s^{-1} °C^{-1} was sufficient to prevent heat loss from the measured steam whilst it was in the pocket, and this flow through the jacket was ensured throughout the measurements of total heat. Below this flow of 1 cal s^{-1} °C^{-1}, the values of H tended to fall. The variation of heat loss with steam flow and with other factors, such as disturbance of the lagging which was a troublesome feature of the older apparatus, had been largely eliminated in the new design. The heat-loss correction factor was reduced to a much smaller proportion of the total heat than in the former apparatus, generally less than ½% and in no case more than about 1%.

The figures in table 18 indicate the effect of steam flow on the observed value of the total heat and the result of applying the correction for heat loss.

TABLE 18. TOTAL HEAT OBSERVED WITH DIFFERENT STEAM FLOWS

steam conditions	steam flow (g/s)	observed H (cal/g)	total heat (cal/g)
75 Kg/cm², 300 °C	2·962	673·18	673·2
	2·164	672·97	673·0
	1·927	672·79	672·8
	1·303	672·98	673·0
100 Kg/cm², 400 °C	3·772	739·85	740·1
	2·547	739·62	740·0
	1·891	739·44	740·0
	1·315	739·48	740·2

The variation of cooling effect with temperature is small at low pressures; at 10 Kg/cm² the cooling effect only varies from 12° at 300 °C to 4° at 550 °C. Temperature is then the significant variable connecting the heat-loss correction factor with the total heat observed. A number (35) of measurements of the total heat at 10 Kg/cm² were obtained between 300 and 550 °C, with different steam flows. The difference of the values of the heat-loss correction factor from the values at the higher pressure of 50 Kg/cm² was small corresponding to only about 0·25 cal/g on the value of the total heat.

(*b*) *The accuracy of the measurements*

All the other precautions described in part I were taken during the many measurements made. The number of separate measurements was about 450, distributed as in six series as shown in table 19.

TABLE 19

series	dates (approx.)	number of measurements	range T (°C)	range P (Kg/cm²)
P	1936	83	275 to 600	50 to 100
R	1936, 1937	55	200 to 400	5 to 150
S	1936, 1937	110	300 to 450	10 to 200
T	1937	107	350 to 560	10 to 225
U	1938	32	400 to 600	50 to 175
V	1939, 1940	53	400 to 600	50 to 200
	total	440		

50 Kg/cm², 400 °C, was used as a check point and 55 separate measurements throughout the series P to V at this point gave a total heat 763·6 ± 0·2 cal/g.

The only real trouble encountered was found to be due to a very small leak of steam into the lagging near a joint leading to the condenser. This was so small that it could only be detected by a slight change in the value of the total heat at the check point. When discovered, however, the trouble was easily eradicated.

At the high temperatures and pressures, it took longer to obtain reliable results; 25 measurements at 600 °C represent twice that number of measurement-days.

The probable error of an observed value of the total heat can be estimated from the dispersion of the single values taken at any one temperature and pressure, or by plotting the set mean values on the H/P diagram when the values should lie smoothly along isotherms on the plot.

The possible error of an observed set mean value of total heat from four observations was estimated to be composed of the following errors:

1.	average observational error	±0·18 cal/g
2.	thermometer constants	±0·14
3.	weight standardization	±0·04
4.	evaporation correction	±0·04
5.	meter time difference	±0·07
6.	correction to even T and P	±0·05
7.	heat-loss correction	±0·33
8.	specific heat of cooling water	±0·20

From these values, the error of an observed value of H was estimated as probably $\frac{1}{2}$ cal/g.

The heat-loss values plotted against temperature and cooling effect lie within 0·5 cal/s of their expected position on the chart and this is equivalent to 0·2 cal/g on the total heat. The error quoted under 7 above is considered on the high side: the error of a set mean value could therefore be a little less than the ±0·5 cal/g given.

9. Results

Table 20 shows the differences between the total heat as measured in the new apparatus and in the old; they are sets of mean measured values compared on the same basis (i.e. on the earlier National Bureau of Standards values of the specific heat of water used in part I).

Table 20. Departure in calories

($H_{new} - H_{old}$) in cal/g.

T (°C) \ P (Kg/cm²)	10	25	50	75	100	150	17
200	+0·3	—	—	—	—	—	
250	—	—	—	—	—	—	—
275	—	—	−0·3	—	—	—	—
300	+0·6	+0·5	+0·2	−0·2	—	—	—
325	—	—	+0·2	—	+0·2	—	—
350	—	—	+0·3	—	0	−0·4	—
375	—	—	+0·5	—	0	—	—
400	0	+0·2	+0·6	+0·5	+0·1	−0·1	−0·5
425	—	—	+0·5	—	−0·1	—	—
450	−0·4	—	+0·3	+0·5	+0·2	−0·4	−0·7
500	−0·7	—	−0·2	—	−0·4	−1·5	—

It was satisfactory that the values obtained in the old apparatus, on which less reliance was placed, are mostly within $\frac{1}{2}$ cal/g of the later values, i.e. within the accuracy of the respective values. The newer values are, however, slightly higher at the low pressures, but lower at the high pressures.

The small change of heat loss with pressure was probably about the same with the old apparatus as with the new, but it was not so easy to determine in the old apparatus on account of the large change with temperature and steam flow. With the new apparatus, the variation of heat loss with steam flow was almost eliminated and the variation with cooling effect could be more easily obtained. The old values were slightly too high at the highest temperatures, even at low pressure; the heat-loss correction was evidently about 15% too great under these circumstances.

The newer measurements have since been corrected for the later National Bureau of Standards values (Osborne, Stimson & Ginnings 1939) for the heat content of water

TABLE 21. OBSERVED VALUES OF TOTAL HEAT (I.T.CAL/G)

T (°C) \ P (Kg/cm²)	5	10	25	50	75	100	125	150	175	200	225
200	682·1	675·5	—	—	—	—	—	—	—	—	—
225	694·8	689·6	—	—	—	—	—	—	—	—	—
250	707·2	702·9	688·2	—	—	—	—	—	—	—	—
275	719·5	715·9	704·0	678·8	—	—	—	—	—	—	—
300	731·8	728·7	718·8	699·1	673·0	—	—	—	—	—	—
325	744·1	741·4	732·9	717·0	697·6	672·4	—	—	—	—	—
350	756·4	754·0	746·7	733·4	717·8	699·3	676·4	647·1	—	—	—
375	768·7	766·7	760·2	748·8	735·8	721·1	704·2	684·1	660·5	627·3	—
400	781·2	779·3	773·6	763·6	752·5	740·2	726·7	711·8	694·8	675·1	651·6
425	793·5	791·9	786·9	778·0	768·4	757·9	746·9	734·5	720·8	705·4	691·0
450	806·0	804·5	800·0	792·2	783·7	774·7	765·0	754·8	743·4	731·4	720·0
475	818·5	817·2	813·2	806·2	798·4	790·3	782·0	773·3	763·9	753·8	744·5
500	831·3	830·0	826·3	820·0	813·0	805·8	798·4	790·6	782·2	773·3	—
525	844·0	842·9	839·5	833·7	827·4	820·9	814·1	807·0	799·5	791·7	—
550	856·8	855·9	852·7	847·3	841·6	835·6	829·4	823·0	816·4	809·5	—
575	869·9	869·0	866·1	861·0	855·8	850·3	844·8	839·1	833·2	827·0	—
600	883·2	882·4	879·7	874·9	870·1	865·2	860·2	855·2	850·0	844·4	—

TABLE 22. TOTAL HEAT (ABS. J/G)

T (°C) \ P (bars)	5	10	25	50	75	100	125	150	175	200
200	2855·3	2827·1	—	—	—	—	—	—	—	—
225	2908·7	2886·5	—	—	—	—	—	—	—	—
250	2960·6	2942·2	2879·4	—	—	—	—	—	—	—
275	3012·2	2996·8	2945·7	—	—	—	—	—	—	—
300	3063·7	3050·5	3008·0	2923·4	2811·3	—	—	—	—	—
325	3115·3	3103·8	3067·3	2999·1	2915·3	2806·8	—	—	—	—
350	3166·8	3156·8	3125·3	3068·3	3001·1	2921·5	2821·2	2694·8	—	—
375	3218·3	3209·7	3182·0	3133·1	3077·3	3014·0	2940·8	2853·5	2749·2	2604·4
400	3270·1	3262·5	3238·2	3195·4	3147·7	3094·8	3036·8	2972·3	2898·4	2812·3
425	3322·2	3315·3	3294·0	3255·9	3214·7	3169·7	3122·4	3068·9	3009·6	2943·6
450	3374·5	3368·2	3348·9	3315·5	3279·1	3240·5	3198·9	3155·0	3105·7	3054·6
475	3426·9	3421·3	3404·2	3374·3	3340·8	3306·2	3270·6	3233·2	3192·8	3149·7
500	3480·5	3474·9	3459·1	3432·1	3402·1	3371·4	3339·7	3306·2	3270·0	3231·8
525	3533·6	3528·9	3514·4	3489·6	3462·6	3434·8	3406·6	3375·2	3343·0	3309·7
550	3587·2	3583·4	3569·8	3546·7	3522·3	3496·6	3470·6	3442·6	3414·3	3384·7
575	3642·1	3638·2	3625·9	3604·0	3581·7	3559·3	3534·8	3510·4	3485·1	3458·5
600	3697·8	3694·3	3682·8	3662·3	3641·8	3620·9	3599·6	3578·2	3556·0	3531·8

between 0 and 100 °C. The 1939 values are 0·067% larger than the 1930 values and this increases the total heat to the extent of +0·38 to 0·49 cal/g in the range 650 to 850 cal/g.

The results of all the most reliable measurements *in the improved apparatus* (series P to V) are summarized in table 21 of approximately smoothed values.

A table (22) converted to joules (abs.)/g and pressure (bars) is also given. Some error is introduced in the conversion, which necessarily involves the values of dH/dP and dH/dT, but independent check of the conversion (by the kindness of Mr Angus) indicates agreement within 0·1 to 0·2 cal/g, except in the high pressure and temperature corner where

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interpolation is difficult and differences up to 0·5 cal/g can occur, which however are within the error of the measurements.

The figures in these tables represent about 100 sets and 392 separate measurements, not including numerous measurements at the check point, 50 Kg/cm², 400 °C. 70 % of the set mean observed values differ by less than 0·2 cal/g from the smoothed values, and only 10 differ by as much as 0·6 to 0·9 cal/g, and nearly all these are exceptional in that the other measurements at the same point fall closer to the smoothed value. The above table of values of enthalpy can therefore be considered to represent the result of the work, without quoting the figures for the individual measurements. Some points are values interpolated from those observed at neighbouring temperatures for, in the region of high superheat (475 and 525 °C) at the lower pressures, the specific heat varies very little with temperature and interpolation is easily made.

From 5 to 100 Kg/cm², the differences between the various values of Havliček and other values obtained indirectly were within ±0·5 cal/g of the above values. Above this pressure, the values here presented are smaller by 1 to 3 cal/g. Such a difference is well outside the possible error. Havliček's observed values at 100 Kg/cm² and above, which were privately communicated, were closer to the present measurements than his formulated values published later (Havliček & Miškowský 1936). It seems unnecessary to discuss further the values obtained, as no other comprehensive direct determinations of the enthalpy of steam have yet been made with which to compare them. Further consideration can be given to them when the measurements are issued which are being made in a new installation in the Department of Chemical Engineering at the Imperial College, South Kensington, under the direction of Professor D. M. Newitt, F.R.S.

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