PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

On the Saturation Pressures of Steam (170 $^{\circ}$ to 374 $^{\circ}$ C)

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V. *On the Saturation Pressures of Steam* (170° *to* 374° *C.*).

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[Plate 9.]

I. *Introduction.*

The efforts which are being made through the agency of the International Steam Tables Conferences to co-ordinate investigations on steam, and to set down its measured properties in a series of tables and figures which shall be within agreed limits of error, and consistent with each other thermodynamically, cannot very well succeed, unless it be proved that steam is consistent in its behaviour. If there are differences, for instance, traceable to the time required for the constituent molecules of steam to reach an equilibrium state, then it might be difficult to achieve concordance between measurements of the properties of steam carried out by different methods. If, on the other hand, no such differences are exhibited, then it would seem that it is only a matter of care and of time to achieve a set of tables which shall represent the true behaviour of steam and which can be brought within a thermodynamically consistent scheme.

The apparatus installed at the Imperial College, South Kensington, which the late Professor H. L. Callendar devised for the determination of the total heat of steam and which he described in the Howard Lectures to the Royal Society of Arts (1926), was easily adapted to the determination of the saturation pressure of steam. In view of the above remark it seemed of importance to measure the saturation pressures in this apparatus, which provides a continuous flow of steam (*i.e.*, " dynamical " condition) and to compare the results with the measurements of Holborn and Baumann,* who used steam in equilibrium with water in a confined space (*i.e.*, a " statical " condition).

It is known that water is a complex mixture of condensed H_2O molecules, and it has been found by Hess† that the surface tension of a freshly formed water surface is momentarily different from that of an older surface; it has also been observed‡ that the presence of dissolved air modifies the properties of steam. It was possible that such changes might be detected in freshly formed steam, as it passed through the

* 'Ann. Physik,' vol. 31, p. 945 (1910).

† Freundlich, "Capillarchemie," p. 101.

‡ Callendar, 'Proc. Roy. Soc.,' A, vol. 120, p. 464 (1928).

apparatus, by a change in the values obtained for the saturation pressure, whereas no such effects would occur in the case of vapour in equilibrium with the liquid phase in a confined space. The apparatus provided a flow of steam and water, the temperature and pressure of which was measured before it passed through a throttle into a condenser. The size of the throttle and the speed of pumping the water into the electrically heated tube which forms the boiler determine the rate of flow and the wetness of the steam.

It may be stated at the outset that no appreciable differences between the results provided by the "Dynamic" and the "Static" methods have been found.

HENNING* has reviewed all the earlier work on the vapour pressure of water; it was not in good agreement at that time in the region 150° C. Subsequently HOLBORN and HENNING† carried out a very accurate investigation both by a dynamic and a static method up to 200° C., which, being supported by a thermometric investigation carried out simultaneously, has been accepted as entirely satisfactory. HOLBORN and BAUMANN‡ then carried the investigation upwards from 200° C. by a static method in a region where errors became more troublesome. These results have not been accepted as bearing the same certainty. The results near the critical point conflicted with some conclusions of CALLENDAR, who criticised them on the grounds that the water attacked the steel of the pressure vessel.§

Measurements by the statical method have been carried out in America by KEYES and SMITH,|| taking great precautions to avoid the presence of air. Though "final" figures are quoted, the investigation does not appear to have been published in full detail. The results of the present investigation lie between these measurements and those of HOLBORN and BAUMANN, but a slightly higher accuracy is claimed than for either of the sets of measurements made by the "statical" methods.

It is satisfactory to conclude that if accurate measurements are made of the properties of steam within defined limits of error that there is no reason to doubt that they may be brought within a consistent thermodynamic scheme, and that the tolerances at present agreed upon may eventually be reduced. The present work should help to reduce the tolerances in the case of the P/T relations for saturated steam.

II. *The Method and Apparatus.*

The description is divided into five sections; the first section gives an account of the apparatus, the second the detail of the temperature measurements, the third the detail of the pressure measurements, the fourth the methods of carrying out the experiment and discussion of the possible sources of error, and the fifth the results.

* 'Ann. Physik,' vol. 22, p. 609 (1907).

† 'Ann. Physik,' vol. 26, p. 833 (1908).

‡ 'Ann. Physik,' vol. 31, p. 945 (1910).

§ "R. Inst. Lectures," 'Engineering,' November 30, p. 7 (1928).

|| 'Mechanical Engineering,' vol. 52, p. 127 (1930).

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Pure distilled water, stored in two stoneware jars, was pumped into a boiler for removal of traces of air, from which it passed into a glass storage vessel, fig. 1. A triple-throw hydraulic pump drew it from this vessel and forced it through the monel

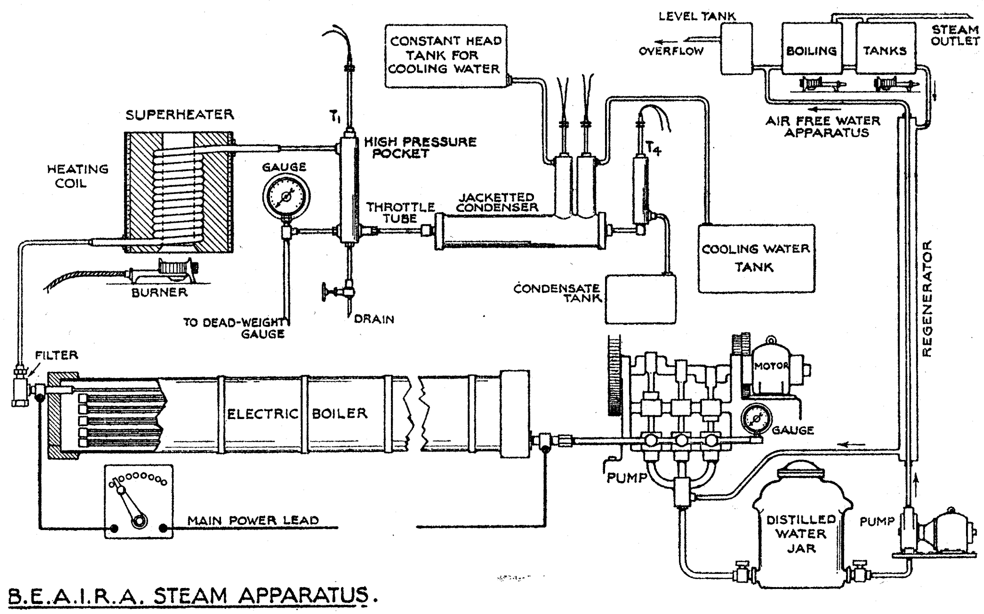

Fig. 1.

metal tube of the boiler (see fig. 15, Plate 9). The pump, driven at constant speed from storage batteries, was capable of delivering a very steady flow of water against pressures up to 5,000 lb. per square inch.

The monel metal tube of the boiler was arranged as a bundle of 19 tubes in series (11 feet × $\frac{5}{16}$ inch internal diameter) installed inside a 10-inch pipe with flanged ends. A carefully adjusted direct current from the main 200-volts supply provided the necessary heat to the boiler tube. The mixture of water and steam then passed through the $\frac{1}{2}$-inch diameter coil of the gas-heated superheater, fig. 2, which served as a fine

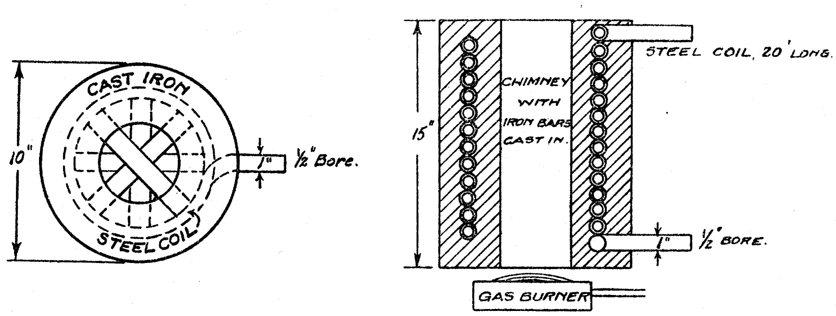

Fig. 2.—Superheater for 4,000 lb. pressure.

adjustment to the temperature to get the steam into a steady state before entering the high-pressure pocket. For a flow of 5 grams per second of steam (20 per cent. wet), the steam required 3·5 seconds to pass through the 20-feet helical coil of the superheater at 500 lb. pressure; at 3,000 lb. it would take nearly 40 seconds. The final measurements have been made with the monel metal larger pocket shown in fig. 3. The thermometer was inserted into the inner tube as close as possible to the point at which the small pipe leading to the pressure gauge was fixed.

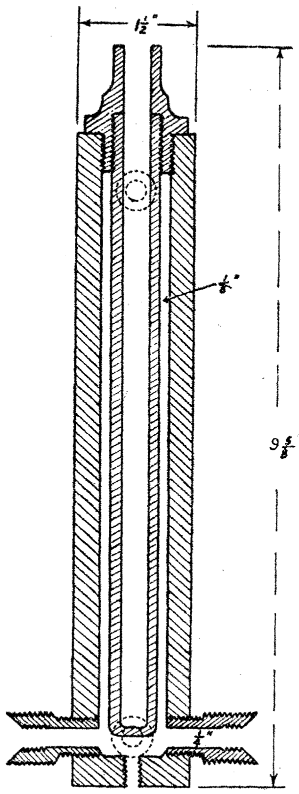

FIG. 3.

The steam from the high-pressure pocket was expanded and condensed after passing through the hole in the throttle disc. The condenser was the double-surface type referred to by CALLENDAR* (fig. 4). The temperatures of the cooling water entering and leaving the condenser, and the temperature and weight of the condensate provided data as to the degree of wetness and the rate of flow.

The pressure of the steam was measured by means of a large differential dead-weight gauge. The steam exerted pressure on a column of water in a fine bore tube, the pressure being communicated through oil to the gauge, fig. 5.

The temperature of the steam was measured by resistance thermometers. It was only by careful attention to the details of the temperature and pressure measurements that the results have been brought to their present accuracy; the method of calibration and the sources of error will be discussed in the next two sections.

There have been four stages of the work; first, a preliminary series of measurements over the whole range with the smaller pressure pocket (March and April, 1930), then a more careful series with the larger pocket after elim-

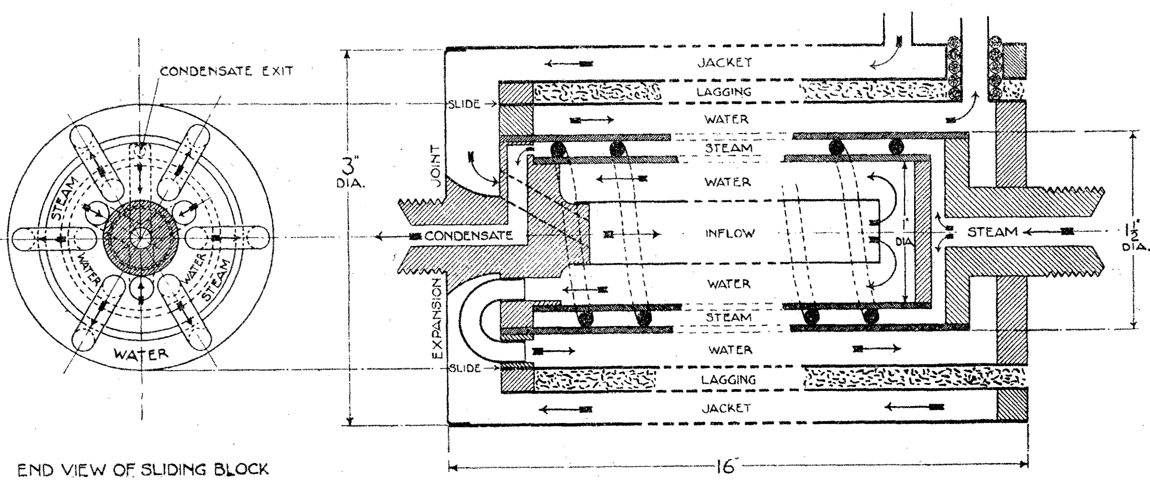

FIG. 4.—Jacketed condenser.

* "Roy. Soc. Arts," 'Howard Lectures,' 1926.

inating many of the sources of error of the temperature and pressure measurements (May and June, 1930), then further investigations of sources of error and a series of final measurements (August and October, 1930). This was followed by final investigations and a check over the range of measurements in January, 1931.

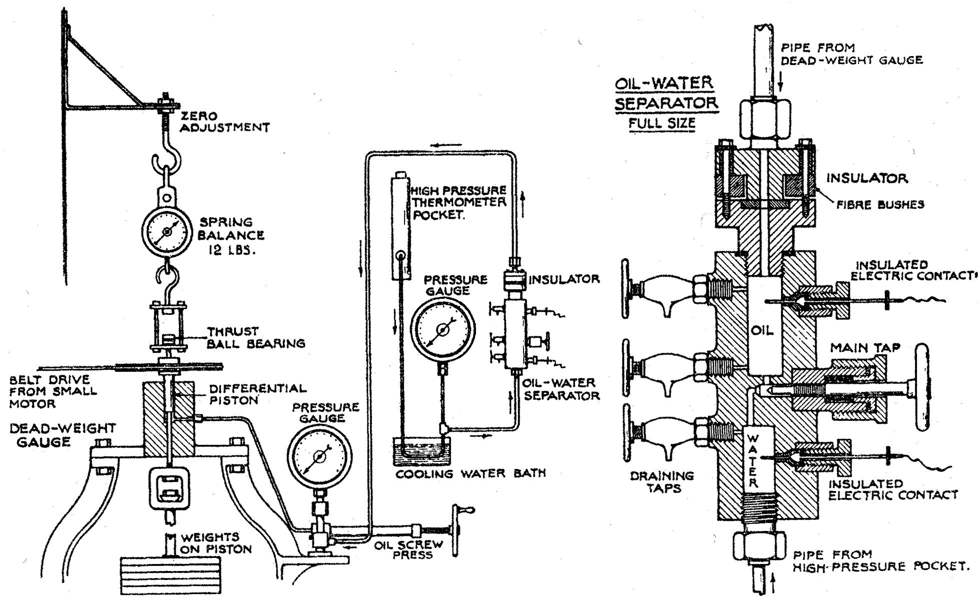

Fig. 5.—General arrangement for direct measurement of high pressures by dead-weight gauge.

III. *The Temperature Measurements.*

The methods of resistance thermometry, as adapted by H. L. Callendar* for the measurements of total heat of steam, have been used for the present investigation.

(*a*) *The Method of Temperature Measurement and Reduction of Observations.*—The thermometers employed had long been in the use of Callendar and were constructed under his supervision. They were compensated, and, using gold leads threaded through many mica discs, were contained in thin-walled resistance glass tubes. The open end was so fitted as to make an airtight joint.

The thermometers in use (either Nos. 4, 2 or 5) were always balanced with No. 3 thermometer in circuit, the latter being maintained in a steam bath. The difference between the resistance of the thermometer and that of No. 3 thermometer was measured. The fixed platinum resistance N (about 20 ohms), wound as a thermometer, but exactly compensated for change of temperature, was inserted in the case of the resistance box for convenience. The fundamental interval of each thermometer was about 5 ohms, so that the unit bridge coil (approx. $0 \cdot 1\ \omega$) corresponded to $2°$ on the platinum scale.

Each resistance coil of the box was compensated as described by Callendar†, in fact, the same bridge was used. All contacts were either copper to copper soldered

* 'Phil. Trans.,' A, vol. 212, p. 17 (1912).

† 'Phil. Trans.,' A, vol. 199, p. 188 (1902).

or by cups filled with clean mercury. The battery current could be reversed so that external effects might be eliminated, and the current could be changed by a plug resistance R.

The galvanometer deflection was zero when the compensation coils of the box, P_z (No. 3 thermometer), C_t (the compensator of thermometer in use), and N balanced the resistance coils, C_z (No. 3 compensator), P_t (the thermometer in use), and C_N (the compensator wound inside N). R being the difference between the values of the resistance and the compensation coils—

$$R + P_t = N + P_z,$$

where $R = N$ when $P_t = P_z$; if the thermometers were both in steam, $R \simeq 19 \cdot 2$ ohms.

Heating effects in the thermometers due to the currents were largely eliminated by this arrangement, the current in the circuit being maintained constant (see CALLENDAR, *loc. cit.*).

Having obtained an approximate balance by means of the resistance box coils, the total deflection on either side of the zero position was observed by reversing the current. A change of 1 unit (0·1 ohm) in the coils was made and the deflection again observed. The standard thermometer was maintained in the steam bath, the working thermometer being removed to the temperature point and the deflection again observed. The working thermometer was then taken out, cooled and returned to the steam bath, and the "zero" measurements again checked. By adjustment of the external resistance each galvanometer scale division was made to correspond to about 1/100° C., but for some tests the sensitiveness was increased.

If the barometer does not change, the two measurements give

$$R_t - R_z = R_t - R_{t \simeq 100}.$$

Now, if C_z represents the number of box coils for the "zero" measurement and C_t for the other, $\Delta R_z = (C_z + 1) - C_z$ and $\Delta R_t = (C_t + 1) - C_t$, and both were approximately 0·1 ohm, but not exactly, because of the corrections to be applied to the different box coils used to make the unit difference.

If f_z° and f_t° are the observed total galvanometer deflections and the galvanometer scale reading is f mm. per $0 \cdot 1\ \omega$ unbalanced, then $f_x = f_x^\circ / \Delta R_x$ at any resistance x on the bridge.

As the change of scale reading was proportional to the change of current flowing in the circuit, for small changes in the latter

$$f_t = f_z + \alpha\,(C_z - C_t),$$

and α was easily determined by observing the total deflection (f_t°) and finding f_t, at any steady temperature points.

$$\alpha = \frac{f_t - f_z}{C_z - C_t} = 0 \cdot 037, \text{ or } 1/27.$$

This was found to be constant between 0 and 450° C. within the errors of observation.

Thus when observing some temperature which was not absolutely steady, the galvanometer scale reading at that temperature could be found from the zero scale reading, with an accuracy equal to that of a direct determination, although owing to slight fluctuations of temperature this might not have been possible during an actual saturation pressure measurement.

The value of α has been derived from the mean of over 20 observations at the steady standard points (sulphur, naphthalene, benzophenone and ice), the probable error of the mean value being less than corresponds to a change of 1/1,000° C.

Change of the zero deflection of the galvanometer during the saturation pressure observations was largely eliminated by the method, as zeros were taken before and after the temperature observations, the mean of these being used. The accuracy depended mainly on the care with which the "zero" observations were taken, but as these were under standard conditions, the accuracy required was easily attained.

Special tests were made to show that stray e.m.fs., effects of temperature on the torsion of the galvanometer suspension, etc., were satisfactorily eliminated by the reversal of the current.

The following is given as an illustration of the reduction of observations:—

Sulphur Point. Date, 27.8.30.

Bar: 765·7 at 29·1° C. = 762·65 at 0° C.

(1) Zero. Both thermometers Nos. 3 and 4 in steam.

Box coils . . . 192. Difference in scale reading of galvanometer deflection 172 mm. on reversing battery current.

Box coils . . . 193. Difference in scale reading of galvanometer deflection 24 mm. on reversing battery current.

(2) No. 4 in sulphur, No. 3 in steam.

Box coils . . . 32, deflection 164·5.

Box coils . . . 33, deflection 36.

Difference of resistance, 193–192 coils = 0·099 units of the box resistance.

In steam, total galvanometer deflection—

$$172 + 24 = 196 = f_z^\circ.$$

Therefore total galvanometer deflection for 0·1 unit—

$$\frac{196}{0 \cdot 099} = 198 = f_z.$$

With box coils (= 192·005 corrected) in "unbalanced resistance" (R_u) the deflection was equivalent to—

$$\frac{172}{198} = 0 \cdot 869 \text{ unit.}$$

Therefore $R_z = 192 \cdot 005 + 0 \cdot 869 = 192 \cdot 874 \left(\text{or} = 192 \cdot 995 - \frac{24}{198} = 192 \cdot 874\right)$.

The galvanometer deflection for box coils = 32, was—

$$f_z + \frac{192 - 32}{27} = f_z + 5\cdot9 = 198 + 5\cdot9 = 203\cdot9 = f_t.$$

(The 'observed value' obtained from the mean deflection, corresponding to this value was—

$$\frac{200\cdot5}{0\cdot99} = 202\cdot5.)$$

No. 4 in sulphur when box coils = 32 gave a deflection of 164·5 mm., therefore

$$R_t = 31\cdot985 + \frac{164\cdot5}{204} = 32\cdot791,$$

and

$$R_z - R_t = 160\cdot083.$$

Since the resistance of the thermometer had been so arranged that 1 box unit ($\simeq 0\cdot1$ ohm) = 2° C. on the platinum scale, the corresponding difference of platinum temperature would be double ($R_z - R_t$), if the fundamental interval was 5·000 ohms. The fundamental interval of each thermometer was not exactly 5 ohms, so that in converting to platinum degrees, a fundamental interval correction entered. The steam temperature then has to be added to provide the platinum temperature. The corrections to gas scale from platinum scale are taken from tables by HOARE.*

The platinum temperature t_{pt} was given by—

$$t_{pt} = \left(\frac{R_t - R_z}{R_{100} - R_0}\right) 100 + \left(\frac{R_{t\sim 100} - R_0}{R_{100} - R_0}\right) 100,$$

where

$$R_{100} - R_0 = 50 - r \left(\text{units of } \frac{1}{10} \text{ ohm}\right),$$

r being a small correction to the fundamental interval found from the resistance at 0° C. Therefore

$$t_{pt} = \left(\frac{(R_t - R_z)}{50 - r}\right) 100 + \left(\frac{R_{t\simeq 100} - R_0}{50 - r}\right) 100$$

$$= 2\,(R_t - R_z) + 2\,(R_t - R_z)\left[\frac{2r}{100}\cdot\frac{50}{50 - r}\right] + pt_z,$$

where pt_z was the platinum temperature at $t \simeq 100$ and was the same as the boiling point of steam on the gas scale at the observed atmospheric pressure unless the barometer was appreciably different from 760 mm.

If

$$\frac{100r}{50 - r} = 2\left[r + \frac{r^2}{50 - r}\right],$$

* 'J. Sci. Inst.,' vol. 6, p. 99 (1929).

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was called the fundamental interval correction I, then

$$t_{pt} = 2(\mathrm{R}_t - \mathrm{R}_z) + 2(\mathrm{R}_t - \mathrm{R}_z)\frac{\mathrm{I}}{100} + pt_z,$$

or

$$\simeq 2(\mathrm{R}_t - \mathrm{R}_z) + 2(\mathrm{R}_t - \mathrm{R}_z)\frac{\mathrm{I}}{100} + t_{\mathrm{B}},$$

corrections being applied if the barometer was appreciably different from 760 mm.; it was not usually necessary to correct t_{B} to pt_z unless the pressure difference was more than 5 mm. pt_z was given by $t_z - (t_z - t_{pt_z})$ obtained from the tables; it was also equal to

$$2(\mathrm{R}_z - \mathrm{R}_0) + 2(\mathrm{R}_z - \mathrm{R}_0)\frac{\mathrm{I}}{100}.$$

For the present example

$$t_{pt} = 2(160\cdot083) + 2\left(\frac{160\cdot08 \times 0\cdot502}{100}\right) + \left(100\cdot000 + \frac{2\cdot65}{27\cdot25}\right)^* = 421\cdot877°,$$

which corrected to gas scale with $\delta = 1\cdot4974$, becomes

$$421\cdot877 + 22\cdot968 = 444\cdot840° \text{ C.}$$

The sulphur boiling point at the pressure 762·65 mm. = 444·841° C.

(*b*) *The Calibration of Resistance Box.*—The binary scale compensated resistance box was calibrated in terms of the 25·6 ohm coil by the method of substitution, using another Callendar-Griffiths resistance box in the external circuit. The measurements were carried out in a special room maintained at a constant temperature. The results obtained are given in Table I.

TABLE I.—Temperature, 20·0° C. Correction in 0·01 ohm.

Coil.	Nominal Value, ohms.	Correction July 3.	Correction July 4.	Mean.
A	25·6	0	0	—
B	12·8	+0·245	+0·245	+0·245
C	6·4	—0·193	—0·193	—0·193
D	3·2	—0·151	—0·154	—0·153
E	1·6	—0·023	—0·028	—0·025
F	0·8	—0·238	—0·239	—0·238
G	0·4	—0·090	—	—0·090
H	0·2	—0·057	—	—0·057
I	0·1	—0·098	—	—0·098

* $t_{\mathrm{B}} = 0\cdot03675\,(p - 760) - 0\cdot00002\,(p - 760)^2$.

A further calibration was carried out in August and confirmed the above to $\pm 0{\cdot}0001$ ohm (equivalent to $1/500°$).

Having regard to the effect on the measured temperature of the corrections to the different coils, a special study was made to show that no errors arose from an error in the calibration of any one coil in use.

Although the resistance box was completely compensated for temperature, as tests at 15° and 35° C. showed, there may have been a slight lag in heating up the several portions of the box, which would lead to error. For all the final measurements, a current of water was run through the double walls of the box and through the aluminium cover, thus preventing temperature fluctuations. CALLENDAR* pointed out the advantages of the compensated box over other types of resistance box using manganin coils.

(*c*) *Standardisation of Thermometers.*—The thermometers have not only been standardised at the sulphur point, steam and ice points, but also, for further check upon the temperatures corresponding to the saturation pressures, they have been tested at the secondary points, naphthalene, benzophenone and mercury.

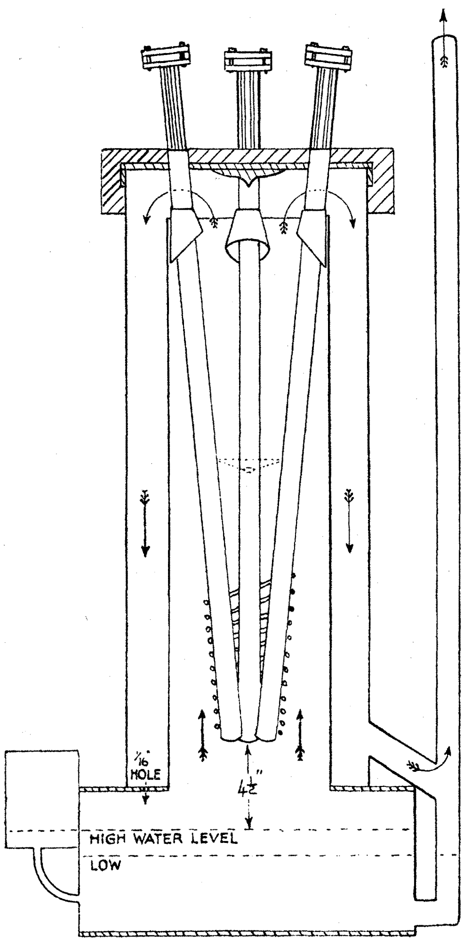

FIG. 6.—Hypsometer for zero temperature.

The steam bath in which the thermometers were kept when not in use and in which No. 3 was always situated is shown in fig. 6. It will accommodate 6 thermometers.

The overpressure was found to be ½ mm. of water (which includes any correction for the weight of the column of steam in the exit tube); the correction of $0{\cdot}04$ mm. of mercury due to this, about balanced the meniscus correction on the barometer (diameter $1{\cdot}5$ cm.) and both could be neglected. The Fortin barometer situated in a truly vertical position on a level with the hypsometer in the next room to the steam laboratory was corrected for gravity and temperature (brass scale). The value of gravity at South Kensington is $981{\cdot}18$, and height is 14 feet above sea-level. The barometer could be read and set to $\pm 0{\cdot}03$ mm. The barometer has been carefully checked against the other two barometers at South Kensington. On correcting for difference of level and temperature, the barometer in use was found, as a mean of three separate tests, to read $0{\cdot}15 \pm 0{\cdot}03$ mm. lower than the other two; but compared with the maker's

* 'Phil. Trans.,' A, vol. 199, p. 87 (1902).

standard barometer (checked at the National Physical Laboratory), it agreed to 0·05 mm. A correction 0·10 ± 0·05 mm. has been accepted in reducing all the observations.

The sulphur bath used in the earlier standardisations was an iron tube $1\frac{1}{2}$ inches diameter lagged outside with asbestos. The thermometers with iron radiation shield attached were immersed direct in the vapour. This method was abandoned and a pyrex glass vessel used, in which the sulphur was maintained in a purer condition. An iron radiation shield was arranged on the end of the thin pyrex tubes, in which the thermometers closely fitted. This shield was essential; the temperature was found to be uniformly 0·4° C. lower without it. With the shield the results agreed well with those given by the iron apparatus and could be relied on with more certainty than when the latter was used. The conditions for obtaining a satisfactory sulphur point have been detailed by BURGESS and MUELLER* and were followed closely.

A similar naphthalene bath was set up and the two kept alongside the steam bath, so that the temperature could be checked after each set of final saturation pressure measurements.

The naphthalene was a specially purified sample; several different samples of naphthalene agreed closely when fresh (purity as used for calorimetric standardisations); the benzophenone (mpt. 48° C.) remained colourless after use for some time; it supercooled very readily. The two samples were probably purer than the specimen used by HOLBORN and HENNING,† which was stated to darken after use. This may explain the somewhat lower boiling point obtained, viz., 305·83, instead of 305·9, agreeing well, however, with FINCK and WILHELM's value 305·84.‡

The mercury was electrically prepared (JOHNSON and MATTHEY) and was vaporised both in a welded steel vessel and a pyrex glass vessel (similar to the sulphur bath). The values agree, but the error in the determination is five times greater than in the other cases. The mercury condenses as a mirror and the radiation from the region of the thermometer was changed; the low latent heat of the mercury also tended to decrease the accuracy. The boiling point obtained, 356·63° C., was slightly lower than that given by MENZIES§ from vapour pressure determinations (356·71° C.), the change of temperature with pressure by observations when the barometer was high and low agreed well with MENZIES' value (0·074 mm. $= dt/dp$).

Thermometer No. 4 proved to be the most reliable and has been used in all the final vapour pressure measurements. No. 5 (a more recently constructed thermometer) had a slightly higher δ value. The final agreement obtained at the standard points when all corrections had been applied was satisfactory and the probable error of the temperature measurements for the saturation pressures is correspondingly small.

* 'Bull. Bur. Stand.,' vol. 15, p. 163 (1919).

† 'Ann. Physik,' vol. 26, p. 867 (1908).

‡ 'J. Amer. Chem. Soc.,' vol. 47, p. 1577 (1925).

§ 'Z. phys. Chem.,' vol. 130, p. 90 (1927).

The Ice Point.—It is important that the fundamental interval correction

$$I = \frac{100r}{50 - r},$$

should be known accurately: $R_{100} - R_0 = 50 - r$, or nearly 5 ohms, hence $2r = 100 - 2(R_{steam} - R_{ice})$.

The accuracy required for 1/100° C. was about 5 in the third place, depending on the temperature. The barometer corrections have therefore to be accurately known.

The thermometers were immersed in washed ice in a vacuum jacketed flask, No. 3 being maintained in steam. The depth of immersion for complete attainment of the ice point was carefully ascertained.

For the later determinations the battery current was increased so as to increase the accuracy of reading of galvanometer deflection; increase of the battery current was shown to be insufficient to cause error due to heating of the thermometer, the compensated circuit eliminates this source of trouble.

The later observations are given in Table II.

TABLE II. (Barometer Correction + 0·15 mm.).

Date.	No. of observations.	Bar.	$(R_t - R_z)$	Steam T° C.	Pt_z.	$2r$.	I.	Thermometer No.
July 21	3	749·56	99·122	99·619	99·625	0·505	0·507	4
	3	749·56	99·113	99·620	99·626	0·514	0·516	5
Nov. 4	2	755·23	99·327	99·826	99·827	0·502	0·504	4
	2	755·25	99·323	99·827	99·829	0·507	0·509	5
Dec. 10 (ice from air-free distilled water)	1	760·85	99·523	100·031	100·031	0·499	0·501	4
	1	760·85	99·518	100·031	100·031	0·513	0·515	5
						Means	0·504	4
							0·513	5

All the above values have been reduced by 0·002 for barometer correction 0·10 mm. instead of 0·15 mm.; the final value for I was therefore taken as 0·502.

The Sulphur Point.—The observations at the sulphur point, July 1930 to January 1931, are given in Table III.

The same sample of sulphur was used from November 6 to January 5 without change of boiling point. The reproducibility of the sulphur point (*i.e.*, 0·015° C.) was satisfactory and as found at the National Physical Laboratory.* The most careful observations were those on November 6, November 26, January 1 and January 5.

* HALL, 'Phil. Trans.,' A, vol. 229, p. 14 (1930).

Table III.

Correction for Variation of Boiling Point of Sulphur with Change of Barometric Pressure :—

(1) $t_p = 444 \cdot 6 + 0 \cdot 0909\ (p - 760) - 0 \cdot 00005\ (p - 760)^2$.

(2) $t_p = 444 \cdot 6 + 0 \cdot 09\ \ (p - 760) - 0 \cdot 00004\ (p - 760)^2$.

Zero Steam Point* : $(t_p)\ pt = 100 + 0 \cdot 03675\ (p - 760) - 0 \cdot 00002\ (p - 760)^2 - 0 \cdot 00055\ (p - 760)$.

Thermometer.	No. 4.		No. 5.	
I.	+0·502.		+0·511.	
δ	1·4974.		1·5182.	
dt/dp.	(1)	(2)	(1)	(2)
Date. (*p* — 760) mm.				
July 17 . . . . (— 13·6)	(444·598)	(444·582)	—	—
July 29 . . . . (— 4·7)	444·614	444·610	444·600	444·597
Aug. 14 . . . . (— 7·55)	444·599	444·591	—	—
Aug. 27 . . . . (+ 2·65)	444·598	444·599	—	—
Oct. 2 . . . . (+ 11·50)	444·591	444·601	—	—
Nov. 6 . . . . (— 5·08)	444·604	444·599	444·606	444·602
Nov 26 . . . . (— 17·17)	444·616	444·601	444·614	444·600
Dec. 31 . . . . (— 28·2)	444·630	444·600	—	—
Jan. 1 . . . . (— 19·35)	444·630	444·611	444·628	444·607
Jan. 2 . . . . (— 10·05)	444·592†	444·583†	444·587†	444·575†
Jan. 5 . . . . (+ 5·45)	444·598	444·602	444·595	444·599
No. of observations	10	10	5	5
Mean	444·608	444·599	444·609	444·601
Bar. between 750 and 770 mm. . .				
No. of observations	5	5	2	2
Mean	444·603	444·600	444·600	444·600
Maximum deviation 750 to 770 mm.	+0·014°	—0·017†	—0·013	—0·025†

* *cf.* p. 191.

† January 2 : Sulphur point taken from ice zero, 0·1 ohm additional external resistance caused slight uncertainty (±0·02°) from contacts, etc. ; also the last 1/100° C. may not be quite attained in the ice.

The value for δ for No. 4 thermometer obtained from the above observations, viz., 1·4974, has been used for the determination of the saturation temperatures.

Secondary Points.—The observations in Table IV on the secondary points, benzophenone, mercury and naphthalene boiling points show that the temperature scale of the No. 4 and No. 5 platinum thermometers are in close accord with the accepted boiling points of these substances, and provide limits within which the accuracy of the saturation pressure measurements may be set.

TABLE IV.—Benzophenone Point.*

Date.	No. 4. $\delta = 1 \cdot 4974$ $I = 0 \cdot 502$	No. 2. $\delta = 1 \cdot 500$ $I = -0 \cdot 11$	No. 5. $\delta = 1 \cdot 5182$ $I = 0 \cdot 511$
(B.D.H.) Benzophenone.			
June 15	305·795	305·79	—
July 15	305·810	305·78	—
July 16	305·812	305·78	—
(H. & W.) Benzophenone.			
July 29	305·818	305·82	305·830
Nov. 4 (darkened)	305·827	—	—
Nov. 7 (new sample)	305·827	305·82	—
Nov. 7 (new sample)	305·827	305·83	305·843
Mean of determinations from July 29 .	305·825	305·82	305·836

* dt/dp is taken as varying directly with $(p - 760)$ for benzophenone, mercury and naphthalene boiling points. This would only be safe for 760 ± 8 mm.

It is probable that there was actually a slight difference (0·02° C.) in the boiling point of the two samples ; the earlier observations were, however, not so accurately carried out.

TABLE V.—Mercury Points.

Date.	No. 4. $\delta = 1 \cdot 4974$ $I = 0 \cdot 502$	No. 5. $\delta = 1 \cdot 518$ $I = 0 \cdot 510$
	(Barometer zero + 0·10 mm.)	
November 11, iron vessel	356·643	—
November 21, large glass vessel . .	356·629	—
November 25, large glass vessel . .	356·671	—
November 25, large glass vessel . .	—	356·63
November 25	356·622	356·63
Mean	356·641	356·62

TABLE VI.—Naphthalene Point.*

Date.	No. 4. $\delta = 1 \cdot 4974$ $I = 0 \cdot 502$	No. 2. $\delta = 1 \cdot 500$ $I = -0 \cdot 11$	No. 5. $\delta = 1 \cdot 5182$ $I = 0 \cdot 511$
	(Barometer zero + 0·10 mm.)		
July 22, new sample	217·963	217·976	—
July 29	217·968	217·959	217·987
August 27	217·969	—	—
October 2	217·975	—	—
November 5, new sample	217·969	—	217·978
	217·970	217·966	217·983

* See note to Table IV.

The naphthalene appears to become slightly contaminated after continued use, and the boiling point increases slightly. The boiling point is in agreement with that found by EPPLEY 217·97° C.†

No. 2 thermometer was unreliable.

Table VII summarises the results of these boiling point determinations for thermometers No. 4 and No. 5, on the basis of the sulphur boiling point 444·60, giving $\delta = 1 \cdot 4974$ and the ice point 0·502 for No. 4, and $\delta = 1 \cdot 5182$ and the ice point 0·511 for No. 5. (Barometer between 750 mm. and 770 mm.)

TABLE VII.

	Barometer Correction.*	No. 4.	No. 5.	Recent Value.
Naphthalene	0·058 (p — 760)	217·970	217·983	217·97
	No. of observations	5	3	
Benzophenone	0·0633 (p — 760)	305·825	305·836	305·84
	No. of observations	4	2	
Mercury	0·074 (p — 760)	356·64	356·62	356·71
	No. of observations	7	7	

* See note to Table IV.

Observations with thermometer No. 4 are consistent and the results in Table VII show that there is no reason to mistrust the observations of temperature obtained with it throughout the range of saturation pressure for which it has been used.

† 'J. Franklin Inst.,' vol. 205, p. 383 (1928).

TABLE VIII.—No. 4 Thermometer.

—	No. of Observations.	Variation of Observations. Percentage Variation.	Mean Difference from Standard Point.
Ice	6	±0·003 ±0·003	—
Naphthalene . .	5	±0·006 ±0·003	Nil
Benzophenone . .	4	±0·008 ±0·003	—
Sulphur	9	±0·010* ±0·002	Nil

* Between 750 and 770 mm.

The checks given in Table IX at the standard points were made, during the final saturation pressure measurements, in January and February, 1931.

TABLE IX.

—	No. 4 at 760 mm.	No. 5 at 760 mm.	Date.	Barometer.
Sulphur (1) . . .	444·592°	444·604°	30.1.31	752·6
Benzophenone .	305·828	305·830	12.2.31	750·3
Naphthalene . .	217·976	217·965	12.2.31	750·3

The conclusion arising from these investigations regarding the reliability of the temperature measurements was that, using No. 4 thermometer, the probable variations in the measured values of a *constant* temperature were well within ± 1/100° C. and that the temperatures obtained were within ± 1/50° C. of those on the standard platinum scale in the range within which the thermometer has been used. The maximum deviation in the determination of a secondary fixed point was only about 1/50° C., but that deviation includes the special errors of the determination of the boiling point, which would not be the same as those relating to the measurements for which the thermometer was used; those will be discussed in Section 5. This error of ± 0·02° C. included the zero change of the galvanometer, the error of observation of the galvanometer reading and the error of the resistance coil correction (± 0·005° C.).

IV. *Pressure Measurements.*

(*a*) *Introduction.*—The pressures of saturation of steam were measured by the differential (SCHAEFFER and BUDENBERG) dead-weight gauge (fig. 5; the illustration also shows the connection to the high-pressure pocket of the system through the "separator"). The "separator" made it possible to fix the position of the surface separating the water and the oil used to transmit the pressure to the gauge. The copper tube ($\frac{3}{16}$ inch diameter and $\frac{1}{16}$ inch bore) led to the separator from the pocket, the bend being immersed in cold water. The actual level of the water surface during an experiment was close to the entry to the high-pressure pocket; the level did not fluctuate more than 1 cm. The pipe cooled rapidly along its length, and 15 cm. from the pressure pocket was only slightly above room temperature (the difference in density due to the temperature of the water in the two arms made no appreciable difference to the measurements of pressure).

By the aid of the cocks, the exact position of the surface separating the oil and water could be set, the separator being situated on a level with the entry to the pressure pocket. The copper pipe ($\frac{5}{16}$ inch and $\frac{3}{16}$ inch bore), filled with castor oil, connected with the gauge. The approximate dimensions of the gauge are given in fig. 7; the pressure is taken on the rim between the larger and smaller portions. Although the gauge has two gland surfaces where leakage can occur, the fit was so satisfactory that errors from this cause were negligible, while the method of direct suspension of the weights makes this type of gauge suitable for measurements of high pressures.

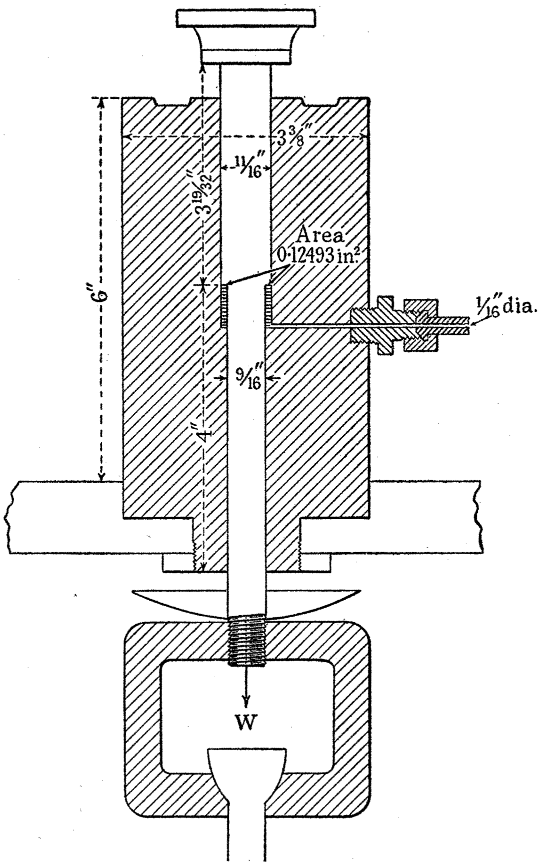

FIG. 7.—Dead-weight gauge cylinder and piston.

The piston carried on its upper end a light wooden disc, by which the piston was rotated by belt drive from an electric motor, fig. 16, Plate 9. To the centre of the disc was attached a collar and ball race, to which the spring balance or the steel yard was connected by a stirrup. The carrier for the weights was fixed directly to the lower end of the piston. Adjustment of the feet enabled the stem of the carrier to be set in a vertical position. A calibrated steel yard was used for the final adjustment of weights on the piston. A setting to horizontal position of steel yard arm could be

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made to $\pm$ 1·5 grams* (which is equivalent to an accuracy of 1 in 60,000 when measuring a pressure of 100 atmospheres). MICHELS † found the sensitivity of his gauge to be $\frac{1}{120000}$ and independent of pressure; CROMMELIN and SMID,‡ on the other hand, gave a much lower accuracy ($\frac{1}{10000}$). MICHELS stated that the rotation of the gauge must be above a certain critical speed in order to attain high accuracy.

The effective area of the gauge is about 0·125 square inch, so that each 1 lb. weight added is equivalent to a pressure of about 8 lb. per sq. inch. The gauge has been carefully calibrated, (i) by checking a smaller Crosby dead-weight gauge against a mercury column and (ii) by balancing the smaller gauge against the larger gauge. The method of calibration is described in this section, and the possible sources of error are discussed.

(*b*) *Calibration of Crosby Gauge against Mercury Column.*—The Crosby gauge consisted of a simple steel piston and gunmetal cylinder, fig. 8. A gunmetal plate screwed into the head of the piston, accurately made so as to turn true, served as the weight carrier; the weights fitted exactly so that when loaded the piston could be rotated by a gentle touch with the hand. The gauge was connected to the reservoir of the mercury column as shown. The Crosby gauge was placed so that no correction entered for height of oil column. A weight of less than 3 grams (about 0·03 lb. per sq. inch = 0·002 atmos.) is sufficient to cause definite movement of the piston up or down from the position of balance which is marked by fixed reference points just below and above the weights. The mercury column (nearly 23 metres high) was situated in a tower of the Imperial College, to which access was provided by a lift; fortunately, the tower was exceptionally even in temperature. The height of the mercury level in the reservoir was set against a steel point, which closed an electrical circuit, fig. 8. The distance from the point of contact to one end of a carefully levelled straight edge was measured, and also the distance from the other end of the steel edge vertically to the top of the column, level with the position of the tangent to the mercury meniscus; an adjustable straight edge which could be set accurately was provided for the setting at the top of the column. For the measurement of the height a steel tape was used. The tape was fixed to a weight of 3 lb., which was set so as to cause a tension of about 2 lb. on the tape. The tape was graduated in mm., and its length was checked at the National Physical Laboratory (May, 1930); the length, supported on the flat under tension of 3·3 lb. weight, from 0 to 2,310 cm. mark, was found to be 2,310·45 cm. at 60° F. to an accuracy of 1 in 100,000.

Thermometers at $3\frac{1}{2}$ metres interval were bound to the steel tube of the mercury column, and were read on each occasion that the height of the column was measured. The temperature did not vary in any case by more than 2° throughout the height of the column. The average temperature was computed graphically from the area of

* See p. 170.

† Ref. p. 172.

‡ 'Verh. Akad. Wet. Amst.,' vol. 14 (1915).

the curve obtained by plotting the observed temperature against the height of the position of the thermometer. The thermometers agreed to 1/10° C. with a thermometer which had been checked against the resistance thermometer; the small corrections found were applied in computing the mean temperature in all the later measurements.

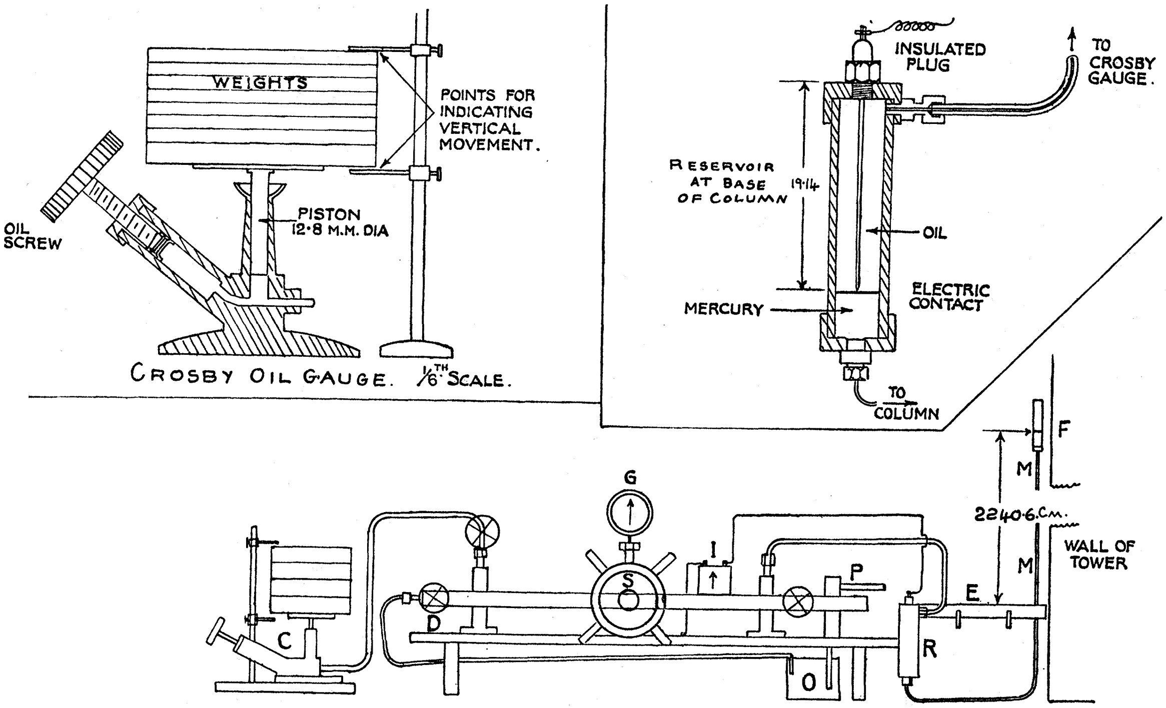

FIG. 8.—Oil press for lifting mercury column, Crosby gauge attached.

General arrangement: C = Oil gauge; D = Drain valve; S = Screw press; G = Pressure gauge approx.; I = Contact indicator; O = Oil reservoir; P = Hand oil pump; R = Mercury reservoir; M = Mercury column; E = Horizontal straight edge; F = Open glass tube.

The heights from the contact point to the straight edge placed level with the position of the meniscus at the top of the column, obtained on various occasions, were as follows :—

September (1930). 2,259·72 cm. corrected to 15·55° C. (Observed at 17·2° C. mean temperature.)

November (1930). 2,259·71 cm. corrected to 15·55° C. (Observed at 12·5° C. mean temperature.)

November (1930). 2,259·74 cm. corrected to 15·55° C. (Observed at 14·6° C. mean temperature.)

Finally, a more accurate measurement gave :—

February (1931). 2,259·73 cm. corrected to 15·55° C. (observed at 13·0° C.), which agrees with the mean value 2,259·73 ± 0·005 cm.

This measurement included length from contact to straight edge 19·14 cm. ± 0·01 and from straight edge to mark at top of column against which the mercury meniscus was set level (2,240·2 cm.), also the correction for the average temperature of the tape (0·000011 × 2·59 × 2,260 = − 0·064) and the standard correction to the tape (+ 0·45 cm.).

(Special tests were made to decide whether any correction entered for the expansion of the wall of the tower to which the column was attached; but the distance as measured on the steel tape remained within 1/10 mm., although the September and February observations referred to a mean wall temperature difference of nearly 10° C. Taking the ordinary coefficients of expansion, a difference of 2 mm. might have been expected. The inside wall temperature differed by considerably less (about 4° C.) and the corresponding small expansion was probably taken up in various ways).

The total weights which balanced the pressure of the mercury column were found and corrected to the same temperature of column and piston as for the last measurement, viz., 13·4° C. for column and 12·5° C. for piston and on the basis of a height of column of 2,259·77 cm. (see p. 167), the following figures were obtained :—

Date.	Weight in grams (*in vacuo*).
May, 1930	39,595·0 ± 12
June, 1930	39,597·0 ± 12
September, 1930	39,596·0 ± 10
February 4, 1931	39,585·6 ± 5
February 6, 1931	39,582·6 ± 4
February 19, 1931	39,584·0 ± 3
February 24, 1931	39,587·4 ± 2
Weighted Mean	39,587·1 ± 1·2

The temperature observations were less certain in the first three cases, the last four measurements were made with particular care, and the last one of all after the column had been thoroughly cleaned out, dried and refilled.

The weight to balance the column was lighter by 7·2 grams for each degree rise in temperature, while an increase of 0·88 is required for each degree rise in piston temperature.

The last measurement was carried out with special precautions. Means were provided to detect very slight upward or downward trend of the piston. Time was allowed for the column to reach equilibrium; there was appreciable inertia and the response to small displacements (0·2 mm.) of the piston required several seconds, during which the mercury would move through 7 mm. in the fine 2·2 mm. bore of the steel column. The natural time of fall of the piston, due to leakage, was found to be about 3 minutes per mm. and in all the later measurements this fall was allowed for and was equivalent to an excess weight of 2 grams. Tests were made to fix the position of the mercury surface in the reservoir at the moment of break of the circuit at the steel point (see below). The piston was raised 1·2 cm. in the cylinder of the gauge during the tests, and was set level with the contact point. In the measurements prior to 1931, there was a difference of level of 1 inch between the piston and mercury surface in the reservoir for which correction has been made in the figures given (amounting to 1 inch oil = 1·80 mm. Hg.). The gauge and the connections to the reservoir were filled with castor oil, and care was taken to ensure that no air was present, tests being also made to detect that no leakage occurred at any of the joints : the column could be maintained at the correct height against the oil pressure throughout the night (the tap to the Crosby gauge being closed).

The temperature at the piston and the mean temperature of the column were obtained from the temperature observations at the time of tests in the same way as already mentioned in describing the measurement of the height of the column.

The equivalent height of a column of mercury at 0° C. was then estimated, taking 0·00001818 per °C. per cm. as the coefficient of expansion, + 1·2 mm. as the correction for compressibility of the mercury, and for the difference in the atmospheric pressure at the top and the bottom of the column — 2·0 mm. The change of gravity constant with height is only a difference of less than 10^{-2} mm. and may be neglected ; the bore of the upper glass mercury reservoir being 2·2 cm., the capillarity correction was also negligible.

Investigation showed that there was an observed rise of between 1·2 and 1·6 mm. (mean 1·4 mm.) in the height of the mercury at the top of the column when the mercury level in the reservoir went from the position when the circuit was just made to that when the circuit was just broken, a height which corresponds to 2·5 grams on the Crosby piston. The corresponding movement of the mercury level in the reservoir (diameter 3·2 cm.) was 0·70 mm., which makes a total change in the height of the column 2·1 mm. It was estimated that the level of the mercury surface corresponding to the moment when the circuit was just broken would be 0·44 mm. lower than the contact point, or about half the 0·70 mm. observed. The measured height of the mercury column at 15·55° C. was, 2,259·73 cm., and to this was added the 0·4 mm., or 2,259·77 cm. for the total height (see p. 165).

If the position of the reference point at the bottom and the top of the column changed with the temperature, a correction would enter for the change of temperature (15·55 — 13·4 = 2·15° C.), but trials showed that the distance between the marks at the bottom and the top of the column varied very little with temperature (see p. 165). The small corrections here investigated have been checked satisfactorily by measuring the actual displacement of the Crosby piston at the moments of make and break, the equivalent displacement at the top of the column was found to be 2·0 mm., which agreed with the result of the more direct measurement. (In the final comparison of the weight on the Crosby gauge against the pressure of the mercury column, the column was set exactly at the top mark at the moment of break and only the 0·4 correction entered).

The height of mercury, 2,259·77, balances a weight of 39,587·1 grams on the Crosby piston, when the mean temperature of the column was 13·4° C. and the temperature of the piston was 12·5° C.

The equivalent height of a column at 0° C., making the aforementioned corrections for expansion, compressibility and air pressure, was $2{,}259 \cdot 77 - 5 \cdot 50_5 + 0 \cdot 12 - 0 \cdot 20 = 2{,}254 \cdot 19$ cm.

Since the pressure corresponding to 76 cm. of mercury (in London, South Kensington, $g = 981 \cdot 18$ height, 14 feet above sea-level) is 14·6959 lb. per sq. inch, the pressure of the column was

$$\frac{2{,}254 \cdot 19}{76} \times 14 \cdot 6959 = 435 \cdot 886 \text{ lb. per sq. inch (London)}$$
$$= 29 \cdot 6761 \text{ normal atmospheres.}$$

The density of the mercury in the column was carefully compared with a sample of specially purified mercury used for the boiling point determinations, also with a sample of mercury purified at Oxford by the Hulett method, the densities agreed with each other, and with the accepted value to 1 part in 70,000. The measurements were carried out in two different pyknometers; the necessary air corrections were applied in order to make an absolute determination to compare with the accepted value.

The weight, 39,587·1 grams, on the piston had to be corrected for air displaced by the weights, whose volume was measured and found to be 5,492 cm.^{3} = 6·9 grams of air at 770 mm. and 12·5° C. (corresponding to the conditions of the trial on February 24) so the actual weight on the piston was 39,580·2 grams. Therefore the area of the Crosby piston was

$$\frac{39{,}580 \cdot 2}{435 \cdot 886 \times 453 \cdot 592}$$

$= 0 \cdot 200190$ square inch at 12·5° C. $= 0 \cdot 200213 \pm 0 \cdot 000008$ square inch at 18° C. (The figure for the probable error of this result includes the probable error of the measurement of the height of the column and of the corrections, viz., ± 0·25 mm., or 0·4 gram, as well as that of the weight on the Crosby piston ± 1·2 grams.)

It is necessary to consider the limits of error within which this figure falls, apart from the probable error of the series of measurements.

Considering first the measurements on which the length of the column depended :—

(i) The standardisation of the steel tape may have a possible error of ± 0·01 cm. The breadth of the divisions on the tape was about 0·4 mm., but observations were taken using the middle of the lines magnified by a lens.

(ii) The length from point of contact to the mark at the top of the column required two settings against the tape, and two on a finely graduated steel rule, while the steel edge needed to be accurately level. The errors here were included in the series of measurements, but it can be supposed that an error of $4 \times 0 \cdot 02 = \pm 0 \cdot 08$ cm. might occur in measuring these heights.

(iii) The mean temperature of the column was estimated correct to $\pm 0 \cdot 2°$ C., so that $\pm 0 \cdot 08$ cm. should be allowed for this error.

(iv) The various corrections (compressibility, expansion of mercury, etc.) are open to error and also—

(v) The determination of the make-and-break position, but these have been already considered in estimating the probable error of the series of measurements. The error in the case of (iv) could, however, be estimated at $\pm 0 \cdot 02$ cm., and of (v) $\pm 0 \cdot 01$ cm.

(vi) The change of position due to the wall temperature and other unaccounted-for effects might be taken to provide an error of $\pm 0 \cdot 05$ cm.

The total limits of error in the measurement of the height of the column are considered, therefore, to be within $\pm 0 \cdot 25$ cm.

Secondly, there is the measurement of the weight on the piston :—

(1) The error of the actual weights used was not more than $\pm 0 \cdot 25$ gram (as the weights were severally checked to $0 \cdot 05$ gram).

(2) The gauge temperature was determined to within $\frac{1}{2}°$ C., or a possible error of $\pm 0 \cdot 5$ gram.

(3) The error of the determination of the position of balance is allowed for in the estimation of the probable error of the series of measurements, but as the number of observations was not large, the limits of error of the last single determination may be taken to be the possible error, viz., ± 2 grams.

(4) The errors of determination of the density of the mercury, of the air corrections and the unaccounted-for effects might amount to $\pm 1 \cdot 25$ grams.

The total error thus becomes $\pm 4 \cdot 0$ grams for the possible error of the determination of the weight on the piston, and the area of the Crosby gauge can therefore be taken to be fixed within a possible error of $\pm 0 \cdot 00004$.

The error of the weight measurement, ± 4 grams, is equivalent to $\pm 0 \cdot 23$ cm. on the height, so that the two errors are taken to be of the same size. Probably the height of the column is more accurately known than the weight which balances it in the ratio 5/3 ; the limits are therefore taken wide.

(c) *Comparison of Crosby Gauge with the Differential Gauge.*—The area of the Crosby gauge having been determined by balancing against the mercury column, it was only necessary to set the Crosby up in connection with the differential gauge and balance the one against the other in order to determine the constant of the latter, fig. 16, Plate 9. The two pistons were placed on the same level, so that no correction for height of oil entered. Great care was taken that no air was trapped in the system; refined castor oil (specific gravity 0·97 at 60° F.) was used throughout. For convenience a pressure tap was inserted in the pipe between the two gauges, so that it was not necessary to move the small gauge during saturation pressure measurements, and the " zero " of the large gauge could be checked at any time.

(α) *Steel Yard Correction.*—Each piston when floating was maintained at a definite height, the Crosby piston was raised 1·2 cm. and the other 1·7 cm.; the latter was prevented from moving more than 3 mm. by means of a brass collar.* This movement, however, was sufficient to deflect the arm of the steel yard off the scale, the magnification of the movement by the lever being about 20 times. The lever arm, 14 inches long, was accurately adjusted to be in a horizontal position when opposite the fixed indicating mark. Pressures were recorded when a point on the arm was level with this mark. The bob on the steel yard could be moved along so as to give a lift equivalent to any pressure from 0 to 40 lb. per square inch, but it was kept in a definite position (at 20 lb.) for nearly all the saturation pressure measurements. By balancing known weights against the bob in various positions, the weight to which the bob in a given position corresponded could be ascertained, and checked from time to time within $\frac{1}{2}$ gram weight. The actual weight found in the final trials (January 12, 1931), when the bob was at the position 20, was equivalent to a lift on the piston of 20·12 lb. per square inch (= 1,141 grams). A weight of 1,141 grams, and the stirrup and ball race balanced the bob at the mark 20, so that the arm remained horizontal. Similarly, with the bob in the first notch, the arm was horizontal with a weight of 60 grams (= 1·05 lb. per sq. in.) added.

Various possible causes of uncertainty were investigated, such as the alignment of the steel yard in relation to the piston, but any small likely movements of the position of the supports and knife edges were not found to make a perceptible effect. The movement of the arm out of the horizontal position was, however, of importance, and partly accounted for small discrepancies between gauge calibrations on different days amounting to about ± 3 grams, particularly in those made before January, 1931.

(β) *Corrections to Weights.*—The weights used on both gauges were carefully checked; the smaller weights to the nearest 1/10th gram on a large 10 kg. balance against a standard set of brass weights† and the nine largest weights were checked to the nearest gram at the National Physical Laboratory. The table below gives the values of the weights in detail. The corrections for true weight have been included in all the final measurements of pressure. The error, after application of corrections, due to any

* MICHELS (Ref. p. 26) has shown the importance of working with the piston at a definite height, so that any effect due to the piston being slightly conical may be eliminated. This was rendered difficult by the natural fall of the piston in his case, but the fall was so slight for the gauge used in the present experiments that there was no difficulty about retaining the piston at a definite height.

† The 5000 gram brass weight was standardised at the National Physical Laboratory (March 1931), and the remaining weights were calibrated accordingly.

single weight, was not more than ± 1 gram (or 0·017 lb. per sq. inch = 0·00116 atmos.) for the larger, and even less (0·1 gram) in the case of the smaller Crosby weights.

The volume of all the weights has been determined, so that the mean density may be known and any necessary air corrections applied.

The buoyancy of the oil on the piston does not enter, as any weight lost reappears as pressure on the oil at the point where the pressure is gauged. This was put to the test on the Crosby piston, which supported a column of castor oil equivalent to its weight (the density of the oil was measured at the same temperature). It was noted that any oil above the piston in the cup had effect in floating the piston.

The gauges were compared at numerous pressures between 100 and 1,000 lb. per sq. inch, the comparison being based on the area of the Crosby gauge determined by the column of mercury at 450 lb. per sq. inch (= 30·6 atmos.). It was seriously considered whether the Crosby gauge should be checked at any other pressure by other means than the mercury column, such as the vapour pressure of carbon dioxide at 0° C. (34·4 atmos.) would provide,* but the suggestion was rejected for three reasons. Firstly, additional errors and uncertainties would be introduced in connection with temperature and purity; secondly, the agreement with the results of other observers on the saturation pressure of steam in the region where the two gauges could be compared was already as good as could be expected, and, thirdly, it is general experience that calibration at a given pressure of a properly proportioned dead weight gauge provides a constant independent of pressure until very high pressures are reached, when the gauge may become appreciably deformed.

TABLE X.—Table of Weights.

Crosby Weights:

W_m (marked).	W_c (in air).	
100 lb. per sq. inch.		Volume, cm.^{3}
Weights 9061·5 grams	9062·6 grams	1286
9068·5 ,,	9069·6 ,,	1264
9065·0 ,,	9066·2 ,,	1267
9066·0 ,,	9066·8 ,,	1275
9065·5 ,,	9066·3 ,,	1270
9064·5 ,,	9065·5 ,,	1285
6—100 lb. weights	54396·8 grams	Density 7·2
+ piston and tray	54851·8 ,,	
5 lb.	454·27	Density for weights used for checking against column 7.36
10 lb.	907·9	
14 of 20 lb.	25410·4†	

* See BRIDGEMAN, 'J. Amer. Chem. Soc.,' vol. 49, p. 1174 (1927).

† Each separate weight checked at time of measurement.

Weights for Differential Gauge.

Nominal.	W_B in air.	No. 1.	No. 2.	No. 3.
5 of 5 lb.	1416·5 } Used together.			
3 of 25 lb.	4253·7 }			
2 of 50 lb.	5671·4	2835·4	2836·0	—
3 of 100 lb.	17607·0	5665·2	5669·6	5672·2
9 of 500 lb.	No. 1 28353	No. 5 28343	Weight of wheel, piston shaft and carrier, 17365·1 ± 0·2	
	No. 2 28352	No. 6 28354		
	No. 3 28349	No. 7 28351		
	No. 4 28351	No. 8 28351		
Density 7·0		No. 9 28357*		

* Checked against smaller weights.

(γ) *Correction for Drive.*—Apart from the weights and the adjustment for the lift of the steel yard, there was one further uncertainty which had yet to be investigated, namely, the effect of the drive which rotates the piston. Part of the weight of the belt fell on the wheel and there was also the torque of the drive. It was necessary to find out the net effect on the piston, and numerous trials were made to determine it. The net effect was found to be very small, and nearly constant under the normal conditions under which the gauge was used. The belt weighed 46 grams, but the effect of the drive was such as nearly to negative the effect of the weight, leaving a resultant weight of only a few grams.

The effect of the drive would be influenced by temperature, because of its effect on the viscosity of the oil. This effect has been carefully investigated (see p. 175). Above 13° the effect of the drive was nearly independent of temperature, but below that temperature the lift, due to the increasing torque, rapidly increased.

The effect of the drive was nearly independent of pressure ; provided the lubricating effect of the film of oil on the piston remains fairly constant, there should be little change in the torque necessary to keep it in rotation. It was essential that the position of the belt should not change or the height of the piston, but in all the final saturation pressure measurements the piston was maintained at the definite height at which the gauge was calibrated.

A theoretical discussion of the differential gauge has been given by MICHELS.† He showed that there was a critical velocity of rotation of the piston above which metallic contact with the cylinder walls was avoided (this contact being due to the lack of perfection of the piston and cylinder) ; the velocity for a given gauge was shown to depend on the viscosity of the oil and the temperature, but not on the load. As the "belt lift" in the present experiments varied only slightly with the temperature above

† 'Ann. Physik,' (4), vol. 72, p. 321 (1923), and vol. 73, p. 577 (1924).

13° C., the rotation was probably above the critical velocity required for the gauge and the oil used, and MICHEL's experiments provide a reason for the "belt lift" remaining constant in spite of change of load. On some occasions $W_B - W_s$ plotted against p was not quite a straight line, and the effects of "drive" varied slightly from day to day. These effects would be explained by small traces of impurities in the oil, or the velocity of rotation being too low.

Fuller details of this part of the investigation are available in a report to the British Electrical and Allied Industries Research Association (J/T72). The following Table, No. XI, gives an illustration of the method of comparison of the two gauges, from which results the effect of the drive could be obtained as well as the area of the differential gauge :—

TABLE XI.—Date : December 12, 1930. Temperature : 17° C.

	lb. per sq. inch.					
Approximate pressure :—	300	400	500	600	700	800
Weight W_c in grams on Crosby . . .	27746·0	36827·8	45921·6	55014·9	64109·7	73203·7
Weight W_B in grams on differential gauge	17305·1	22970·3	28639·9	34312·0	39983·4	45653·5
Weight W_s on 0·125 sq. inch to balance W_c	17322·8	22993·4	28671·1	34347·8	40026·8	45704·6
Difference $W_B - W_s$	—17·7	—23·1	—31·2	—35·8	—43·4	—51·0

$$\left.\begin{array}{c}\text{Crosby area}\\ \text{at } 17^\circ \text{ C.}\end{array}\right\} 0\cdot200211 \; ; \quad r_s = \frac{0\cdot125000}{0\cdot200211} = 0\cdot624341.$$

The weights were the total weights on the Crosby W_c or the large gauge W_B, which included the weights of the carriers, etc., corrected to true weight, but not for air displaced.

The weight W_s on the nominal area A_s of the piston of the differential gauge was obtained from

$$\frac{W_c \times 0\cdot125}{A_c},$$

where $A_c = 0\cdot200211$, the area of the Crosby piston at 17° C.

The ratio r

$$= \frac{\text{area of differential gauge piston}}{\text{area of Crosby piston}} = \frac{W_B\left(1 - \dfrac{\delta}{\rho_B}\right)}{W_c\left(1 - \dfrac{\delta}{\rho_c}\right)} = \frac{W_B}{W_c} = \frac{A_B}{A_c},$$

where δ = density of air and ρ of the iron of the weights, the air correction does not enter, for the weights for each gauge are both calibrated with the same standard brass weights.

At any pressure p, the weight on area A_s will be $W_s = pA_s$, so that

$$A = A_s + \frac{W - W_s}{p}.$$

If there is no effect of drive,

$$\frac{W - W_s}{p}$$

is constant, for $A - A_s$ is constant.

The graph $W - W_s$ against p will be a straight line passing through the origin, where $W - W_s = 0$ when $p = 0$. But if there is an effect of the drive

$$\frac{W - W_s}{p}$$

will not necessarily be constant.

However, on plotting the difference $W_1 - W_{s_1}$, $W_2 - W_{s_2}$, etc., against p_1, p_2, etc., an approximately straight line was obtained, which did not pass through the origin, and for which the distance from the origin of the intercept on the ordinate gave the value of the correction for the drive. The experiments therefore show that the net effect of drive, b, was independent of the pressure.

It follows

$$A = A_s + \frac{(W_B - W_s) - b}{p},$$

where $W = W_B - b$.

It is then only necessary in order to find the area A of the differential gauge to plot a number of values at different pressures in order to determine p or to take a number of pairs of values at widely separated pressures and so eliminate b: for instance, from the above results at 300 and 800 lb. pressure.

$$A = A_s + \frac{-33 \cdot 3}{500 \times 453 \cdot 59} = 0 \cdot 125000 - 0 \cdot 000145 = 0 \cdot 124855 \text{ sq. inch at } 17^\circ \text{ C.}$$

The results of 30 comparisons at various pressures have been plotted. The observations on different days lay on slightly different straight lines, due to small variations in the setting of the steel yard or in the torque required to turn the piston, and small changes in the lubrication of the piston by the oil, but each curve was nearly straight and nearly parallel to a line passing through the origin corresponding to a piston area of 0·124858 sq. inch at 18° C.

The weighted mean of all those results gave a straight line which cut the ordinate at − 2·3 grams, so that the effect of drive was equivalent to a pressure of only 0·04 lb. per sq. inch; in fact, the part of the weight of the belt taken by the wheel was almost completely annulled by the lift of the drive. This result was further checked by determining the line of closest fit to the observation by the method of least squares.

It was necessary to show that the slight variation in the value of b was not due to temperature change. A number of trials was made, keeping the Crosby gauge at room temperature, and the differential gauge jacketed so that the temperature could be varied between 0 and 40° C. The results are tabulated. The determination of b and the area A_B do not necessarily involve the finding of the weight W_s on the standard area A_s, for since—

$$\frac{A_B}{A_c} = \frac{W_B - b}{W_c} = r = \frac{dW_B}{dW_c}$$

$$r = \frac{W'_B - W_B}{W'_c - W_c} \text{ and } b = \frac{W_B W'_c - W_c W'_B}{W'_c - W_c},$$

in which the weights W and W′ are observed at two pressures p and p'.

Since the piston area increases with temperature according to $A_t = A_{18^\circ \mathrm{C.}} (1 + 2\alpha (t - t_{18^\circ}))$, where $\alpha = 0\cdot000011$, the coefficient of expansion of the piston steel, $b = W_B - rw_c (1 + 0\cdot000022 (t_B - t_c))$, where W_B is the weight on the large gauge at t_B and W_c that on the Crosby at t_c; if t_c is arranged to be nearly constant, the above relation holds.

Table XII.—Observations January 9 and 12, 1931.

Crosby Temperature. °C.	Differential Gauge Temperature. °C	$t_B - t_c$.	Differential Gauge. W_b.	Crosby Gauge. W_c.	$+W_c [1 + 2 \alpha (t_B - t_c)]$.	b.	p.
18	0	−18	17305·1	27738·5	17292·3	−12·8	300
18	7·5	−10·5	17305·1	27748·5	17301·4	− 3·7	300
21	21	0	17305·1	27753·5	17308·5	+ 3·4	300
19	19	0	17305·1	27753·5	17308·5	+ 3·4	300
18	37	+19	17305·1	27745·5	17310·3	+ 5·2	300
18	9	− 9	28639·9	45929·1	28638·0	− 1·9	500
19	19	0	28639·9	45926·6	28643·5	+ 3·6	500
20	20	0	28639·9	45925·6	28642·5	+ 2·6	500
18	38	+20	28639·9	45907·6	28644·1	+ 4·2	500
18	0	−18	34312·0	55016·0	34297·1	−14·9	600
18	0	− 9	34312·0	55029·0	34312·0	0	600
18·5	18·5	0	34312·0	55026·0	34317·0	+ 5·0	600
18	9	− 9	39983·4	64126·2	39984·3	+ 0·9	700
18	13·5	− 5·5	39983·4	64123·2	39985·6	+ 2·2	700
18	18·0	0	39983·4	64118·2	39986·8	+ 3·4	700
19	19·0	0	39983·4	64116·2	39986·1	+ 2·7	700
18·5	38·0	+19·5	39983·4	64086·2	39984·5	+ 1·1	700

The influence of temperature on the drive effect was thus found to be very slight, above 13° C. over the range of pressures investigated, but below this temperature, owing to the viscosity of the oil, the torque necessary to turn the piston, and therefore the lift, increased rapidly. For the saturation pressure measurements the Differential Gauge was always used above 13° C., so the effect of drive may be taken as constant and independent of temperature.

Collecting the results, the means at the different temperatures were as follows :—

t_B, °C.	b, grams.
0	$-$ 13·3
8·5	$-$ 1·2
13·5	+ 2·2
19·1	+ 3·8
37·7	+ 3·5

The effect of drive in this series of experiments was a little greater (or the belt lift a little less) than obtained in the first series, but lies well within the error $\pm$ 2 grams.

From 14 separate trials the mean effect of drive may be taken as equivalent to a weight of 2·5 grams, with a probable error of the mean of $\pm$ 0·5 gram and a maximum deviation in any trial of 3·5 grams.

From the mean of these 27 results of the determination of the belt lift between 15° and 20° C., giving weight to the later determinations, in which all the necessary refinements were attended to, and allowing in each case the average effect of the drive, namely, a weight of 2·5 $\pm$ 0·5 grams on the piston, the final value of A at 18° C. for the differential gauge was 0·124858 $\pm$ 0·000002 ; the minimum detectable change in balance position, due to a weight of 1·2 grams, would cause a change of area of about $\pm$ 0·000006 and the maximum departure from this mean result in any single determination was $\pm$ 0·000020, when a small pressure interval was used.

In order to determine the area, a series of careful determinations on the same day would provide the most accurate figure, since the drive effect may vary slightly on different dates ; a final test, to check the above result, was therefore carried out on March 4, 1931.

The pistons were level, the Crosby piston was 1·2 cm. "up," the piston of the differential gauge 1·5 mm. above the stop ring, the steel yard lift was 60 grams $\pm$ 0·3 at 18° C., its arm was horizontal when opposite the mark, the ball race hanger was set central when it hung free, the motor drive was clockwise at 12 revolutions per minute, the driving belt tension such that 100 grams deflected the belt 15 mm. at its centre, and the pulleys were in their normal fixed position and well lubricated. Two grams on the Crosby (= 1·2 grams on the large gauge) made a detectable movement of the steel yard arm. The conditions were checked before the measurement at each pressure.

TABLE XIII.—Date : March 4, 1931.

Approx. Pressure lb. per sq. in.	Weight on Differential Gauge.	Temperature °C.	Weight on Crosby A = 0·200319 sq. in.	Temperature of Crosby. °C.	W_s.	$W_s - W_B$.
300	17305·1	19·2	27753·6 ±1·5	18·0	17327·6	—22·5
400	22970·3	19·3	36838·9 ±2·0	18·0	22999·8	—29·5
500	28639·9	19·3	45925·7 ±2·0	17·6	28673·3	—33·4
600	34312·0	19·4	55022·8 ±2·0	17·7	34353·0	—41·0
700	39983·4	19·4	64115·7 ±2·0	17·8	40029·9	—46·5
800	45653·6	19·1	73205·4 ±3·0	17·5	45705·2	—51·6
	45656·2		73211·7 ±3·0		45709·1	—52·9
900	51321·4	19·0	82296·5 ±3·0	17·5	51381·2	—59·8
1000	56991·0	18·8	91388·6 ±3·0	17·3	57058·0	—67·0

Taking x as the difference in area from the standard,

$$A_s = 0\cdot125 \text{ sq. inch, } x = 0\cdot125\left\{\frac{(W'_s - W'_B) - (W_s - W_B)}{W'_s - W_s}\right\}.$$

From each pair of values W_s and W_B, 102 in all, the mean change of $W_s - W_B$ is found to be 6·17 grams per 100 lb., giving proportionate weight to the size of the pressure interval, or $A_B = 0\cdot124864$ at 19·2° and 0·124861 at 18° C.

From the results at 300 and 1,000 lb. alone, the area would be 0·124859 at 18·0° C.; the difference is only equivalent to an error of 1 gram on the large gauge in the observations at the two pressures. The ratio r of the differential gauge and Crosby gauge pistons at equal temperature then became

$$r = \frac{0\cdot124861}{0\cdot200213} = 0\cdot623640,$$

and from $b = rW_c - W_B$, with differential gauge piston at 19·2° and Crosby at 18° (*i.e.*, $r' = 0\cdot623656$), $b = 4\cdot0$ grams from the mean of the values at all the different pressures. The greatest divergence was at 800 and 1,000 lb., where the larger weights had to be used, viz., ± 1·5 grams on the differential gauge; in all other cases the difference from the mean was less than 1 gram. It follows that the area was 0·124861 at 18° C. ± 0·000003, and as determined on March 4 the effect of the drive was + 4 grams (0·07 lb. per sq. inch).

The result closely confirmed the previous determinations, the effect of the drive was the same as determined on September 25 and January 12, *i.e.*, within the detectable difference 1 gram. There was no doubt that it varied a little from time to time—for instance, the slightly smaller mean figure for the drive effect (+ 2·3 grams) was due only to the observations on December 12, probably because of the change of oil or owing to particles of extraneous matter altering the piston lubrication, but if the conditions were very carefully attended to, the variation was certainly smaller than the extreme variation ± 3 grams found in all these trials.

The main object of this part of the investigation (the details of which have not been given in full) has been attained, namely, to ascertain the limits of error which the effect of the drive might introduce, and these are fixed, and found to be very small.

By the kindness of the Director and of the Superintendent of the Engineering Department of the National Physical Laboratory, the gauge was compared against the gauge of the latter Department and re-standardized. The gauges were placed so that the pistons were at the same level. The nominal piston areas of the N.P.L. gauges were 0·1 sq. inch and 0·02 sq. inch. The diameters were accurately known by direct measurement; the effective diameter being taken as the mean of the maximum diameter of the working part of the piston and the minimum diameter of the cylinder. The results of the comparison are given in Table XIV.

TABLE XIV.

Differential Gauge E and C.* lb. per sq. inch.	N.P.L. Gauge. Piston. in.	N.P.L. Gauge. lb. per sq. inch.	Difference. lb. per sq. inch.	Parts in 10,000.
505·67	0·1	505·5	—0·2	4
1006·18	0·1	1006·1	—0·1	1
1506·66	0·1	1506·3	—0·4	3
2007·10	0·02	2006·4	—0·7	3
3008·21	0·02	3007·4	—0·8	3

* $P = \frac{W + b}{A_B}$; W is the weight less buoyancy correction; A_B is corrected for temperature.

The agreement is as close as could be expected, particularly taking into account the entirely different basis of calibration of the two gauges. (The leak of oil past the piston was greater for the N.P.L. gauge than for the differential, and this may have slightly affected the accuracy of the first of the above measurements.)

(δ) *Leakage and other Corrections.*—The forces on the piston are (*a*) the direct hydrostatic pressure, (*b*) the friction due to the liquid forced to move in the space between cylinder and piston, and (*c*) the friction of the liquid on the wall due to the fall of the piston. MICHELS, *loc. cit.*, has shown that for stationary streaming, provided the cylinder and piston do not taper, and even when they are not perfectly concentric, half the pressure on the area of section of the oil between the piston and cylinder is communicated to the piston, so that half the mean clearance should be added to the piston diameter on account of the friction (*b*) due to the oil film. The rate of fall of the piston is so small in the present case that the effect (*c*) is quite negligible. The effects of fluid friction can be represented by an increase in the effective diameter of the piston. They are included in the effective diameter as determined by comparison with the mercury column, and that effective diameter is independent of the load.

The only effects which may give rise to a change of effective diameter with load are those due to deformation of the gauge by the pressure.

MICHELS has considered the effect of (*a*) stretch due to the load on the piston in an axial direction, (*b*) the compression of the piston, and (*c*) the expansion of the cylinder. For Michels' gauge the net increase in effective diameter was only $\frac{1}{23000}$ at 200 atmos.; in the present case the effects work out to be smaller, so that the resulting deformation does not appreciably affect the accuracy of the measurements.

In the case of the Crosby gauge with gunmetal cylinder, the external shape rendered an estimate of the effect of deformation difficult; it would not enter at the pressure at which comparison with the mercury column was made, but it might have just begun to be detectable at the highest pressures (1,000 lbs. per sq. inch), at which comparison was made with the large gauge.

The effective areas of the pistons of the N.P.L. gauges were found by direct measurement, so that it was thought to be of interest to compare the "effective area" of the differential gauge with the measured dimensions. The diameter at position 1 was 0·69097 ± 0·00004 inches, and, at position 2, 0·56408 ± 0·00002 inches (at 62° F.). (The accuracy of the determination being ± 0·00002 inches.) The two positions were separated by $\frac{11}{16}$-inch, position 1 being close to where the diameter of the piston increased.

The internal diameter of the cylinder could not be measured sufficiently accurately in the case of this differential gauge by measuring the volume of a known length, as was done by Wagner in the case of a simple gauge, so an attempt has been made to estimate the mean cross-sectional area of the oil film from the rate of efflux of oil. The flux on the annulus is given by LAMB ("Hydrodynamics," Camb. Univ. Press) as

$$v = \frac{\pi\,(\Delta P)}{8\eta L}\left(R^4 - r^4 - \frac{(R^2 - r^2)^2}{\log R/r}\right)$$

when η is the viscosity, L the length, and R and r the inner and outer radii of the two concentric cylindrical walls respectively. The flow is therefore $\frac{\pi \Delta p}{6\eta L} R (R - r)^3$. The leakage of castor oil at the lower gland at 2,000 lb. per sq. inch ($= 137 \cdot 7 \cdot 10^6$ dynes per sq. cm.) was found to be $1 \cdot 41 \cdot 10^{-4}$ c.c. per sec., $L = 10 \cdot 16$ cm., $R_1 = 0 \cdot 716$ cm., and $\eta = 9 \cdot 9$ poises at 20° C., so that $R_1 - r_1 = 0 \cdot 00065$ cm. $= 0 \cdot 000256$ inch. Similarly, for the upper gland, where $L = 7 \cdot 62$ cm., $R_2 = 0 \cdot 877$, and $v = 0 \cdot 75 \cdot 10^{-4}$ c.c./sec. $R_2 - r_2 = 0 \cdot 00045$ cm. $= 0 \cdot 000177$ inch. These measurements gave an "effective area" of $\pi \left\{ \left(r_1 + \frac{R_1 - r_1}{2} \right)^2 - \left(r_2 + \frac{R_2 - r_2}{2} \right)^2 \right\} = 0 \cdot 125030$ sq. inch, instead of 0·125086 sq. inch for the measured area of the differential piston, or of 0·124861 sq. inch for the effective area determined by calibration. The effect of pressure on the viscosity of the oil, the effect of rotation of the piston, the net expansion of the gauge due to deformation, the fall of the piston, and the *lack of parallelism* of the walls and circularity of piston and cylinder are not allowed for in this estimate, and may affect it appreciably, but possibly not sufficiently to account for the difference $\frac{1}{750}$ being altogether outside the error ($\frac{1}{3000}$) of the "effective area."

If the pressure on the upper oil film is considered as balancing that on the same area of the lower film, and the whole, instead of half, the pressure on the remaining oil film was to be exerted on the piston in a downward direction, then the "effective area" would become 0·124922, which is closer to the effective area obtained by calibration, but such procedure is not justified theoretically unless the clearance is too small for the ordinary Poiseuille conditions to apply. It is noteworthy that the effective area of the gauge used by WAGNER* was slightly less than the area determined by direct measurement of cylinder and piston. These discrepancies are possibly of interest from the point of view of the theory of lubrication, but they may well be ascribed to the piston not being a true cylinder. It was found that the rate of leakage of oil only increased by about 30 per cent. on rotation of the piston.

The leakage was determined by measuring the fall of the piston in a given time at various pressures, under conditions such that the oil supply was confined. The oil which leaked out from the two glands was also caught and measured, and in any actual saturation pressure measurement allowance was made; the leakage, however, was very small, and only amounted to 22 grams in the 30 hours of measurement during August (1930). From the Crosby piston the leakage was relatively slightly greater, viz., 0·6 c.c. per hour at 600 lb. pressure.

(*d*) *Measurement of Pressure.*—Having arrived at the most probable value of the area of the differential gauge, viz., $0 \cdot 124861 \pm 0 \cdot 000005$ at 18° C., having regard to all the comparisons with the Crosby gauge and the probable error in the determination of the area of the Crosby piston, the required corrections to the observations of pressures applied to the differential gauge could be made.

* 'Ann. Physik,' vol. 15, p. 906 (1905).

The correction a, which has to be added to the pressure p, which has a nominal value marked on the weight, for a piston area of 0·125 sq. inch, was given by

$$\frac{P'}{p} = \frac{0 \cdot 125}{0 \cdot 124861} = 1 \cdot 00111 \text{ at } 18^\circ \text{ C.};$$

hence $P' = p + 0 \cdot 00111\, p$. A change of 2 in the last place of this factor, equivalent to a change of area from 0·124930 to 0·124926, only makes 1/10 lb. per sq. inch difference (= 0·0046 atmosphere) at 3,000 lb. ($\backsimeq$ 200 atmospheres) total pressure. The factor 0·00111 changes with temperature to a slight extent, and can be corrected thus, $0 \cdot 00111 - 0 \cdot 000022\,(18 - t)$. In measuring a pressure there will also be a correction c for the air displaced by the weights, *i.e.*,

$$W_B = {}_V W_B \left(1 - \frac{0 \cdot 00121}{d}\right),$$

where $d = 8 \cdot 4$ for the smaller iron weights checked against brass weights in air, and uncorrected to weight *in vacuo*, and $d = 7 \cdot 0$ for the larger iron weights checked at the N.P.L. and corrected to true weight *in vacuo*, *i.e.*, 0·015 lb. per sq. inch per 100 lb. up to 800 lb. pressure and 0·017 lb. per sq. inch per 100 lb. from 800 upwards.

Each weight corresponded approximately to a certain pressure on the piston, the area of which was supposed to be 0·125 square inches, and was marked accordingly; there are, however, the corrections above mentioned to be made for the defect in area a and buoyancy c of the weights, and also for corrections to the weights themselves (w'), for the lift of the steel yard s, and for the zero of the gauge (Z), *i.e.*, the weight of the driving wheel, piston, and the effect of drive, etc., which should cause a minus reading of pressure if the pressure applied were reduced to zero (normal atmospheric pressure).

So Z, the zero correction, is given by

$$Z = P'\,(1 - a + c) - p + S$$

(the steel yard correction (s) was found from the weights (W) needed to balance the bob at the position used when the arm was in the horizontal position

$$= -\frac{8W}{453 \cdot 6}).$$

The pressure P′ is given by

$$P' = (p + z - s)\,(1 + a - c) + w',$$

where w' is the sum of the weight corrections in grams divided by 56·7, reducing to lb. per sq. inch.

Thus, taking

$$p = 300,\ s = 1 \cdot 06,\ c = 0 \cdot 00015,\ a = 0 \cdot 00111,$$

P′ is given by the weight on the Crosby piston (corrected for air displaced, 2,7749·5 grams), which balances the pressure on the differential gauge piston at 300 lb. approximate pressure, *i.e.*, 305·562 lb. per sq. inch.

Therefore

$$Z = 305 \cdot 56\ (0 \cdot 99904) - (300 - 1 \cdot 06) = 6 \cdot 33 \pm 0 \cdot 02.$$

(The value of this zero correction is only affected by the probable error of the weight on the Crosby, not by the area of the Crosby; it was checked and agreed with the pressure equivalent of the actual weights of the piston, wheel, etc., allowing for the effect of the drive.) If a mean value of 0·00016 P is taken for the air displaced correction, it follows that

$$P = p + 6 \cdot 33 - s + 0 \cdot 00095\, p + w'$$

will give the "true" gauge pressure (for 18° C.). (It makes no appreciable difference if p is used instead of P in the fourth term of this equation.)

Now for all the saturation pressure measurements, the barometric pressure (B) had to be added, and correction made for the pressure difference corresponding to the height of the pressure point above the piston (fig. 5) the pipe connection being filled with oil.

This was determined by three methods :—

(1) From the specific gravity of the oil (0·97) and the measurement of the height in mm., which gave 0·87 lb. per sq. inch.

(2) From the height of the mercury in an open manometer which balanced the column of oil (0·87 lb. per sq. inch), and

(3) From a direct determination of the weight on the Crosby placed as nearly as possible at the position of the pressure point either by balancing against the weight on the large gauge in the usual position, or by measuring saturation pressures of steam on the Crosby in the two positions. This comparison resulted in the mean value of 0·86 ± 0·04 lb. per sq. inch.

The mean value by the three methods is 0·87 ± 0·01 and therefore

$$P'' = B + p + 5 \cdot 46 - s + 0 \cdot 00095\, p + w',$$

where P″ is the absolute pressure at the oil/water separation point.

It remains to summarise the errors of the pressure measurements. It has been the aim to determine the probable error of the result of the series of determinations which have led to the standardization of the instruments used for measuring the saturation pressures, while at the same time estimating the possible limits of error which any single measurement might possess.

TABLE XV.—Summary of Errors of Determination of Pressure.

	Probable lb. per sq. inch.	*Possible* lb. per sq. inch.
Z = 6·33 . . .	±0·02	±0·07 (taken as ±4 *grams*, *i.e.*, maximum error in any single comparison).
s	±0·005	±0·01.
(*a* and *c*) . . .	±0·002 per 100 lb.	±0·02 per 100 lb. per sq. in. (possible Crosby error).
W′ (1 g.)	±0·02	±0·02 per 1000 lb. per sq. in.
Oil height . . .	±0·01	±0·02.
Total . . .	±0·075 at 1000 lb.	±0·32 at 1000 lb.

The possible error does not seem to be greater than $\frac{1}{3000}$, and the intercomparison with the N.P.L. gauge agrees within this figure. The point of doubt referred to in the remarks on p. 180 could only be settled by an investigation on lubrication, using apparatus at present not available. Those remarks need not be considered to affect the validity of the saturation pressure measurements, for the larger piston area would lead to a pressure difference altogether outside the error of the saturation pressures which are known with certainty at the lower pressures (about 15 atmos.).

MICHELS (*loc. cit.*) obtained the working area of his differential gauge by comparison with a mercury column of 485 cm. height in conjunction with a Cailletet manometer filled with hydrogen, and provided with an electric contact: the result, 0·99885 ± 0·0003, was found to be independent of the pressure, and is about the same order of accuracy (possible error $\frac{1}{3000}$) as the present measurement of the gauge area.

V. *Saturation Pressure Measurements.*

In the two previous sections the methods used for the temperature measurements and for the pressure measurement have been detailed. It remains to describe the carrying out of the saturation pressure measurements, and to discuss the remaining possible sources of error.

Pure distilled water from the stoneware vessels was drawn by the three-stage pump and forced into the monel metal tube of the boiler. Thence the steam passed through the steel tube of the superheater into the monel metal pressure pocket, and out through the aperture in the throttle disc, into the double condenser. The power used in the boiler tube amounted to about 10 to 15 kw., regulated by large adjustable resistances. The speed of the pump (which was driven off secondary batteries at constant voltage) was very constant and slow (10 to 12 r.p.m.); the speed was checked from time to time by a stop-watch. The superheater was maintained at a definite temperature so as to provide a store of heat in the system and prevent fluctuations in the wetness of the steam. The temperature of the superheater was adjusted by the gas flame, which did not come into contact with the tubes, but only with the 250 lb. block of metal in which they were embedded; a Whipple Indicator roughly checked the temperature of the block, but the thermometer was hardly near enough the coil to give an accurate indication of the temperature of the steam. The size of hole in the throttle was suited to the pressure range and mass flow required. The holes varied from 0·025 cm. to 0·125 cm. diameter, *e.g.*, for 3000 lb. per sq. inch pressure, 12 mils up to 40 mils for 300 lb. per sq. inch, with eight intermediate sizes.

The plant has to be run about three-quarters of an hour before readings are steady enough for measurements to be made, but it could be set in operation and adjusted to the required temperature in a remarkably short time, and also could be shut down very quickly, owing to the small capacity of the boiler.

The flow was determined by measuring the total water (*i.e.*, condensed steam and unvaporised water) flowing out per half-minute. The wetness was found by observing the difference in temperature of the inflowing and outflowing condenser water, and the temperature of the condensed water flowing away. From the approximate value of the total heat so obtained, the wetness could be obtained from tables. The temperatures (of the condenser water, etc.) were observed by mercury thermometers to 1/10° C., *i.e.*, to ± 3 cals. per lb. The wetness could be varied over a range 10 to 75 per cent. without appreciable effect on the saturation temperature, as shown by the results in Table XVI :—

TABLE XVI.

Temperature, ° C.	p lb. per sq. inch.	Flow.	Wetness, Percentage.
368·633	3003·30	4·2	20
368·643	3003·30	4·2	83
303·119	1301·39	4·6	13
303·133	1301·40	4·5	70

The actual velocity of flow was not high, but it could be varied through a considerable range without effect on the saturation pressure. It was obtained from the dimensions of the pressure pocket and the known total flow, *e.g.* :—

TABLE XVII.

P. obs. lb. per sq. inch.	800·53	801·03	800·97	2302·44	2302·24	2302·44
t ° C. obs.	270·209	270·239	270·228	346·746	346·743	346·738
t at 801·00 lb.	270·247	270·237	270·230	—	—	—
Flow, g./sec.	1·9	3·0	5·9	3·5	4·0	6·0
Wetness, percentage	50	17	25	35	55	18
Velocity, ft. per sec.	0·65	1·45	2·8	0·42	0·32	0·72

The volume of the wet steam was obtained sufficiently accurately from

$$\frac{\pi\,(\mathrm{H} - st)}{\mathrm{P}},$$

where

$$\pi = \frac{\mathrm{PV}_s}{\mathrm{H}_s - st},$$

where P is the saturation pressure, V_s the volume of the saturated steam, H_s the total heat of the saturated steam, and s the specific heat of the water. The area of the passage past the thermometer was 0·29 sq. inch.

The experiments showed no indication of change of observed pressure with change of rate of flow within the range which could be investigated without difficulty in the apparatus. The actual rates of flow are limited by the size of the aperture in the throttle disc, and the rate at which the steam can be generated in the boiler. Effects due to transfer of momentum or impact of the water particles can be shown to make no appreciable difference to the measured pressure at such rates of flow.

The pressure in all the experiments was measured close to the end of the re-entrant tube in which the thermometer is placed. The latter could be withdrawn 3 cm. (at all temperatures) without any alteration of the reading becoming noticeable. Loss of heat by radiation from the thermometers was shown not to influence the observed temperature to an appreciable extent; the steam maintained the surfaces of the metal in the pocket at its own temperature, and supplied heat at such a rate that radiation from the exterior of the pocket (which is surrounded with an aluminium casing) had no appreciable effect on the temperature of the interior surfaces. Neither additional lagging (1 inch asbestos) round the pocket nor different rates of flow of steam made any difference to the temperature ascribable to difference of radiation from the thermometer tube.

If steam were in equilibrium with a particulate mist of water, the condition would not be stable unless the vapour pressure were that corresponding to the normal vapour pressure for droplets of appreciable size. But, as already mentioned in the introduction, there are conditions in which a slightly different vapour pressure might have been discernible from that of the vapour in equilibrium with the liquid in an evenly heated enclosure; for instance, if the rate at which complex molecules dissociate into simpler ones is such that equilibrium is not established during the time in which the steam is generated and flows through the vessel where the pressure is measured.

The careful experiments at different flow rates and wetnesses of steam show that no such effects due to lack of equilibrium amongst the molecules are observable; indeed, at the flow rates available it would hardly be expected that equilibrium would not be established.

There is necessarily a slight difference in pressure in the case when the number of molecules evaporating is equal to the number condensing at the same temperature (*i.e.*, the statical case), in comparison with the case where the pressure is measured at some place where there is a certain amount of condensation (*i.e.*, the dynamical case). The change in momentum of the molecules at a surface would be $2\,mn\bar{c}$ in the former case and $(mn\bar{c} - mn'\bar{c})$ in the latter where n', the number leaving the surface at the position where the pressure is measured, is less than n, the number meeting the surface. In the present apparatus the tube leading to the pressure gauge is of small diameter and the heat conducted away is so small compared with the total supply of heat in the steam, that the loss of pressure due to this cause is beyond the limits of accuracy of measurement.

The pressure directly measured by the dead weight gauge could only be less than the saturation pressure by loss due to leakage of oil or movement of the oil and water with loss by friction. The leakage at the joints of the system and around the piston were so small as to make an indetectable difference to the pressure. The observed pressures could be maintained very steady; a slight regular fluctuation due to the thrust of the pump was observed at the highest pressures, but it could generally be avoided.

It remains to discuss the influence of the quality of the water itself on the saturation pressure measurements.

Distilled water from a large block tin still was run into the storage system and pumped round and round a closed system through a series of three copper boilers, which could remove the air very completely, fig. 9. The water was taken from the top

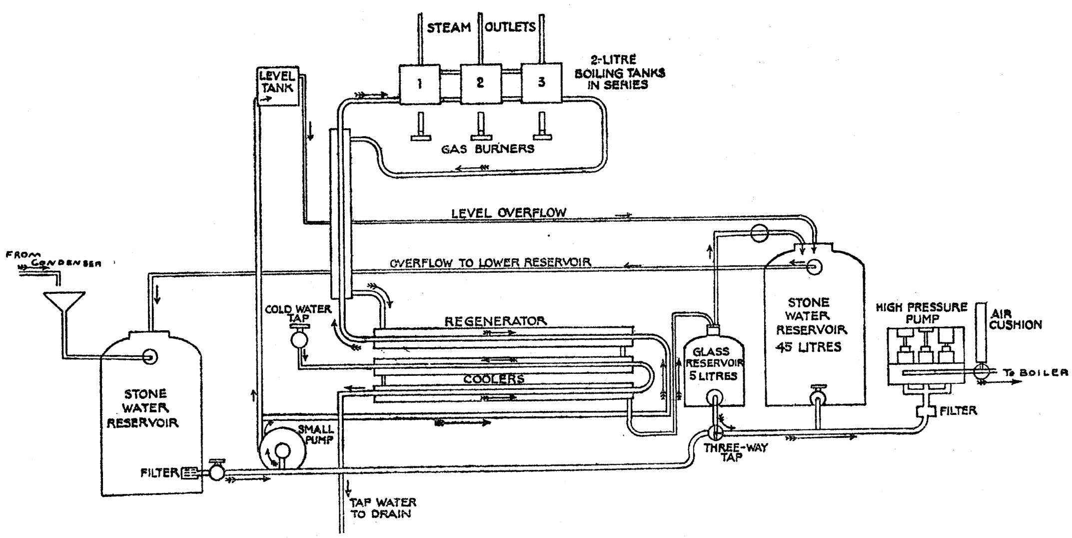

FIG. 9.—Supply System for Air-free Water.

layers of a closed glass vessel, and pumped into the plant as described. It was found that the monel metal tubes were attacked very little during the whole course of the experiment, and the condensed steam was quite clear. The residue on evaporation of 20 cc.^{3} in a platinum basin gave a barely visible unweighable residue (*i.e.*, difference less than 1/20 mg.).

The water leaving the condenser situated beyond the throttle, passed through a glass trap so that any air liberated and not re-dissolved could be rendered visible, and collected if necessary. The boiling arrangement freed the water of air to such an extent that no bubbles of air were visible (nor of hydrogen which might possibly arise from the attack of steam on the metal at the high pressures). With ordinary distilled water which had not been subjected to the boiling treatment, considerable numbers of bubbles of air were caught in the trap, but apparently the saturation pressures were unaffected. Pure air-free distilled water was, however, used for all the final measurements, and minor alterations were made so as to replace all rubber connections by metal (German silver) tubes, without, however, making any appreciable effect on the values obtained. The apparatus is continually being washed out with fresh distilled water and remains very clean, unlike, in the case of measurements by the statical method, when contamination is likely to accumulate.* The only contamination that was sometimes noticeable was an almost indetectable trace of oil, probably from the pump leathers, which caused the water to wet glass a little irregularly; the agreement at the low pressures with statical measurements indicates that the effect of such traces was too small to influence the saturation pressures. Furthermore, the hypsometer used for the standard point was filled with water which had passed through the plant, and gave identical boiling points to water taken direct from the still.

The above discussion indicates that such errors as arise are only liable to be those of the actual measurement of the pressure and of the temperature in the pressure pocket, which have already been discussed in their respective sections.

The following Table, No. XVIII, summarises the probable and possible errors (as given in the sections dealing with the calibration of the pressure and the temperature measuring arrangements) at various pressures for the final sets of measurements :—

TABLE XVIII.

		500 lb.		1000 lb.		2000 lb.		3000 lb.	
		Probable.	Possible.	Probable.	Possible.	Probable.	Possible.	Probable.	Possible.
Pressure . . .		±0·065	0·21	0·075	0·32	0·095	0·54	0·115	0·76
Temperature .		±0·07	0·14	0·15	0·30	0·25	0·50	0·40	0·80
Total	lb. per sq. in.	±0·135	0·35	0·225	0·62	0·345	1·04	0·515	1·56
	° C. . . .	±0·015	0·040	0·015	0·043	0·014	0·041	0·015	0·044

These figures are a measure of the reliability of the results, but do not include the variations of the actual observations due to the pressure observed not corresponding exactly to the temperature observed.

* At the completion of the work, the superheater pipes, etc., were examined and found to be clean.

If the mean error of observation of temperature is taken as $\pm 1/100°$ C. and the mean error of observation of pressure is $\pm 0\cdot07$ lb. per sq. inch (which is equivalent to $\pm$ 2 grams for observation of the pressure with steel yard at the mark and $\pm$ 2 grams for variation of the belt lift on different occasions), then the mean observational error would amount to :—

$\pm$ 0·14 lb. per sq. inch (= 0·016° C.) at 500 lb. per sq. inch.
$\pm$ 0·22 lb. per sq. inch (= 0·015° C.) at 1000 lb. per sq. inch.
$\pm$ 0·32 lb. per sq. inch (= 0·013° C.) at 2000 lb. per sq. inch.
$\pm$ 0·47 lb. per sq. inch (= 0·013° C.) at 3000 lb. per sq. inch.

(These figures do not include the calibration errors, but are the errors expected for a series of measurements made on different occasions at the same temperature and pressure, assuming the two exactly to correspond.) Comparing these figures with those in the previous table, the results are *probably* correct within the errors of observation of the temperature and pressure.

Four series of experiments have been carried out, as already mentioned. [The preliminary experiments from March to May, 1930, the second series in June, the final series in August and in October, and the final check in January, 1931.] The results throughout agreed satisfactorily. Experiments have been made, using air-free and ordinary distilled water, with two different pressure gauges, with two different thermometers, at various flow rates, using different pressure pockets, and before and after the apparatus had been partially dismantled, without any constant errors becoming manifest.

In making an actual experiment, having inserted the necessary throttle disc, the water is first pumped into the boiler, the current through which is then switched on and adjusted to give the required pressure as approximately measured on a Bourdon gauge. The oil to water level is carefully adjusted, and when the pressure is steady the cock is opened to the dead weight gauge and loaded. By regulating the current through the boiler the steel yard arm is maintained at the mark, and measurements of the temperature are taken (having previously observed the thermometer zero and the barometer, etc.). The measurements are repeated several times, because it is found that the pressure measurement lags a little behind the temperature to which it corresponds. The thermometer zero is taken again after the measurement. Measurements are repeated at about 100 lb. pressure intervals, until it becomes necessary to change the throttle disc.

Special precautions were taken during the final measurements in January :—

(*a*) The galvanometer deflection was not taken till the pressure had been steady at the required point for 10 seconds at least.

(*b*) The pressure was brought to the point four or five times, and the mean galvanometer reading was taken.

(*c*) The barometer was very carefully read at each observation.

(*d*) The oil, if any, was removed from the tray of the gauge under the piston before each observation.

(*e*) The height of the oil in the separator was checked twice during an experiment at each point.

(*f*) The steel yard arm was adjusted to the mark before experiment at each point, and checked for the correct lift.

(*g*) The temperature of the gauge piston was maintained at 17 ± 1° C. and the zero was checked against the Crosby on January 19, 26 and 27, without change being observed.

(*h*) The thermometers were checked at the naphthalene, benzophenone and sulphur points, the calibration agreeing very satisfactorily with the former results.

The following are the data of an experiment on January 27, 1931 :—

Zero deflections 120 . . . . Box at 15° C.
79·5

Coils 192–193.

Time : 11.25 a.m. Barometer 767·50 at 56° F.

Coils 75, deflection — 35 (obs. G.S.C.), steady 1 minute.

Time : 12.15 — 35.
— 35 (obs. A.E.)
— 36 (obs. A.E.)

Barometer 767·25
at 59° F. — 35 (obs. A.E.)

Time : 12.50. Barometer 767·25 at 59° F.

Zero : 1.20 p.m., deflection 120·5. Box at 17° C.
84

Volts : 146.

Gas pressure : 15 cm.

Revolutions : 11 per minute.

Flow : 3·85 g./sec.

Rise of Cooling Water : 34½°.

Temperature of condensate 25°.

Pressure Gauge :

Wts. . . . . . . 2400, actual wts. 3, 4, 7, 6 and 1 h.
Steel yard — 20.
Tested : wt. on Crosby 27,754 ± 1, Differential Gauge 17,305 grams.

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These data are reduced as follows :—

As barometer and f_z change with time, the values are interpolated for time of test and are marked below * :—

Temperature.		*Pressure.*	
Bar. at 0° C.	766·26	Wt. on Differential Gauge ..	2400·00
Pt_z — 100	+ 0·225	Correction for wts.	+ 0·01
Pt_z	100·225	Bar. correction	14·81
f°_z	201*	Zero	+ 5·46
f_z	203*	0·095 per 100	+ 2·28
C_z	192·005	Steel yard	— 20·12
Ru_z	0·591*	Total correction	+ 2·44
R_z	192·596	P obs...	2402·44
Coil (corrected)	74·941	Flow	3·85
ΔC/27	4·3	Rise	34·5
f_t	207·3	Cals.	530
Observed deflection	— 35	Wetness, per cent.	45
Ru_t	— 0·169		
R_t	74·772		
2 (R_z — R_t)	235·648		
I (0·502)	1·183		
+ Pt_z = Pt	337·056		
X (1·5)	13·146		
K Δ (1·5)	— 0·025		
t° C.	350·177		

The basis of the reductions is summarised here for convenience :—

1. Barometer : zero .. .. .. + 0·10 mm.
   latitude 45° .. .. + 0·45 mm.
   temperature .. .. $(P - P_0) = (t - t_0)\ [0{\cdot}1235 + 0{\cdot}00016\ (p - 760)]$ (when t is 15 to 23°).

2. Steam temperature t_p° C. $= 100 + 0{\cdot}03670\ (p - 760) - 0{\cdot}000023\ (p - 760)^2$, and

   platinum scale $(t_p)\ pt = 100 + 0{\cdot}03615\ (p - 760) - 0{\cdot}000023\ (p - 760)^2$ (for 740 to 780 mm.).

3. Temperature, No. 4 thermometer, $\delta = 1\cdot4974$ and $\mathrm{I} = 0\cdot502$.

$$t^\circ \mathrm{C.} = (t_p)\, pt + 2\,(\mathrm{R}_z - \mathrm{R}_t)\left(1 + \frac{\mathrm{I}}{100}\right) + \delta\,(t - 100)\,t.$$

$$\delta\,(t - 100)\,t = 1\cdot5\,[(t - 100)\,t]\,(1 + \mathrm{K}),$$

where

$$\mathrm{K} = 0\cdot74\,(\delta - 1\cdot5) \text{ for small changes in } \delta \text{ to } 375^\circ.*$$

4. Pressure :—

$$\mathrm{P}'' = \mathrm{B} + p + 5\cdot46 - \mathrm{S} + 0\cdot00095\,p + \mathrm{W}'.$$

VI. *Results.*

The numerous measurements made in May and June, 1930, are not included in the following tables of results, because the final refinements had not then been applied. Nevertheless, those measurements agreed satisfactorily enough with the later results carried out in August and October.

Table XIX contains the results of the observations made in August and October, reduced on the above basis, viz., for the temperature $\mathrm{I} = 0\cdot502$ and $\delta = 1\cdot4974$ (No. 4 thermometer) and for the pressure $\mathrm{P} = 5\cdot46 + 0\cdot00095\,\mathrm{P}$.

Corrections for barometric height, for the position of the bob on the steel yard arm (usually at 20 mark = — 20·12 lb.), for the weight of oil collected in the cup of the dead weight gauge, and for the weights used were applied. The approximate figures for the rate of flow and degree of wetness are given in columns 5 and 6 respectively. Column 4 gives the difference from the figures derived from the *mean curve* finally adopted.

Table XX contains results of the January, 1931, observations, which were carried out with the greatest care (p. 188).

* When $\delta = 1\cdot5$, the values of $t - t_{pt}$ are available from tables, but when $\delta \neq 1\cdot5$, correction by solution of the quadratic becomes cumbersome and since we can write—

$$t - t_{pt} = 1\cdot5\,(t' - 100)\,t'\,\{1 + (\delta - 1\cdot5)\,f(t)\}\,10^{-4}$$

t' being the value if $\delta = 1\cdot5$, and $f(t) = \dfrac{1}{0\cdot00015 - \delta^2\,(2t - 100)}$. To 375°, $f(t) = \mathrm{K}' = 7400$ or with closer approximation $k' = (6500 + 2\cdot5\,t)$. [Justification for this procedure is given in a recent communication to the Philosophical Magazine.]

TABLE XIX.

Date.	$t°$ C.	P. obs. lb. per sq. inch. (S. Kensn.)	P — P′.	Flow, g. per sec.	Wetness. Per cent.
2.6.30	171·686	119·71	+0·02	—	—
2.6.30	186·637	169·07	—0·02	—	—
2.6.30	198·456	218·32	—0·02	—	—
7.8.30	218·264	325·37	+0·02	3·0	60
7.8.30	235·804	450·44	—0·15	4·0	60
8.8.30	244·604	525·88	+0·10	4·0	35
7.8.30	245·127	530·59	—0·05	4·5	60
8.8.30	254·920	625·94	—0·06	4·2	15
6.8.30	261·365	695·60	—0·01	2·0	20
8.8.30	264·013	726·02	+0·05	4·7	5
6.8.30	267·805	770·65	—0·45	2·1	15
8.10.30	270·209	800·53	—0·28	1·9	50
11.8.30	270·228	800·97	—0·17	5·9	25
8.8.30	270·239	801·03	—0·23	3·0	17
8.10.30	277·828	900·64	—0·08	2·8	60
11.8.30	277·860	900·94	—0·20	3·3	17
11.8.30	284·893	1000·84	—0·07	3·6	13
11.8.30	291·368	1101·23	+0·43	3·8	7
11.8.30	297·440	1201·33	+0·30	4·3	14
11.8.30	303·119	1301·39	+0·26	4·6	13
12.8.30	303·133	1301·40	+0·08	4·5	70
12.8.30	308·482	1401·46	+0·10	4·2	60
12.8.30	313·552	1501·44	—0·15	4·0	40
12.8.30	318·359	1601·60	+0·34	4·0	25
12.8.30	322·957	1701·67	—0·37	4·2	30
12.8.30	327·306	1801·72	+0·67	4·1	15
13.8.30	327·348	1801·92	—0·17	3·3	10
13.8.30	331·558	1902·10	—0·36	4·2	40
13.8.30	335·563	2002·05	+0·16	4·1	25
2.10.30	335·554	2002·15	+0·11	5·4	25
13.8.30	339·433	2102·23	—0·20	4·1	20
2.10.30	339·400	2102·23	+0·54	5·6	22
3.10.30	339·413	2102·33	+0·50	2·6	75
3.10.30	343·131	2202·37	+0·21	2·6	70
13.8.30	343·143	2202·25	+0·04	4·2	10
14.8.30	343·163	2202·29	—0·27	4·2	60
2.10.30	343·162	2202·29	+0·27	5·6	12
1.10.30	345·005	2252·41	—1·50	3·6	40
7.10.30	346·716	2302·04	—0·58	3·9	70
3.10.30	346·709	2302·44	+0·11	2·6	70
14.8.30	346·743	2302·24	—0·82	4·0	60
2.10.30	346·738	2302·44	—0·82	6·0	18
1.10.30	346·746	2302·44	—0·92	3·5	30
6.10.30	348·407	2352·10	+0·90	3·6	55
18.8.30	350·139	2402·63	+1·00	4·0	60

TABLE XIX.—(continued).

Date.	$t°$ C.	P. obs. lb. per sq. inch. (at S. Kensn.)	P − P′.	Flow, g. per sec.	Wetness. Per cent.
6.10.30	350·164	2402·33	+0·12	3·6	55
14.8.30	350·172	2402·53	+0·03	3·9	50
6.10.30	353·479	2502·28	+0·32	3·6	55
18.8.30	353·485	2502·60	+0·32	3·9	50
14.8.30	353·496	2502·48	+0·08	3·5	40
18.8.30	356·720	2602·74	+0·68	3·9	4
15.8.30	356·743	2602·84	+0·19	3·4	25
18.8.30	359·846	2702·81	+0·70	3·9	50
15.8.30	359·882	2702·91	−0·23	3·8	40
18.8.30	362·860	2802·86	+0·95	4·2	50
19.8.30	362·889	2803·06	+0·24	4·1	45
15.8.30	362·902	2802·96	−0·25	3·8	15
19.8.30	365·806	2903·24	+0·22	4·0	15
19.8.30	368·633	3003·30	+0·23	4·2	20
27.8.30	368·643	3003·30	−0·17	4·2	83
20.8.30	368·644	3003·30	−0·17	3·4	50
20.8.30	371·371	3103·33	+0·05	3·3	50
7.10.30	371·388	3102·87	−1·15	3·6	20
20.8.30	374·023	3203·40	−0·10	3·8	90
7.10.30	374·001	3202·90	+0·20	4·0	50
7.10.30	375·310	3252·95	−0·60	4·1	50

TABLE XX.

Date.	$t°$ C.	P. obs. lb. per sq. inch. (at S. Kensn.)	P − P′ lb. per sq. inch.	Flow, grams per sec.	Cals.	Wetness. Per cent.
19.1.31	229·265	400·29	+0·03	2·0	520	36
19.1.31	241·735	500·37	+0·04	2·4	520	36
2.2.31	270·203	800·68	+0·03	2·2	580	25
2.2.31	277·817	900·82	+0·28	2·3	600	20
20.1.31	284·875	1000·92	−0·13	4·5	530	40
20.1.31	291·382	1101·10	+0·02	4·8	550	33
20.1.31	303·141	1301·30	−0·22	5·75	540	35
21.1.31	313·550	1501·45	−0·08	4·0	550	36
21.1.31	318·345	1601·57	+0·35	4·0	590	21
21.1.31	327·360	1801·82	−0·40	5·0	520	42
23.1.31	327·312	1801·47	+0·39	3·7	530	40
23.1.31	331·532	1901·47	−0·20	3·6	580	22
23.1.31	334·739	1981·39	−0·80*	3·6	620 ?	5*
26.1.31	335·563	2001·93	−0·09	3·0	510	46
26.1.31	343·118	2202·19	+0·16	3·4	500	51
26.1.31	346·702	2302·26	+0·15	3·4	525	42
27.1.31	346·706	2302·41	+0·15	3·8	515	45
27.1.31	350·177	2402·44	−0·18	3·8	530	45
27.1.31	353·515	2502·52	−0·56	4·0	530	40
27.1.31	359·870	2702·75	−0·17	4·5	510	40

* Probably superheated.

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Vapour pressure measurements can be represented with fair accuracy by the straight line relation

$$\log p = -\frac{A}{T} + B.*$$

It is obvious that, as A changes with T, the relation is not strictly accurate ; nevertheless it often holds for practical purposes as well as any other empirical equation.

Plotting, therefore, the value for log p against 1/T from the January observations, they were found to lie very nearly on a straight line, except for the values above 330° C. and below 200° C., which begin to diverge slightly from the line. The straight line

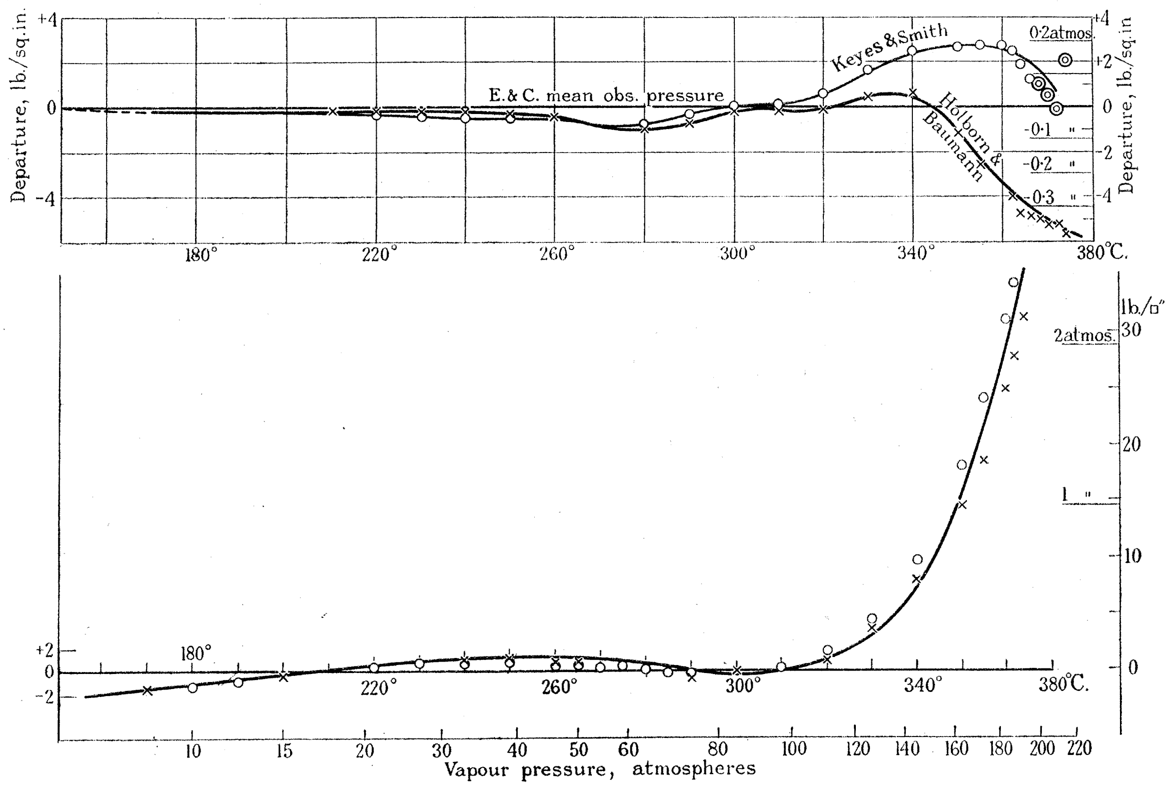

FIG. 10.—Curve 2.—Departure from present observations of previous work.

KEYES and SMITH mean line = ○○○○ HOLBORN and BAUMANN mean line = × × ×

Observed points = ⊙⊙ At 374° C.

K and S = 218·192 At

E and C = 218·048 ,,

H and B = 217·666 ,,

Curve 1.—Observed and smoothed pressure (normal lbs./in.^{2}) as a difference from Log P= $b - a$/T.

KEYES and SMITH ○○○ HOLBORN and BAUMANN × × ×

* See EGERTON, ' Phil. Mag.,' vol. 48, p. 1048 (1924), also T. S. WHEELER, ' Phil. Mag.,' vol. 11, p. 442 (1931).

obtained is chosen from the points log $p = 2\cdot2600$, $1/T = 0\cdot00158$ and log $p = 1\cdot4355$, $1/T = 0\cdot001990$, so that

$$\log_{10} p_{\text{atmos.}} = -\frac{2010\cdot97}{T} + 5\cdot43733$$

or

$$\log_{10} p_{\text{lb.}} = -\frac{2010\cdot97}{T} + 6\cdot60452_6.$$

The differences between the pressures obtained from this formula (which is only used as an empirical reference line) and the pressures observed can then be plotted.

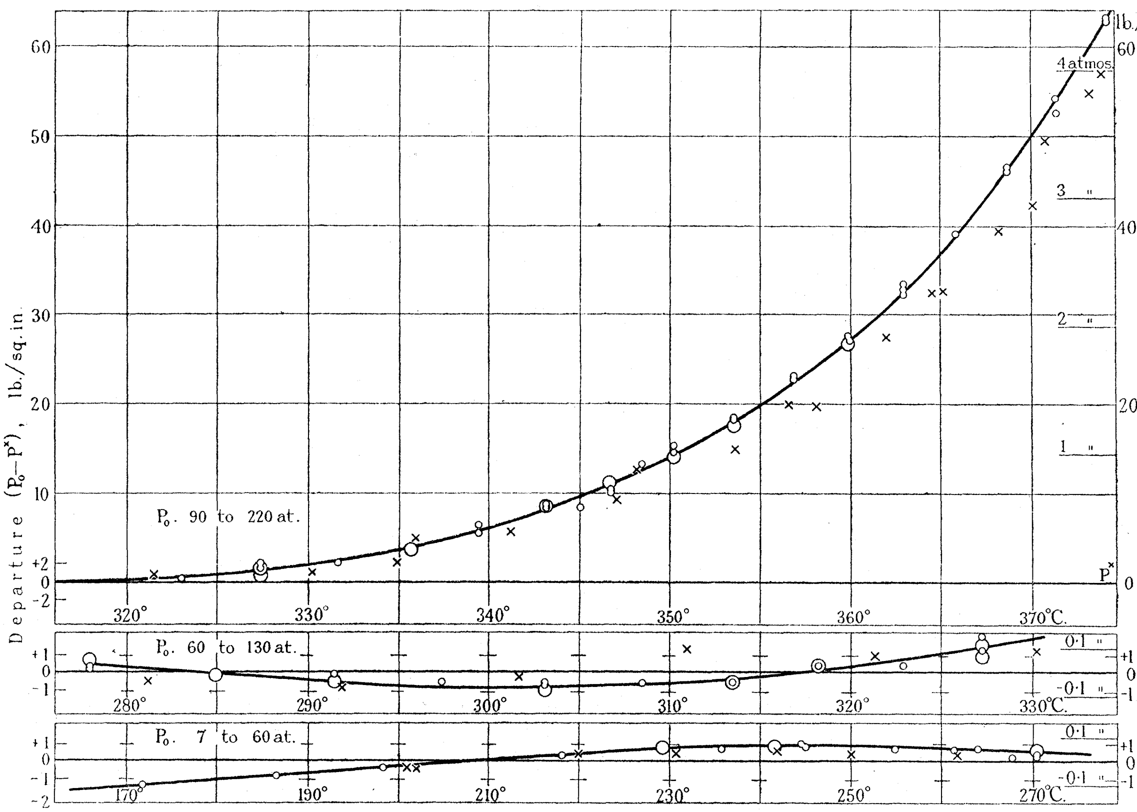

FIG. 11.—Curve 3.—Departure of *observed* pressures from P where log $P = b - a/T$. Observations taken January, 1932 ○ ○. Observations taken Aug.–Oct., 1930 ○ ○. Observations taken by HOLBORN and BAUMANN (1908) × × ×. E and C mean line shown full.

The curves obtained are curves 1 and 3, figs. 10 and 11. (See also Table XXI, column 2, which gives the difference between observed and calculated values in lb./sq. inch (London).)

Up to 330° C. the deviation from the straight line is quite small, but above this temperature the pressures increase more rapidly with temperature than the straight line relation requires. The real

$$\log p \Big/ \frac{1}{T}$$

TABLE XXI.

$t°$ C.	Δ P.	P. lb./sq. inch (L).	P. atmos. normal	$t°$ C.	Δ P.	P. lb./sq. inch (L).	P. atmos. normal
165	—1·76	101·63	6·9192	290	— 1·06	1079·15	73·471
170	—1·57	114·93	7·8246	295	— 1·41	1159·82	78·964
175	—1·40	129·53	8·8187	300	— 1·57	1245·29	84·782
180	—1·18	145·54	9·9086	305	— 1·51	1335·55	90·927
185	—1·00	163·04	11·100	310	— 1·40	1430·82	97·414
190	—0·83	182·13	12·400	315	— 1·06	1531·17	104·245
195	—0·65	202·93	13·816	320	— 0·61	1636·78	111·436
200	—0·47	225·54	15·355	325	0	1747·82	118·996
205	—0·27	250·07	17·025	330	+ 0·91	1864·60	126·946
210	—0·08	276·66	18·835	335	+ 2·48	1987·61	135·322
215	+0·07	305·39	20·792	340	+ 5·02	2117·32	144·152
220	+0·25	336·41	22·903	345	+ 8·47	2253·85	153·447
225	+0·41	369·81	25·177	350	+12·91	2397·47	163·224
230	+0·56	405·69	27·621	355	+18·55	2548·18	173·485
235	+0·65	443·19	30·242	360	+25·45	2707·00	184·299
240	+0·64	485·41	33·048	362	+29·06	2773·03	188·794
245	+0·59	529·48	36·048	364	+33·04	2840·55	193·393
250	+0·55	576·54	39·252	366	+37·60	2909·68	198·092
255	+0·46	626·79	42·674	368	+42·67	2980·40	202·912
260	+0·36	680·42	46·325	370	+48·25	3052·77	207·839
265	+0·32	737·53	50·213	371	+51·36	3089·62	210·358
270	+0·24	798·22	54·345	372	+54·59	3126·85	212·883
275	+0·10	862·56	58·725	373	+57·96	3164·58	215·452
280	+0·23	930·72	63·366	374	+61·34	3202·71	218·048
285	+0·62	1002·86	68·277	375	+65·24	3241·40	220·681

curve for water is S-shaped, and it is evident why the straight line holds so well between 200° C. and 330° C. (change in specific volume compensates the change in λ the latent heat). Exaggerating the shape of the curve, the straight line is chosen to cut the real curve as shown, so that the small positive values between 220°–270° and the negative values between 280° C. and 320° C. are real deviations due to the shape of the curve. The straight line would give a value for the normal boiling point of water (100° C.) 1·11 atmospheres, so that it cannot be used to compute even approximate values below 180° C.

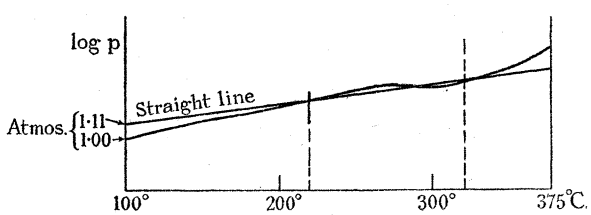

FIG. 12.

The pronounced change in the slope of the curve as the critical point is approached, which commences about 330°, was considered by H. L. CALLENDAR to be due to disaggregation of the molecules of the liquid, and he attempted to reproduce the lie of the curve in the equation*

$$\log p = 21\cdot07434 - 4\cdot7174 \log \mathrm{T} - \frac{2903\cdot4}{\mathrm{T}} + 0\cdot20956 \log \frac{1+\mathrm{ZP}}{1-\mathrm{ZP}} + 0\cdot001138 \frac{\mathrm{P}}{\mathrm{T}}$$

the deviations from which (see Table XXVI) gave a curve of the shape given in fig. 14. From the sharp maximum at about 350° it is clear that the function does not entirely reproduce the actual behaviour of steam.

Somewhat better agreement is obtained using the modified VAN DER WAALS type of equation of CEDERBERG†

$$\log \frac{\pi_0}{p} = a\left(\frac{\theta_0}{\mathrm{T}} - 1\right),$$

where π_0 and θ_0 are the critical pressure and temperature respectively and

$$a = \alpha\,\beta^{\left(\frac{\mathrm{T}}{\theta_0} - \gamma\right)^2}$$

where $\alpha = 3\cdot1244$, $\beta = 1\cdot7887$, and $\gamma = 0\cdot7500$ (for p in mm.).

The differences in atmospheres between the observed figures and those calculated by this formula are given in Table XXV.

In drawing the mean curve through the points representing the departure of the observations from the straight line equation, three times the weight was given to the January observations as to those of August-October. The mean line through the January observations was nearly coincident, however, with that through the August-October measurements alone. The individual values of pressure, tabulated for every 5° C., were found from the dp/dt values to be smooth to about $\pm 0\cdot2$ lb. per sq. inch, and the values were then further smoothed by making the $\log p_1 - \log p_2$ differences change as regularly as possible; the final individual values of the pressure were consistent and showed no irregular variation of more than $\pm 0\cdot02$ lb. per sq. inch up to 2400 lb. The experimental points might have been smoothed by means of an empirical equation, but it is hoped that when other properties of steam are known satisfactorily, that a vapour pressure equation, in which the constants have a physical significance, may be found to fit the observed results.

* $\mathrm{Z} = f\left(\frac{c}{\mathrm{T}}\right)$ where c is "coaggregation volume."

† 'Phys. Z.,' vol. 15, p. 697 (1914).

TABLE XXII.

$t°$ C.	$\frac{dp}{dt}$ lb./sq. inch (London).	$\frac{dp}{dt}$ atmos. (normal).	$t°$ C.	$\frac{dp}{dt}$ lb./sq. inch (London).	$\frac{dp}{dt}$ atmos. (normal).
170	2·79	0·190	290	15·69	1·068
175	3·05	0·208	295	16·59	1·129
180	3·35	0·228	300	17·54	1·194
185	3·66	0·249	305	18·53	1·262
190	3·98	0·271	310	19·55	1·331
195	4·33	0·295	315	20·60	1·402
200	4·71	0·321	320	21·70	1·477
205	5·11	0·348	325	22·83	1·554
210	5·53	0·377	330	24·01	1·635
215	5·97	0·406	335	25·25	1·719
220	6·44	0·438	340	26·57	1·809
225	6·93	0·472	345	27·96	1·904
230	7·43	0·506	350	29·38	1·999
235	7·96	0·542	355	30·93	2·106
240	8·52	0·580	360	32·67	2·224
245	9·10	0·620	362	33·41	2·275
250	9·72	0·662	364	34·16	2·326
255	10·38	0·707	366	34·93	2·378
260	11·06	0·753	368	35·74	2·433
265	11·77	0·801	370	36·60	2·492
270	12·50	0·851	371	37·04	2·522
275	13·25	0·902	372	37·49	2·552
280	14·03	0·955	373	37·94	2·583
285	14·84	1·010	374	38·40	2·614

TABLE XXIII.

Pressure. lb./sq. inch.	No. of Observations.	May and June. *Δ lb./sq. inch.	Aug. and Oct. Δ lb./sq. inch.	January. Δ lb./sq. inch.
800	3	1·0	0·2	—
900	7	1·0	0·1	—
1900	3	1·3	0·8	0·2
2300	2	1·5	1·1	0·2
2500	4	1·0	0·3	—
2600	3	2·5	0·7	—
2700	4	2·5	1·0	—

* Δ = average dispersion.

Table XXI gives the smoothed value of the pressures in lb. per sq. inch (London) and in normal atmospheres for every 5° up to 365° and for every 2° beyond. Table XXI, column 2, contains the difference of the smoothed values of the pressure as observed at South Kensington ($g = 981 \cdot 187$) from the values of the pressure from the straight line equation already cited (*cf.* p. 195).

Table XXII gives the values for dp/dt for the smoothed curve, in lb. and in atmos. Table XXV gives the differences between the "smoothed" results of the present measurements and the "smoothed" results given by HOLBORN and BAUMANN and by KEYES and SMITH, all reduced to standard lb. per sq. inch (see also curves 1 and 2). There are no other measurements of sufficient accuracy above 200° C. to warrant comparison. Before discussing the small differences, it is necessary to consider the errors of the present observations.

The variation of a number of measurements made at the same temperature on different occasions gave a measure of the observational error of the determinations which are seen to diminish as the precautions increased (Table XXIII). The January observations were given the greatest weight; they lay very close to the smooth curve through the August and October values, as the plot, fig. 13, of the departures of the observed results from the final smoothed values demonstrates.

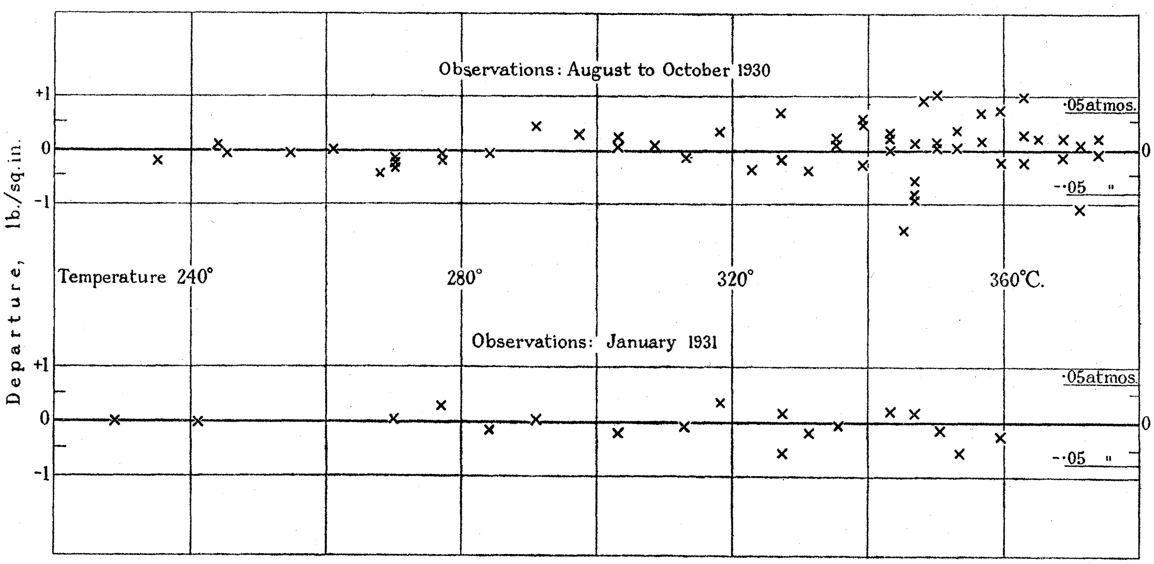

FIG. 13.—Showing departure of individual observations from the chosen mean curve.

The sum of the squares of the observed differences from the smoothed curve for the January observations gives the probable error of the resulting mean line to be ± 0·04 lb. up to 800 lb. per sq. inch or ± 0·07 up to 3000 lb. The mean observational error, as determined from a number of observations at the same temperature, increases with the pressure and for the August and October set varies from about 1 in 6000 at the higher pressures to 1 in 10,000 at the low (± 0·1 lb. at 300 lb. to ± 0·5 at 3000 lb. per sq. inch).* These figures are slightly less than the mean observational error allowed

* Actual mean errors for sets of 3 or 4 separate measurements at 800·07 lb., 2300·77 lb. and 2401·0 lb. per sq. inch were + 0·08, + 0·32 and + 0·44 respectively.

for the pressure and temperature measurements given on p. 188. The results can, therefore, be regarded as determined within those limits of error, for the probable errors of the temperature and pressure standardization lie within those observational errors. The probable error of the individual points on the smoothed curve being about 0·85 of the above figures, the accuracy of the result may be given as at least 1 in 6000 over the range of the pressures measured, if sufficient observations are taken and they are satisfactorily averaged.

The *maximum* divergence of any single observation from the mean curve was about ± 1·5 lb. per sq. inch for the August and October series and ± 0·5 lb. for the January set (*i.e.*, about 1 in 4000). From the discussion on p. 187, about various possible errors which affect the calibrations, a tolerance of not more than ± 1·6 lb. at 3000 lb. per sq. inch and 0·4 lb. at 500 lb. could be fixed. The maximum observational deviations do not lie outside this tolerance permitted for the standardization. Any other measurements of saturation pressure of steam lying outside these tolerances would require to be explained by some experimental error or different physical condition of the steam (unless some altogether unexpected source of error influences the present results).

The agreement with HOLBORN-HENNING'S and HOLBORN-BAUMANN'S data* up to 320° C. and with the results given by KEYES and SMITH up to the same temperature is satisfactory (*i.e.*, to 0·1 per cent.). Beyond 320° C. there are definite slight discrepancies (see figs. 10 and 11).

Before discussing the appreciable deviation from the results of HOLBORN and of KEYES and SMITH above 320° C., some measurements carried out in the neighbourhood of the critical point will be cited.

In Table XXIV are collected the results of experiments made at the highest pressures investigated. Up to a temperature of 374° C. behaviour was quite normal. Beyond this temperature it was possible to maintain the pressure steady at a given temperature and then, having changed the conditions, to return nearly to the same temperature again at the same pressure; but if the temperature were raised or flow reduced, the temperature would sometimes continue to rise although the pressure was diminished, which meant that the vapour was superheated. The general indications were that above 374° the steam behaved as a superheated vapour. The method was not adaptable to an exact determination of the critical point: once the critical temperature is passed in any portion of the system there is no longer latent heat to maintain constant conditions. It was found difficult to ascertain whether there was a definite small region of saturation, as has been suggested by the experiments of the late Professor H. L. CALLENDAR on the total heat of steam between 374° and 380·5° C. (from which the figures in column 7 of the table have been derived in order to provide a figure for possible wetness). At 374·5° it still seemed possible to repeat measurements of the pressure

* Their smoothed values corrected to I.C.T. temperature scale, see vol. iii, "International Critical Tables," p. 233.

TABLE XXIV.

Date.	Thermo-meter.	$t°$ C.	p. lb./sq. inch (L).	Volts on Boiler.	Flow, $g/sec.$	Cals.	$P-P_m$.	Remarks.
7.5.30	2	371·075	3098·1	125	3·0	124	+ 5·6	
6.5.30	2	371·154	3099·0	140	3·7	91	+ 3·6	80 per cent. wet.
7.10.30	4	371·388	3102·9	140	3·7	20	— 1·15	
20.8.30	4	371·371	3103·4	147	3·35	55	+ 0·05	
6.5.30	2	373·914	3203·0	148	3·6	29	+ 3·6	
7.10.30	4	374·001	3202·9	146	4·0	34	+ 0·20	
20.8.30	4	374·023	3203·4	143	3·85	70	— 0·10	
7.5.30	2	374·632	3228·1	139	3·0	72	+ 1·0	
6.5.30	2	374·621	3228·0	148	3·6	24	+ 1·3	
6.5.30	2	375·296	3243·0	144	3·5	25	—10·0	
7.10.30	4	375·31	3252·9	146	4·1	23	— 0·6	Raised flow, temp. fell.
8.10.30	4	376·12	3303·0	144	4·15	30	—	
7.10.30	4	376·45	3303·0	147	4·1	15	—	
6.5.30	2	376·628	3283·2	144	3·6	17	—	0·15° C. per 10 lb.
8.10.30	4	376·68	3303·0	144	3·75	30	—	0·18° C. per 10 lb.
8.10.30	4	383·51	3303·0	150	3·2	—	—	0·11° C. per 10 lb.

fairly accurately. The experiments at 376° indicated that the steam was probably entirely vapour, and this was certainly the case at 383° C.; the temperature observed for a given pressure in this region depends on the rate of flow instead of this rate merely altering the degree of wetness as in the case of saturated steam.

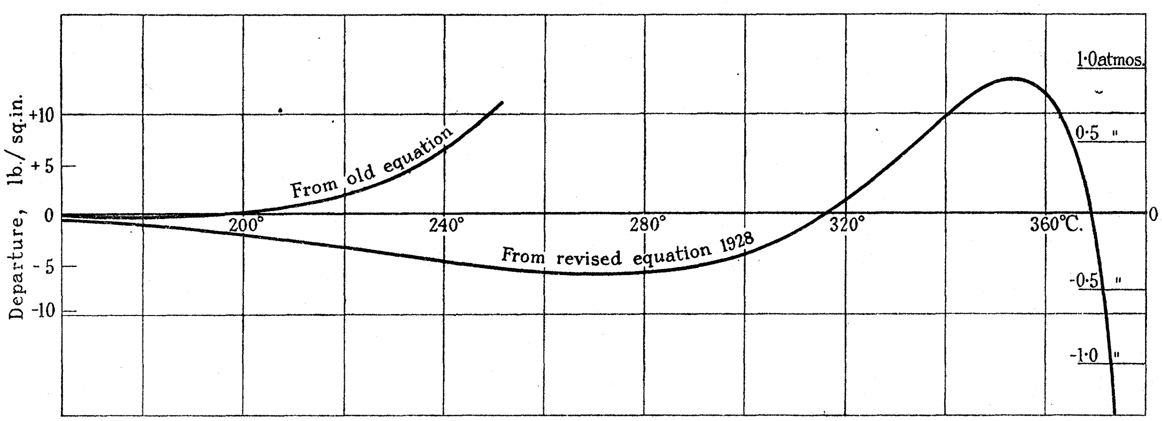

FIG. 14.—Departure from Callendar's vapour pressure equations.

HOLBORN and BAUMANN gave the critical temperature 374·0° C. (corrected to I.C.T. scale), but this corresponded to the last isothermal which showed any horizontal portion. The next isothermal was 374·56°, and did not appear to exhibit any region where $dp/dt = 0$. There was nothing to show that the critical point may not have lain somewhere between 374 and 375·5° C. according to their measurements. TRAUBE and

TEICHNER* gave 374·07 to 374·62 from direct observations (but the exact temperature scale is in doubt). KEYES and SMITH give the critical point from their isothermals to be 374·11° C.

In Table XXIV the May values are based on observations with thermometer No. 2, which provided results of less concordance than No. 4. They were reduced with I = − 0·12 and δ = 1·50, but if I = − 0·10 (which was an equally probable value from the ice point measurements) the differences in column 8 (pressure observed − pressure from the smoothed curve) would be 2 lb. per sq. inch less. These

TABLE XXV.—Temperature basis.

t° C.	(Normal) P_0 atmosphere.	HOLBORN and BAUMANN Departure.			KEYES and SMITH Departure.			Departure from CEDERBERG formula (atmosphere).
		Atmosphere.	lb. per sq. inch.	Equivalent. °C.	Atmosphere.	lb. per sq. inch.	°C.	
170	7·824	−0·006	−0·09	+0·032	−0·007	−0·10	+0·035	—
180	9·908	−0·012	−0·18	+0·054	−0·013	−0·19	+0·057	—
190	12·400	−0·014	−0·20	+0·050	−0·015	−0·22	+0·056	—
200	15·355	−0·014	−0·20	+0·042	−0·011	−0·16	+0·035	+0·004
210	18·835	−0·010	−0·15	+0·027	−0·016	−0·24	+0·044	+0·006
220	22·903	−0·015	−0·22	+0·034	−0·022	−0·32	+0·050	+0·014
230	27·621	−0·018	−0·26	+0·034	−0·030	−0·44	+0·058	+0·024
240	33·048	−0·021	−0·31	+0·036	−0·035	−0·51	+0·060	+0·038
250	39·252	−0·017	−0·25	+0·026	−0·032	−0·47	+0·048	+0·037
260	46·325	−0·028	−0·14	+0·012	−0·039	−0·57	+0·052	+0·055
270	54·345	−0·054	−0·79	+0·063	−0·055	−0·81	+0·065	+0·087
280	63·366	−0·071	−1·04	+0·074	−0·051	−0·75	+0·054	+0·102
290	73·471	−0·050	−0·74	+0·047	−0·021	−0·31	+0·020	+0·101
300	84·782	−0·003	−0·04	+0·002	+0·003	+0·04	−0·002	+0·110
310	97·414	−0·012	−0·18	+0·009	+0·009	+0·13	−0·007	+0·130
320	111·436	−0·008	−0·12	+0·006	+0·037	+0·54	−0·026	+0·147
330	126·946	+0·033	+0·48	−0·021	+0·114	+1·67	−0·070	+0·132
340	144·152	+0·044	+0·65	−0·025	+0·169	+2·48	−0·093	+0·171
350	163·224	−0·059	−0·87	+0·030	+0·183	+2·69	−0·092	+0·297
355	173·485	−0·160	−2·36	+0·077	+0·171	+2·52	−0·082	—
360	184·299	−0·227	−3·34	+0·102	+0·190	+2·79	−0·086	—
362	188·794	−0·270	−3·97	+0·118	+0·164	+2·41	−0·072	+0·508
364	193·392	−0·319	−4·69	+0·138	+0·126	+1·85	−0·054	—
366	198·092	−0·329	−4·84	+0·136	+0·079	+1·16	−0·033	—
368	202·912	−0·338	−4·97	+0·140	+0·007	+1·03	−0·029	—
370	207·839	−0·355	−5·22	+0·143	+0·035	+0·51	−0·019	+1·09
372	212·883	−0·351	−5·16	+0·138	−0·002	−0·03	+0·001	—
374	218·048	−0·382	−5·60	+0·145	+0·144	+2·12	−0·055	+1·50

* 'Ann. Physik,' vol. 13, p. 620 (1904).

TABLE XXVI.—Pressure Basis.

P_o lb./sq. inch (Standard).	$t°$ C.	Departure of other Values in lb./sq. inch (Standard).				
		HOLBORN and BAUMANN, 1908.	KEYES and SMITH, 1931.	CALLENDAR, 1928.	MOLLIER, 1927.	KEENAN, 1930.
100	164·328	—0·10	—0·12	+ 0·5	—	0
200	194·301	—0·20	—0·20	+ 1·7	—	— 0·1
300	214·061	—0·18	—0·37	+ 3·1	—	0
400	229·204	—0·26	—0·42	+ 4·0	—	0
500	241·670	—0·31	—0·50	+ 4·9	—	0
600	252·340	—0·27	—0·47	+ 5·6	—	+ 0·3
700	261·717	—0·42	—0·58	+ 5·9	—	+ 0·2
800	270·109	—0·80	—0·81	+ 6·0	—	+ 0·2
900	277·745	—1·00	—0·77	+ 5·8	—	— 0·1
1000	284·770	—0·74	—0·54	+ 5·6	—	+ 0·2
1200	297·342	—0·27	—0·05	+ 4·8	—	+ 0·7
1400	308·368	—0·16	+0·13	+ 2·0	+ 1·0	+ 1·0
1600	318·244	—0·16	—0·40	+ 1·0	+ 2·0	+ 1·2
1800	327·221	+0·30	+1·3	— 4·0	+ 2·0	+ 1·9
2000	335·447	+0·50	+2·0	— 7·3	+ 1·0	+ 2·9
2200	343·010	+0·10	+2·5	—11·0	0	+ 2·4
2400	350·042	—0·70	+2·7	—13·4	0	+ 2·3
2600	356·611	—2·60	+3·0	—13·2	— 1·0	+ 1·8
2800	362·756	—4·50	+2·1	—10·4	— 2·0	+ 1·2
3000	368·495	—5·0	+0·2	— 2·0	— 3·0	+ 1·5
3200	373·883	—5·5	+1·2	+20·0	— 4·5	+ 1·7

early measurements were, in fact, less reliable. Column 7 gives the difference between the total heat calculated from the CALLENDAR equation and the total heat observed. Columns 5 and 6 give figures for voltage on the boiler and flow to indicate the conditions under which the experiments were made.

The outcome of these measurements at high pressures is to show that there is fairly good agreement between the several investigations as to the value of the critical temperature 374–374·5, *i.e.*, within 0·5° C. The corresponding critical pressures are given on curve 1.

Returning now to such differences as there are between the present measurements, those of KEYES and SMITH, and of HOLBORN and BAUMANN respectively, KEYES and SMITH* have already discussed the discrepancy† between their results and those of HOLBORN and BAUMANN; they concluded that a difference in the temperature scale was not the cause of the error, but more likely a difference in the pressure as measured by the dead weight gauges. They considered that the Reichsanstalt gauge might have given slightly lower pressures as the pressures increased, owing to leakage of oil past

* "Mechanical Engineering," vol. 52, p. 126 (1930).

† at 360° C, 1 in 450.

the piston; the method of electrically testing the level in a mercury U tube placed between the gauge and the source of pressure being stated to avoid such a possible source of error.

In view of the substantial agreement at the highest pressures with KEYES and SMITH's results, those of HOLBORN and BAUMANN are probably slightly low in that region, due perhaps to some slight attack of the steel vessel (*cf.* p. 148). In the region 300 to 360° C., the present measurements provide a very fair mean of the former ones. Agreement with the Reichsanstalt values is good up to 350°, particularly when the individual measurements are considered (see curve 3, fig. 11), for a comparison of actual experimental results on the same basis, viz., departure from the empirical equation on p. 195 in lb. per sq. inch (standard). Inclusion of a doubtful value at 310·99° C. (5/11/09) influences the smoothed values of HOLBORN and BAUMANN and causes the somewhat higher pressures between 320 and 340° which will be noted on the curve 2, giving the comparison of the smoothed results.

KEYES and SMITH state that the maximum deviation of the observed values from their final smoothed values is 0·1 per cent. (in the region near 2500 lb. per sq. inch) and the present measurements are not different by more than about 0·1 per cent. from their final figures. At the lower pressures the present measurements are consistently higher (about 0·2 lb. per sq. inch) than those of HOLBORN and BAUMANN and of KEYES and SMITH, which agree in that region, but they are within the error of those measurements. Although reduction of the standard of pressure to that of the N.P.L. gauge would partly remove this small difference, at the same time reducing all the saturation pressures throughout the range by 1 part in 2500, it is not thought that there is justification for such alteration so far as the present investigation is concerned. It can, perhaps, be taken into account when considering a mean of all the separate measurements by different observers.* Greater refinement of the present experimental

* [*Footnote added October* 2, 1932.—The values given in Table XIX below 200° C. were obtained using the Crosby gauge direct, and have not the accuracy of the other measurements, because of the uncertainties introduced by the arrangements for supporting the steelyard. Observations have since been collected, using the differential gauge, the bottom weight having been removed to render it possible to measure smaller pressures. All the temperature and pressure constants were verified, and two independent thermometers used to measure the temperature at each pressure. The following results were obtained:

Date.	Pressure lb. per sq. in. (normal).	T° C.	$P - P_m$ lb. per sq. in.
21·7·32 } 25·7·32 }	100·00	164·310	+0·05
26·7·32	150·00	181·318	−0·09
26·7·32 } 29·7·32 }	200·00	194·317	−0·09
2·8·32	250·00	204·964	−0·12
2·8.32	300·00	214·056	+0·08

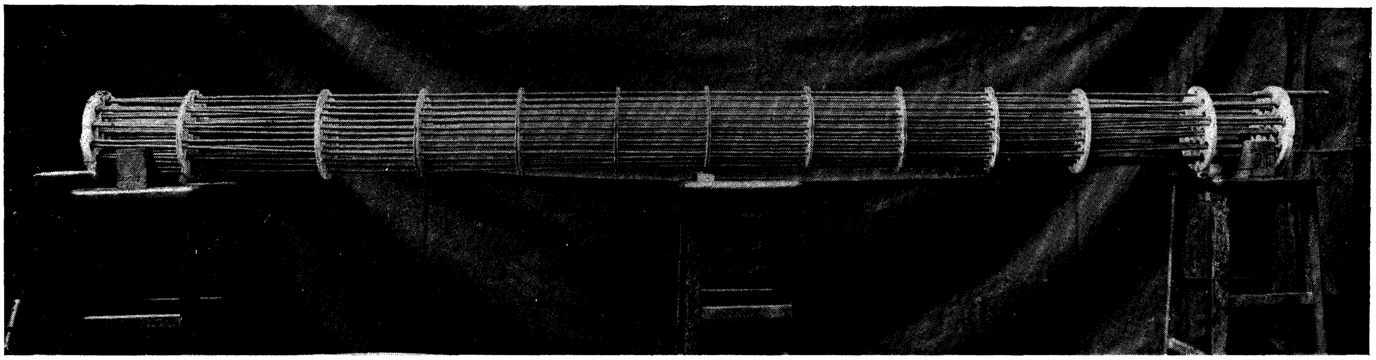

FIG. 15.—Monel Metal Boiler.

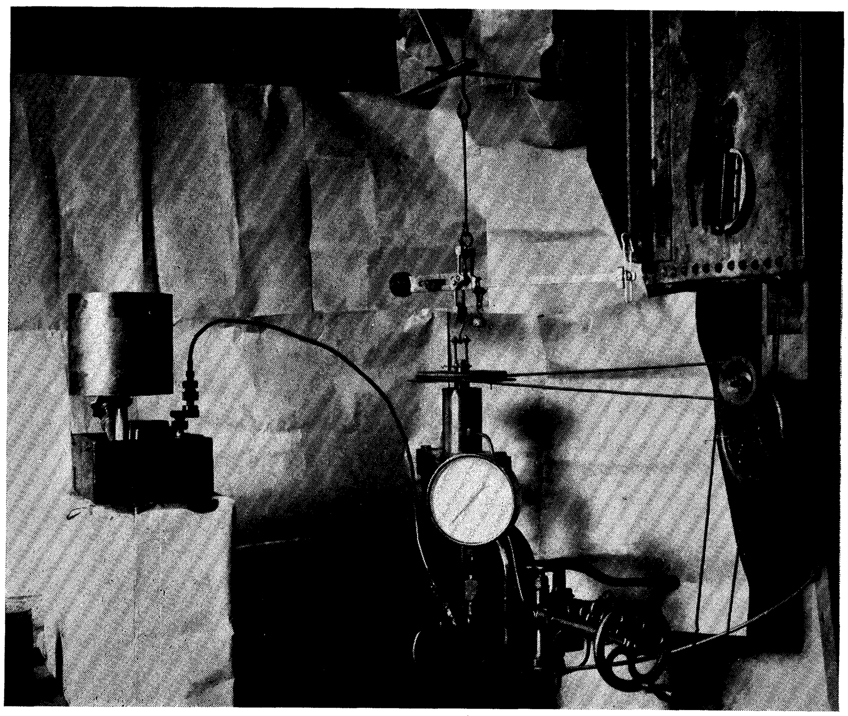

FIG. 16.—Arrangement of Pressure Gauge, Showing Cylinder and Steel Yard.

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results is hardly possible: the accuracy has been pushed as far as possible with the apparatus available.

The outcome of these measurements is that one thermodynamical property of steam—the saturation pressure—is now capable of being fixed within narrow limits of error throughout the whole temperature range to the critical point and the present tolerances allowed for can be diminished.

This work has been carried out with funds provided by the British Electrical and Allied Industries Research Association. We are greatly indebted to the members of the Turbine Committee for their support and encouragement. We take the opportunity of thanking various friends (Mr. A. R. UBBELOHDE and Professor R. H. FOWLER, F.R.S., and others) for their help in clearing up various little difficulties.

Summary.

(*a*) As a stage in the systematization of the thermodynamic properties of steam, the accurate determination of the saturation pressures has been carried out by a "dynamic" method from 160° C. to the critical point 374° C.

(*b*) The methods of temperature and pressure measurement are described, and the errors affecting calibration of the resistance thermometers and the dead weight pressure gauge discussed.

(*c*) The saturation pressures are given in Tables for every 5° C. in lb. per sq. inch and atmospheres, together with values for *dp/dt*. The measurements are probably accurate to about 1 in 6000. The errors of the actual measurement lie within the errors of the standardization of the temperature and pressure measurements: consideration of the latter suggests a tolerance of about 1 in 1500.

(*d*) The results are in general agreement with the measurements of HOLBORN and BAUMANN and of KEYES and SMITH, who used "static" methods, particularly with the latter, at the highest pressures.

(*e*) Measurements have been made in the neighbourhood of the critical point, which lies between 374 and 374·5° C., as found by other observers.

Below 200° C. the values, though in better agreement, are still definitely about 0·1 lb. per sq. inch higher than the mean of previous results (H. and B. and K. and S.). The method is not quite suitable for measurements in this region below 200° C. where the temperature changes more rapidly for a small change in pressure; the accuracy is correspondingly less. The values obtained were independent of the rate of flow of the steam. Other points at 700 lb. and at 1400 lb. per sq. inch on the saturation pressure curve have also been carefully rechecked, and show agreement with the results given in this paper, within 0·01° C. in spite of the thermometer circuit having been altered.]

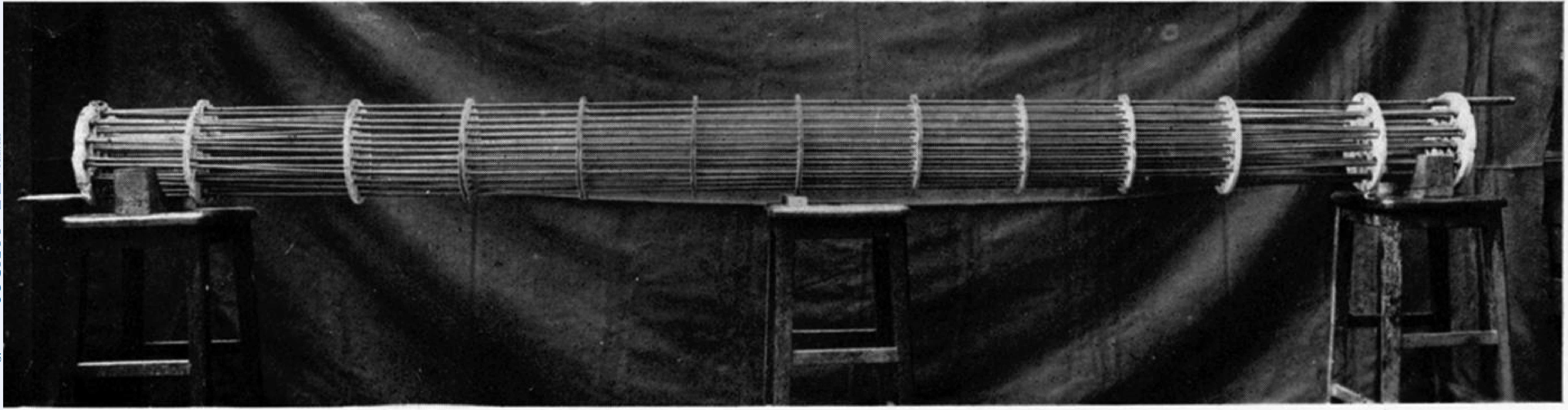
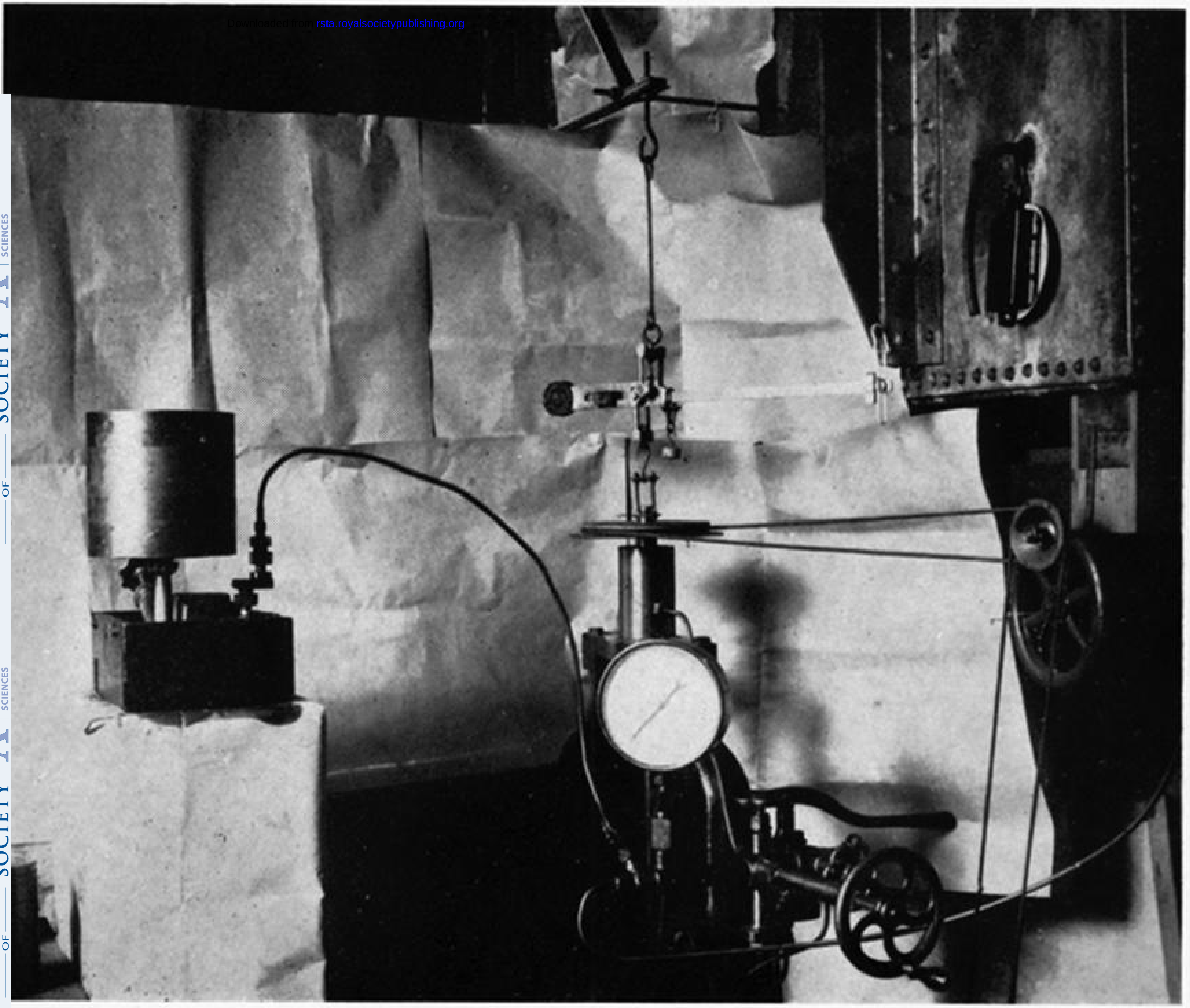


FIG. 15.—Monel Metal Boiler.



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IG. 16.—Arrangement of Pressure Gauge, Showing Cylinder and Steel Yard.