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On the Determination of Some Boiling and Freezing Points by means of the Platinum Thermometer

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II. *On the Determination of some Boiling and Freezing Points by means of the Platinum Thermometer.*

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[PLATES 4, 5.]

1. CALLENDAR, in his exhaustive comparison of the platinum and air thermometers ('Phil. Trans.,' A, 1887), suggested the introduction of the term "platinum temperature" (denoted by *pt*).

Pt is obtained by assuming the temperature to vary as the resistance. Thus

$$pt = \frac{R - R_0}{R_{100} - R_0} \times 100.$$

A curve is then constructed, having $t - pt$ (t being temperature as indicated by the air thermometer) as the ordinate and *pt* as abscissa. I have adopted this method of expressing my results throughout this paper.

If CALLENDAR'S conclusion is correct, viz., that whatever be the coefficient of increase in resistance from 0° to 100° of the platinum wire used, then for the same t all wires will give the same *pt*, the difficulty of determining high temperatures with accuracy has been overcome.

Unfortunately my experiments have driven me to the conclusion that the *pt* given by platinum thermometers made from different samples of wire differ considerably for the same value of t. However, in my thermometers the wire throughout is in contact with glass or asbestos, or both, and its behaviour is probably much influenced thereby. In CALLENDAR'S thermometers the coil was in contact with the glass only at its extremities.*

Later on I give particulars of the thermometers used in these experiments.

I was anxious to adopt a form of thermometer which would (1) quickly assume the surrounding temperature, (2) occupy little space, and (3) bear a reasonable amount of

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* See note in Appendix (p. 70).

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rough usage. I believe that the thermometers referred to hereafter as E, F, and G fulfil these requirements.

2. I proposed to graduate the thermometers by exposing them to the vapour of certain substances under known pressures, the substances selected being as follows :—

TABLE I.

	Temperature.	Authority.	References.
(1) *Melting ice*	0°		
(2) *Steam at* 760 *mm.*	100		
(3) Aniline at 760 mm.* . . .	184·41	RAMSAY .	'Chem. Soc. Journ.,' vol. 47
(4) *Naphthalene at* 760 *mm.* . .	218·06	CRAFTS .	'Paris Soc. Chimique Bull.,' vol. 39
(5) Methyl salicylate at 760 mm.	222·88	RAMSAY .	'Chem. Soc. Journ.,' vol. 47
(6) *Benzophenone at* 760 *mm.* .	306·08	CRAFTS .	'Paris Soc. Chimique Bull.,' vol. 39
(7) Mercury at 760 mm. . . .	357·25 358·2	REGNAULT RAMSAY	'Mémoires l'Académie des Sciences,' vol. 26 'Chem. Soc. Journ.,' vol. 47
(8) *Sulphur at* 760 *mm.* . . .	448·38	REGNAULT	'Mémoires l'Académie des Sciences,' vol. 26

The change in temperature of the vapour of these substances due to changes in pressure appeared also to have been satisfactorily determined.

In the following pages I endeavour to show how the adoption of the numbers given for (1), (2), (4), (6), and (8) in the above table was forced upon me to the exclusion of the others.

The Apparatus Used.†

3. The resistance box (of the four dial pattern) was one constructed for me by Messrs. ELLIOTT in 1886. I have had occasion to test this box severely during some investigations on which I have been engaged for the last two years, and I believe it to be a most reliable instrument. Messrs. ELLIOTT were good enough to ascertain for me the coefficient of alteration per 1° C. for each set of dials. Although all the wire used in the box was from one casting, these coefficients differ slightly and are as follows :—

TABLE II.

Unit dial = ·000413 per 1° C.
10 ohm ,, = ·003733 ,,
100 ,, ,, = ·03773 ,,
1000 ,, ,, = ·38036 ,,
} box right at 17°.

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* Most of these substances were suggested to me by Messrs. HEYCOCK and NEVILLE. I wish that I could adequately express my indebtedness to these gentlemen, who have not only assisted me in my observations, but have freely placed at my disposal the apparatus used by them in their investigations on the melting point of alloys.

† All the apparatus used in these experiments, with the exception of the galvanometer and resistance box, was constructed by Mr. F. THOMAS, of Jesus Lane, Cambridge, and, like all other work that he has done for me, leaves nothing to be desired either in design or workmanship.

The accuracy of the coefficients will best be understood by reference to the Tables in the Appendix (pp. 65–69).

The chief difficulty has been that of ascertaining the real temperature of the coils, for the mere suspension of a thermometer within the box afforded but little information as to the temperature of the wires, unless the temperature of the box was steady.

The rapid changes of temperature in the air of the room in which the experiments were conducted made it necessary to place the resistance box, etc., in an adjoining room, which, unfortunately, had only an unprotected iron roof. Attempts were made to keep the temperature constant by means of a gas stove, but with little success.

A large copper bath with double walls was constructed, the bottom of the resistance box was cut out, and the top, with the exception of openings for the dials, was covered with a board, the under part of which was lined with swansdown. A gas jet beneath the bath was controlled by a mercury gas regulator of the usual form, but having a very large bulb about a half-inch broad and eight inches long, reaching from nearly the top to the bottom of the bath. This maintained the bath night and day at a temperature which was never observed to vary by ·1°.

However, the radiation from the top of the box could not be prevented, and during some of the frosty nights near the end of March its temperature fell as low 16°.

The thermometer in the box was coated with paraffin of about the same thickness as that on the coils. Later, Messrs. ELLIOTT constructed for me a bobbin in all respects similar to those in the box, and the thermometer was placed with its bulb in the centre of this coil. It appeared probable, therefore, that its rate of change would be about equal to that of the bobbin.

The observations made after March 21st, from which date the regulator was constantly at work, showed a greater agreement than those taken before that date, and as the greatest divergence from the normal temperature (17°) was ·8°, the residual errors due to temperature could not in any case be very great.

4. The galvanometer was a high-resistance one, made for me by the Scientific Instrument Company. Its total resistance was between 8000 and 9000 ohms; however, its coils being connected in parallel arc, its resistance was about 2000 ohms. Although this was far too high a resistance, as compared with the other resistances of the bridge, I considered it advisable to use it, an important consideration being that any thermal effects were unlikely to affect it. The galvanometer was nearly dead beat, and was so arranged as to be extremely sensitive. The scale was about two yards from the galvanometer, and thus a very small deflection was easily noted.*

For some time commutators were used, all connections reversed, and the observations repeated to eliminate the effect of thermal currents. In no case, however, could any such effect be traced, so that in my later experiments I only reversed the connections occasionally.

A double contact key of the usual kind was used.

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* A low-resistance galvanometer was tried and rejected.

It was found necessary not only to place the galvanometer on an insulating stand, but also the batteries and key. All connecting wires were run through india-rubber or glass tubes. Until this was done the galvanometer showed a permanent deflection after the wires were attached to the batteries. The whereabouts of this leakage I never discovered.

5. The apparatus was placed in rooms adjoining the Sidney Laboratory, and I was much troubled by the vibration caused by the traffic. In fact it was only possible to take some of the observations (such as those in which I wished to trace the process of surfusion during the freezing of metals) late at night. One great difficulty I met with at the outset, *i.e.*, the warming of the thermometer-coil by the current used when determining its resistance, and since it was necessary, during some of the observations on surfusion, to maintain the current for several seconds at a time, the point was one of considerable importance.

Callendar mentions that he used six Leclanché cells without any trouble of this kind. I found it impossible to use two unless I lowered the current by introducing extra battery resistance. The effect was clearly traceable if too strong a current was used. If the arms of the bridge were in equilibrium and the key held down, the spot would gradually slide away in the direction indicating a steady increase in the resistance of the coil. A few experiments showed that this rate of increase was nearly as the square of the current, thus indicating the cause. Again, the stouter the wire in the thermometer, the greater the E.M.F. that could be used without producing this effect. For instance, the thermometer A, in steam under 755 mm., gave a reading of 14·068 when used with one Leclanché cell, and of 14·080 when used with two Leclanché cells. The same difference was observable throughout all the readings of A, B, and C, at different temperatures. This effect was particularly marked in E* (whose coil was formed of exceedingly fine wire), particulars of which I have given later on.

I found it convenient in my later experiments to work with a large number of cells, introducing into the battery-circuit sufficient resistance to reduce the current to harmless dimensions.

On the determination of the "fixed points."

6. *Freezing-point of water.* The method described by Guillaume (see 'Traité Pratique de la Thermométrie de Précision') was adopted with this addition, that the vessel filled with finely powdered ice was surrounded by a larger one packed with large lumps. In some of the experiments the ice in the inner vessel was drained, in others, a mixture of ice and water was used. Snow was also tried (see Table XVIII.). In all cases the ice had been thoroughly washed with distilled water.

Boiling-points. A hypsometer of the usual form was used for water. The gauge connected with the instrument showed that the internal pressure rarely exceeded the external by more than 1 mm. of water.

The remaining boiling points were all determined in glass vessels. Round bottomed, long necked flasks, having a capacity of about 2½ litres, were used for aniline, naphthalene, and sulphur; somewhat smaller ones for the remaining substances. At about 1½″ from the top, a side tube was fitted into the neck, and through this tube the vapours passed into the condenser. The bulb of the thermometer just projected into the body of the flask (in no case touching the liquid), and the vapour on its way to the condenser had to pass the whole of the immersed portion of the thermometer. The top of the flask and the mouth of the condenser were closed with cotton wool or asbestos cloth, in which the vapours condensed, while the risk of increased internal pressure was diminished.

7. The difficulty with regard to super-heating was overcome as follows: An oven was built up with asbestos cards and in the roof a circular hole was cut in which the base of the flask was placed. The surface of the liquid in the flask was always maintained at a higher level than the rim of this hole, and it was, therefore, impossible for the flame to play on any portion of the glass above the liquid. To prevent radiation through the liquid a smoky flame was used until the exposed portion of the flask was covered with carbon.

Asbestos cloth was then wound round the flask, completely covering it from the roof of the oven to the exit tube, and on removing the cloth after distillation no signs of condensation were observable on the sides of the flask. From the time that these precautions were taken no indications of super-heating presented themselves, the temperature during distillation being independent of the size of the flame.

Every endeavour was made to secure pure specimens of the selected substances.

In most cases the observations were repeated from the commencement of distillation until about two-thirds of the sample had distilled over, the process was, therefore, practically, one of fractional distillation. Occasionally the distillate was separated after about half the sample had come over, and the residue and distillate experimented upon separately; and in one or two cases the process was repeated on the portions thus separated.

The only substances which showed slight signs of change when thus treated were methyl salicylate and triphenyl methane.

It is worthy of notice that the same specimens of naphthalene and benzophenone were boiled or distilled between twenty and thirty times, and yet their boiling-points showed no signs of change—a strong argument in favour of the purity of the samples, and of their adoption for the determination of fixed points.

As large a quantity as possible was used in each case.*

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* Crafts, in the paper referred to in Table I., writes as follows:—" . . . La naphtaline du commerce ne varie plus de 0°·1 dans son point d'ébullition quand elle a été purifiée, par une méthode quelconque, jusqu'à ce que la substance fonde à 79°·9–79°·6. La même chose est vraie pour la benzophénone préparée par l'oxychlorure de carbone, quand son point de fusion est amené par une purification convenable à 48°–47°·7. On voit que des limites considérables peuvent être tolérées dans

The aniline, naphthalene, and sulphur (when liquid) measured nearly 1 litre; the mercury about 200 c.c. (2600 grms.); the quantities of benzophenone and methyl salicylate were rather smaller. In those cases in which different specimens were tried, the results were the same (see Table XIV.).

Comparison of readings taken under different pressures.

8. If R_t be the resistance at a temperature $t°$ C.,

then $\frac{R_{t_2} - R_{t_1}}{t_2 - t_1}$ will give the approximate increase per 1° C. at a temperature $\frac{1}{2}(t_1 + t_2)$.

The accuracy of the result depends of course on the nearness of t_1 and t_2.

Observing the pressure (during my first series of observations with each thermometer) at the time of the determination of the B.P. of water, naphthalene, benzophenone, and sulphur, I was able (from the data supplied by CRAFTS and REGNAULT) to determine the actual temperatures t_1, t_2, &c., corresponding to observed resistances R_1, R_2, &c. The resistance at 0° being also known, the approximate increase in resistance per 1° at temperatures $\frac{1}{2}(t_0 + t_1)$, $\frac{1}{2}(t_1 + t_2)$, &c., could be deduced.

After plotting the points thus obtained I was enabled to determine the approximate increase per 1° at intermediate points.

On examination of the change in temperature due to increased pressure as given by different observers (in the case of the selected substances) it was evident that however they might differ in regard to the actual temperature, they were in practical agreement as to the *change* over a range of about 30 mm. above and below 760 mm. For instance, both REGNAULT and RAMSAY agree in giving ·0760° per 1 mm. as the change in mercury vapour through the above range, although they differ by nearly 1° in the actual temperature.*

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les points de fusion sans que le point d'ébullition change, ou, en d'autres mots, des impuretés font varier plus vite le point de fusion que le point d'ébullition; et cette qualité, qui donne un moyen sûr de reconnaître la pureté, est indispensable pour l'usage en question."

On May 11th I determined the melting-points of the samples of naphthalene and benzophenone used during the experiments. The thermometer used was a small sensitive one of GEISSLER'S.

The results were as follows:—

Benzophenone.

Melting-point of a portion which had not been boiled or distilled	(1)	47·8.
	(2)	47·9.
Melting-point of a portion which had been used throughout all the experiments		47·8.

Naphthalene.

Melting-point of a portion which had not been boiled or distilled	79·7.
Melting-point of a portion which had been used throughout all the experiments .	79·65.

* A considerable variation in this coefficient would have but a small effect on the fifth figure of the

Tables were thus constructed, giving in each case the change in resistance of the wire for a difference of 1 mm. pressure in the vapour of the substance.

I give the tables used for comparison of observations with E, F, and G; similar ones having been constructed for the other thermometers* :—

TABLE III.

Substance, vapour of.	Temperature of vapour at 760 mm.	Difference in temperature due to difference of 1 mm. in pressure (K).	Increase in resistance due to an increase of 1° in temperature.			± for each 1 mm. difference in pressure (K × I).		
			I_E	I_F	I_G	E	F	G
Water	100°	·0375°	·00913	·01481	·01558	·00034	·00056	·00058
Aniline	184·4	·053	·00884	·01432	·01508	·00047	·00076	·00080
†Naphthalene . .	218·06	·058	·00871	·01410	·01486	·00051	·00081	·00086
Methyl salicylate.	222·88	·057	·00870	·01406	·01482	·00050	·00080	·00084
†Benzophenone . .	306·08	·0636	·00834	·01343	·01420	·00053	·00085	·00090
Mercury . . .	357·25	·076	·00810	·01298	·01377	·00062	·00099	·00105
Sulphur . . .	448·34	·082	·00759	·01211	·01293	·00062	·00099	·00106

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resistance. For example, if ·0780 be taken it would produce a change of ·0106 per 10 mm. in the resistance of G instead of ·0105, the number obtained by assuming it to be ·0760.

* Subsequent experiments have shown that the approximate corrections thus obtained are sufficiently accurate.

For example, the resistance of G at 200° C. is 8·0639,

and ,, ,, ,, 0° C. is 4·9543,

$$\therefore \frac{8{\cdot}0639 - 4{\cdot}9543}{200} = \text{approximate increase per } 1° \text{ at } 100° = {\cdot}\mathbf{0155}.$$

Now (see Table XIX., experiments 6, 7, and 14 and 15) the true resistance

of G in steam under 746·8 mm. = 6·5321,

,, ,, ,, 772 ,, = 6·5469,

∴ Difference for 25·2 mm. = ·0148.

Now the difference in temperature of steam at 746·8 and 772 is given by the accepted authorities as ·945°.

∴ Increase per ·945° = ·0148.

∴ ,, ,, 1° (at 100°) = **·0156**.

Here the result as obtained by experiment differs from the approximate result by only 1 in 156 over a range of 25·2 mm., which is the extreme variation in pressure met with during the experiments, and this difference would only cause a change of 1 in the fifth figure of R.

The value of $t_2 - t_1$ used in Table III. was in no case so large as 200 (greatest value 142·3), consequently the above is an extreme case.

The value given by Table III. for G at 100° = ·01558.

† CRAFTS gives the following formulæ for the boiling-points of these substances :—

$$\text{Naphthalene} \quad . \quad . \quad . \quad . \quad t = 218{\cdot}06 + \frac{H - 760}{17{\cdot}1},$$

$$\text{Benzophenone} \quad . \quad . \quad . \quad t = 306{\cdot}08 + \frac{H - 760}{15{\cdot}8}.$$

Freezing Points of Metals.

9. The apparatus used was similar to that described by Messrs. HEYCOCK and NEVILLE in their paper on the melting-point of alloys ('Chem. Soc. Trans.,' May, 1890). A large iron block, about 8 inches in height, had a circular hole about $1\frac{1}{8}$ inch in diameter, bored from the top to within 2 inches of the bottom.* The capacity for heat of this block was very great, and, therefore, its rate of alteration in temperature very slow. The block stood on a large FLETCHER'S burner and was surrounded by two circular burners, thus the heating effect was fairly uniform. A circular ring, having a slight spiral twist, and worked by a water-motor, moved rapidly up and down through the melted metal, stirring it thoroughly. Down the centre passed the thermometer, its lower end reaching nearly to the bottom of the hole.

The space above the melted metal was filled with paraffin, oxidation was thus prevented, and that portion of the rod of the stirrer which passed out of the metal during the ascent, kept at an even temperature.

It was found possible to use paraffin with all the metals employed, except zinc, although, in some cases, the "fuming" was excessive. Zinc was, in consequence, a difficult metal to work with.

I endeavoured to prevent oxidation and surface cooling by covering its surface with finely powdered charcoal. The result was not entirely satisfactory, and I found it impossible to prevent a certain amount of oxidation during the experiments with that metal. I do not know that this would affect the freezing-point (unless the oxide was soluble in the molten metal), but it prevented any surfusion. The temperature throughout the process of solidification was, however, very constant, and could be determined without difficulty.

From 400 to 600 grms. of metal were used in each case, and as far as time permitted, I tested samples from different makers. It appears to be fairly established that, with certain rare exceptions, the presence of any foreign metal will be shown by the lowering of the freezing-point; therefore, when different samples give different freezing-points, I have adopted the higher.† The phenomenon of surfusion was, in some cases, very marked. When taking observations, the key was held down and the resistance of the box lowered as the metal cooled, so as to maintain the spot in its zero position. When solidification commenced, the process had to be reversed, and the resistance rapidly increased; for example, in one experiment on Sn the resistance of E fell to 5·1330, and then rapidly rose to 5·1578. When making these observations I was in a different room from that in which the metal was cooling, and this rise was my only indication. It was, however, unmistakable, and, after the first few trials, easily measured. The stirrer was usually arrested by the solidification of the

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* The surface of this hole and the stirrer were coated with Fe_3O_4 by raising the block to a high temperature and passing steam into the hole for several hours.

† See freezing-point of Pb, Table XV.

metal within 30 to 60 seconds after the rise. In those cases where surfusion was absent, the cessation of cooling was sufficiently marked to allow of accurate determination.

Thermometers A, B, C, and D.

10. The platinum wire used for A, B, and C had a diameter of ·005 inch. Glass tubing was drawn out until of just sufficient bore to admit this wire, and was then cut into lengths of about 1¼ inch. The wire was then threaded through these pieces, the ends of which were heated until they adhered to the wire. About two yards of the platinum wire were thus covered, and a stout silver wire was hard-soldered on to each end of it. One of these pieces of silver wire was passed through a fine glass tube about 18 inches long, placed within a second glass tube of about ¼ inch in diameter; and the second silver wire was passed up the annular space between these two tubes. The outer tube was widened at its lower end to ½ inch external diameter, the glass-covered platinum wire was folded up at the junctions of the glass threads and thrust into this wider portion, which was then fused at the open end. The bulb thus formed was heated to a red heat, and allowed to cool slowly. The whole apparatus had much the size and appearance of a sensitive mercury thermometer, with a bulb about 1⅜ inch long.

The upper end was fixed to a small board, and the ends of the projecting silver wires were soldered to two heavy brass connecting screws, insulated by ebonite.

The same sample of platinum wire was used in all three.

The silver wire in A was "standard silver," in B and C pure silver.

The total resistance of the silver wires was as follows:—

A = ·100; B = ·087; C = ·101 ohm at 17° C.

From the connecting-screws well-insulated stout copper wires ran to the resistance box, the same wires being used in all experiments with these thermometers. The resistance of the wires and the connecting-screws was ·089 ohm. The external resistance (meaning thereby all resistance except that of the platinum wire in the bulb) was of no consequence provided that it remained constant, nor would its variation be of any consequence provided that it was regular, which would probably be the case if the same portion of the stem was always immersed.

I scarcely anticipated that my measurements would be sufficiently exact to render appreciable the alteration in resistance due to different immersions of the stem, the coefficient of increase of silver being less than that of platinum, and the external resistance only about $\frac{1}{150}$ of the coil. Herein I was mistaken, and I afterwards ascertained that the consequent error might amount, in some cases, to nearly ·2° C.*

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* For example:—*Thermometer B; Vapour of H_2O; Barometer at 770 mm.*

Bulb only just within hypsometer . . . . Resistance = 17·467
,, and 14 in. of stem within hypsometer . . . . ,, = 17·477

This was an extreme case, and here the difference = ·01 ohm = ·2°, *nearly.*

However, in nearly all my experiments with these thermometers the same fraction of the stem was immersed, and the error due to this cause inappreciable. This difficulty could, of course, be met by using stouter silver wires.

A large number of determinations were performed with thermometers A, B, and C, and they have remained quite constant although roughly used. I have compared them with several large bulb mercury thermometers, and find that they assume the surrounding temperature more rapidly than some and less rapidly than others.

To illustrate the close correspondence of the experimental results, and also the accuracy of the corrections used for the variations in the temperature of the box and the height of the barometer, I extract the following page from my note-book. (The resistances in all cases include the exterior resistance.)

TABLE IV.—Resistance of A at Temperature 100° C.

Date.	Observed resistance.	Temperature of coils.	Resistance after correction for temperature of coils.	Barometer.	Correction for barometer.	Resistance at 100°.
		°		mm.		
Jan. 25th, 1890	18·585	16·5	18·582	749·5	+ ·017	18·599
„ „ „	18·584	16·5	18·581	749·5	+ ·017	18·598
„ 27th „	18·622	14·5	18·605	762·4	— ·004	18·601
„ „ „	18·623	14·5	18·606	762·4	— ·004	18·602
„ 28th „	18·628	12·2	18·594	755·0	+ ·008	18·602
„ 29th „	18·649	12·4	18·617	771·0	— ·018	18·599

Although I afterwards discarded this form of thermometer, I have described it fully, because it is inexpensive, easily made, and may be used in all cases where an accuracy bounded by 1° C. is sufficient.

11. The results obtained from these thermometers are as follows (I consider it unnecessary to give the records of individual experiments) :—

TABLE V.

In all cases one Leclanché cell was used, and the arms of the bridge $\frac{1000}{10}$.	Resistances of A, B, C, after correction for temperature of coils and height of barometer.		
	A.	B.	C.
Melting ice	14·068	13·202	14·552
B.P. of H_2O	18·601	17·462	19·247
„ aniline	22·283	20·918	23·060
„ naphthalene	23·720	22·272	24·544
„ methyl salicylate	23·934	22·475	24·770
„ benzophenone	27·389	25·716	28·344
„ mercury	29·452	27·653	30·480
„ sulphur	32·915	30·914	34·067

Denoting the platinum temperatures by pt_a, pt_b, and pt_c, respectively, then

$$pt_a = \frac{R - 14{\cdot}068}{4{\cdot}533}\,; \qquad pt_b = \frac{R - 13{\cdot}202}{4{\cdot}260}\,; \qquad pt_c = \frac{R - 14{\cdot}552}{4{\cdot}695}\,.$$

Table V. gives us the following results :—

TABLE VI.*

	pt_a.	pt_b.	pt_c.	Assuming values of t given in Table I., then		
				$t - pt_a$	$t - pt_b$	$t - pt_c$
B.P. (at 760 mm.) aniline	181·19	181·12	181·18	3·22	3·29	3·23
,, ,, naphthalene . .	212·88	212·91	212·84	5·18	5·15	5·22
,, ,, methyl salicylate	217·60	217·67	217·64	5·28	5·21	5·24
,, ,, benzophenone .	293·81	293·76	293·78	12·27	12·32	12·30
,, ,, mercury . . .	339·31	339·26	339·27	17·94	17·99	17·98
,, ,, sulphur . . .	415·68	415·76	415·66	32·70	32·62	32·72

12. On plotting these numbers it was evident that they were not as concordant as might have been expected, considering the close agreement in the experimental results. No difficulty was experienced in drawing a smooth curve through the points determined from melting ice, steam, naphthalene, benzophenone, and sulphur, but the curves thus drawn passed *above* mercury (REGNAULT) and methyl salicylate (RAMSAY), but *below* aniline (RAMSAY).

Again, RAMSAY's boiling-point for mercury (358·2) gave a value of $t - pt$, which fell considerably *above* the curves. Further, it was found impossible to draw a consistent curve through the points obtained from melting ice, steam, aniline, methyl salicylate, and mercury, even if the remaining points were disregarded.

The experiments were repeated with great care, and all the precautions mentioned in Sections 3 to 7 were adopted (with the exception of the thermo-regulator to the resistance box). The results, however, were practically the same.

An equation of the form $y = ax + bx^2 + cx^3 + dx^4$ was taken (where y, the ordinate, $= t - pt$, and $x = pt$), the values of y and x given by the boiling-points of water, naphthalene, benzophenone, and sulphur were substituted, and some intermediate points then deduced.

Curves A, B, and C (Plate 4) were then drawn on a large scale, the vertical spaces (on the original plan) representing ·1° and the horizontal ·5°.†

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* All these thermometers were constructed from the same sample of platinum wire and glass, and the resistances of the coils are nearly equal. The results are sufficiently close to lead to the conclusion that the *pt* is the same for A, B and C at any given temperature, the greatest variation from the mean *pt* being ·06°.

† By means of curve A the mercury thermometers used by Messrs. HEYCOCK and NEVILLE were

The values of the boiling-points of the remaining substances, as obtained from curves A, B, and C, are as follows:—

TABLE VII.

	Aniline.			Methyl salicylate.			Mercury.		
	A.	B.	C.	A.	B.	C.	A.	B.	C.
pt	181·19	181·12	181·18	217·60	217·67	217·64	339·31	339·26	339·27
$t - pt$ . . .	3·13	3·15	3·11	5·48	5·45	5·52	18·30	18·33	18·38
t	184·32	184·27	184·29	223·08	223·12	223·16	357·61	357·59	357·65
Mean t . .	184·29			223·12			357·62		

On comparing these curves with one plotted from the numbers given by CALLENDAR ('Phil. Trans.,' A, 1887), it was evident that they differed considerably: the rise is steeper, and $t - pt$ is invariably a larger quantity. This difference may be in some measure due to the behaviour of the glass with which the wire is in contact throughout. If, however, this is the case, it will not affect the temperatures deduced from the curve, provided that the resistance remains constant for each temperature. I was anxious to see if a thermometer constructed from a different sample of wire would give the same platinum temperatures, and, if these differed, to ascertain if the resulting values of t differed.

13. *Thermometer D.*—The platinum wire used was ·007 inch diameter. No silver or solder was used within the instrument. A thick rod of platinum ran through the inner tube, and down the annular space between the two glass tubes was passed a tube of platinum foil, terminating about $1\frac{1}{2}$ inch from the lower end. One end of the fine wire was welded to the rod, and the wire was then wound as a spiral round the lower $1\frac{1}{4}$ inch of the inner tube. This spiral was then entirely covered by fine threads of glass (laid lengthwise), and over them the wire was wound downwards to the end. This process was repeated until five layers had been formed, and the end of the coil was then welded to the platinum tube. The glass bulb enclosing the coils was about the same size as in A, B, and C. This coil contained nearly 9 feet of wire.

Very few experiments were performed with this thermometer as, owing to the large mass of glass in the bulb, it was very slow in acquiring the temperature of the surrounding vapour. I, however, obtained one reading at all the previous points—with the exception of methyl salicylate.

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graduated. I believe that they have given an account of the method adopted in their paper ('Chem. Soc. Trans.,' May, 1890).

TABLE VIII.—Thermometer D.

	Resistance after correction for temperature of coils and height of barometer.	pt_d.	$t - pt_d$.
Melting ice	14·953	0	0
B.P. of H_2O	19·501	100	0
,, aniline	23·155	180·34	. .
,, naphthalene . . .	24·588	211·85	6·21
,, benzophenone . .	28·220	291·71	14·37
,, mercury	30·248	336·30	. .
,, sulphur	33·653	411·17	37·21

Plotting the same 5 points as before, and deducing from the curve (curve D) the remaining temperatures, we get

Aniline . . . . . . 180·34 + 3·87 = 184°·21
Mercury . . . . . . 336·30 + 21·24 = 357°·54.

Curve D (Plate 4) follows quite a different path from Curves A, B, and C (the platinum temperature of the vapour of S differing by as much as 4°·5), yet the values of *t*, deduced from the curves, differ by less than ·1°. It must be remembered that the above represent solitary determinations, and, therefore, the resulting values are of little importance in themselves. Nevertheless, they point to the conclusions (see Curves A, B, C, and D) :—

(1.) That the platinum temperatures obtained by using different samples of wire, differently arranged, are not equal.

(2.) That the "fixed points" (viz., those obtained by assuming previous determinations of melting ice, steam, naphthalene, benzophenone, and sulphur) give, in each case, a consistent curve.

(3.) That the temperatures of the vapour of aniline, methyl salicylate, and mercury, deduced from these curves, are practically identical, but differ slightly from previous determinations.

These conclusions were borne out by subsequent experiments.

14. A different form of thermometer was now adopted.

I obtained from Messrs. JOHNSON and MATTHEY a thick platinum tube, $\frac{1}{16}$th inch internal diameter, and $16\frac{1}{2}$ inches long, having a resistance of about ·04 ohm. Through this a hard glass tube was passed, projecting $1\frac{3}{4}$ inch at one end. Round this projecting portion was wound a slip of asbestos paper* (obtained from BELL

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* The non-conductivity of this asbestos paper was exposed to severe tests. As compared with glass, it proved much the better insulator. A tube formed of it was placed within a hard glass tube, and two tightly-fitting wires thrust within until the ends were as close as possible without contact. This was placed in the circuit between four Leclanché cells and the galvanometer. It was then slowly heated to a bright red heat, but no deflection was observed. If, however, the wires were allowed to touch the glass, the deflection was considerable.

and Co.) until the thickness of the roll of paper was equal to that of the platinum tube.

On this roll of asbestos the wire was wound, one end being welded to a projecting slip on the lower end of the platinum tube, the other to a bundle of thick platinum wires passing down the centre glass tube.

The coil consisted of about thirty turns. The coil and the asbestos were then heated to a red heat and allowed to cool gradually. A thin hard glass tube, closed at the lower end, was then slipped over the whole. The top portion of the instrument was filled with paraffin, and the upper $8\frac{1}{2}$ inches surrounded by an outer tube covered with asbestos yarn to prevent surface condensation. Water was kept running through this outer tube during each experiment, the change in resistance of the connections caused by the changes of temperature in the tap water being less than could be measured. One advantage of this form of thermometer is, that, owing to the diameter being the same throughout, it can be thrust through perforated corks, etc. The asbestos roll being of an elastic nature, presses the coil against the exterior tube, and thus the instrument is extremely sensitive. If the hand be placed within an inch or two of the coil, when at the ordinary temperature of the room, the spot of light will be deflected off the scale.

In order still further to reduce the external resistance, silver wires, running from the upper end of the platinum tube to within 1 inch of its lower end, were hard-soldered to the platinum connections. Similar wires were added in the same manner to the platinum wires in the inner tube. Since the resistance of the platinum is so small, any current caused by differences of temperature within the thermometer will be short circuited, and thus will not visibly affect the galvanometer. As the silver wires terminated about $1\frac{1}{2}$ inch above the coil, the flow of heat along them was not likely to influence its temperature.

Thermometers thus constructed have proved satisfactory in every respect, and can be safely exposed to any temperature up to a dull red heat.

Thermometers E, E, F, and G.*

15. I obtained from Messrs. JOHNSON and MATTHEY some exceedingly fine platinum wire—diameter ·001 inch, and a resistance of about 48 ohms per foot. Great difficulty was experienced both in welding this wire to its connections and in winding the coil. A piece of this wire, about 20 inches in length, was wound into a coil $1\frac{3}{8}$ inch in length. The external diameter of the thermometer was only $\frac{3}{16}$ inch, and was the same throughout its length. Eight inches projected below the condenser tube. The total resistance from the coil to the connecting screws at the top of the instrument was about ·021 ohm. About two-thirds of the thermometer was kept at a constant temperature by the tap water. Thus the part exposed to change of temperature was about ·007 ohm, and as the greater portion of it was always immersed, any variation caused by difference of immersion could be safely disregarded.

The same remarks apply to E, F, and G, which were constructed in the same manner, except as regards the wire used for the coil.

Before using these thermometers the wires running to the resistance box in the next room were replaced by thick copper rods, carefully insulated, the resistance of which, and all connecting screws, was ·014 ohm.

These rods were only subjected to the same changes of temperature as the air of the room, and any difference thus produced was not measurable. E*, however, had one fatal defect. The capacity for heat of the coil was so small that the difficulty previously referred to (the raising of its temperature by the current used when determining the resistance) compelled the reduction of the E.M.F. used to such an extent, that the deflection of the galvanometer was too slight to be accurately measured.* I determined, however, before destroying the thermometer, to ascertain the resistance at the "fixed points," using seven cells with a battery resistance of 1000 ohms, and using $\frac{10000}{100}$ for the arms of the bridge.

The results were as follows :—

TABLE IX.

	Corrected resistance.	*pt.*	$t - pt.$
Melting ice	43·795	0	0
Steam (760 mm.)	56·733	100	0
Aniline (760 mm.)	67·353	182·08	
Naphthalene (760 mm.)	71·524	214·32	3·74
Benzophenone (760 mm.)	82·098	296·06	10·02
Sulphur (760 mm)†	98·010	419·04	29·34

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* For example

Arms of bridge.	E.M.F.	Observed R.	
$\frac{10000}{100}$	2 Leclanché cells	56·927	(1)
$\frac{10000}{100}$	1 Leclanché cell and 100 ohms placed in battery connection	56·887	(2)
Again, $\frac{10000}{100}$	7 Leclanché cells and 1000 ohms in battery connection	56·875	(3)
$\frac{1000}{10}$	7 Leclanché cells and 1000 ohms in battery connection	56·925	(4)
Again, $\frac{10000}{100}$	2 Leclanché cells	43·862	(5)
$\frac{1000}{100}$	1 Leclanché cell and 100 ohms in battery connection	43 762	(6)

(1) and (2) the thermometer in steam under same pressure (781).
(3) and (4) " " " " (772·5).
(5) and (6) " in melting ice.

The fall in the resistance of the coil due to a diminution in the current passing through it, is here very marked.

† I omitted to determine mercury B.P. by means of E*.

This curve (Curve E*, Plate 4,) differs considerably from the preceding curves; it, however, approaches more nearly to the curve plotted from CALLENDAR'S numbers. Ascertaining from it the temperature of aniline B.P. at 760 we get 182·08 + 2·16 = 184·24, thus bearing out the conclusions arrived at in section 13.

The thermometer was reconstructed and a wire of diameter ·007 inch (the same sample of wire as that used for D), and length about 20 inches, was substituted for the previous coil. This thermometer was labelled E.

Diameter of wire in F = ·005 inch (the same sample of wire as that used for A, B, and C).

F was destroyed during some experiments with melted Zn and was replaced by G, whose coil was constructed of a rather greater length of the same wire. Both F and G had an external diameter of a quarter of an inch. As regards the external resistance, length, etc., they practically coincide with E*.

16. A series of observations led me to the conclusion that the current produced by the following arrangement was the greatest that I could use if I wished to prevent any observable rise in temperature due to the current.

F. 7 Leclanché cells and 500 ohms introduced into battery, arms of bridge $\frac{10000}{10}$.
E. ,, ,, 200 ,, ,, ,, ,, ,,
G. ,, ,, 500 ,, ,, ,, ,, ,,

These conditions were maintained throughout all the remaining experiments.

TABLE X.—Resistances of E, F, and G after correction for temperature of coils and height of barometer.*

	E.	F.	G.
Melting ice	3·0569	4·7662	4·9543
Steam	3·9848	6·2715	6·5399
B.P. of aniline	4·7384	7·4922	7·8288
,, naphthalene	5·0355	7·9709	8·3351
,, benzophenone	5·7896	9·1833	9·6175
,, mercury	6·2149	9·8668	10·3410
,, sulphur	6·9276	11·002	11·552

From Table X. we get the following results:—

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* Tables of the individual experiments from which these numbers are obtained are given in the Appendix (pp. 65–69), except those of aniline and mercury which are given in Table XIV.

TABLE XI.

	pt. E.	*pt.* F.	*pt.* G.	$t - pt$. E.	$t - pt$. F.	$t - pt$. G.
B.P. of aniline	181·24	181·08	181·28	. .	. .	. .
,, naphthalene . . .	213·27	212·89	213·22	4·79	5·17	4·84
,, benzophenone . .	294·57	293·44	294·10	11·51	12·64	11·98
,, mercury	340·40	338·83	339·72	. .	. .	. .
,, sulphur	417·22	414·25	416·10	31·16	34·13	32·28

These numbers (with the exception of those deduced by assuming the standard numbers for aniline and mercury) give, as in previous cases, a smooth curve, although $t - pt$ differs considerably in the last three columns.

Assuming, as before, $y = ax + bx^2 + cx^3 + dx^4$, and substituting the values of y and x given by the above table, we get

TABLE XII.

	E.	F.	G.
a	— ·026724	— ·025479	— ·0229155
b	·00032537	·00029505	·000260768
c	— ·00000070247	— ·00000050	— ·0000004013
d	·00000000121	·0000000010	·00000000085

From Table XII. we get the following values of y :—

Table XIII.—Values of $y = (t - pt)$.

	E.	F.	G.
When $x = 50$	— ·60	— ·59	— ·54
$x = 150$	1·56	1·63	1·49
$x = 250$	7·40	8·16	7·61
$x = 350$	18·60	20·74	19·47
$x = 450$	39·47	43·74	41·22

Ten points were thus obtained on each curve, five by direct experiment (Table X.) and five from the equation.

The curves (Curves E, F, and G, Plates 4 and 5) run without the slightest difficulty through these points. They are plotted on a scale in which a vertical distance of $\frac{1}{2}$ inch corresponds to a difference of 1° in y, and its value can be read with certainty to ·02°.

The marked difference in the coefficients of the equations may be due (1) to differences in the quality and thickness of the platinum wire used; (2) to differences in the total external resistance; (3) to differences in the asbestos and glass, different samples being used in each.

That, under the same circumstances, the resistance of each thermometer remains constant is, I believe, clearly shown by the Tables given in the Appendix.

The temperatures of the boiling-points of aniline and mercury (at 760 mm.), deduced from curves E, F, and G (using the numbers given in Tables X. and XI.), are as follows:—

		E.	F.	G.	Mean t.
Aniline.	$pt =$	181·24	181·08	181·28	
	$y =$	2·96	3·15	2·95	
	$t =$	184·20	184·23	184·23	184·22*
Mercury.	$pt =$	340·40	338·83	339·72	
	$y =$	17·24	18·85	17·90	
	$t =$	357·64	357·68	357·62	357·65*

The greatest variation from the mean value being 0°·03.

My attention was, henceforward, confined to determining various temperatures by means of these curves.

After having used thermometer F for the determination of the boiling-point of methyl salicylate and the melting-points of Sn and Pb, it met with an accident, and thereafter I was dependent upon E and G.

At regular intervals I tested these thermometers by means of a hypsometer, but was not able to detect any alteration in them.

I give particulars of the remaining experiments in full, without omission, as I wish to show how comparatively insignificant the variations are in each case.

I hope that the replacement of glass by porcelain tubes will hereafter enable me to determine the freezing-points of metals melting at higher temperatures.

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* Mean of previous results (curves A, B, C, D, and E*):—

Aniline	184·25
Mercury	357·60

TABLE XIV.—DETERMINATION of the B.P. of Aniline, Methyl Salicylate, Triphenyl Methane, and Mercury.

Nature of experiment.	Date.	Therm.	R.	Temp. of coils.	R. after correction for temp. of coils (right at 17°) (see Table II.).	Ht. of bar.	Correction for bar. to 760 (see Table III.).	R. at 760.	Mean resulting pt.	Diff. taken from curve = $t-pt$.	t.	Mean t.	Previous determination.	Remarks.
	1890.			°		mm.						°		
B.P. of aniline A	March 1	F	7·4959	17	7·4959	765	−·0038	7·4921	181·08	3·15	184·23	184·22	Ramsay 184·41 Thorpe 183·7	Two different samples used—(A) supplied by Harrington Bros., (B) supplied by Burgoyne, Burbidges, and Co. Curves (A, B, and C) gave 184·29 Curve (D) gave 184·21 Curve (E*) gave 184·24
	,, 1	,,	7·4954	17·15	7·4958	765	−·0038	7·4920						
	,, 2	,,	7·5066	14·6	7·5498	769·5	−·0073	7·4925						
	,, 22	,,	7·4893	16·9	7·4890	756·2	+·0029	7·4919						
	,, 22	,,	7·4896	16·9	7·4893	756·2	+·0029	7·4922						
	,, 22	,,	7·4895	16·85	7·4892	756·3	+·0028	7·4920						
	,, 22	E	4·7368	16·85	4·7366	756·8	+·0015	4·7381	181·24	2·96	184·20			
	,, 22	,,	4·7369	16·85	4·7367	756·8	+·0015	4·7382						
	,, 22	,,	4·7366	16·85	4·7364	756·8	+·0015	4.7379						
B	,, 26	,,	4·7369	17·1	4·7371	757·6	+·0011	4·7382						
	,, 26	,,	4·7371	17·1	4·7373	757·6	+·0011	4·7383						
	,, 26	,,	4·7380	16·65	4·7374	757·2	+·0013	4·7387						
	,, 26	,,	4·7378	16·7	4·7373	757·2	+·0013	4·7386						
	,, 26	G	7·8268	16·9	7·8266	757·5	+·0020	7·8286	181·28	2·95	184·23			
	,, 26	,,	7·8269	17	7·8269	757·5	+·0020	7·8289						
B.P. of methyl salicylate	March 22	F	8·0403	17·05	8·0404	756·3	+·0029	8·0433	217·70	+ 5·51	223·21	223·19	Ramsay 222·88 Cahours 222	Not satisfied as to purity of sample; some time before temp. was steady. Curves (A, B, and C) gave 223·12
	*March 22	E	5·0778	17	5·0778	756	+·0020	5·0798	218·08	+ 5·10	223·18			
	,, 22	,,	5·0782	17	5·0782	756	+·0020	5·0802						
	,, 22	,,	5·0784	17	5·0784	756	+·0020	5·0804						
B.P. of triphenyl methane	April 1	E	6·2138	16·6	6·2129	770·8	correction not known	..	340·18	17·20	357·38	357·35 (bar. 770·8)	Kekulé 355 (760) Crafts 358 (754) Schwarz 330 (760)	Quantity (2 ozs.) too small for satisfactory determination No data for correction of pressure
	,, 1	G	10·339	16·6	10·337	770·8	,,	..	339·47	17·86	357·33			
B.P. of mercury	March 7	F	9·8623	16·6	9·8608	753·7	+·0062	9·8670	338·83	18·85	357·68	357·65	Regnault 357·25 Ramsay 358·2	About 2600 grms. of mercury in flask Curves (A, B, C) gave 357·62 Curve (D) gave 357·54
	,, 22	,,	9·8648	16·6	9·8633	756·5	+·0035	9·8668						
	,, 22	E	6·2135	16·8	6·2130	757	+·0019	6·2149	340·40	17·24	357·64			
	,, 22	,,	6·2133	16·8	6·2128	757	+·0019	6·2147						
	,, 26	,,	6·2134	17·3	6·2141	758·8	+·0007	6·2148						
	,, 26	,,	6·2136	17·3	6·2143	758·8	+·0007	6·2150						
	,, 26	G	10·339	17·2	10·340	759	+·0010	10·341	339·72	17·90	357·62			
	,, 26	,,	10·339	17·2	10·340	759	+·0010	10·341						

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* In every case where the date is repeated, the experiment was a distinct one, the substance being boiled again after cooling.

TABLE XV.—Freezing-points of Metals.

Nature of experiment.	Date.	Therm.	Observed R.	Temp. of coils.	R. after correction for temp. of coils.	Resulting *pt.*	Diff. taken from curve = (*t*—*pt.*)	*t.*	Mean *t.*	Previous Observers.	Remarks.
Freezing-point of Sn	Mar. 9*	F.	8·1660	16°·9	8·1657	225·87	6·13	232·00	232°·03	REIMSDYK 228·5 KUPFFER 230· PERSON 232·7 CRICHTON 238·	Weight of Sn, Mar. 9, 500 grms. Weight of Sn, Mar. 28, 600 grms. Surfusion was in many of the experiments *very* marked. Spec. of Sn supplied by Messrs. JOHNSON and MATTHEY.
	,, 9	,,	8·1662	16·9	8·1659						
	,, 9	,,	8·1659	16·9	8·1656						
	Mar. 28	G.	8·5430	16·88	8·5427	226·30	5·72	232·02			
	,, 28	,,	8·5426	16·9	8·5423						
	,, 28	,,	8·5434	16·9	8·5431						
	,, 28	,,	8·5425	17·	8·5425						
	,, 28	E.	5·1578	17·05	5·1579	226·45	5·63	232·08			
	,, 28	,,	5·1576	17·1	5·1578						
Freezing-point of Bi A	Mar. 28	E.	5·4825	16·75	5·4820	261·38	8·30	269·68	Spec. A. and B. 269·68	PERSON 273·5 REIMSDYK 268·3	Weight of Bi used, Spec. A. 600 grms., Spec. B. 550 grms. Both these specimens were supplied by Messrs. JOHNSON and MATTHEY, but with an interval of nearly twelve months. Surfusion very slight, but temp. very steady from commencement of solidification.
	,, 28	,,	5·4822	16·72	5·4817						
	,, 28	,,	5·4823	16·7	5·4817						
B	April 2	,,	5·4820	16·8	5·4816	261·39	8·30	269·69			
	,, 2	,,	5·4826	16·8	5·4822						
	,, 2	,,	5·4825	16·8	5·4821						
A	Mar. 28	G.	9·0960	16·8	9·0953	261·16	8·53	269·69			
	,, 28	,,	9·0962	16·8	9·0955						
	,, 28	,,	9·0958	16·8	9·0951						
B	April 2	,,	9·0955	16·8	9·0948	261·15	8·53	269·68			
	,, 2	,,	9·0960	16·8	9·0953						
	,, 2	,,	9·0959	16·8	9·0952						

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* In every case where the date is repeated, the experiment was a distinct one, the substance being allowed to solidify, then re-melted and again cooled.

TABLE XV.—Freezing-points of Metals—(continued.)

Nature of experiment.	Date.	Therm.	Observed R.	Temp. of coils.	R. after correction for temp. of coils.	Resulting *pt.*	Diff. taken from curve = (*t*—*pt.*)	*t.*	Mean *t.*	Previous Observers.	Remarks.
Freezing-point of Cd A	Mar. 27	E.	5·9175	17·3	5·9182	308·43	13·08	321·51	Spec. A. 321·50	PERSON 320·7 REIMSDYK 320 VAN DER WYDE 325	Spec. A. supplied by HARRINGTON BROS., weight used 500 grms. Spec. B. supplied by Messrs. JOHNSON and MATTHEY, weight used 459 grms. Surfusion very marked in the experiments on sample B.
	,, 27	,,	5·9176	17·3	5·9183						
	,, 27	,,	5·9174	17·35	5·9182						
	,, 27	G.	9·8346	17·4	9·8361	307·92	13·57	321·49			
	,, 27	,,	9·8350	17·45	9·8366						
B	April 1	E.	5·9208	16·1	5·9199	308·58	13·12	321·70	Spec. B. 321·67		
	,, 1	,,	5·9206	16·65	5·9195						
	,, 1	G.	9·8400	16·65	9·8387	308·04	13·60	321·64			
	,, 1	,,	9·8405	16·7	9·8394						
	,, 1	,,	9·8400	16·75	9·8391						
Freezing-point of Pb A	Mar. 15	F.	9·4820	16·35	9·4797	313·14	15·13	328·27	Spec. A. 328·27	PERSON 326·2 KUPFFER 334 QUINCKE 330	Spec. A. supplied by HARRINGTON BROS., granulated, 600 grms. used. Spec. B. supplied by Messrs. JOHNSON and MATTHEY, foil, 600 grms. used.
	,, 15	,,	9·4820	16·45	9·4800						
	,, 15	,,	9·4814	16·6	9·4800						
B	Mar. 29	G.	9·9392	17·02	9·9393	314·40	14·39	328·79	Spec. B. 328·78		
	,, 29	,,	9·9395	17·02	9·9396						
	,, 29	,,	9·9392	17·05	9·9395						
	,, 29	E.	5·9789	16·65	5·9782	314·91	13·86	328·77			
	,, 29	,,	5·9788	16·75	5·9784						
	,, 29	,,	5·9787	16·9	5·9786						
Freezing-point of Zn	Mar. 31	G.	11·203	16·4	11·200	393·90	27·31	421·21	421·23	REIMSDYK 420 WRIGHT and TUFF 420 PERSON 433·3. Other observers range from 342 (DANIELL) to 450 (BOUSSINGAULT)	Spec. of Zn supplied by HARRINGTON BROS., 450 grms. used. No surfusion, but temp. during solidification very steady.
	,, 31	,,	11·200	16·6	11·198						
	,, 31	,,	11·202	16·6	11·200						
	April 1	E.	6·7204	16·8	6·7199	394·84	26·41	421·25			
	,, 1	,,	6·7202	16·8	6·7197						
	,, 1	,,	6·7205	16·8	6·7200						

Summary of Results.

17. (1.) Different thermometers, whose coils are formed of different specimens of platinum wire, encased in glass or wound on asbestos, do *not* give the same platinum temperature when at the same actual temperature.

(2.) The readings of each thermometer are constant, whenever its temperature is the same.

(3.) The platinum temperatures obtained by assuming CRAFTS' numbers for the B.P. of naphthalene and benzophenone, and REGNAULT's for that of sulphur, are consistent with each other, and with 0° and 100°.*

(4.) Using the substances mentioned in (3) for the determination of the "fixed points," of platinum thermometers, the thermometers thus graduated agree in assigning the values given in Table XVI. as the air thermometer temperatures of the boiling and freezing points of the different substances. The difference between the numbers obtained by using different thermometers on the same specimen in no case affects the fourth figure of the results.

TABLE XVI.

		Temp. by air therm.
Boiling-points—		
(Bar. 760)	Aniline	**184·22**
,,	Methyl salicylate	**223·19**
(Bar. 770·8)	Triphenyl methane	**257·35**
(Bar. 760)	Mercury	**357·65**
Freezing-points—		
	Tin	**232·03**
	Bismuth	**269·68**
	Cadmium	**321·67**
	Lead	**328·78**
	Zinc	**421·23**

APPENDIX.

I give, in full, tables showing the results of the individual experiments by which the "fixed points" on E, F, and G were determined.

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* It must be remembered that these determinations were obtained by use of the air thermometer, whose readings agree with the mercury thermometer at 0° and 100°. It follows that all the temperatures ascertained by my thermometers are expressed in terms of the air thermometer. If subsequent investigations establish new values for the air-temperature at these points, the figures given in the Tables in Appendix would supply sufficient data for the correction of the temperatures deduced from them.

TABLE XVII.—Determination of "Fixed Points" on E. (Seven Leclanché Cells. 200 ohms in Battery Connection. Bridge $\frac{10000}{10}$.)

Nature of experiment.	No.	Date.	Observed R.	Temp. of coils.	R. after correction for temp. of coils (by Table III.).	Ht. of bar.	Correction for bar. 760 (by Table III.).	R. bar. at 760.	*pt.*	*t.*	*t—pt.*	Remarks.
				°		mm.						
Melting ice . . .	* 1	March 22	3·0568	17	3·0568							In all cases the inner vessel filled with finely powdered ice and distilled water
	* 2	,, 22	3·0569	17	3·0569							
	* 3	,, 26	3·0570	17·1	3·0571							
	* 4	,, 26	3·0569	17·2	3·0571							
	* 5	April 2	3·0570	16·9	3·0569							
	* 6	,, 2	3·0571	16·9	3·0570							
				Mean	3·0570							
B.P. of water . . .	7	March 20	3·9826	15·65	3·9806	747	+·0044	3·9850				Thus $pt_e = \frac{R - 3\cdot0570}{\cdot9277}$
	8	,, 21	3·9829	16·1	3·9815	752·5	+·0027	3·9842				
	* 9	,, 23	3·9811	17·5	3·9819	751·5	+·0029	3·9848				
	*10	,, 23	3·9812	17·5	3·9820	751·5	+·0029	3·9849				18. E had before this experiment been immersed in melted Sn, Bi, Cd, and Pb
	*11	,, 23	3·9810	17·5	3·9818	751·5	+·0029	3·9847				
	*12	,, 24	3·9822	16·2	3·9810	749·6	+·0036	3·9846				
	*13	,, 25	3·9802	16·8	3·9799	746·5	+·0046	3·9845				
	*14	,, 25	3·9801	16·9	3·9800	746·5	+·0046	3·9846				
	*15	,, 25	3·9798	17·1	3·9800	746·5	+·0046	3·9846				19. This experiment was performed within half-hour after the immersion of E in melted Zn
	*16	,, 26	3·9843	17·25	3·9846	759·5	+·0002	3·9848				
	*17	,, 26	3·9844	17·25	3·9847	759·5	+·0002	3·9849				
	*18	,, 31	3·9894	16·45	3·9885	770·5	—·0036	3·9849				
	*19	April 1	3·9899	16·4	3·9889	772·2	—·0041	3·9848				
							Mean	3·9847				

TABLE XVII.—(continued.)

Nature of experiment.	No.	Date.	Observed R.	Temp. of coils.	R. after correction for temp. of coils (by Table III.).	Ht. of bar.	Correction for bar. 760 (by Table III.).	R. bar. at 760.	*pt.*	*t.*	*t*—*pt.*	Remarks.
				°		mm.						
B.P. of naphthalene .	20	March 21	5·0319	16·95	5·0318	753·5	+·0039	5·0357	213·29			
	21	,, 21	5·0317	17	5·0317	753·5	+·0039	5·0356	213·28			
	*22	,, 25	5·0306	17·1	5·0308	751	+·0046	5·0354	213·26	218·06 (CRAFTS)	4·79	
	*23	,, 25	5·0307	17·1	5·0309	751	+·0046	5·0355	213·27			
	*24	,, 25	5·0307	17·25	5·0312	752	+·0041	5·0353	213·25			
	*25	April 2	5·0382	17·1	5·0384	765·5	—·0028	5·0356	213·28			
	*26	,, 2	5·0380	17·1	5·0382	765·5	—·0028	5·0354	213·26			
								Mean	213·27			
B.P. of benzophenone	27	March 21	5·7875	16·6	5·7866	754·7	+·0028	5·7894	295·55			
	28	,, 21	5·7878	16·6	5·7869	754·7	+·0028	5·7897	295·58	306·08 (CRAFTS)	11·51	
	29	,, 21	5·7880	16·6	5·7871	754·7	+·0028	5·7899	295·60			
	*30	,, 25	5·7833	17·2	5·7837	749	+·0058	5·7895	295·56			
	*31	April 2	5·7922	17·1	5·7924	765	—·0027	5·7897	295·58			
								Mean	295·57			
B.P. of sulphur . .	32	March 21	6·9239	17	6·9239	754·5	+·0034	6·9273	417·17			
	33	,, 21	6·9237	17	6·9237	754·5	+·0034	6·9271	417·15	448·38 (REGNAULT)	31·16	
	*34	,, 24	6·9200	17·25	6·9208	748	+·0074	6·9282	417·26			
	*35	,, 24	6·9198	17·25	6·9206	748	+·0074	6·9280	417·24			
	*36	,, 25	6·9198	17·2	6·9203	748	+·0074	6·9277	417·21			
	*37	April 2	6·9300	17·2	6·9305	764·5	—·0028	6·9277	417·21			
								Mean	417·22			

* Numbers thus marked were obtained after the gas regulator and bath had been used for coils; the resulting numbers are therefore more trustworthy.

TABLE XVIII.—Determination of "Fixed Points" on F. (Seven Leclanché Cells. 500 ohms in Battery Connection. Bridge $\frac{10000}{10}$.)

Nature of experiment.	No.	Date.	Observed R.	Temp. of coils.	R. after correction for temp. of coils (by Table III.).	Ht. of bar.	Correction for bar. to 760 (by Table III.).	R. at 760.	Resulting *pt*.	*t*.	*t*—*pt*.	Remarks.
Melting ice	1	Feb. 26	4·7688	15·8°	4·7666	mm.						No. 1. Ice in inner vessel drained
	2	,, 27	4·7745	12·6	4·7664							No. 2. Ice in inner vessel with water
	3	,, 28	4·7658	16·6	4·7652							No. 3. } Snow instead of
	4	March 1	4·7683	15·8	4·7661							No. 4. } ice
	*5	,, 22	4·7662	17	4·7662	. .	. .	. .	. .	0	0	No. 5. Same as 2 but ice very finely powdered
				Mean	4·7662							
B.P. of water . . .	6	Feb. 26	6·2839	15·4	6·2801	774·3	—·0081	6·2720				Thus $pt_f = \frac{R - 4{\cdot}7662}{1{\cdot}5053}$
	7	March 1	6·2760	15·5	6·2724	760·7	—·0004	6·2720				
	8	,, 20	6·2680	15·5	6·2644	747	+·0073	6·2717				
	9	,, 20	6·2679	15·6	6·2645	747	+·0073	6·2718				
	*10	,, 21	6·2694	16·15	6·2674	752·7	+·0041	6·2715				
	*11	,, 21	6·2693	16·2	6·2675	752·8	+·0040	6·2715				
							R. adopted	6·2715				
B.P. of naphthalene .	12	March 1	7·9758	16·6	7·9746	764·3	—·0035	7·9711	212·90			
	*13	,, 21	7·9660	16·8	7·9654	753	+·0056	7·9710	212·89	218.06 (CRAFTS)	5·17	
	*14	,, 21	7·9658	16·8	7·9652	753	+·0056	7·9708	212·88			
								Mean *pt*.	212·89			
B.P. of benzophenone	15	Feb. 27	9·2007	14·8	9·1931	771·5	—·0097	9·1834	293·45			
	16	,, 28	9·1955	16·5	9·1936	771·6	—·0099	9·1837	293·47	306·08 (CRAFTS)	12·64	
	17	,, 28	9·1950	16·6	9·1935	771·6	—·0099	9·1836	293·46			
	*18	March 21	9·1798	16·7	9·1788	754·7	+·0045	9·1833	293·44			
	*19	,, 21	9·1798	16·7	9·1788	754·7	+·0045	9·1833	293·44			
								pt. adopted	293·44			
B.P. of sulphur . .	20	March 6	11·004	15·5	10·998	757·2	+·003	11·001	414·19			
	21	,, 7	11·005	16	11·001	754·5	+·005	11·006	414·49	448·38 (REGNAULT)	34·13	
	*22	,, 21	10·996	16·95	10·996	754	+·006	11·003	414·25			
	*23	,, 21	10·996	16·95	10·996	754	+·006	11·002	414·25			
								pt. adopted	414·25			

The numbers marked * were taken after the gas regulator and bath had been used for coils; the resulting numbers are, therefore, more trustworthy.

TABLE XIX.—Determination of "Fixed Points" on G. (Seven Leclanché Cells. 500 ohms in Battery Connection. Bridge $\frac{10000}{10}$.)

(All observations with G were taken after the gas regulator, &c., had been used for coils.)

Nature of experiment.	No.	Date.	Observed R.	Temp. of coils.	R. after correction for temp. of coils (by Table III.).	Ht. of bar.	Correction for bar. 760 (by Table III.).	R. at 760.	*pt.*	*t.*	*t—pt.*	Remarks.
Melting ice . . .	1	March 26	4·9538	17·2°	4·9542	mm.						In all cases inner vessel filled with finely-powdered ice and distilled water G was left standing in the ice for two hours between observations 2 and 3
	2	,, 26	4·9539	17·2	4·9543							
	3	,, 26	4·9536	17·35	4·9543							
	4	April 2	4·9542	17	4·9542							
	5	,, 2	4·9544	17	4·9544							
				Mean	4·9543							
B.P. of water . . .	6	March 25	6·5318	17·15	6·5322	746·8	+·0077	6·5399				Thus $pt_g = \dfrac{R - 4{\cdot}9543}{1{\cdot}5856}$ (13) G had before this experiment been immersed in melted Bi, Cd, Sn, and Pb (14) and (15) These experiments were performed after G had been immersed in melted Zn
	7	,, 25	6·5316	17·15	6·5320	746·8	+·0077	6·5397				
	8	,, 26	6·5391	17·25	6·5397	759·5	+·0003	6·5400				
	9	,, 26	6·5389	17·25	6·5395	759·5	+·0003	6·5398				
	10	,, 26	6·5389	17·25	6·5395	759·5	+·0003	6·5398				
	11	,, 27	6·5410	17·5	6·5422	764	—·0023	6·5399				
	12	,, 27	6·5409	17·55	6·5422	764·2	—·0022	6·5400				
	13	,, 31	6·5470	16·6	6·5460	770·5	—·0061	6·6399				
	14	April 1	6·5484	16·35	6·5468	772	—·0070	6·5398				
	15	,, 1	6·5486	16·35	6·5470	772	—·0070	6·5400				
							Mean	6·5399				

TABLE XIX.—(continued.)

Nature of experiment.	No.	Date.	Observed R.	Temp. of coils.	R. after correction for temp. of coils (by Table III.).	Ht. of bar.	Correction for bar. 760 (by Table III.).	R. at 760.	*pt*.	*t*.	*t*—*pt*.	Remarks.
				°		mm.						
B.P. of naphthalene	16	March 25	8·3275	17·2	8·3281	752	+·0069	8·3350	213·21	218·06 (CRAFTS)	4·84	
	17	„ 25	8·3276	17·2	8·3282	752	+·0069	8·3351	213·22			
	18	April 2	8·3394	17·1	8·3396	765	—·0043	8·3353	213·23			
	19	„ 2	8·3390	17·1	8·3392	765	—·0043	8·3349	213·21			
								Mean	213·22			
B.P. of benzophenone	20	March 25	9·6076	17·1	9·6080	749·5	+·0095	9·6175	294·10	306·08 (CRAFTS)	11·98	
	21	„ 25	9·6076	17·1	9·6080	749·5	+·0095	9·6175	294·10			
	22	April 2	9·6226	17	9·6226	765·5	—·0050	9·6176	294·11			
	23	„ 2	9·6222	17	9·6222	765·5	—·0050	9·6172	294·09			
								Mean	294·10			
B.P. of sulphur . .	24	March 25	11·537	17·25	11·538	748	+·013	11·551	416·05	448·38 (REGNAULT)	32·28	(26) and (27) Distilled for twenty minutes between these experiments; about ½ litre distilled over
	25	„ 25	11·539	17·2	11·540	748	+·013	11·553	416·15			
	26	April 2	11·557	17·15	11·558	765	—·005	11·553	416·15			
	27	„ 2	11·556	17·15	11·557	765	—·005	11·552	416·10			
								Mean	416·10			

Note on the Possible Causes of the Differences of pt as shown by Different Thermometers, when t is the same.

If the external resistance is constant, it cannot affect the value of $\frac{R_t - R_0}{R_{100} - R_0} \times 100$, whatever its magnitude.

It has been suggested that the discrepancy between my $t - pt$ curves and CALLENDAR'S, may be accounted for by the difference in the alteration of the "stem" resistance due to changes in its mean temperature. If such were the explanation, it is probable that the discrepancies would be more marked in A, B, C, and D (where the whole of the stem would be liable to alteration in temperature) than in E*, E, F, and G (where nearly the whole of the immersed portion was kept at the temperature of the tap water. No such contrast is, however, observable.

On comparison of the *pt* given by thermometer G with that given by CALLENDAR at the same temperature, I get the following numbers :—

Thermometer G	When $t = 440{\cdot}9$ then	$pt = 410{\cdot}4$
CALLENDAR (Table A., 5. Exp. 30).*	„ $t = 440{\cdot}9$ „	$pt = 417{\cdot}1$
	Difference	6·7

Now the mean temperature of that small portion of the stem which was immersed and exterior to the condenser must, in all cases, have been somewhere between the temperature of the tap water and that of the coil.

Assuming that S_t, S_{100}, and S_0 would be the resistances if the temperature of the stem remained constant at the temperature of the tap water, and R_t, R_{100}, and R_0 the observed resistances, then $R_t > S_t$ and $R_0 < S_0$ $\therefore$ *a fortiori*, $R_t - R_0 > S_t - S_0$.

Assuming the mean resistance of the stem to be a function of *t*, then

$$\frac{R_t - R_0}{R_{100} - R_0} = \frac{S_t - S_0 + f(t)}{S_{100} - S_0 + f(100)}.$$

Denoting the *pt* as given by G by pt_g, and, as given by CALLENDAR by *pt*, then

$$pt_g = \left(pt + \frac{f(t)}{S_{100} - S_0}\right)\left(1 - \frac{f(100)}{S_{100} - S_0}, \text{ \&c.}\right)$$

$$= pt - pt\frac{f(100)}{S_{100} - S_0} + \frac{f(t)}{S_{100} - S_0}, \text{ \&c.}$$

$$\therefore pt - pt_g = pt\frac{f(100)}{S_{100} - S_0} - \frac{f(t)}{S_{100} - S_0}, \text{ \&c.}$$

Now the total stem resistance of G was about ·021 ohm at 0°.

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* 'Phil. Trans.,' A., 1887.

In no case was the portion of the stem immersed and exterior to the condenser more than one-ninth of the whole stem. Assuming, however, that one-fourth of the whole stem is subject to variation, we get ·005 ohm as its resistance. Of this portion one end was at the temperature of the coil, the other at that of the tap water; it is probable, therefore, that its mean temperature was about $t/2$. Taking the circumference of increase of platinum as ·003, we can deduce a rough approximation (taking $S_{100} - S_0 = 1{\cdot}59$; see Table XIX.) for $pt - pt_g$ when $t = 440$.

We get

$$pt \frac{f(100)}{S_{100} - S_0} - \frac{f(t)}{S_{100} - S_0} = {\cdot}2, \text{ etc.}$$

The difference of 6·7 cannot, therefore, be due solely to the difference in the mean stem temperature.

A more probable explanation is to be found in the decrease in the resistance of glass as its temperature rises. The platinum tube and rod in the stem were separated by a thin glass tube only, of which the lower six inches were exposed to the extreme changes of temperature. Again, the coil was in contact with glass throughout its whole length. A fall in the resistance of this large section of glass sufficient to reduce the total resistance at 440°·9 from 11·5678 to 11·4616 ohms would account for the difference between pt_g and pt.

From Everett's 'Physical Constants,' I extract the following numbers :—

Specific resistance of glass at 200°C. = 2230000×10^{10}
,, ,, ,, 300° = 14500×10^{10}
,, ,, ,, 400° = 7210×10^{10}

Assuming these numbers, the above fall in the resistance would be accounted for on the supposition that the total resistance of the glass at 200° did not exceed about 6×10^5 ohms, which, bearing in mind the large section, is not an impossible number. This explanation is borne out by the fact that Curve D is the steepest, showing the greatest falling off in the increase of resistance. In D the section of the glass conductor was much greater than in any of the others, the wire being in close contact with glass on *both* sides throughout the whole length of nine feet. Again, slight differences in the quality of the glass, or in the nature of the contact between it and the platinum would be sufficient (on this hypothesis) to account for the differences between the curves.

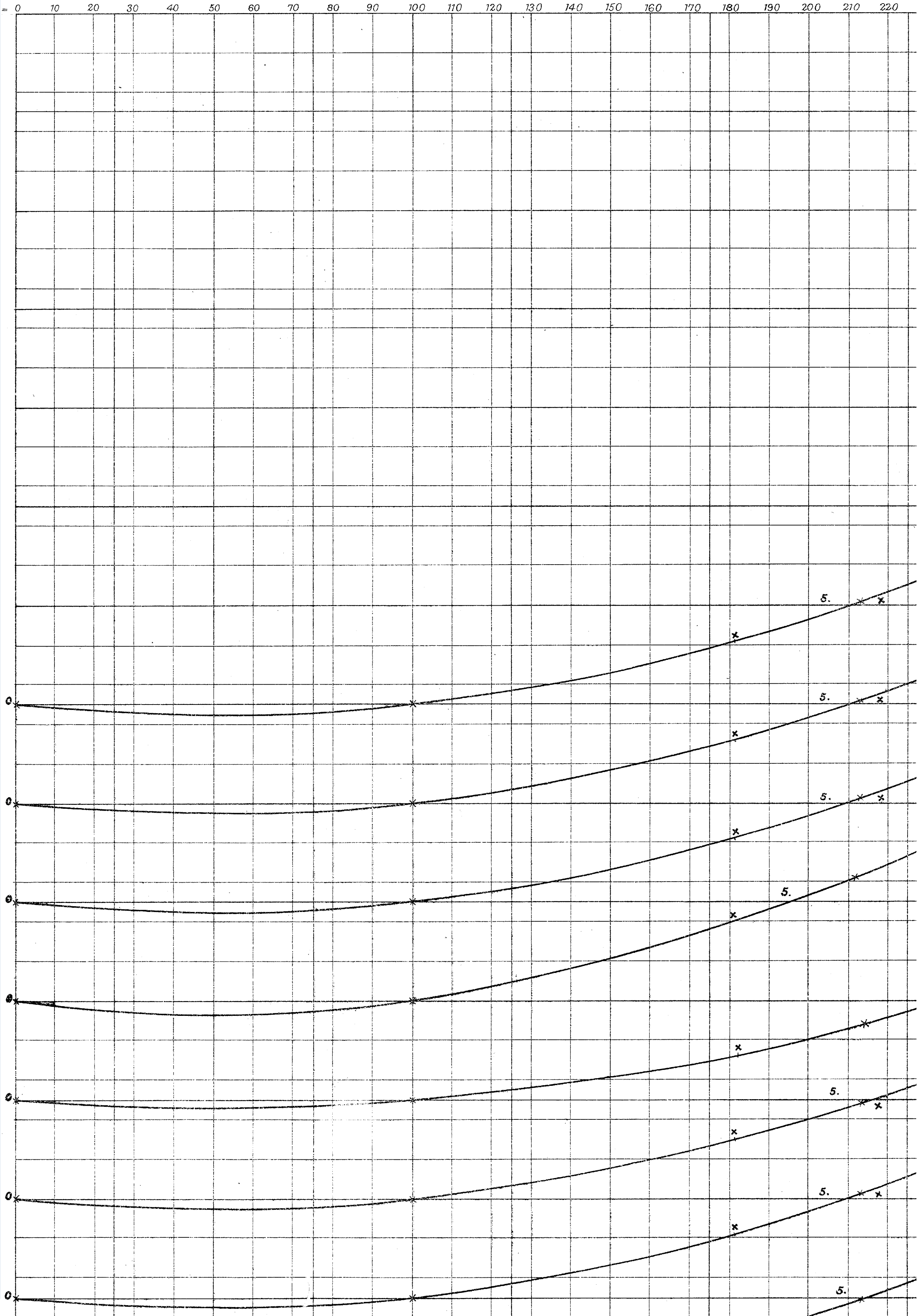
It is, however, conclusively shown by the experimental results that, whatever is the cause of the discrepancy, it does not affect the determinations of temperature made by these thermometers.

[January, 1891.—In a communication which Mr. Callendar and I had the honour of presenting to the Royal Society on December 18th, 1890, we gave the results of an investigation into the boiling-point of sulphur. We found that the temperature by normal air thermometer of the saturated vapour of sulphur under a pressure of 760 mm. of mercury at 0° C. and $g = 980{\cdot}61$ C.G.S. (sea-level in lat. 45°), is $t = 444^{\circ}{\cdot}53$ C.

It follows that the numbers given on page 64 require revision in the sense indicated by the note on that page.

A constant error of ·5 mm. in the barometer scale used by me has subsequently been discovered.

The numbers obtained by the revision thus rendered necessary are given by us in the communication above referred to.]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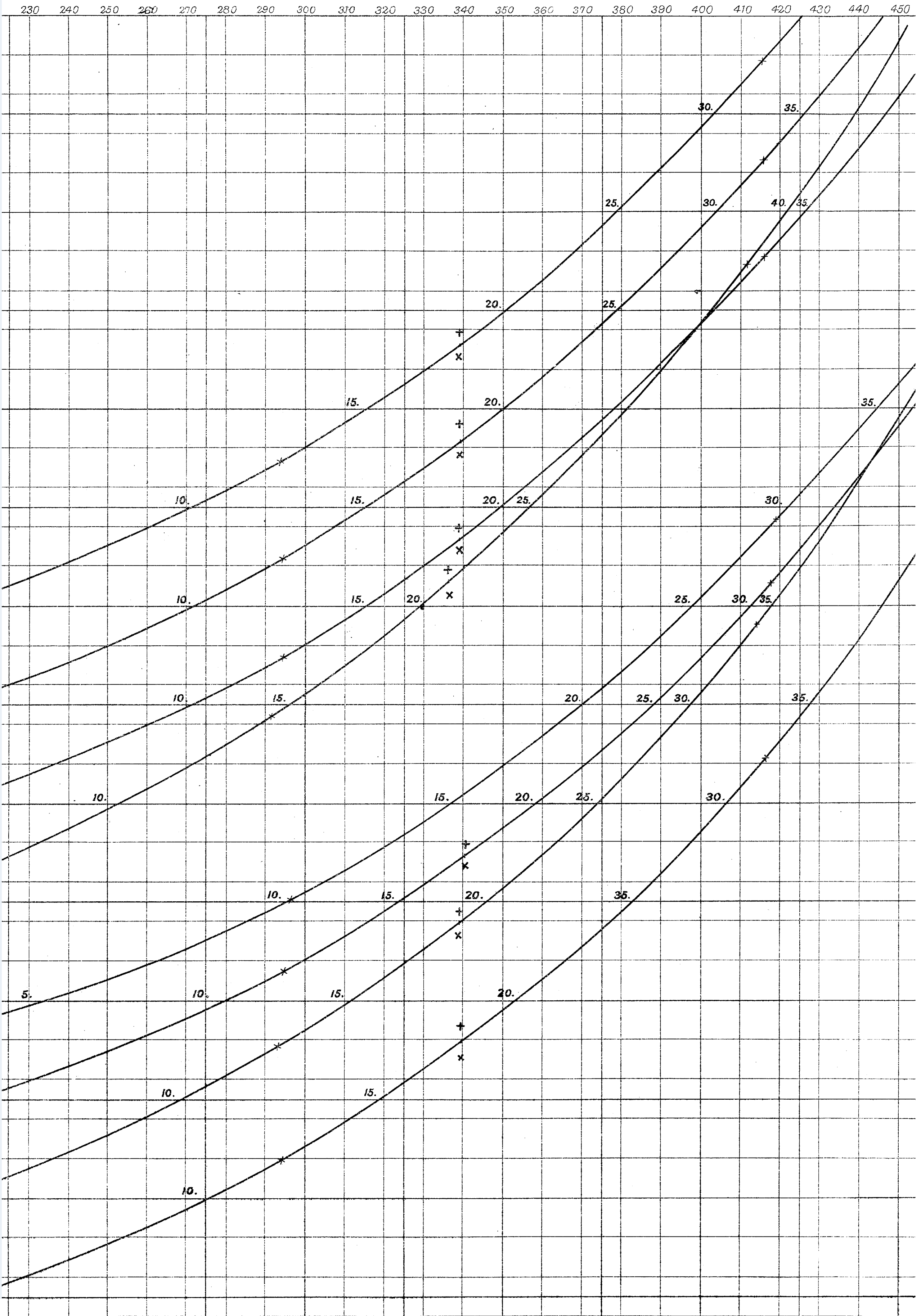
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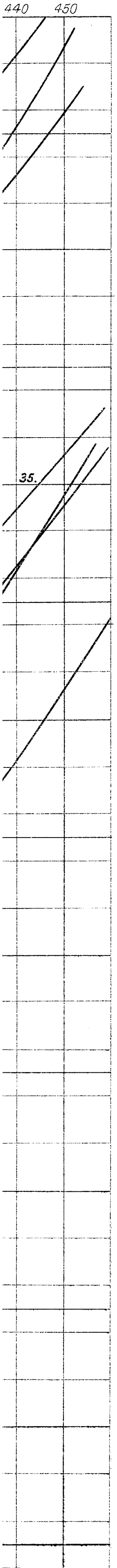
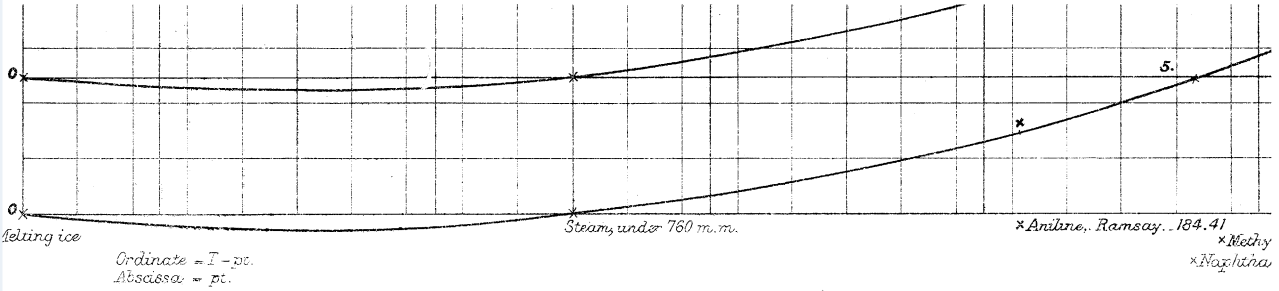
Plate 4.




0
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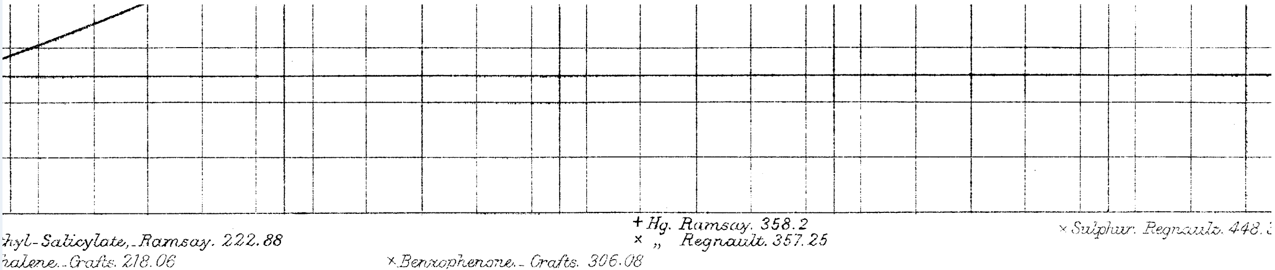
Melting ice
Steam, under 760 m.m.
× Aniline, Ramsay 184.41
× Methy
× Naphtha
Ordinate = T − pt.
Abscissa = pt.


hyl-Salicylate, Ramsay. 222.88
halene. Crafts. 218.06
× Benzophenone. Crafts. 306.08
+ Hg. Ramsay. 358.2
× „ Regnault. 357.25
× Sulphur. Regnault. 448.

West, Newman

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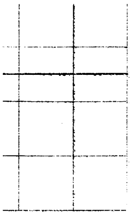

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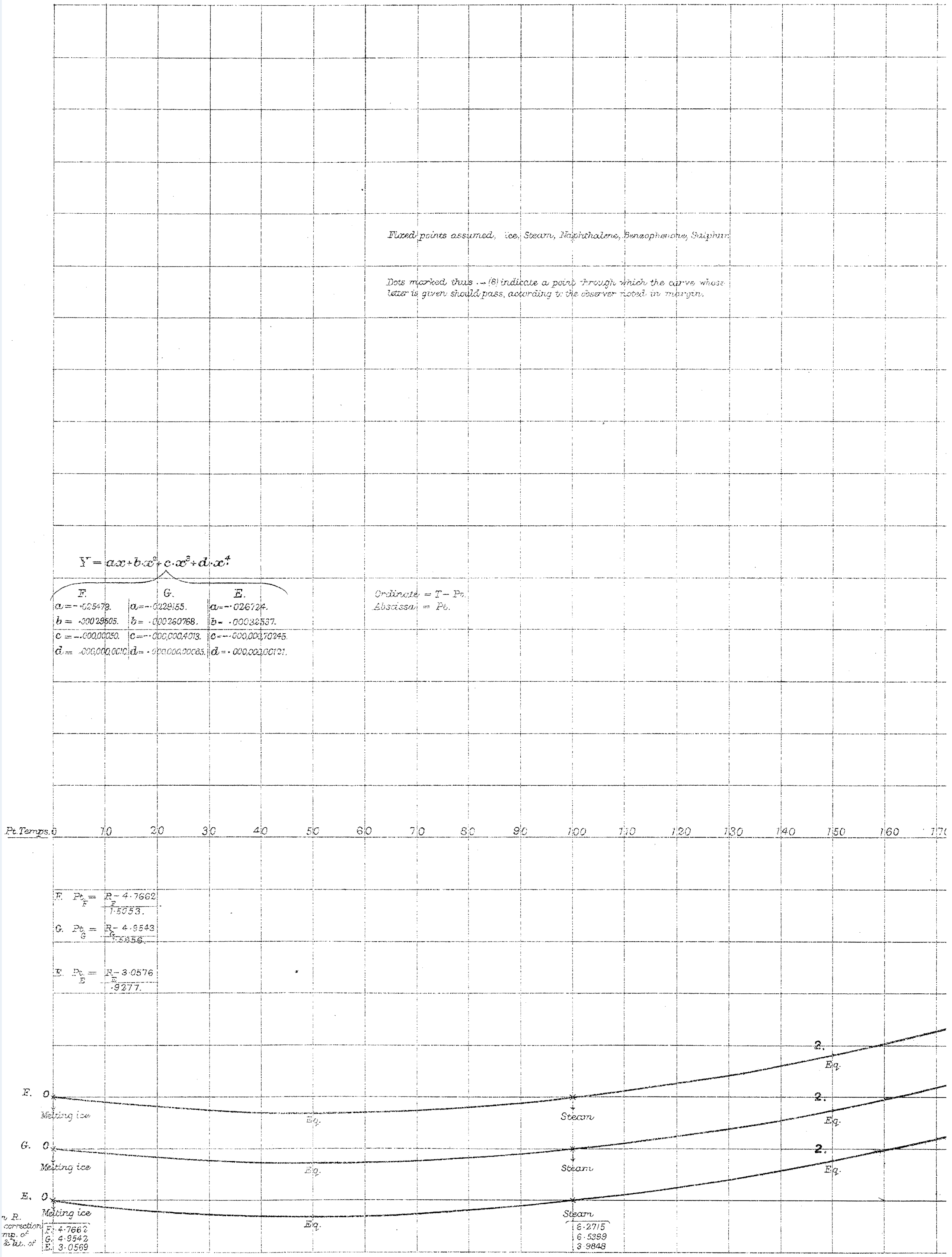

Fixed points assumed, Ice, Steam, Naphthalene, Benzophenone, Sulphur.

Dots marked thus . → (8) indicate a point through which the curve whose letter is given should pass, according to the observer noted in margin.

$$Y = ax + b\cdot x^2 + c\cdot x^3 + d\cdot x^4$$

F.	G.	E.
$a = -\cdot 025479.$	$a = -\cdot 0229155.$	$a = -\cdot 026724.$
$b = \cdot 00029505.$	$b = \cdot 000260768.$	$b = \cdot 00032537.$
$c = -\cdot 000,00050.$	$c = -\cdot 000,000,4013.$	$c = -\cdot 000,000,70245.$
$d = \cdot 000,000,0010.$	$d = \cdot 000,000,00085.$	$d = \cdot 000,000,00121.$

Ordinate = T − Pt.
Abscissa = Pt.

F. $Pt_F = \dfrac{R_F - 4\cdot 7662}{1\cdot 5053.}$

G. $Pt_G = \dfrac{R_G - 4\cdot 9543}{1\cdot 5856.}$

E. $Pt_E = \dfrac{R_E - 3\cdot 0576}{\cdot 9277.}$

Points marked Eq. were deduced from equation.

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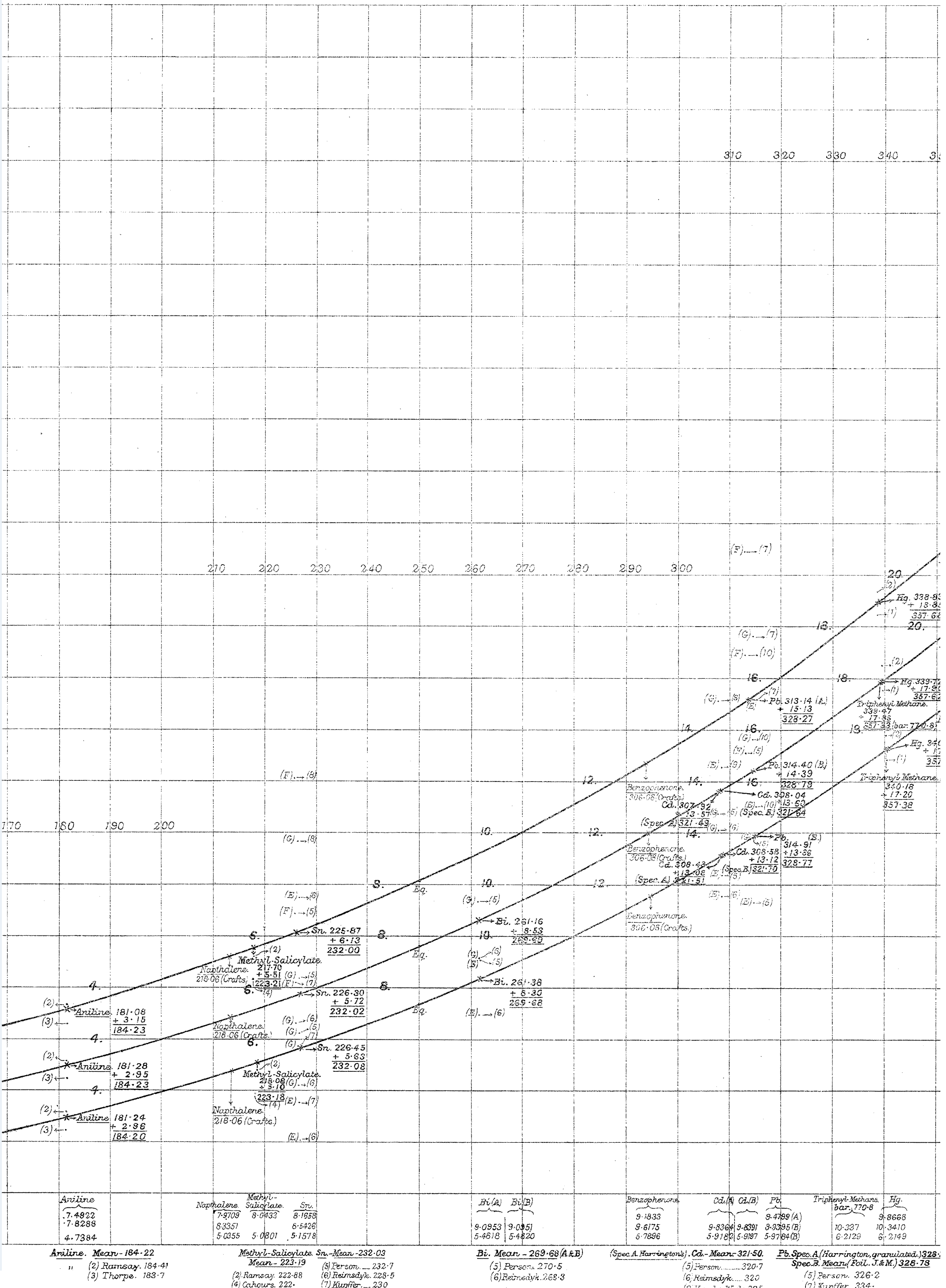
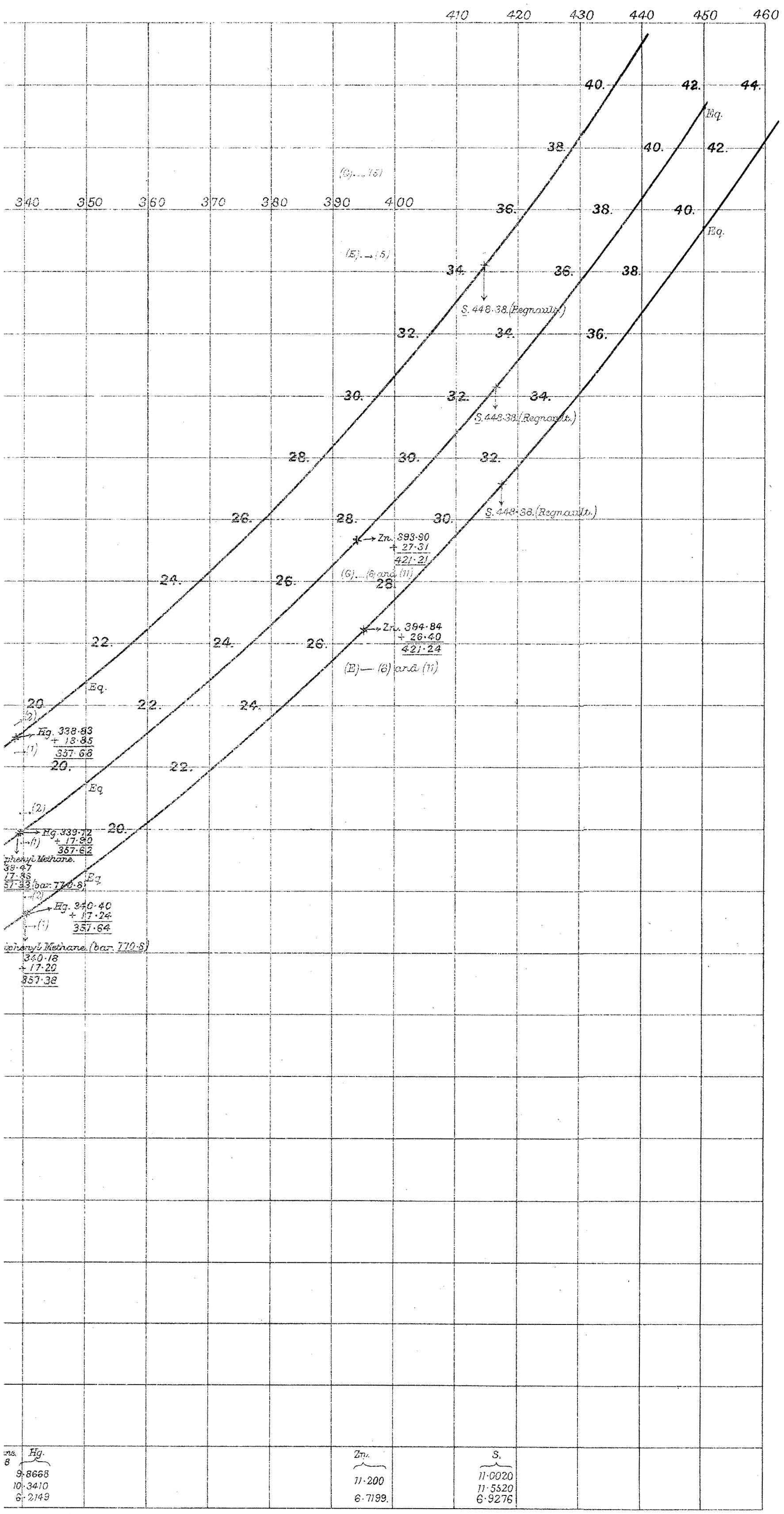




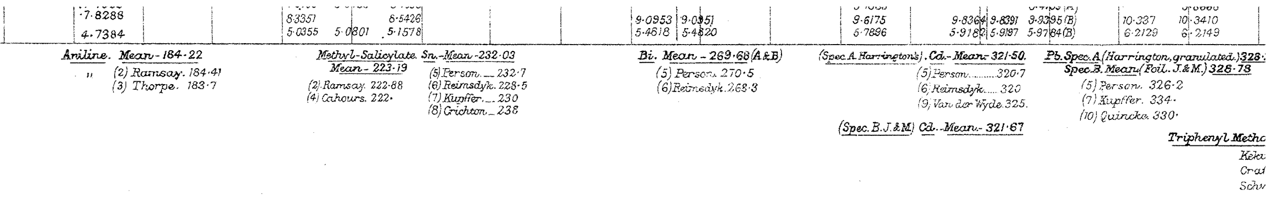
,granulated.) **328·27**
.J.&M.) **328·78**
·2

Hg. Mean. 357·65
" (1) Regnault. 357·25
" (2) Ramsay. 358·2

Zn. Mean. 421·23.
(6) Reimsdyk. 420
(11) Wright & Luff. 420

[illegible]	[illegible]	4·7667					[illegible]					[illegible]							
mp. of	G.	4·9542										6·5399							
& lat. of	E.	3·0569										3·9848							

Points marked Eq. were deduced from equation.



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

10·3410					11·200		11·5520				
6·2149					6·7199.		6·9276				

,granulated.) **328·27**
.J.&M.) **328·78**
·2
0·

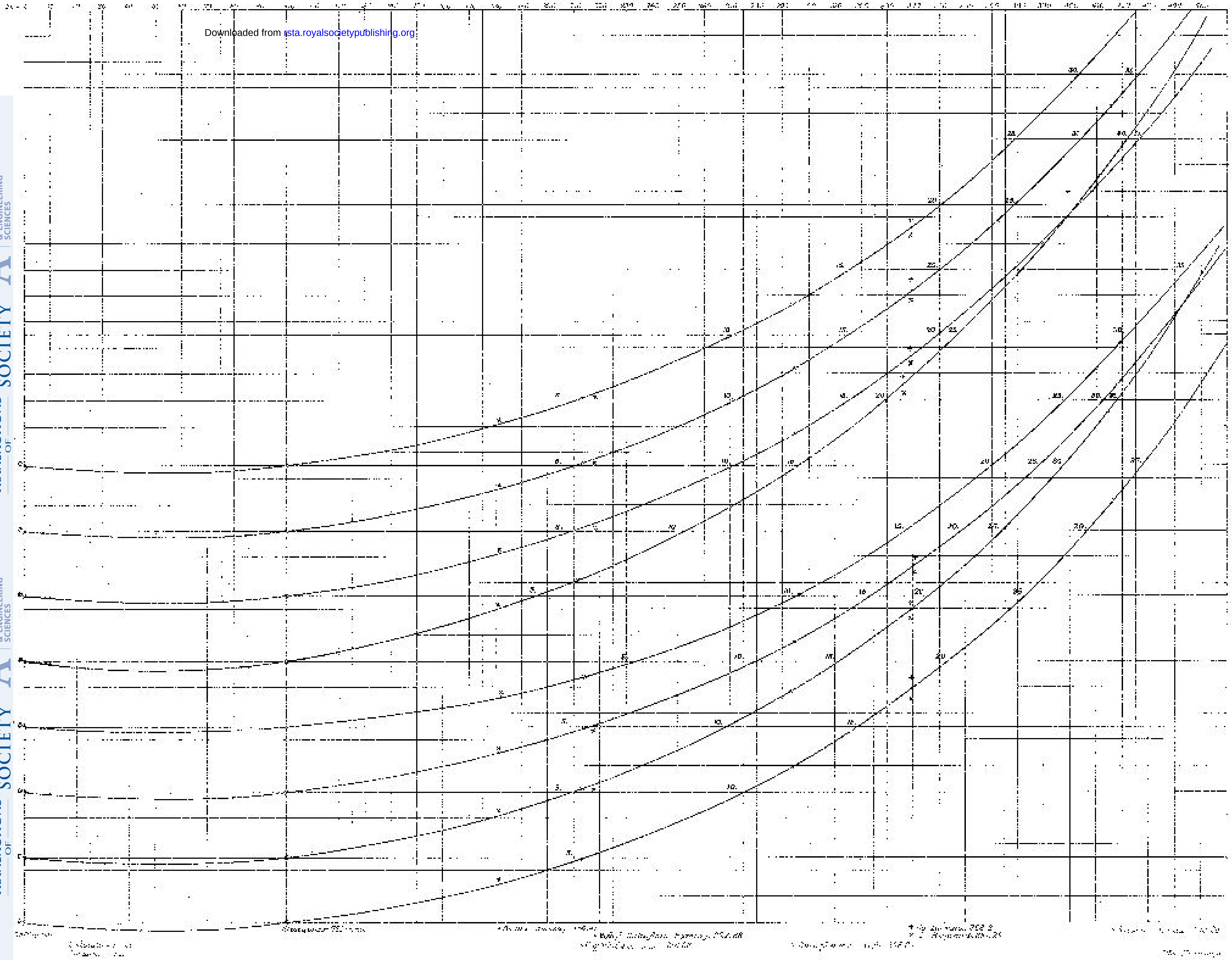
Hg. Mean. 357·65
„ (1) Regnault. 357·25
„ (2) Ramsay. 358·2

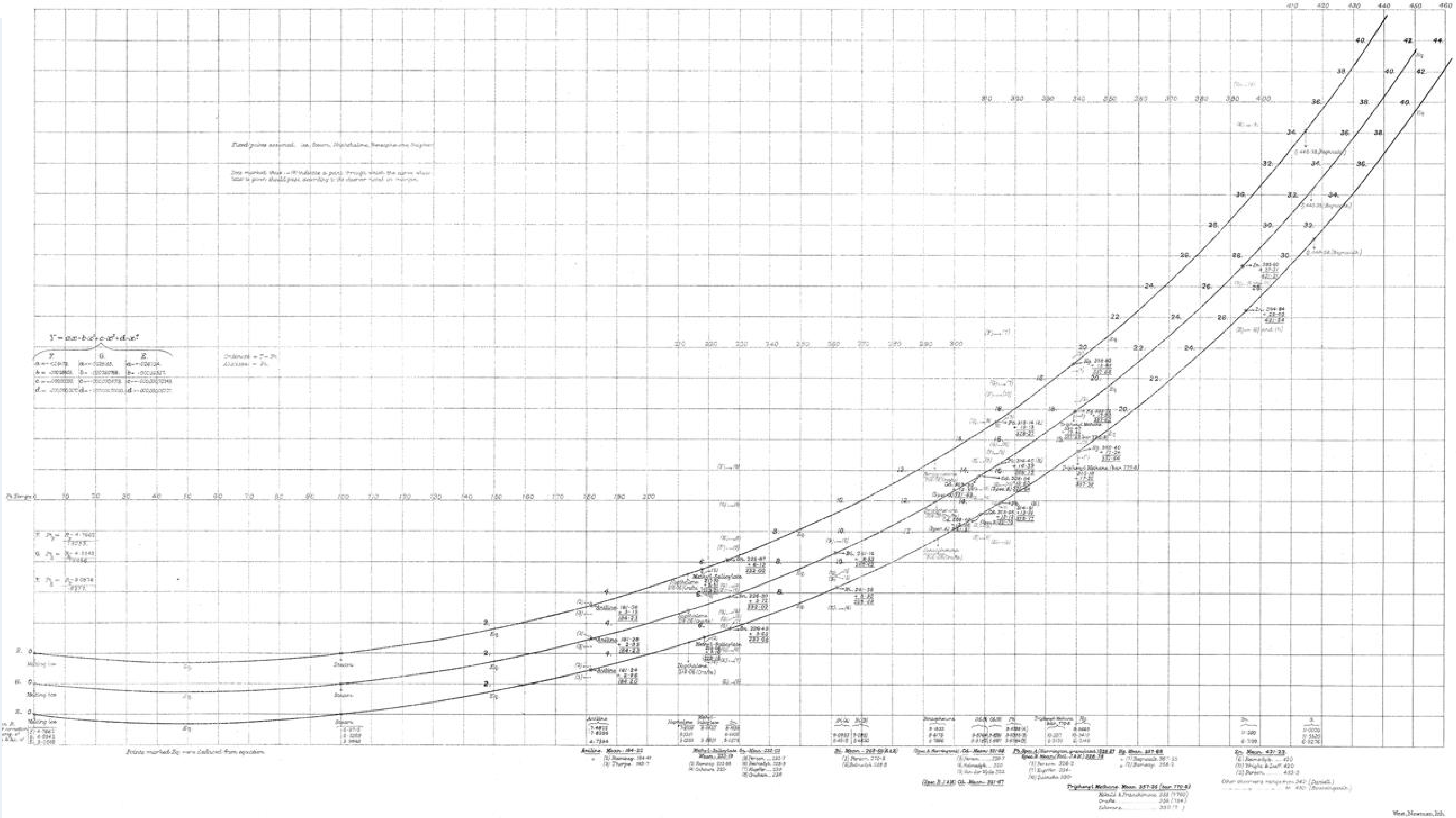
Zn. Mean. 421·23.
(6) Reimsdyk. 420
(11) Wright & Luff. 420
(5) Person. .... 433·3

Other observers range from 342· (Daniell.)
.... „ .... „ .... „ ...... to 450· (Boussingault.)

Triphenyl Methane. Mean 357·35 (bar. 770·8)
Kekulé & Franchimont. 355 (? 760)
Crafts. 358 (754)
Schwarz.......................... 330 (?)

West, Newman, lith.





$Y = a.x + b.x^2 + c.x^3 + d.x^4$

Points marked Eq. were deduced from equation.

West, Newman, lith.