XXV.—*On High Melting Points, with Special Reference to those of Metallic Salts.*

By THOMAS CARNELLEY, B.Sc., F.C.S., Demonstrator in the Chemical Laboratory of The Owens College.

PART I. *Description of a New Method proposed for Determining the same.*

WITH the exception of a few, which melt at a comparatively low temperature, the melting points of the different metallic salts, and even of the high-melting alloys, &c., have not been determined and represented numerically, so far as I have been able to ascertain; and what we know with reference to these points is of a very indefinite character, such as that the salt in question melts just below a red heat, at a dull red heat, or at a full red heat, &c.; while with respect to any connection there may be between this physical property and others, or between it and the chemical composition and properties, we know still less. Further, in the accurate comparison of some other physical properties of salts, it would be necessary that the determination of the figures representing the numerical relation between these properties should be made at their melting points, or at any rate at equal distances from them, such, for instance, as the determination of the specific heats, and also of the specific gravities, when the latter are employed in the calculation of the molecular volumes by dividing the molecular weights by them; other cases also might be mentioned. So that taking these things into consideration, and at the same time not forgetting the great difficulty of determining high temperatures, it appeared that it would be useful to have a method by which the fusing points of the different metallic salts could be determined, if not with the accuracy attainable in other cases, yet at the very least with some approach to the correct number.

Though the melting points of the principal metals have been determined, as is well known, by means of pyrometers, especially by Daniell, yet neither he nor others extended their investigations to the metallic salts; and even if that method could be conveniently used for the latter purpose, it would require too large an amount of the substance to be generally useful.

In the present paper I wish to bring before the Society the description of a method, which I have employed for the above-mentioned purpose, and also the results which I have so far obtained. The method is applicable when only a small quantity of the salt is at hand, for it requires no more than a few centigrams to make several determinations.

When I had almost completed the work which I have so far done in this direction, I saw in the Society's Journal (vol. xxviii, 996), an extract from *Poggendorff's Annalen* (cliv, 161—196) of a paper by F. Braun, "On the Electric Conductivity of fused Salts," in which he gives the melting points of a few metallic salts, obtained in a secondary manner by the method employed by him for the estimation of their electric conductivity.

The present paper I have divided, for the sake of clearness, into the following headings:—

- (1.) The description of the method which I propose to employ for the determination of high melting points.
- (2.) An account of the results so far obtained.
- (3.) Determination of the corresponding solidifying points and results.
- (4.) An account of a few tests employed to prove in some measure the correctness of the method now described.
- (5.) A comparison of some of these results with those obtained by Braun, and also of the respective methods by which they were arrived at.

The Description of the New Method.—The principle of the method is this:—When a small quantity of the salt is placed in a weighed platinum crucible, and the latter suspended in the flame of a Bunsen's burner or of a blowpipe, the temperature of the crucible after a time reaches that at which the salt fuses, if the latter is not beyond a certain limit; and now if the crucible, the instant the salt is seen to melt, be dropped into a known weight of water of known temperature, and the rise in temperature noted, then, from the well known equation for specific heats, we obtain the initial temperature of the crucible at the moment the salt melted, and therefore the temperature at which the fusion occurred, assuming that the mean temperature of the crucible is the same as that of the salt at the moment of melting.

The details of the apparatus employed will be easily understood with the help of the accompanying figures.

Fig. I represents the crucible employed, and is of about the actual size. It is of platinum, and is 25 mm. across on the outside each way, and 16 mm. in height; it is 9.5 mm. deep, the walls being 2.5 mm. thick; the inside floor of the crucible is flat, and the whole weighs 128 grams. It can be suspended by means of four thin platinum

wires attached to each corner respectively and united at (*g*) to a platinum wire, about 180 mm. long, and this again to a fine twisted iron wire 100 mm. long, and the latter to whipcord of convenient length.

FIG. I.

FIG. II.

FIG. III.

In Fig. II is represented the calorimeter and its casings. The former (C) is of copper, thinly coated on the inside with polished tin, and has a capacity of about 200 c.c. It has a pretty wide lip round its mouth by which it can be suspended in an empty beaker of thin glass (B), leaving an empty space between it and the latter, which is in turn placed in another beaker (A), the space between the two being filled with cotton wool. The calorimeter can be covered by a cardboard lid (*mn*) Fig. III, provided with a slit (*d*), for the suspending wire of the crucible; it is also perforated by a hole, in which the thermometer (*ab*) is permanently fixed by a cork (*c*). The thermometer used reads as high as 40° C., and is divided so that 0.05° can be read off with tolerable ease; it is placed so that the bulb may be in about the centre of the water.

In Fig. IV is shown the arrangement of the apparatus during the course of a determination. $\alpha\beta\gamma\delta\theta$ is a kind of oblong wooden box set on end, the top and the side towards H being wanting. The sides $\alpha\beta$, $\beta\gamma$ and $\gamma\delta$, have the following lengths respectively, 200, 170, and 400 mm.

FIG. IV.

The crucible (A) is suspended in the flame of the lamp (B) by means of the wire (C), which passes over the pully (N), and can be attached

by the peg (M) at any point. N consists of a piece of bent glass rod attached to the horizontal support (ON), which can be fixed at any height on the vertical rod (PQ) by means of the screw at O. Round the interior of the box, at about 170 mm. from the top, there runs a ledge on which slides a movable floor (K), which consists of the horizontal piece (*cefdg*), and the vertical piece (*abcd*), both firmly united together; by means of the handle (*g*) this floor can be slid in and out. That part of the box above K, together with the upper surface of the latter, and the inside of *abcd*, is lined with sheets of polished tin.

D represents the calorimeter, which stands on a small carriage (E), running on wheels in a smooth groove, so that it may be brought up opposite the telescope, H, by pulling the cord GF. *mn* is a vertical slit in the back of the box, wide enough to admit the tube of the Bunsen's burner (B), the foot of which rests outside the box on a wooden support (L), the height of which can be varied at pleasure; the lamp can also be moved easily backwards and forwards in or out of the slit, and even to a small extent horizontally, and to greater extent vertically over a small arc with the slit as centre. In making an experiment the tube of the lamp is not quite horizontal, but inclined slightly upwards.

In making a determination the following is the method of procedure:—A quantity of water is weighed out into the calorimeter, and the latter brought on the carriage before the telescope (H); the lid and the thermometer (Fig. III) having been placed in position, the calorimeter is allowed to stand for some time, so that the temperature may become the same as that of the air. In the meantime 1 or 2 milligrams of the pure dry salt are placed as nearly as possible in the centre of the platinum crucible, which is next suspended over the pulley (N), and the latter so arranged that the crucible may be in the centre of the flame, and also exactly drop into the calorimeter at the requisite moment on releasing the cord at M.

The temperature of the calorimeter having been noted, the telescope is raised to about the height to which the mercury will rise after the crucible has been dropped into the water; the thermometer and lid of the calorimeter are then removed, and the lamp lit. The salt in the heated crucible is carefully watched, and a few seconds before the salt melts (which can be pretty nearly judged by a previous rough experiment), the calorimeter is run under the crucible. The observer, who holds the handle (*g*) in his left hand, and the cord (MC) in his right, the moment the salt melts removes the floor (K), and at the same time drops the crucible into the water, while an assistant immediately pulls up the carriage before the telescope (H), and by working the platinum wire attached to the crucible mixes the water in the calorimeter so as to insure its being of the same temperature

throughout; in the meantime the lid carrying the thermometer is placed over the water by the observer, who also reads off the highest temperature to which the mercury rises. The whole operation, from the moment of the melting of the salt to the reading off of the final temperature, can be done, after a little practice, in a few seconds, while the mercury, after it has risen to its highest point, does not visibly begin to fall for about half a minute, and then only very slowly, depending of course on the temperature, so that the error of reading, arising from the loss of time between the dropping of the crucible into the calorimeter and the reading off, would not at the most amount to more than 0.05° .

When the blow-pipe is used, if it be properly arranged, the observer can, while watching the crucible, also work the blast, but it is much more convenient if this is done by an assistant.

The open part of the slit (*mn*) above the lamp is closed by a piece of tin, so as to prevent any draught. A small telescope (T) supported on the rod (*s*), so that it can be moved in both a vertical and a horizontal plane, and provided with a lens of pretty long focal length, may be used to observe the moment of fusion.* For most cases, however, it is more convenient to use the naked eye.

The moment at which the salt melts can be readily seen, this only being at all difficult when it fuses at a very high temperature, and even this is soon overcome by a little practice.

Calculation of the Results.—For this purpose the data required are the following:—

Weight of water in calorimeter	..	..	..	..	= W.
Specific heat of water	..	..	..	..	= <i>r</i>
Value of calorimeter + mercury and glass of thermometer					
in grammes of water	..	..	..	..	= <i>w</i> .
Weight of platinum crucible	..	..	..	..	= M.
Specific heat of platinum for $(0-T)^{\circ}$ C.	..	..	..	..	= <i>s</i> .
Initial temperature of water	..	..	..	..	= <i>t</i> .
Final temperature of water	..	..	..	..	= θ .

the values of which, inserted in the following equation, give on calculation the value of T, which represents the temperature of the hot crucible at the moment the salt fuses, and therefore, making the assumption already mentioned, the melting point of the salt.

$$M \times s \times (T - \theta) = (W + w) \times r \times (\theta - t)$$

$$\text{or} \quad (T - \theta) = \frac{(W + w) \times r \times (\theta - t)}{M \times s}$$

The value of (*r*) was taken as 1.008, being the specific heat of water for $(13-98)^{\circ}$ C.

* Of course care must be taken that the lens is not cracked by the heat.

The value of the calorimeter, &c. (w) was found to be equivalent to 9.487 grms. of water.

The value of s for the different values of T was calculated from the table of the specific heats of platinum at different temperatures found by Pouillet, and given in Watts's *Dictionary* (vol. iii, p. 36).

M indicates the weight of the crucible together with that of the wires crossing its upper surface. The very small quantity of heat given up by the short portion of the suspending wire, which was immersed in the water, was neglected, as it and the small quantity which would be lost in dropping the crucible into the water would tend to compensate each other.

The quantity of salt used (1 or 2 milligrams) was too small to produce any sensible error through the heat which it would give up to the water, so it was not taken into account.

The Results so far obtained.—The determinations which I have made up to the present are preliminary to a systematic estimation of the melting points of the more important metallic salts, which I hope in time to execute, and have been carried out more for the sake of testing the method, as to whether the results it gives agree among themselves, and also as to how far they agree with those few which have been got by other observers by other methods.

I have so far carefully determined the melting points of 28 different salts, ranging from silver nitrate, the most easily fusible, to sodium sulphate, the most difficult of fusion, and the results obtained are given in Table I, from which it will be seen that they agree sufficiently well among themselves, considering the difficulties in the way of estimating high temperatures. The extent to which they coincide with the results obtained by others will be pointed out further on.

Every result which has been obtained for each salt, is given together with the data required for the calculation, in order that the extent to which the numbers differ from one another may be seen in every instance. Those melting points which differ much from the rest of the same salt are marked with an asterisk to show that they are not taken into account in calculating the mean. There are seven of these cases, and it will be seen that of these, four were the first determination that was made of the salt in question, when the eye had not become sufficiently accustomed to the appearance of the salt just before fusion, and was therefore not so fully prepared for the exact moment of melting.

In the second column, under the heading "Source of Heat," L signifies that the Bunsen's burner, and B that the blowpipe was used in each particular case respectively. The symbols heading the other columns have the signification attached to them on page 494.

TABLE I.

1. Salt.	2. Source of heat.	3. W + w	4. M.	5. S	6. <i>t</i> .	7. θ	8. $\theta - t$.	9. Melting point.	10. Mean.
AgNO ₃	(1) L	183·92	127·932	0·03400	18·20	22·88	4·68	222	} 224° C.
	(2) "	184·16	"	at	19·30	24·07	4·77	228	
	(3) "	184·68	"	(0—220)° C.	19·43	24·10	4·67	224	
	(4) "	166·48	"		19·60	24·79	5·19	225	
	(5) "	184·44	"		20·59	25·13	4·54	219	
HgCl ₂	(1) L	191·28	127·478	0·03434	13·30	19·78	6·48	305	} 302° C.
	(2) "	182·38	"	at	13·52	20·15	6·63	299	
	(3) "	185·34	"	(0—300)° C.	13·60	20·20	6·60	302	
NaNO ₃	(1) L	183·01	128·933	0·03447	16·92	24·60	7·68	343*	} 330° C.
	(2) "	183·01	"	at	16·80	24·10	7·30	327	
	(3) "	182·33	"	(0—330)° C.	16·80	24·24	7·44	332	
	(4) "	181·44	"		16·85	24·30	7·45	331	
KNO ₃	(1) L	183·77	128·933	0·03455	15·07	22·98	7·91	352	} 353° C.
	(2) "	184·18	"	at	15·35	23·23	7·88	352	
	(3) "	183·83	"	(0—350)° C.	15·60	23·58	7·98	355	
KClO ₃	(1) L	183·29	128·933	0·03467	14·37	22·78	8·41	370	} 372° C.
	(2) "	182·19	"	at	14·62	23·20	8·58	376	
	(3) "	182·20	"	(0—380)° C.	15·10	23·55	8·45	371	
AgBr	(1) L	184·51	128·696	0·03489	19·91	30·00	10·09	448*	} 434° C.
	(2) "	184·14	"	at	18·40	28·30	9·90	437	
	(3) "	184·67	"	(0—430)° C.	18·66	28·42	9·76	433	
	(4) "	183·97	"		18·78	28·58	9·80	433	
TiCl	(1) L	184·21	128·571	0·03493	18·50	28·37	9·87	436	} 434° C.
	(2) "	184·47	"	at	18·60	28·50	9·90	438	
	(3) "	184·54	"	(0—440)° C.	18·70	28·40	9·70	430	
	(4) "	184·03	"		18·95	28·71	9·76	432	
LiI	(1) L	184·18	128·696	0·03501	16·80	27·26	10·46	458	} 453° C.
	(2) "	183·13	"	at	16·65	26·99	10·34	451	
	(3) "	183·49	"	(0—460)° C.	17·00	27·28	10·28	449	
TiI	(1) L	184·63	128·571	0·03497	20·30	30·59	10·29	456*	} 446° C.
	(2) "	184·33	"	at	20·40	30·40	10·00	444	
	(3) "	183·93	"	(0—450)° C.	20·60	30·68	10·08	446	
	(4) "	184·19	"		20·80	30·90	10·10	448	
AgCl	(1) L	184·59	128·696	0·03501	20·26	31·10	10·84	478*	} 457° C.
	(2) "	184·02	"	at	20·60	31·00	10·40	459	
	(3) "	183·89	"	(0—460)° C.	20·35	30·60	10·25	452	
	(4) "	184·07	"		19·65	30·00	10·35	456	
	(5) "	184·54	"		19·99	30·38	10·39	459	
TiBr	(1) L	183·95	128·571	0·03506	19·70	30·30	10·60	466	} 463° C.
	(2) "	184·38	"	at	19·60	30·10	10·50	463	
	(3) "	184·36	"	(0—470)° C.	19·60	30·02	10·42	460	

TABLE I (continued).

1. Salt.	2. Source of heat.	3. W + w	4. M.	5. S.	6. <i>t</i> .	7. θ	8. $\theta - t$.	9. Melting point.	10. Mean.
AgI	(1) I ₂	184.29	128.571	0.03530	19.73	31.88	12.15	529	} 530° C.
	(2) „	183.92	„	at	20.01	32.20	12.19	530	
	(3) „	184.56	„	(0—530)° C.	19.82	31.98	12.16	530	
LiCl	(1) L	182.72	128.933	0.03560	17.00	31.30	14.30	605	} 602° C.
	(2) „	184.27	„	at	17.11	31.39	14.28	609	
	(3) B	181.61	„	(0—600)° C.	17.12	31.20	14.08	592	
	(4) „	182.84	„	„	17.35	31.53	14.18	601	
NaI	(1) B	184.24	128.696	0.03573	16.45	31.39	14.94	635	} 633° C.
	(2) „	184.31	„	at	16.35	31.00	14.65	623	
	(3) „	184.49	„	(0—630)° C.	16.65	31.70	15.05	640	
	(4) „	185.05	„	„	16.80	31.05	14.25	610*	
	(5) L	183.43	„	„	16.80	31.90	15.10	639	
	(6) „	184.19	„	„	16.82	31.85	15.03	638	
	(7) B	184.14	„	„	17.05	31.75	14.70	625	
KI	(1) L	183.85	127.932	0.03577	20.39	35.40	15.01	643	} 639° C.
	(2) „	184.61	„	at	20.39	35.00	14.61	629*	
	(3) „	183.81	128.571	(0—640)° C.	20.70	35.52	14.82	633	
	(4) „	184.49	„	„	20.80	35.70	14.90	638	
	(5) „	183.88	„	„	20.82	35.81	14.99	640	
	(6) „	184.67	„	„	20.61	35.60	14.99	642	
CaBr ₂	(1) L	183.90	128.696	0.03594	13.90	30.59	16.69	699	} 680° C.
	(2) „	184.94	128.933	at	14.78	30.60	15.82	667	
	(3) B	184.30	„	(0—680)° C.	14.55	30.75	16.20	680	
	(4) L	182.96	„	„	14.88	31.10	16.22	677	
	(5) „	183.43	„	„	15.50	31.00	15.50	650*	
	(6) „	182.59	„	„	15.00	31.30	16.30	679	
KBr	(1) B	183.69	128.696	0.03602	18.40	35.07	16.67	701	} 703° C.
	(2) „	184.24	„	at	18.55	35.20	16.65	702	
	(3) „	182.99	„	(0—700)° C.	18.65	35.50	16.85	706	
Li ₂ CO ₃	(1) L	183.84	128.933	0.03602	15.80	32.60	16.80	703	} 699° C.
	(2) „	184.93	„	at	16.19	32.87	16.68	702	
	(3) B	183.54	„	(0—700)° C.	15.50	32.04	16.54	691	
	(4) „	184.39	„	„	15.70	32.40	16.70	701	
NaBr	(1) B	184.86	128.696	0.03610	18.32	35.00	16.68	704	} 712° C.
	(2) „	183.84	„	at	18.43	35.52	17.09	717	
	(3) „	184.21	„	(0—720)° C.	18.12	35.35	17.23	724	
	(4) „	183.95	„	„	18.20	35.00	16.80	706	
	(5) „	183.22	„	„	18.40	35.33	16.93	708	
	(6) „	183.84	„	„	18.50	35.55	17.05	716	
CaCl ₂	(1) L	184.72	128.571	0.03610	20.90	38.00	17.10	724	} 723° C.
	(2) „	183.77	„	at	21.20	38.35	17.15	723	
	(3) „	183.97	„	(0—720)° C.	20.99	38.10	17.11	722	
	(4) „	183.84	„	„	20.40	37.60	17.20	724	

TABLE I (*continued*).

1. Salt.	2. Source of heat.	3. W + w	4. M.	5. S.	6. <i>t</i> .	7. θ	8. $\theta - t$.	9. Melting point.	10. Mean.
KCl	(1) B	184·69	128·696	0·03619	18·27	35·70	17·43	732	} 738° C.
	(2) „	184·09	„	at	17·32	35·80	17·88	748	
	(3) „	184·06	„	(0—740)° C.	18·25	35·82	17·57	736	
	(4) „	183·24	„		18·40	36·10	17·70	738	
NaCl	(1) B	184·05	128·696	0·03636	17·20	36·30	19·10	793	} 776° C.
	(2) „	183·86	„	at	18·32	36·80	18·48	769	
	(3) „	183·91	„	(0—780)° C.	18·80	37·40	18·60	774	
	(4) „	182·91	„		18·03	36·80	18·77	776	
	(5) „	187·79	„		18·45	36·81	18·36	779	
	(6) „	190·02	„		18·52	36·70	18·18	781	
	(7) „	182·05	„		18·77	37·22	18·45	761	
	(8) „	188·36	„		19·00	37·20	18·20	776	
Na ₂ CO ₃	(1) B	185·05	127·478	0·03652	12·15	32·00	19·85	827	} 818° C.
	(2) „	185·93	„	at	19·00	38·20	19·20	811	
	(3) „	184·97	„	(0—820)° C.	16·78	36·21	19·43	814	
	(4) „	184·38	„		16·30	35·95	19·65	820	
Li ₂ SO ₄	(1) B	182·28	128·933	0·03657	16·90	37·10	20·20	824	} 822° C.
	(2) „	181·26	„	at	18·88	39·00	20·12	819	
	(3) „	184·07	„	(0—830)° C.	18·85	38·82	19·97	825	
	(4) „	184·66	„		18·78	38·62	19·84	822	
SrCl ₂	(1) B	184·73	128·696	0·03657	17·02	36·90	19·88	823	} 829° C.
	(2) „	183·39	„	at	17·10	37·35	20·25	833	
	(3) „	184·72	„	(0—830)° C.	17·20	37·25	20·05	830	
K ₂ CO ₃	(1) B	183·88	128·933	0·03660	18·45	38·80	20·35	838	} 838° C.
	(2) „	181·73	„	at	18·60	39·22	20·62	840	
	(3) „	182·93	„	(0—840)° C.	18·40	38·80	20·40	836	
Na ₂ SO ₄	(1) B	183·78	127·478	0·03673	15·60	36·60	21·00	867	} 865° C.
	(2) „	184·74	„	at	14·85	35·75	20·90	867	
	(3) „	182·50	„	(0—870)° C.	14·62	35·60	20·98	860	
PbCl ₂	(1) L	184·12	127·478	0·03518	14·50	26·01	11·51	502	} 501° C.
	(2) „	182·53	„	at	14·07	25·65	11·58	501	
	(3) „	181·75	„	(0—500)° C.	13·75	25·35	11·60	499	

Determination of Solidifying Points.

This is done by the same method as that employed for the estimation of the melting points, but with this difference, viz., that when the salt has completely melted the lamp is turned out, and the crucible, still suspended from the pulley, carefully watched, and the moment the salt begins to solidify, dropped at once into the calorimeter, after which the process is the same as in the former case. The same

amount of salt, viz., 2 or 3 milligrams, is used as in the determination of the melting points.

It is usually pretty easy to see when the salt solidifies, but it not unfrequently occurs that the solidified salt forms a transparent glass not in the least opaque, in which case it is very difficult, if not impossible, to tell when the salt becomes solid. The best way to do so is to place a bright gas flame at the opposite side of the crucible, so that its image may be seen reflected from the surface of the melted salt, which image, the moment the salt solidifies, becomes blurred and indistinct, or disappears altogether.

In the following table are given the solidifying salts I have determined, together with the corresponding mean melting points given in Table I.

TABLE II.

Salt.	Solidifying point.	Mean S.P.	Melting point.	Difference.
KNO ₃ (1) (2) (3)	324 } 333 } 338 }	332° C.	353° C.	21° C.
KClO ₃ (1) (2)	351 } 351 }	351° C.	372° C.	21° C.
TlCl (1) (2)	412 } 417 }	415° C.	434° C.	19° C.
KI (1) (2)	621 } 622 }	622° C.	639° C.	17° C.
KBr (1) (2)	681 } 688 }	685° C.	703° C.	18° C.
K ₂ CO ₃ (1) (2) (3)	825 } 841 } 829 }	832° C.	838° C.	6° C.

From this table it will be seen that the solidifying and melting points as found agree very nearly, considering the difficulty of registering high temperatures, and they do so much better than one would expect previous to making the determinations. The different estimations of the solidifying points of the same salt also agree very well among themselves, as well in fact as the melting points; it is, however, more difficult to hit the exact point of solidification than that of fusion.

Two experiments were also made in the case of potassium chlorate, in order to see if the same results, with respect to the solidifying point, were obtained when the crucible was full of salt as when there were

only 2 or 3 millegrams placed in it for each determination, the point of solidification being taken as that at which the first appearance of a crust or scum was seen on the surface of the fused salt. In this case of course the heat which the salt itself would give up to the water had to be taken into account. The numbers obtained are given in Table III, the specific heat of potassium chlorate used in the calculation being that obtained by Kopp (First Supplement to Watts's *Dictionary*, p. 667).

TABLE III.

Salt.	Source of heat.	W + w	M.	S.	Weight of salt.	Specific heat of salt.
KClO ₃ (1)	L	185·45	127·478	·03459 at	4·179	·194
(2)	L	180·83	—	(0 – 360°)	4·311	—

t.	θ.	Solidifying point.	Mean.	Melting point.
13·10	22·82	371	} 358° C.	372°
13·40	22·70	346		

This method, as the above results show, gives good results, the mean of the two determinations approaching nearer to the melting point even than the first method; I am, however, inclined to think that the latter would, as a rule, give the more correct results.

Tests employed to Prove in some measure the Correctness of the Method.

Though the method I have described for the determination of high melting points be theoretically correct, yet, as practically it might give results varying considerably from the true ones, it seemed desirable to submit it to all the tests that could be brought to prove or disprove in any way the correctness of these results; but owing to the difficulties in the way, very few tests, at least of any weight, could be applied, and these by no means conclusive ones in either direction. Such tests as I have so far been able to bring to bear on the point are as follows:—

(a.) First and foremost, of course, come the few determinations which have been made by other observers by other methods, of which the following table gives a view. In it I have not included the more numerous results obtained by Braun, to which attention has already

been drawn, as I wish to speak of them more fully in a subsequent paragraph.

TABLE IV.

Salt.	New method.		Melting point, as found by other observers.
	Melting point.	Mean.	
AgNO ₃	219—228	224° C.	219° C., Watts's <i>Dictionary</i> . { 265° C., Watts's <i>Dictionary</i> . I found it to be (275°—278°) by the mercurial thermometer, and this corrected gave (285°—288°) as the true melting point. { 310° C., as found by Person. Schaffgotsch found the solidifying point to be 313° C. { 339° C., Person. { About 260° C. is given as the melting point in Gmelin's <i>Handbuch der Chemie</i> , 4te Auflage iii, 619, and in Watts's <i>Dictionary</i> ; but this must certainly be wrong, since I found that AgCl does not melt at the highest tempera- ture at which the mercurial thermometer can be used (300°—320°); nor does it melt even in molten zinc, whose melting point is 412° C.
HgCl ₂	299—305	302° C.	
NaNO ₃	327—332	330° C.	
KNO ₃	352—355	353° C.	
AgCl	452—459	457° C.	

Of the melting points of the different salts which I have determined by the new method, only those of the five given in the above table have been estimated by other observers (*i.e.*, not including Braun's results), and of these the last must be omitted, as 260° C. cannot very well be its melting point, for the reason already given; of the remaining four, that of silver nitrate agrees sufficiently well with that obtained by the ordinary method, so that only those of mercuric chloride, sodium nitrate, and potassium nitrate are left, which, though agreeing moderately well, differ by more than I like from the melting points usually ascribed to them, *viz.*, mercuric chloride by 16°, sodium nitrate by 18°, and potassium nitrate by 14°.

(*b.*) That the temperature at different parts of the crucible was appreciably the same the following results show:—

Small portions of potassium chlorate or of potassium iodide placed in each of the four corners of the crucible, and heated over the lamp, melted at exactly the same moment.

Small portions of either of the same salts placed in the centre and one corner respectively, on heating as before, melted simultaneously.

Small portions of potassium chlorate placed on the top of the walls of the crucible at different points melted as nearly as possible together, provided of course that the flame did not play directly on the salt. The same result was also got when one portion of the salt was placed

on the top of the wall and another at the middle of the inside of the crucible.

From the above it appears that when the Bunsen's burner is used the temperature at all parts of the crucible is appreciably the same. Similar results with the same salts were obtained when the blowpipe was employed, the salts melting, as nearly as the eye could judge, at the same time at whatever part of the crucible they were placed. One or two of the experiments, however, appeared to show that the temperature of that side of the crucible nearest the blowpipe was, if anything, slightly higher than the side *b* furthest removed from it. But, even if this were the case, it would not make any material difference, since the salt, in making a determination, being always placed in the centre of the crucible, would have the mean temperature of the latter. This is also borne out by the results given in Table I, where the same or nearly the same melting point is obtained whether the lamp or blowpipe be used.

(*c.*) The same results were obtained whether the salt, whose melting point was required, had been previously fused or not.

(*d.*) In order to prove whether the values obtained for the melting points of the different salts given in Table I were correct with respect to the order of melting, small portions of two of the salts were placed in the crucible at the same time, beginning with the two most easily, and going on successively to the more difficultly fusible, and the order of their melting observed, with the following results :—

TABLE V.

Salt.	Melting point.	Order of melting, as found by trial.
NaNO ₃	330	1
KNO ₃	353	2
KClO ₃	372	3
AgBr	434	4
TlCl	434	4 } Melted at the same time.
LiI	453	4
TlI	446	7
AgCl	457	8
TlBr	463	8 } Melted as nearly as possible together, if any- thing, AgCl rather the first.
AgI	530	10
NaI	633	11
KI	639	11 } Melted simultaneously.
CaBr ₂	680	13
Li ₂ CO ₃	699	14
KBr	703	15
NaBr	712	16
CaCl ₂	723	16 } Ditto.
KCl	738	18
NaCl	776	19
SrCl ₂	829	20

The above table needs, I think, scarcely any comment, since it is seen at once that it supports the correctness of the method as fully as could be expected, for there is only one case, viz., that of lithium iodide, whose melting point = 453, in which the order of melting, as found by experiment, is the reverse of what might be expected from the determined melting points, for it was found to melt before thallium iodide (whose melting point as estimated = 446), and as nearly as possible simultaneously with silver bromide and thallium chloride. In other cases of course, where the melting points are very near together, the salts appeared to melt at the same moment.

(e.) Another test employed was the following :—Small portions of the finely powdered salts were placed in capillary tubes, and the latter then immersed in baths of molten lead or zinc, kept as nearly as possible at their melting points, by allowing a portion of the metal to remain unfused.

The melting points of these metals being known, those salts which had been found to fuse below those temperatures ought of course to melt when immersed in the molten metals; while those on the contrary, which had been found to melt higher, ought not to fuse in them.

The following table gives the results obtained :—

TABLE VI.

In molten lead, M.P. = 335.			In molten zinc, M.P. = 412.		
Salt.	M.P.	Effect.	Salt.	M.P.	Effect.
NaNO ₃	330	Melted.	AgBr	434	Melted, but only just, and after remaining in the bath for a long time.
KNO ₃	353	Melted.	TlCl	434	Ditto.
KClO ₃	372	Shrank, but did not melt.	TlI	446	Did not melt, only changed to a red colour.
AgBr	434	Did not melt.	AgCl	457	Did not melt.
TlCl	434	Did not melt.			

Whatever conclusions may be drawn from the above results will of course have to assume the correctness of the melting points assigned to the two metals employed; the numbers given are those found by Daniell.* I hope shortly, by a modification of the present method, to be able to determine the melting points of the more easily fusible metals and alloys, when the fusing points of lead and zinc, as found by the above observer and by this method, can be directly compared.

* Lead begins to fuse at 325°, and is completely melted at 335° C.

(f.) It has already been seen that the melting and solidifying points of the several salts as found agree very well, and more nearly almost than one would have expected; and this fact, though affording only a secondary kind of argument in favour of the correctness of the results, is of considerable value when more direct proofs are so difficult and so little available. The same may be said of the different melting points of the same salt.

Of the above tests *b*, *c*, *d*, and *f*, such as they are, speak decidedly in favour of the correctness of the method, while *a* and *e* seem to show that the results it gives are a little too high, 22° C. being the greatest divergence between the numbers as found and what they ought to be according to *a* and *e*.

Comparison of some of the results obtained with those of Braun, and also of the respective methods by which they were arrived at.

As mentioned at the beginning of this paper, Braun has lately published the results of some determinations which he has made of the melting points of a few metallic salts. The following is his account of the method somewhat curtailed:—"A thermo-element of platinum and iron was used for this purpose (viz., the determination of the melting points of metallic salts). In order to protect the iron from being attacked by the fused salt, it was surrounded by a thin piece of platinum foil, which was pressed close to the iron by means of platinum wire twisted round it. Up to temperatures of 260° C., the thermo-electric power of the combination showed itself proportional to the differences of temperature at the points where the metals were soldered together, as has already been shown by Gauguin (*Ann. Chim. Phys.* [3], lxx, 1862), and recently by Beetz (*Pogg. Ann. Jubelband*); but at temperatures above 260° C., I have found, with the materials I have used, that the temperature and the thermo-electric power of the combination no longer exhibited the simple proportional relation asserted by Beetz. The thermo-electric power, it is true, still increased with a stronger heat but more slowly than the temperature.

"I used as fixed points, (1) the boiling point of water; (2) the melting point of zinc (262° C. as determined by the mercurial thermometer); (3) the melting point of galvanically reduced copper (1200° C.). As the places of contact of my thermo-element were not completely immersed in the fused copper, an error will be produced in the case of difficultly fusible salts, whose melting points will be found too high. The resistance of the element, which consisted of two wires each 200 mm. in length, amounted to 0.25 Siemen's units; the changes of resistance of the small heated parts of the same can be neglected, compared with the six Siemen's units' resistance of the circuit. The intensity of

the current was read off on a Wiedemann's compass, provided with a scale and mirror. A difference of temperature of 80° C. caused a mean divergence of 55.2 divisions on the scale, a difference of temperature of 242° caused a divergence of 265.4, and finally, a difference of 1200° a divergence of 460.5. According to the first and last numbers, I represented the difference of temperature (T) of the two places of contact as a function of the electromotor power or of the current intensity (i), here proportional to it, in the form.

$$T = ai + ci^3$$

in which $a = 55.2$ and $c = 0.0000054$.

Table VII represents the results obtained by Braun, and also the corresponding melting points obtained by the method proposed in the present paper:—

TABLE VII.

Salt.	p .	Intensity of current. i .	Mean melting point. (Braun.)	p' .	Mean melting point (new method).	Difference.
ZnCl ₂	7	165.4	262° C.	—	—	—
NaNO ₃	8	180.6	314° C.	3	330° C.	+ 16
KNO ₃	8	194.5	342° C.	3	335° C.	— 7
PbCl ₂	4	289.0	580° C.	3	501° C.	— 79
KI	5	321.0	666° C.	5	639° C.	— 27
KCl	5	341.6	730° C.	4	738 C.	+ 8
SrCl ₂	4	390.0	910° C.	3	829° C.	— 81
Na ₂ CO ₃	6	393.0	920° C.	4	818° C.	— 102
NaCl	5	402.0	960° C.	8	776° C.	— 184
K ₂ CO ₃	10	447.0	1150° C.	3	838° C.	— 312
Na ₂ SO ₄	4	472.0	1280° C.	3	865° C.	— 415

Under column p is given the number of observations which Braun made in the case of each salt, and under column p' the number made by the author.

From the last column, which gives the difference between the melting points as determined by the two methods, it will be seen that up to potassium chloride the two give moderately concordant results, with the exception perhaps of lead chloride; but with those salts which fuse above potassium chloride, Braun's method gives higher results than the new one, the difference between the two increasing considerably as the temperature rises, even to as much as 415° in the case of sodium sulphate. It is to be regretted that Braun does not give the several determinations from which his mean melting point is calculated, in order that one might have seen how they agreed among themselves, for he does not say whether the results were concordant or

not. In the case of the method above described, however, it has already been seen that the results obtained by it agree very well *inter se* for the same salt. Table VII, shows that at temperatures above 800° C. not only do the two methods not agree with each other as to the actual melting points they ascribe to the same salt, but also that they do not agree as to the order of melting of some of the salts, as in the case of strontium chloride, sodium carbonate, and sodium chloride, which according to Braun's method melt in this order, while according to the new method the following is the order of melting—sodium chloride sodium carbonate, and strontium chloride. In order to prove which of these is correct, small portions of sodium chloride and strontium chloride were placed in the crucible at the same time, and their order of melting tested as described on p. 502. The result was, that in the four experiments made it was always found that the sodium chloride melted decidedly and some seconds before the strontium chloride, the blowpipe being used. The position of the two salts in the crucible was reversed in each of the experiments made, so as to avoid any error that might arise from the crucible being differently heated at the two points at which the salts were respectively placed. This test is, I think, a very severe one, and fully decides the question as to the order of fusibility of sodium chloride and strontium chloride, and also speaks very much in favour of the new method.

The following are the chief sources of error in the two methods, from which one may form an idea of the value of the two :—

New Method.—(1.) A very small quantity of heat may be given up to the calorimeter by the short length of platinum wire, used to suspend the crucible, and whose weight is not included in that of the latter, for if it were, an error greater in the opposite direction would arise, owing to its having nothing like the same temperature as the crucible. This error will be positive.

(2.) It is possible that the temperature of the crucible may not be exactly the same throughout, though the experiments described on p. 501 seem to show that it is ; in any case the salt at the moment of melting would have the mean temperature of the crucible, since it is as nearly as possible in the centre of the same. The error, therefore, which might arise from this cause would be extremely small, and could be neglected. This of course assumes that the salt at the moment of fusion has the same temperature as that part of the crucible on which it rests, which I think is very probable ; if it had not, its temperature would be slightly lower than that of the platinum, in which case the error in the melting point would be positive.

(3.) A small error might also be caused by the temperature of the calorimeter altering slightly during the few seconds which elapse between the first reading off of the temperature and the dropping of

the crucible into the water. The direction of this error would vary according to circumstances, but would as a rule bring the melting point too low. With proper care, however, any error that might arise from this source could be entirely avoided.

(4.) The crucible will lose a small quantity of heat while being dropped into the calorimeter; this will cause a minus error, and, together with (5), is, I consider, the greatest source of error; but it cannot be very great, as the time which elapses during the dropping of the crucible into the water is only a small fraction of a second.

(5.) Heat lost by the calorimeter. This would cause a minus error, the amount of which, and of that due to the source of error mentioned in (4), will be the greater of course the higher the temperature. This error, however, can be lessened by using a larger calorimeter or a smaller crucible, so that the rise in temperature of the calorimeter may not be so great, or best of all by using Rumford's method. The use of a smaller crucible, however, is not to be recommended, as in that case the error in (4) would be greater. When, with the crucible described above, the fusing point of the salt cannot be reached, a smaller one would have to be used; so far, however, this has not been found necessary, but sodium sulphate appeared to be about the limit to which a crucible so large could be employed.

Of the above sources of error (1) and (2) would bring the melting point too low, while (4) and (5) would act in the opposite direction, and as they will cause an error larger than that arising from the former, the melting point will, for higher temperatures at any rate, tend to be a little too low. The error in (3) may be neglected.

Braun's Method.—(1.) From the comparatively large quantity of salt used, and the relatively low conducting power of the same for heat, it will probably not have the same temperature throughout. The direction of the error would be variable.

(2.) The source of error mentioned in (1) might lead to another, from an extra current being produced by the differently warmed portions of the same salt behaving like two different liquids. The direction of this error would depend on circumstances.

(3.) Might not the current produced by the heat also act electrolytically on the salt? If so, the temperature would be slightly affected by the heat changes caused by the chemical decomposition, and the salt would be rendered to some extent impure by the products of decomposition. The error, however, from this source would, I think, be very small, and its direction would depend on circumstances.

(4.) As mentioned by Braun himself, the places of contact of his thermo-element not having been completely immersed in the fused copper (in determining the highest fixed point of his scale), an error

would be produced in the case of difficultly fusible salts, their melting points as found by him being too high.

(5.) Though the lower fixed points of Braun's scale are correct (viz., that of boiling water and the melting point of zinc chloride), yet a very important error may arise, especially with the less easily fusible salts, by taking the melting point (1200° C. according to Braun) of fused copper as the highest fixed point, for the temperature at which it fuses is by no means certain, as the determinations which have been made of it by different observers vary from $1,000^{\circ}$ to $1,398^{\circ}$ C. The melting point given in Fownes's *Manual of Chemistry*, as determined by Daniell, is 1091° C.

(6.) The number of fixed points taken by Braun in the construction of his scale is hardly sufficient, for the gap between the melting points of zinc chloride (262° C.) and that of copper (1200°) is a long one, in which the relation between the difference of temperature and the thermo-electric power of the combination may vary considerably.

The above enumeration speaks for itself, and no further remarks are needed on that head, except that I may mention that the new method possesses a considerable advantage over Braun's, in that while the latter requires a comparatively large amount of salt, the former needs only 2 or 3 centigrams for several determinations, so that it can be employed when only a small quantity of the salt is at hand. The correctness of the results obtained, however, is the all-important requisite.

Finally, I believe that for high temperatures, Braun's method gives too high results, while the new method yields results somewhat too low.

Conclusion.—The results which have so far been obtained are too few to allow any relation, that may exist between the melting points and other physical and chemical properties, to be fairly seen. The following table gives a view of the melting points of all the salts I have so far determined:—

TABLE VIII.

	NO ₃ .	ClO ₃ .	I.	Br.	Cl.	CO ₃ .	SO ₄ .
Hg.....	—	—	—	—	302	—	—
Tl.....	—	—	446	463	434	—	—
Ag.....	224	—	530	434	457	—	—
Pb.....	—	—	—	—	501	—	—
Li.....	—	—	453	—	602	699	822
Ca.....	—	—	—	680	723	—	—
K.....	353	372	639	703	738	838	—
Na.....	330	—	633	712	776	818	865
Sr.....	—	—	—	—	829	—	—

From which it is seen that, with the exception of thallium chloride, and silver iodide, the order of the fusibility of salts containing the same metal but different acid radicals, is the same as the order of the columns in the table, beginning with nitrates, which are the most fusible, and ending with sulphates, which are the least; while with salts containing the same acid radical but different metals, the order of fusibility appears to exhibit few signs of constancy.

The melting points of the corresponding salts of potassium and sodium appear to run very near together from one end of the scale to the other, the greatest difference being 38° , which occurs in the case of the chlorides.

If we compare the melting points of the halogen salts with the quantity of heat evolved by the union of equivalent quantities of halogen and metal, we find that those salts, in whose formation the greater amount of heat is evolved, have in general (the only important exception being silver iodide) the higher melting point, as is seen from Table IX, compiled from that given in Miller's *Chemical Physics*, p. 389, 4th edition.

TABLE IX.

Salt.	Heat evolved by the union of the constituents of the salt.	Melting point.
KCl	100960	738
NaCl	94847	776
KBr	90188	703
KI	77268	639
PbCl ₂	44730	501
AgCl	34800	457
AgBr	25618	434
AgI	18651	530

At present it is not possible to make a similar comparison in the case of the other salts, as the quantities of heat evolved in their formation have not yet been determined. Whether this is a real relation or not, cannot however be decided by the few examples above given.

In a subsequent paper I hope to bring before the Society further tests as to the correctness of the method, and the results of a systematic determination of the melting points of metallic salts.