SOME NEW STANDARD MELTING POINTS AT HIGH TEMPERATURES

By Howard S. Roberts

Abstract

Melting points of salts for use as standard temperatures for thermocouples, 400° to 1100°C.—After purification by crystallization from solution, a gram of the salt is placed in a Pt crucible 18 mm by 10 mm in diam., the junction is placed in the axis and 3 to 4 mm from the bottom, and the temperature is raised about 5° per minute. For most pure substances and certain eutectics the heating curve becomes quite flat at the melting point and hence the form of curve obtained is a sensitive test of purity. The couples used were carefully calibrated with standard metals, and gave the following results, accurate to ±0.5°: *potassium dichromate* 397.5°; (30.5 $NaCl$+69.5 Na_2SO_4) 627.0°; KCl 770.3°; $NaCl$ 800.4°; Na_2SO_4 884.7°; K_2SO_4 inversion point 583±1°, melting point 1069.1°; also $Ca_2B_2O_5$ 1304±5°. Detailed suggestions as to technique are given, also a *convenient method of using pure metal strips or wires in calibrating couples.*

THE fixed points by means of which the high temperature scale is at present reproduced are for the most part the melting points of pure metals. While these leave little to be desired by way of reproducibility, it is often inconvenient or impossible to use them directly for the calibration of a thermometer under its everyday working conditions. Furthermore there is also a need for a series of easily obtainable materials which may be used without purification for a moderately accurate calibration. It is the purpose of this paper to present a series of salts which may be employed for calibrations of moderate accuracy without purification, or may be carefully purified and used for an accurate calibration. The series is intended primarily for the calibration of thermocouples.

The use of salts as standards has been objected to on the ground that their low thermal conductivity makes them less accurate than the metals. This is not because the salts are necessarily less able to reproduce their melting points accurately but because of the limitations of the thermometers and of the methods used. It is particularly the case where a large volume of the thermometer must be in contact with the melting salt; but it must be remembered that, with the exception of the resistance thermometer, such instruments are seldom used for precise measurements at high temperatures. On the other hand, in the calibration of optical pyrometers, fine wire thermocouples, etc., the effect of low conductivity can be made negligible by the employment of a suitable technique, and here a suitable series of salts will be found quite as satisfactory as a series of metals. The fact that there are so many salts to choose from makes it possible in most cases to obtain fixed points at short intervals and to confine the choice to those salts which are easily purified.

In a paper on "Melting point determination" White[1] has called attention to the remarkably sharp melting curves obtained with certain substances, notably sodium chloride and sodium sulphate. His discussion of the causes for obliquity in the melting curve makes it evident that only under very unusual conditions can such a sharp melting curve be obtained with any but an "ideally pure"[2] substance, and that such a curve represents the constant melting temperature of the substance in question. In the form of the melting curve we have, therefore, an almost infallible check on the purity of such a salt and on the reliability of any given determination with it.

With one exception the salts were chosen from standard chemical reagents with the restriction that they must be easy to purify by simple methods. As will be brought out later, this purification will nearly always be found advisable, if only to get rid of the inevitable dust, paper, and bits of wood.

The melting curves were obtained with powdered charges, in a crucible 10 mm in diameter and 18 mm deep, using a bare thermocouple whose junction was located as nearly as possible in the axis of the crucible and

TABLE I

Fixed points used in the calibration

Substance	Source	Melting point	Authority
Lead	Bur. of Stds. Std. sample No. 49	327.3°	Bur. of Standards[4]
Zinc	Bur. of Stds. Std. sample No. 43a	419.4	Bur. of Standards
Aluminum	Bur. of Stds. Std. sample No. 44	658.7	Bur. of Standards
Gold	Heraeus	1062.6	Day, Sosman, Allen[5,6]
Lithium metasilicate	Synthetic	1201.	Day, Sosman, Allen[6]
Palladium	American Platinum Works	1551.5	L. H. Adams[7]

[1] White, Am. J. Sci. **28**, 453, 1909; also J. Phys. Chem. **24**, 393-416, 1920

[2] For our purpose an "ideally pure" substance is to be defined as any solid or mixture of solids that is free from melting hysteresis and gives, on melting, a liquid whose composition remains constant throughout the melting interval. This definition is worded in such a way as to include eutectic mixtures and certain cases of transformation and of solid solution. It does not, however, apply to most of the silicates.

[3] L. H. Adams, J. Am. Chem. Soc. **36**, 65-72, 1914

[4] Bur. Standards Circ. 66 (1917)

[5] Day, Sosman and Allen, Am. J. Sci. **33**, 587 (1912)

[6] Day, Sosman and Allen, Carnegie Institution Publ. No. 157 (1911); J. de Phys. (5) **2**, 911, (1912).

[7] This lot was found by Adams to melt 2° higher than the standard palladium.

3 to 5 mm above the bottom. The thermocouple was standardized at the melting points given in Table I, using a method to be described below. An electric furnace wound with resistance wire was used for heating, the rate being about 5° per minute.

The deviation curves for the three couples used are given in Fig. 1. They represent the difference between an arbitrary standard curve[3] of temperature and e.m.f., and the observed values of e.m.f. at the melting point, plotted against the observed value. Element A was used for the dicalcium borate point, B for all the others, and Y as a check at the sodium chloride point.

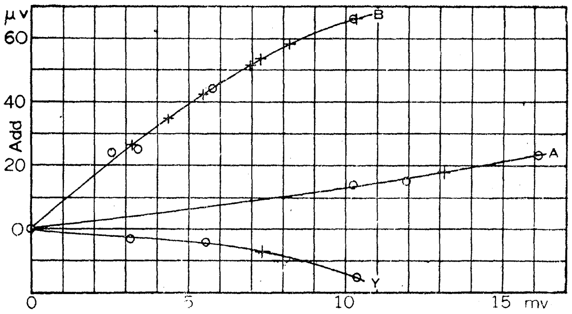

Fig. 1. Calibration curves for the three couples used. The circles represent melting points used in the calibration (Table I); the crosses, melting points determined with the couple (Table II).

TABLE II

Melting points of the purified salts

Substance	Melting point	Probable accuracy	Microvolts[8]
Potassium dichromate	397.5°C	±0.5°	3220
$45KCl+55Na_2SO_4$ by weight[9]	517.1	±1.0°	4385
$30.5NaCl+69.5Na_2SO_4$ by weight	627.0	±0.5°	5499
Potassium chloride	770.3	±0.5°	7008
Sodium chloride	800.4	±0.5°	7335
Sodium sulphate	884.7	±0.5°	8262
Potassium sulphate[10]	1069.1	±0.3°	10372
Dicalcium borate[9] ($Ca_2B_2O_5$)	1304.	±5°	13176

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[8] According to Adams' standard curve, J. Am. Chem. Soc. **36**, 68, 1914; Bull. Am. Inst. Mining Met. Eng., 159, 2114. 1919; Pyrometry Volume, Am. Inst. Mining Met. Eng., p. 168, 1920; reprinted in Bur. Standards Tech. Paper 170, 308. 1921.

[9] Give more or less oblique melting curves

[10] Potassium sulphate passes through a sharp inversion at 583° ±1° which may be used to obtain a second calibration point with a single charge. This point, together with the melting point of potassium sulphate will often be sufficient for a complete calibration.

The results for the purified materials are given in Table II, and the melting curves are shown in Figure 2.

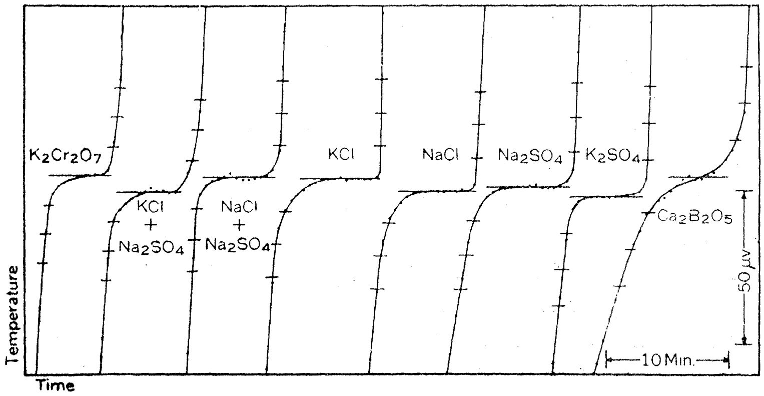

Fig. 2. Melting point curves for the various salts after purification. Short, horizontal lines are drawn through the curves at intervals of 1° above and below the melting point.

The column headed "probable accuracy" gives the maximum departure to be expected from the scale as defined by the fixed points listed in Table I.

The mixture of potassium chloride and sodium sulphate is an approximation to the ternary eutectic[11] $(43Na_2 \cdot 57K_2)$ $(46Cl_2 \cdot 54SO_4)$. The eutectic composition may be obtained more accurately by mixing 44.5% KCl, 2.5% NaCl, 53% Na_2SO_4 or 37% NaCl, 11% Na_2SO_4, 52% K_2SO_4 by weight; but the melting point so obtained does not differ materially from that of the mixture given in Table II.

The melting point of sodium chloride was measured several times with particular care. It is given by White[12] as 801° ± 1°, but a more recent determination by Ferguson[13] gives 803° ± 1°. This difference of 2° seemed rather more than could be explained by the uncertainty of the temperature scale or of the standard calibration curve for the platinum-platinrhodium thermocouple. Therefore, through the courtesy of Dr. Day, "Element Y," which had been compared with the gas thermometer by Day and Sosman[5] was used to check the interpolation between the fixed points. For this purpose a calibration of Element Y was made at the melting points of potassium dichromate, the sodium chloride-sodium sulphate eutectic, and potassium sulphate. The melting point of sodium chloride then obtained with this couple was 800.4°, in entire agreement

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[11] Jänecke, Z. phys. Chem. **64**, 351, (1908)

[12] White, Am. J. Sci. **28**, 470, (1909)

[13] Ferguson, J. Phys. Chem. **26**, 626, (1922)

with that obtained by the use of Element B. The value in Table II of 884.7° for sodium sulphate is in satisfactory agreement with White's[12] value 885° ± 1°. There seems, therefore, to be little doubt that Ferguson's[13] 803° for the sodium chloride point is too high.

The desirability of potassium sulphate as a fixed point has been known for some time; but it has been suspected of having two or more dimorphous forms with different melting points,[14] as is the case with sulphur. No evidence was found to support this belief; two such forms are indeed known, but the transformation from one to the other takes place with unusual promptness at 583°. It seems unlikely that the whole, or even any considerable portion of a powdered charge should remain in a metastable condition; and should it consist of a mixture of dimorphous varieties, the melting point curve would of necessity be oblique except in the remote contingency of the formation of a eutectic mixture of the two forms. On the other hand, a reason for the earlier uncertainty is to be found in the high temperature at which this salt melts, which makes the observed melting point particularly susceptible to impurity in the salt and to various defects in the method of measurement.

FACTORS INFLUENCING THE SHAPE OF THE MELTING CURVE

While the melting curve obtained under satisfactory conditions with an "ideally pure" substance is unmistakable, it may be well to consider the more common causes of variations from the normal curve, for by so doing we may know when to eliminate the cause and when the effect may be ignored.

The curves of Fig. 3 are hypothetical time-temperature curves for the melting of an ideally pure substance, assuming a linear heating rate for the furnace, a long, cylindrical charge of small diameter and no change in the size of the charge on melting. Curve *a* gives the temperature at the center of the charge, *b* at a point near the center, and *c* at the surface. Since the heating rate is linear, the small charge quickly reaches a steady state in which all parts of the charge have the same heating rate. This linear rate and temperature distribution continue unchanged until the instant t_1, when the hottest portion (the surface) of the charge reaches the melting temperature. The linear rate for the unmelted interior now becomes a decreasing rate, approaching the constant melting temperature. The time lag through the charge is usually so small that the temperature at the center becomes sensibly equal to the melting temperature within a much smaller fraction of the melting interval than is indicated in the figure. As soon as melting passes any point *b* in the interior, the tempera-

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[14] Burgess and Le Chatelier, The measurement of high temperatures, p. 451 (1912).

ture at this point immediately begins to rise; at the instant t_2 when it reaches the center the temperature there rises very rapidly and the charge as a whole approaches a new steady state, somewhat different from the first on account of changes that have taken place in the thermal conductivity and specific heat.

Aside from the effect of impurity which White[1] has discussed elsewhere, the most common variation from the normal is curve *b*, caused, usually, by an error in centering the junction. This is evident in the curve for sodium sulphate in Figure 2. It need cause no concern if the horizontal portion is very well defined. Small fluctuations of temperature may be caused by local heat effects involving bits of foreign matter in the charge or, at the beginning of melting, by imperfect thermal contact between the charge and the thermocouple. If the charge is placed too high in the furnace the bottom may melt first and subsequently bits of unmelted material fall into the melt from the top; these may give rise to a false start toward the sudden rise at the end, as is the case in the curve for sodium chloride in the figure.

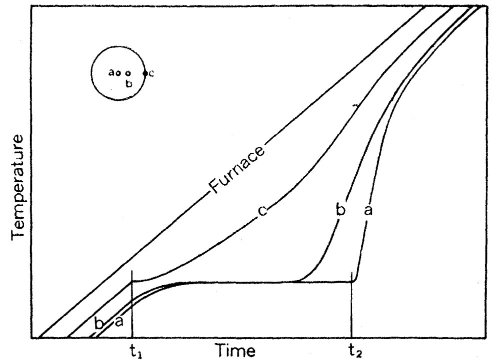

Fig. 3. Hypothetical time-temperature curves for different parts of a cylindrical mass of an "ideally pure" substance melting under idealized conditions. *a* at the center of the cylinder; *b* at a point within, but not at the center; *c* at the surface.

If the thermocouple has been rendered inhomogeneous by contamination, its indications may change while the gradient along it is changed during the melting interval. This may cause the flat portion of the curve to slope either up or down, giving an erroneous idea of the purity of the salt. The effect of this on the calibration will probably not be greater than the uncertainty inherent in the use of the contaminated couple; it may be reduced by employing a slow heating rate.

In general, given a suitable, pure salt, and a good thermocouple well centered in the charge, the melting curve should not be very different from *a* in Fig. 3. If such a curve is not obtained, the foregoing discussion, together with White's discussion of the effect of impurities, should be sufficient to locate the cause.

Dicalcium borate in my table and the silicates in that of Day, Sosman, and Allen fail to conform to our definition of an ideally pure substance and our discussion does not apply to them. In using such salts it is suggested that particular care be taken in centering the thermocouple and that the heating rate be slow. If there is any uncertainty about either the technique or the homogeneity of the thermocouple, these may be checked by a calibration at one of the other points.

SUGGESTED TECHNIQUE FOR BARE THERMOCOUPLES

The size of crucible used here, 10 mm in diam. and 18 mm deep, will probably be found most satisfactory for the calibration of thermocouples not more than 0.6 mm in diameter (No. 22 B & S wire gage). It is large enough to allow a leeway of a millimeter or so in centering the junction and small enough to avoid too much rounding of the ends of the melting curve. For the large wires of the usual base metal couples the crucible should be much deeper, in order to provide sufficient depth of immersion, and somewhat larger in diameter. The minimum thickness of salt outside the thermocouple need not be much more than 5 to 10 mm.

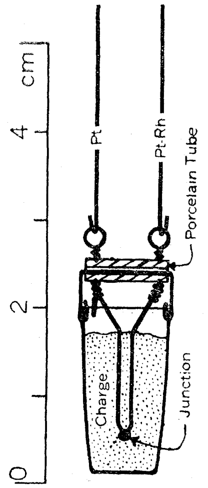

Fig. 4. An arrangement which has proven satisfactory, in the calibration of thermo-couples, as a container for the melting salt.

For a great deal of our work with platinum-platinrhodium couples we have found the arrangement shown in Figure 4 very satisfactory.[15] A short tip is made of the thermocouple wires, terminating in eyelets at the top and hung on a cross bar of porcelain tubing. The crucible has two small holes drilled opposite each other near the top and is supported by a bent platinum wire which passes through these holes and through the porcelain tube. The thermocouple to be calibrated is cut apart at the junction and the crucible hung from it by means of the eyelets, taking care that the wires are not interchanged.

In many cases it will be found convenient to melt the salt cautiously over a Bunsen burner, adding more salt until the crucible is nearly full. The thermocouple may then be thrust into the melt and the salt allowed

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[15] Smyth and Roberts, J. Am. Chem. Soc. **42**, 2589, 1920

to freeze around it, after which it is placed in a furnace for the melting point determination. This preliminary melting is not to be recommended for exact work on account of the danger of partial dissociation or contamination of the salt.

These salts (with the exception of dicalcium borate) are very soluble in water, so that the crucible may be cleaned out after a determination, by washing. Dicalcium borate is readily soluble in dilute hydrochloric acid (equal parts of acid and water) especially on heating.

PREPARATION OF THE SALTS

The curves of Figure 5 indicate forcefully both the desirability of purifying the salts, and the seriousness, for exact work, of even small amounts of impurity.

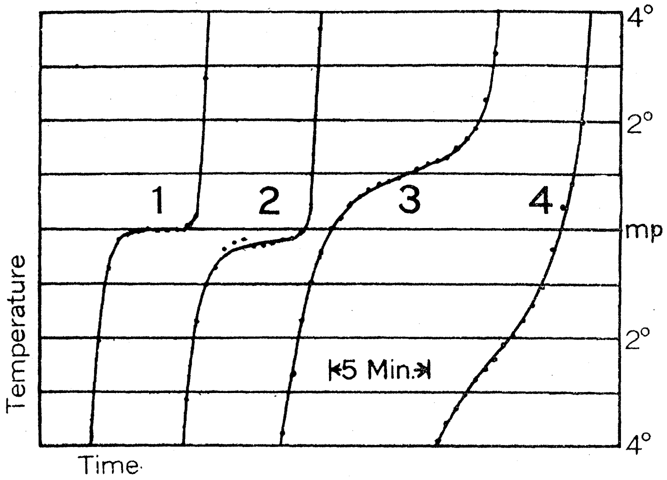

Fig. 5. Melting point curves for sodium sulphate showing the effect of impurities. The horizontal lines are drawn at intervals of 1° above and below the melting temperature (884.7°). (1) purified material; (2) as received from the manufacturer; (3) with the addition of 0.5% $CaSO_4$ to show raising of the melting point; (4) with the addition of 0.3% NaCl to show lowering of the melting point.

The chief impurity met with in these salts has been dust and foreign matter of various sorts, and when these were removed by dissolving the salt and filtering the solution, a single recrystallization was sufficient. With the exceptions of sodium chloride and potassium dichromate, as much of the salt as possible was dissolved in boiling water, the solution filtered and allowed to cool.[16] The liquid was then poured off and the

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[16] Sodium sulphate has a maximum solubility at about 32°. It is therefore advisable to cool the solution considerably below this temperature, e.g., in an ice bath, in order to obtain a reasonable quantity of the solid from it. The decahydrate so obtained melts about 32° and the liquid should then be evaporated to dryness rather cautiously in order to avoid undue loss by spattering.

remaining crystals tamped with a glass rod to remove as much more of the mother liquor as possible; after which the mass of crystals was dried at about 200°.

Very little of the sodium chloride was obtained from the solution by this method; so in this case the filtered saturated solution was boiled down to about half its volume, the crystals freed of mother liquor and dried.

Potassium dichromate solution reacts with organic impurities when heated; so a cold, saturated solution was made, filtered and subsequently boiled down until crystals began to appear on the bottom of the vessel. The solution was then cooled, etc., as before.

All of these salts decrepitate more or less violently when first heated, and some of the salt usually flies out of the crucible. This may be prevented by preheating in a closed crucible to a temperature 100° short of the melting point or until decrepitation ceases. This operation may of course be carried out once and for all on the whole stock of material.

The components of the two eutectics should be very intimately mixed, preferably by grinding them together in a mortar until quite fine. It is well also to preheat the ingredients before mixing.

Dicalcium borate was prepared from a particularly pure supply of calcium carbonate and either boric acid glass (B_2O_3) or recrystallized boric acid (H_3BO_3) which had been dried at a temperature below 100°.

TABLE III

Melting points of salts from different sources

Substance	Source	Melting points	Difference
Potassium dichromate	Purified	397.5°C	....
" "	Squibb	397.3	0.2°
" "	Baker and Adamson	397.1	0.4
" "	Merck	396.8	0.7
Potassium chloride	Purified	770.3	....
" "	Squibb	770.1	0.2
" "	Kahlbaum	770.1	0.2
Sodium chloride	Purified	800.4	....
" "	Squibb	800.4	0.0
" "	J. T. Baker	800.1	0.3
" "	Morton[17] (Purified)	799.9	0.5
Sodium sulphate	Purified	884.7	....
" "	Merck	884.6	0.1
" "	Squibb	884.4	0.3
Potassium sulphate	Purified	1069.1	....
" "	Merck	1069.0	0.1
" "	Squibb	1068.9	0.2
" "	J. T. Baker "Special"[18]	1067.9	1.2

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[17] This was table salt, "Morton's Free Running Salt—It Pours." It was further purified by dissolving, filtering the solution and recrystallizing it.

[18] This bottle had been opened for some time and may possibly have become contaminated, though there was no evidence that such was the case.

The two ingredients were weighed out into a tared platinum crucible, heated slowly to about 1000° and held there for an hour to drive off the H_2O and CO_2. The crucible was cooled and weighed and enough boric acid added to bring the contents up to $2CaO{\cdot}B_2O_3$, stirring it into the partly sintered mass with great care in order to avoid loss of material. The process of heating and adding boric acid was repeated until the theoretical weight was attained. The latest obtainable value, 69.66 was used for the formula weight of B_2O_3. This is a slow process but, owing to the volatility of boric oxide, it seems the surest way to secure the pure compound. I have employed the same method successfully for preparing lithium metasilicate for use as a fixed point.

Table III is a list of the melting points of several samples of these salts as received from different sources, as compared with the melting points of carefully recrystallized samples of the same salts. All of the determinations for a given substance were made and the first determination of the group repeated before going on, in order to provide a check against any possible change in the thermocouple. The small differences, therefore, are independent of its calibration.

A SIMPLIFIED METHOD FOR THE MELTING POINTS OF CERTAIN METALS

For the primary calibration of the thermocouples used in this work, a method was used which has been found particularly useful at the gold and palladium points. It may also be used with other metals or eutectics whose melting points are not affected by slight oxidation, provided a satisfactory melting point curve is obtained.

Except in the case of gold and palladium, which were furnished in the form of 0.6 mm wire, the metals were hammered out into a sheet about 1 mm thick. Dirt and iron were removed from the surface with a knife. A strip of this sheet 6 to 8 mm wide was bent double over the junction, the wires insulated from the strip with paper, and the metal squeezed down tightly on the couple. The paper, of course, chars, but the ash is found to provide sufficient insulation.

For the wire samples, a tight coil of 5 or 6 turns was made, just large enough inside to admit the two wires of the couple, which had been cut apart at the junction. These were thrust in from opposite sides and the coil flattened to hold them in place. It was not found necessary to insulate the wires, probably because melting began at the outside of the coil.

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