

THE
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TEMPERATURE MEASUREMENTS TO 1600° C.

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IN a recent study of the isomorphism and thermal properties of the feldspars¹ in the laboratory of the U. S. Geological Survey, the authors prepared certain apparatus for generating, regulating and measuring high temperatures, which has proved easy of manipulation and uncommonly exact and which may have a wider interest. Through the courtesy of President Kohlrausch and Professor Holborn, of the Reichsanstalt, we were also enabled to obtain unusually direct comparisons with the gas thermometer scale of that institution, and to establish this scale in a conveniently accessible form for use in this country.

It is not our purpose at this time to enter upon an extended discussion of methods or principles of temperature measurement in the upper ranges. This has been done elsewhere,² and the difficulties to be dealt with have also received considerable attention. We desire merely to describe the application of the Reichsanstalt high temperature scale with such detail as may be necessary to make it

¹ The entire investigation will appear in a few months as a professional paper of the U. S. Geological Survey.

² See Le Chatelier and Boudouard, "High Temperature Measurement." (Translated by Burgess.) Ludwig Holborn and Arthur L. Day, "Ueber das Luftthermometer bei hohen Temperaturen." *Ann. d. Phys. u. Chem.*, 68, p. 817, 1899. (Translated, *Am. Jour. Sci.*, 4, 8, p. 165, 1899.) *Ann. d. Phys.*, 4, 2, p. 505, 1900. (Translated, *Am. Jour. Sci.*, 4, 10, p. 171, 1900.)

By the same authors: "Uber die Thermoelectricität einiger Metalle." *Sitzungsber. Berl. Akad.*, p. 691, 1899. (Translated, *Am. Jour. Sci.*, 4, 8, p. 303, 1899.)

And many others.

serviceable and with sufficient data to enable measurements of the order of accuracy of the scale itself to be made without the trouble of the inconvenient official calibration and incidental loss of time.

In the ordinary routine of temperature measurement in the laboratory it is rarely necessary to refer back to the fundamental temperature scale—the errors at ordinary temperatures are for most purposes insignificant—but in pyrometry, temperature is almost without significance until some specific reference to fundamental measurements is made.

The general plan of the apparatus used in these determinations may be assumed to be fairly well known. It is the same in all essential particulars as that used by Holborn and Day¹ in establishing the high temperature scale with the gas thermometer at the Reichsanstalt. And yet it is plain that such a scale requires some care in the transplanting, particularly as the authors were without a gas thermometer and were therefore not in position to make direct comparisons with the gas scale.

The temperatures were measured with thermo-elements exclusively. We obtained from Dr. Heraeus (Hanau, Germany) a set of four elements cut successively from the same roll of wire, which, when joined together, proved to be identically alike in their readings over the range of temperature covered by the gas scale of the Reichsanstalt (250° to 1150° C.), within the limits of observation error. Through the courtesy of Professor Holborn these were taken to the Reichsanstalt and measured in the original melting-point furnace with the same elements in terms of which the gas thermometer scale had been expressed, and five careful comparisons made. These were the melting points of the pure metals, cadmium (in air), zinc (in air), antimony (reducing atmosphere), silver (reducing atmosphere) and copper (in air). A fortunate circumstance made it possible to send these carefully calibrated elements to Washington by messenger, which made it certain that they suffered nothing in transit.

The elements were then further compared in an electric furnace, which will be described below, and the melting points of the same group of metals again determined in our laboratory. The metals

¹Ludwig Holborn and Arthur L. Day, *Am. Jour. Sci.*, 4, 8, 165, 1899.

used, however, were from other sources than those which had served for the calibration at the Reichsanstalt. When this test was finished, we were able to assure ourselves that, although all the constants in the measuring apparatus — thermoelements, resistances, standard cells, metals, etc. — had been changed in the transfer from the Reichsanstalt to the Geological Survey at Washington, the aggregate error nowhere exceeded 1° over the entire range from 250° to 1150° . It will be remembered that 1° was about the accuracy which the standard gas thermometer showed at 1000° . Our thermoelectrical system is therefore now doubly established — (1) by direct comparison and (2) through an independent series of metal melting points — upon the gas thermometer scale of the Reichsanstalt within the limits of error of the latter, and can be verified at any time with the help of two of the elements which have been laid aside for this purpose, or by means of the melting points of the metals. The scale is therefore permanent.

As the introduction of the standard high temperature scale of the Reichsanstalt into this country and its establishment by proper fixed points may be a matter of considerable interest to other investigators, some further details regarding the metals chosen for these fixed points are added. We tried to find metals which should not only be of the purity necessary for such standards, but which should be easily obtainable in uniform quality. With four of the five metals of the Reichsanstalt series — cadmium, zinc, silver and copper — no difficulty was experienced, but we were not able to find satisfactory antimony in this country. This need not prove an obstacle, for the four points mentioned will serve most purposes without a fifth, while if the needs of an experiment are so exacting as to require an intermediate melting point, antimony can be imported from Kahlbaum of Berlin without great delay or excessive cost, in the same purity as that originally used at the Reichsanstalt.

The cadmium and zinc in our series were taken from the regular listed chemicals of Eimer and Amend (zinc, "C.P. in sticks"; "cadmium, metal sticks"), the silver was the well-known test silver of the Philadelphia Mint laboratory, while the copper was also from Eimer & Amend ("C.P. copper drops, cooled in hydrogen").

Careful analyses of samples of the cadmium, zinc and copper follow :

Zinc.		Cadmium.		Copper.	
Eimer & Amend's "c. p. in Sticks."		Eimer & Amend's in Sticks.		Eimer & Amend's "c. p. Drops, Cooled in Hydrogen."	
As	none.	As	none.	Te and Se	none.
Cu	trace.	Cu	trace.	Sb	trace?
Pb	.0412%	Pb	.0860%	As	none.
Cd	.0021	Zn	trace.	Bi	none.
Fe	.0053	Fe	.0025	Ag	.018%
Co and Ni	none.	Co and Ni	none.	Pb	.001
S	.005	S	.0005	Co and Ni	none.
	.0005			Zn	.010
				Fe	.011 ¹
Total Impurities, .0491%		Total Impurities, .0890%		Total Impurities, .040%	

It was not deemed necessary to make an analysis of the silver as we were assured that it contained no impurity which could be quantitatively determined.

The melting temperatures of cadmium and zinc are relatively low and those of silver and copper comparatively high on the gas scale, with a long interval between, so that it sometimes becomes very desirable to have an intermediate point. The two melting points which are most conveniently located are aluminium and antimony. Aluminium, on account of its low density, and perhaps because it has been less successfully purified than the other metals, does not give a sharp and satisfactory melting point. The melting point of Kahlbaum's antimony, of which a recently published analysis is reproduced here, serves this purpose excellently. It rarely solidifies without considerable undercooling, but the point to which the temperature rises after crystallization begins is sensibly identical with the melting point.

Antimony (Kahlbaum, Berlin).²

Fe	.012%
Cu	.004
Pb	.003
	<u>.019%</u>

The C. P. antimony obtained from Eimer & Amend and from Merck & Co., in a careful analysis for which we are indebted to

¹ This figure is doubtless somewhat too high.

² Fritz Henz, Inaugural Dissertation, Zürich. Published Leipzig, 1903.

Dr. W. F. Hillebrand, of the Geological Survey, each showed about one per cent. of the sulphide still present and traces of other impurities. The melting temperatures of these varied under different conditions as much as fifteen degrees and were totally unsuited to this work.

Inasmuch as the melting points of these metals were determined with thermoelements which Professor Holborn had just calibrated with the metals in use at the Reichsanstalt for this purpose, a comparison of the values obtained will show the accuracy with which one may reproduce the Reichsanstalt scale entirely from local sources :

	Reichsanstalt.	Day & Allen.	Difference.
Cadmium.	321.7° (Kahlbaum)	321.7 (Eimer & Amend).	0.0°
Zinc.	419.0 (Kahlbaum)	420.0 (Eimer & Amend.)	1.0
Silver.	961.5 (Gold u. Silber Scheideanstalt).	962.2 (Philadelphia Mint).	0.7
Copper (in air).	1064.9 (Haddernheim Kupferwerk).	1065.3 (Eimer & Amend).	0.4
Copper (reducing atmosphere).	1084.1 (Haddernheim Kupferwerk).	1083.6 ⁽¹⁾ (Eimer & Amend).	0.5

For the method of extrapolation of the scale and further information regarding the use and accuracy of thermo-elements at these temperatures, reference is made to the papers of Holborn and Day already cited.

For everyday use, four more elements were prepared and calibrated in the same way. Of these, two are of the usual form (Fig. 1) and two are of a new design (Fig. 2), which has proved very effective in the determination of the melting points of non-metallic substances. It will be seen from the diagram of the insulated element that the hot junction is protected from the melting charge by a casing of platinum-iridium (0.1 mm. thick) and by a protecting tube of refractory Berlin (Marquardt) porcelain (1.5 mm. thick). Very early in our experiments upon the mineral silicates we became

¹ A single determination with one element, all others are mean values with two or more elements.

aware that the conductivity of these materials for heat would be much poorer than in similar charges of metal. Furthermore, the charge of mineral which the furnaces could carry was only one fourth to one third as great as the metal charges used in the calibrations because of the great difference in specific gravity and the limited space which could be heated to a fairly uniform temperature.

For these reasons the changes of state would be less sharply marked upon the heating and cooling curves than metal melting points, and it was feared that the readings of the protected element might prove too high or too low through inability to take on the temperature of the surrounding mass promptly. It

was to discover and obviate this possible source of error that the form of thermo-element indicated in the adjoining diagram was devised. It really amounts to nothing more than the ordinary form of platinum—platin-rhodium element with the platinum wire insulated from the other by a very slender porcelain (Marquardt) tube and the platin-rhodium wire broadened out and wrapped around this tube like a cap over the portion which dips into the charge. The hot junction (*a*) is then the lower extremity of the cap where the platinum wire emerges from its insulating tube and is welded inside the platin-rhodium cap.

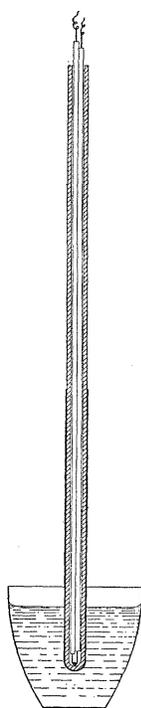


Fig. 1.

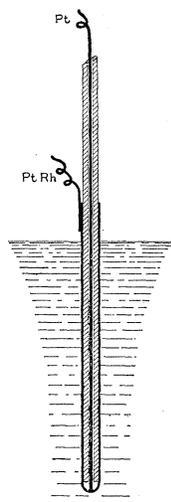


Fig. 2.

This form was dictated entirely by experience to meet conditions where an exposed element might be necessary or desirable. The wires of an ordinary element, if imbedded without protection, are rather frail for the wear and tear of breaking or drilling mineral charges out of the crucibles after the measurements, and they can not be strengthened without introducing a greater error through the

amount of heat conducted away from the junction than the one which it is desired to obviate.

It has furthermore been the almost invariable experience of one of the authors¹ that when an element, through exposure to combustion products or otherwise, no longer gives normal readings, the seat of the trouble lies in the five or six centimeters of the *platinum* wire immediately adjacent to the hot junction, and not in the alloy. The pure platinum sometimes seems to absorb enough volatile or other contact products, when unprotected in a furnace at very high temperatures, to alter both its resistance and its thermo-electric potential.² Changes of this kind are not serious when a number of control elements are constantly available, and they are usually permanently corrected by half an hour's glowing in the open air at full white heat. The glowing must be done by passing a suitable current through from end to end, and not with a Bunsen burner or gas blast.

In event of a serious accident involving an exposure of the element which can not be corrected by glowing, cutting out the exposed portion of the *platinum* wire and reconnecting will almost always restore the normal readings.

The new form of element seeks to avoid both these difficulties, it offers the advantage of an exposed junction without exposing the platinum wire, and by making the platin-rhodium cap project but little above the surface of the melting charge, it avoids excessive loss of heat by conduction away from the hot junction. In fact in this latter particular the new form enjoys a distinct advantage over the usual form of heavily protected element. It has the disadvantage of being more frail to handle, but there is little danger of anything more serious happening than the breaking of the porcelain tube, which is readily replaced.

These elements are calibrated in metal baths like the others by enclosing in a porcelain protecting tube.

The furnace, in plan, differed but little from that in use for melting-point determinations at the Reichsanstalt. In the working out, two important changes were introduced, in order to enable it to

¹ Day.

² Holborn & Day, *Am. Journ. Sci.*, 4, 10, 171, 1900.

reach the higher temperatures of the mineral melting-points. A more refractory and better insulating material was substituted for fire clay in the hotter parts and the coil was wound on the inside of the oven tube instead of outside. The latter involved some little mechanical ingenuity and skill in winding, but the gain in economy and in the rapidity with which changes could be effected or constant conditions established more than repaid any additional labor in preparation.

A diagram of the furnace in section is shown in Fig. 3. It could be used for any temperature up to 1600° C. without any difficulty

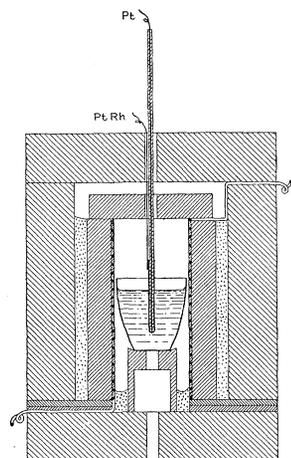


Fig. 3.

or especial precautions, and could be regulated to maintain a constant temperature at any particular point for long periods of time.

The coil, which was obtained from Dr. Heraeus, was of platin-iridium wire (90 parts Pt, 10 parts Ir), 1.5 mm. in diameter, and required about 3,000 watts to maintain a constant temperature of 1600° C. The furnace was carried at times on a 110-volt direct current street main, but accurately constant temperatures could not be depended upon without a storage battery.

The insulation in these furnaces was so perfect that shutting off or reversing the heating current at the highest temperatures did not produce a quiver in the galvanometer to which the thermo-element was connected, although the sensitiveness of the system was such that a leakage from the heating current into the thermo-element, amounting to a single micro-volt (corresponding to less than 0.1°) at 1600° would have caused a displacement of about twenty divisions on the scale.

The thermo-electrical potential was measured upon a potentiometer (Wolff, Berlin, Reichsanstalt calibration) in terms of a standard cadmium cell (saturated) prepared by ourselves. Two of these cells were used interchangeably during the earlier measurements. Toward the close of the series four fresh cells were prepared for

comparison with the earlier ones and were found to agree with them within 0.0001. One of these later cells (the readings of the four were identical to the fifth significant figure) was verified by Dr. Wolff of the Bureau of Standards, by comparison with the standard Clark cells of that institution, and found to be 1.0195 V. at 20° C., assuming the legal value (United States) of the Clark cell, 1.434 V. at 15° C. Substituting the Reichsanstalt value, $\text{Clark}_{15} = 1.4328$,¹ our cells would give the normal potential difference of 1.0186 at 20°.

With the apparatus here described, the authors were enabled to command any furnace temperature up to 1600° conveniently, to regulate it quickly and with great exactness or to hold it constant for long intervals. It could also be easily arranged to introduce an oxidizing or reducing atmosphere whenever desired.

With the help of the metals mentioned, which are readily obtainable and can be used repeatedly, thermoelements or resistance pyrometers can be calibrated in any laboratory, and used for all measurements up to the limit of the Reichsanstalt scale (1150° C.)

Anorthite. First Preparation.

Date.	Element.	Electromotive Force in MV.	Temperature.	Remarks.
Oct. 7, 1903.	A	15939	1534°	Solid charge, open crucible.
" " "	A	15914	1532	" " " "
" 10, "	A	15878	1530	Covered crucible.
" " "	No. 3	16074	1533	" "
" " "	" 3	16058	1532	" "
" " "	" 3	16068	1532	" "
" " "	" 2	16095	1532	" "
			Mean, 1532°	

Second Preparation.

Jan. 16, 1904.	A	15860	1532°	Covered crucible.
" " "	A	15864	1532	
" 20 "	No. 3	15960	1533	
" " "	" 2	16102	1532	
" " "	" 2	16092	1532	
Mar. 31 "	" 3	15932	1531	1st and 2d preparations together.
			Mean, 1532°	

Melting temperature, 1532°.

¹ Jaeger u. Kahle, Wied. Ann., 65, 926, 1898.

with no greater error than that inherent in the scale itself. Above this temperature to 1600° the continuation of the thermoelectric scale probably still furnishes the most convenient and trustworthy extrapolation which has yet been perfected.

The uniformity and certainty of this extrapolation will best be illustrated by a table taken from our measurements upon anorthite (the highest melting point we measured). The melting temperature of a mineral of very poor conductivity for heat and relatively low specific gravity is much more difficult to measure than that of a metal, but the agreement of the results tabulated above is sufficiently good to demonstrate the accuracy of the extrapolation.

These measurements were made with three different thermoelements, the individual constants of each being determined independently by separate calibration with the cadmium (321.7°), zinc (419°), silver (961.5°) and copper (1065°) melting points as described. The thermoelectric potential therefore appears to deserve entire confidence for consistent extrapolation through the 450° immediately above the present Reichsanstalt scale.

U. S. GEOLOGICAL SURVEY,
WASHINGTON, D. C., June, 1904.