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ART. XVIII.—*On the Gas Thermometer at High Temperatures*; by LUDWIG HOLBORN and ARTHUR L. DAY.

Second Paper.

[Communication from the Physikalisch-Technische Reichsanstalt, Charlottenburg, Germany.]

IN a former paper* we described our measurements with the gas thermometer in some detail. The investigation was concerned principally with establishing the conditions under which this instrument may be used with certainty as a standard at high temperatures. We have shown that this is possible using pure nitrogen as the expanding gas in a bulb of platin-iridium, this material being much superior to the porcelain so long in use for the purpose, both in the accuracy of the results obtainable and the convenience in handling.

Since then the work has been continued in the direction indicated at the close of the previous paper. In order to obtain the full advantages of the exactness which the use of the platin-iridium bulb has rendered possible, the first step was to measure the undetermined coefficient of expansion of this metal at high temperatures. This was very necessary because the correction which the observations with the gas thermometer require on account of the expansion of the bulb increases more rapidly than the temperature to be measured. With the platin-iridium bulb, for instance, it amounts to 10° at 500° , 30° at 1000° and 40° at 1150° , while the increase in the coefficient of expansion with the temperature, which of course is not taken into account in the earlier paper, affects the measurement 1° , 5° , and 7° at the above temperatures respectively.

Secondly, the influence of the pressure which the expanding gas exerts on the glowing walls of the bulb was investigated

* Ludwig Holborn and Arthur L. Day, this Journal (IV), viii, 165, 1899.

by a simple method, and finally a second platinum-iridium bulb with walls of double the thickness of the first was used in a somewhat different oven in verification of the earlier results. The use of the same thermo-element throughout enabled the observations to be compared with those of the previous series. The thermo-electric force of this element (platinum—platinum-rhodium), like the others involving the use of combinations of metals of the platinum group, may be represented by an equation of the second degree within the limits of temperature covered by the investigation (250–1150°). The form of the curve is therefore known when such elements are calibrated at three known temperatures.

To render such calibration independent of the gas-thermometer, a series of melting points of pure metals was determined in which we took advantage of the opportunity to investigate rather carefully the conditions which may affect the melting temperature in certain cases.

To this is further added a chapter on the measurement with thermo-elements, the accuracy obtainable and their lasting qualities.

1. *Determination of the Expansion.*

To determine the expansion of the platinum-iridium bulb, a bar of the same alloy (80 Pt, 20 Ir) was obtained, 500^{mm} in length and 5^{mm} in diameter and its linear expansion studied up to 1000°. In connection with this we also undertook the measurement of the expansion of several other substances at high tem-

peratures and hope to communicate in detail the full results of the investigation at another time, restricting ourselves for the moment to such as are necessary to the discussion of the gas thermometer. Slight changes which the figures here commu-

nicated may undergo in the further investigation of the problem cannot sensibly affect the matter in hand.

The method may be described briefly as follows: The bar is laid for the measurement of its expansion symmetrically in an electrically heated fire-clay tube, 80^{cm} long, in which two lateral holes are bored 10^{mm} in diameter and 485^{mm} apart.

This tube is protected against loss of heat by radiation by two concentric fire-clay jackets with corresponding lateral openings, and the whole placed in a horizontal position upon two brick pillars in such a way that the openings are directed downward. Underneath these, two microscopes are mounted with the aid of which readings can be made of the position of certain marks cut upon a flat polished surface near the ends of the expanding bar.

The heating coil which is wound upon the innermost tube extends for a good distance beyond the ends of the bar so that the temperature opposite the opening differs in maximum only 10 per cent from that at the middle. On account of the increase in the coefficient of expansion with the temperature an average temperature for the bar is not sufficient if considerable local differences exist, hence it is eminently desirable that the differences of temperature along the bar be not too great. We are accordingly making an effort to improve upon our present coil in this direction in the hope that an even greater uniformity in the temperature distribution may be secured.

The microscopes were mounted upon sliding bases upon a long horizontal support and could be fixed in the proper positions with clamping screws. To protect them from the radiation of the oven a diaphragm through which water circulated constantly was introduced between.

With this apparatus the expansion was then measured with the eyepiece micrometers of the microscopes, the reading before heating being verified after the oven had cooled down again. No measurable displacement of the microscopes was observed throughout the series but displacements of the bar occurred now and then at the higher temperatures; symmetrical observations upon both ends, however, eliminate any error from this cause in the results.

The observations were usually made at 250°, 500°, 750° and 1000°, and for the same temperature upon different days agree to within $\pm 0.01^{\text{mm}}$, whereby it should be remarked that one whole turn of the micrometer screw corresponds to about 1^{mm}.

The divisions, which were situated in the axis of the bar to diminish the effect of a possible slight bending or warping, were cut with the dividing engine, rather deep but with sharp edges, and rubbed with Parisian red (iron oxide). They were

illuminated from below with incandescent lamps. After the temperature has reached a bright red heat where the bar itself gives out light, the divisions still show very sharply by contrast with the polished metal surface as bright marks upon a dark ground.

But with the metals which oxidise and even with platinum-iridium which tarnishes before reaching 1000° , it is better to illuminate the glowing rod from outside also. The divisions then appear as dark lines upon a bright ground exactly as at the lower temperatures.

The temperature of the bar thus heated was measured at nine different points with a thermo-element, both wires being insulated with thin porcelain tubes so that the junction could be brought to any desired point along its length.

Platin-iridium (80 Pt, 20 Ir).—The following values were obtained for the expansion λ_s of the platin-iridium bar, which together with a similar bar of pure platinum mentioned below, was kindly loaned by the firm of Heraeus in Hanau:

t	λ_s (mm)	
	Observed.	Calculated.
250°	1.033	1.033
500	2.150	2.151
750	3.357	3.355
1000	4.645	4.645

The mean length included between the two groups of five divisions each at the two ends of the bar was 483.07^{mm} at 0° . From these figures the expansion λ of a bar of unit length at 0° may be represented by the formula

$$\lambda = [8198t + 1.418t^2] 10^{-9}.$$

Platinum.—We had no bar of the alloy 90 Pt, 10 Ir, of which the second bulb was made, but one of pure platinum was measured under the same conditions and yielded the following results, which we combined with the foregoing and used the mean for correcting the gas thermometer measurements made with the bulb of the lower alloy:

t	λ_s (mm)	
	Observed.	Calculated.
250°	1.114	1.113
500	2.309	2.304
750	3.570	3.571
1000	4.909	4.914

The length at 0° was 483.52^{mm} and the corresponding formula for a unit bar takes the form

$$\lambda = [8889t + 1.274t^2] 10^{-9}$$

The difference between the observed expansions and those calculated according to the formula amounts in both cases to less than 0.01^{mm} .

The largest measured difference between the observations upon the cold bars before and after heating to 1000° was 0.025^{mm} ; it was generally much smaller.

Porcelain.—The expansion of Berlin porcelain was also measured upon a bar of similar dimensions—unglazed in order that it might afterward be used at still higher temperatures. Plane surfaces were ground upon each end in the same positions as for the metallic bars, and upon these, divisions about 0.15^{mm} wide but very sharply defined were cut upon a lathe with a thin copper disc, five at each end. The readings at the highest temperature were at first somewhat difficult, for the divisions are but little brighter than the background. With illumination from outside, however, excellent readings could still be obtained after the candle power had been increased.

This bar had a mean length at 0° of 483.47^{mm} and yielded the following results for the expansion:

t	λ_s (mm)		λ (mm)
	Observed.	Calculated.	
250°	0.382	0.391	0.790
375	0.628	0.612	1.299
500	0.845	0.850	1.749
625	1.093	1.105	2.261
750	1.307	(1.377)	2.703
875	1.615	(1.666)	3.340
1000	1.977	(1.972)	4.089

Observations were made with the porcelain bar at temperatures between the original four, when it was found that the observed expansions could not be represented by a curve of the second degree. The following formula is approximately true between 250° and 625° ,

$$\lambda = [2954t + 1.125t^2] 10^{-9}$$

and yields the observed value again at 1000° , while for 750° and 875° the differences are considerably larger than the errors of observation. Below 250° also the values obtained from the formula are too large. The coefficient of expansion clearly increases more rapidly after red heat is reached than below 500° , and for the interval between remains nearly constant. The observed value at 1000° coincides with the calculated value again, which shows this temperature to be the point of intersection of two curves.

It may be further remarked that the various series of observations, after the preliminary heating to remove any tension

remaining from the grinding, agree quite as well for porcelain as for the metals. These observations were all made with a rising temperature, however, and it is not impossible that different values would be obtained for the expansion of porcelain if the temperatures observed were approached from the other direction, i. e. in the order 1000° , 875° , 750° , etc. It also remains to be investigated what differences exist between different bars of the same manufacture.

The expansion of Berlin porcelain formed the subject of an earlier investigation by Holborn and Wien,* who heated porcelain plates 9^{cm} in length in a gas furnace and measured them at the temperatures 550° and 1050° nearly. The mean value then arrived at, $44 \cdot 10^{-7}$ for the linear expansion coefficient, agrees with the present value at the higher temperature within the limits of accuracy then obtainable; at the lower temperature the earlier value is too large.

More recently Bedford† determined the expansion of French porcelain (Bayeux) between 0° and 800° . His formula is

$$\lambda = [3425t + 1.07t^2] 10^{-6}$$

A comparison with our results is not instructive, however, for the expansions of porcelains from entirely different sources are not properly comparable.

Our measurements with the gas thermometer and porcelain bulbs, for the calculation of which the Holborn and Wien value was used, require only a slight correction for the new determination of the expansion, partly because the absolute expansion is very small and partly because the use of too large a value for the bulb expansion between 0° and 100° makes it also necessary to correct (diminish) the coefficient of expansion of the gas about $\frac{1}{700}$. The required correction, therefore, remains less than 1° for the whole range from 500° to 1000° .

Jena Glass 59^{III}.—For the measurement with the gas thermometer below 500° a bulb of Jena glass 59^{III} and a nitre bath were used. We have, therefore, undertaken to measure the expansion of this material up to 500° , but the results which have so far been obtained only serve to emphasize how much depends upon the way the glass is treated. We were able, however, to establish the fact that the mean error of the gas thermometer observations in this region, $\pm 0.5^{\circ}$, is not exceeded in assuming for all temperatures up to 500° the constant value $18 \cdot 10^{-6}$. For more accurate measurements it is certainly advisable to employ the platin-iridium bulb for these temperatures also, the expansion of which is much better defined. In the nitre bath it will be necessary to protect it with a thin glass tube, however, as the bath becomes alkaline with use.

* L. Holborn and W. Wien, *Wied. Ann.*, xlvii, 121, 1892.

† T. G. Bedford, *Phil. Mag.* V, xlix, 90, 1900.

2. Influence of Pressure on the Gas Thermometer Bulb.

At the highest temperatures measured the inside pressure in the platin-iridium bulb exceeded that outside by nearly an atmosphere. Although no permanent change in the volume of the bulb after heating could be detected, it seemed, nevertheless, not impossible that a temporary yielding of the glowing walls under the comparatively high pressure might take place. We have investigated this question by redetermining the higher temperatures with a much diminished pressure.

This was accomplished by allowing a portion of the expanding gas to pass over into the closed tube of the manometer, thus varying pressure and volume simultaneously. The expansion-coefficient of the gas suffers a small change thereby which we estimated to be about 0.1 per cent and therefore neglected it.

The closed manometer tube had already been provided with two points (see first paper—loc. cit.) at which readings could be made for volumetric purposes, so that by bringing the mercury tangent to the lower point a definite volume could be added to that of the bulb. To enable a more accurate measurement of the temperature of this supplementary volume to be obtained than was possible with the small thermometer in the cap, a second and more sensitive thermometer was fastened to the tube and the whole carefully packed in a thick layer of cotton batting containing only the two small openings necessary to make the readings above and below.

As a rule the observations were made in sets of three, the first and last with the mercury adjusted to the lower, the second to the upper point. Since it was necessary to wait some time between observations until the temperature conditions in the manometer became uniform, the temperature in the oven had opportunity to change a few degrees. These changes (δ) were measured with the thermo-elements. The supplementary volume between the two points was measured by weighing the mercury required to fill it, the results being as follows:

50.630^{cm³}
50.609
50.641
50.658

Mean 50.635^{cm³}

The differences between the determinations are largely due to an imperfectly formed meniscus at the lower point, the adjustment being necessarily made with a falling column as the mercury was drawn off through a fine capillary tube. The adjustment with a rising column as used for the temperature measurements gives much more exact results. Also the deter-

mination of the distance between the two points, 161.60^{mm} contained variations of only 0.02^{mm} in the individual readings. An error of 0.1 per cent in the determination of the supplementary volume would cause an error of 1° in the temperature at 1000° as determined at the lower point.

For the verification of the method several measurements of the volume of the bulb at 0° were made. For the first platinum bulb the determination by filling with water and weighing yielded 208.49^{cm³}, the volumetric determination 208.45 and 208.51^{cm³}; for the second bulb the results obtained by the two methods were 195.87 and 195.91^{cm³} respectively.

Table XII contains the temperature measurements at the two different pressures. *H* and *t* represent the pressure meas-

TABLE XII.

1899	<i>H</i> (mm.)	<i>t</i>	<i>H'</i> (mm.)	<i>t' - δ</i>	<i>δ</i>	<i>t - t'</i>
July 22	871.71	553.0°	524.13	550.9°	+2.0°	+0.1°
			526.38	556.6	-3.4	-0.2
	877.37	558.7	526.80	557.8	+1.5	-0.6
			528.35	562.0	-2.9	-0.4
	1339.50	1022.7	663.06	1015.4	+6.3	+1.0
			666.71	1030.1	-7.6	+0.2
Aug. 2	848.68	531.1	514.76	527.9	+2.5	+0.7
			517.07	533.8	-2.9	+0.2
	855.11	537.4	517.76	535.5	+1.6	+0.3
			519.05	539.1	-1.6	-0.1
	1047.86	728.2	581.57	721.9	+5.3	+1.0
			585.81	734.9	-7.3	+0.6
Aug. 3	1055.69	736.1	585.80	734.8	+1.1	+0.2
			586.89	737.9	-1.9	+0.1
	952.97	633.9	551.09	629.4	+3.5	+1.0
			558.78	651.4	-18.4	+0.9
	974.06	654.8	559.11	652.5	+1.6	+0.7
			560.58	656.7	-2.4	+0.5
	1242.43	924.5	638.41	921.4	+1.5	+1.6
			639.87	926.7	-3.1	+0.9
	1243.62	925.8	639.62	925.5	-0.6	+0.9
			639.63	925.6	-0.6	+0.8

ured upon barometer and manometer, and the temperature calculated from it for the readings made at the uppermost point; *H'* and *t' - δ*, the corresponding magnitudes for the readings

below. If to $t' - \delta$ the change in the oven temperature δ be added, the results contained in the column $t - t'$ or the difference between the results obtained at the two pressures is obtained. The mean value of this difference is $\pm 0.7^\circ$ and exceeds 1.0° only in a single instance.

It follows from this that within the given limits of accuracy, the measurements with the gas thermometer equipped with the platinum-iridium bulb were not disturbed by the pressure upon the walls of the hot bulb. The initial pressure of the gas at 0° was 294.40^{mm} , nearly the same as in the earlier measurements, and its coefficient of expansion 0.003666 .

It has been suggested that this method be employed for obtaining the volume of the bulb at high known temperatures. It would then be possible to arrive at its coefficient of expansion in this way. In addition to the usual equation for the calculation of the temperature with constant volume,

$$\frac{HV}{1 + \alpha t} = H_0 V_0$$

a second relation is, to be sure, obtainable

$$H \left(\frac{V}{1 + \alpha t} + \frac{V_i}{1 + \alpha t_i} \right) = H_0 V_0$$

if t_i be used to represent the temperature of the supplementary volume V_i . The equations are nevertheless not independent of each other and are therefore not sufficient for the determination of the two unknown quantities V and t .

3. Comparison of the Thermo-element with the Gas Thermometer.

Second Platinum-iridium Bulb.—The second platinum-iridium bulb had nearly the same form and size as the first. It was, however, made from the alloy 90 Pt. 10 Ir., and its walls (1^{mm}) were twice as thick as those of the earlier bulb. Its volume at 0° was 195.87^{cm^3} .

After being boiled with concentrated nitric acid and several times rinsed with distilled water the bulb was carefully dried and attached to the manometer. Then it was evacuated with a mercury pump and maintained for several hours at a temperature of 1300° , being "rinsed" from time to time with fresh nitrogen and again evacuated. The gas for the final filling was also admitted at the high temperature and the exact pressure regulated after the bulb had cooled.

The new bulb was used for several series of measurements and proved to be quite as satisfactory as the old. The gas pressure at 0° remained constant to within 0.1^{mm} throughout.

The comparisons of the gas thermometer and the thermo-element T_2 which are contained in Table XIII agree among themselves exceedingly well and with the earlier comparisons also. The differences, which amount to about 1.0° , are of the same order of magnitude as in all the other measurements made under the given conditions, the bulb with its extended volume and the minute thermo-electric junction being contained in an air bath. The highest temperatures are most favorable in this respect, as the radiation acts most strongly there to equalize the temperature distribution.

Below 500° where the air bath gave place to nitre, the uniformity is also greater of course.

The conditions under which the second bulb was heated were also considerably varied in order that the substantiation of the earlier results might be as complete as possible. The observations under "October 12" in the table, for example, were made with the bulb in the same oven which had served for the measurements with the first bulb, the others in a newer and larger one, but with two different heating coils on the different days—both wound logarithmically as described in the former paper. The tubes carrying these new coils were 42cm long and 6cm inside diameter while the older one was only 35cm long and 4.8cm in diameter. The fire-clay jackets were also correspondingly larger.

TABLE XIII.

Platin-iridium Bulb No. II (90Pt, 10Ir) Gas-Nitrogen.

 $V_0=195.87\text{cm}^3$ $V_s=0.904\text{cm}^3$ $H_s=276.35\text{mm}$ $\alpha=0.003666$

1899	t	$e_2(\text{MV})$	Obs.— Calcul.	1899	t	$e_2(\text{MV})$	Obs.— Calcul.
Oct. 9	562.1°	4759	0.0°	Oct. 12	822.9°	7497	-1.5
	571.7	4861	-0.5		822.5	7496	-1.9
	573.2	4877	-0.6		1093.5	10558	-0.7
	829.5	7568	-1.5		1096.1	10598	-1.5
	1080.9	10423	-1.8		1097.4	10616	-1.7
" 12	552.0	4668	-1.0	" 21	669.1	5836	$+1.1$
	552.2	4670	-1.0		917.4	8526	-0.2
	552.6	4674	-1.0		1063.3	10189	$+0.5$
	821.2	7478	-1.5				

In Table XIII, t represents the temperature observed with the gas thermometer, e_2 the thermo-electric force of the element T_2 in microvolts. The last column (Obs.—Calcul.) contains the difference between t and the temperature in degrees calculated from the curve for e_2 . This curve will be referred to again further on.

The Observations with the first Platin-iridium Bulb.—The earlier observations (loc. cit. Tab. IX, p. 189) with the first bulb (80 Pt, 20 Ir), which were calculated with a constant coefficient of expansion, can now be corrected for the increase in the expansion with the temperature. The corrected values are contained in Table XIV, the numbers printed in italics in Table IX being here omitted. They were made with a uniformly wound oven coil, and a comparatively large (former paper, Table VIII, p. 189) fall in temperature along the bulb, roughly corrected with the help of the thermo-elements.

TABLE XIV.
Platin-iridium Bulb I (80Pt, 20Ir). Gas-Nitrogen.

After filling.	<i>t</i>	<i>e</i> ₂ (MV)	Obs.— Calcul.	After filling.	<i>t</i>	<i>e</i> ₂ (MV)	Obs.— Calcul.
2d day	529.1°	4429	+0.3°	22d day	1052.8°	10073	—0.1°
	614.8	5289	+0.1		1102.5	10653	+0.4
	1008.8	9555	+0.6				
20th "	625.6	5401	—0.1	24th "	541.2	4552	+0.1
	812.1	7356	+0.6		542.8	4569	—0.2
	907.3	8396	+1.2		615.5	5297	0.0
	1014.8	9622	+0.9		717.3	6343	+0.7
	1113.9	10770	+1.7		814.3	7385	—0.2
					919.7	8550	+0.2
22d. "	511.8	4252	+1.1		1017.6	9661	+0.1
	512.7	4268	+0.2		1106.6	10700	+0.4
	551.5	4655	—0.2	25th "	516.4	4304	+0.2
	659.3	5754	—0.8		616.3	5303	—0.1
	703.8	6217	—0.9		721.3	6382	+0.7
	757.0	6775	—0.5		821.9	7462	+1.6
	859.4	7881	—0.3		913.4	8458	+1.8
	949.2	8890	—0.6		1026.0	9756	+0.5
	1001.5	9496	—1.6		1134.5	11031	+0.7
	1050.4	10044	—0.1				

The temperatures *t* are raised by the new coefficient of expansion 0.7° at 500°, 4.9° at 1000° and 7.5° at 1150°.

In the recalculation a small correction has also been added for the slight over-compensation of the heating coil (Table VIII)—13 microvolts at 500°, and 5 at 1150°. This corresponds to the measured temperature distribution according to which the junction of T₂ opposite the middle of the bulb reads smaller than the integral temperature—at 620° 1.2° smaller, at 820° 1.0°, at 1010° 0.5° and at 1150° 0.4°.

Observations below 500°.—After the observations in the electric oven between 500° and 1150° were completed, the thermo-element T₂ was compared with the gas thermometer

equipped with a bulb of Jena glass 59^{III} between 250° and 500° in a nitre bath. These observations were designed partly to verify the earlier observations below 500°, with which the element T_2 was connected only indirectly by comparison with T_1 ; and partly to enable us to compare the absolute values obtained from observations in the nitre bath and in the electrically heated air bath.

This nitre bath was considerably smaller than the one used for the earlier observations and was heated electrically, whereby we were enabled to secure constant temperatures more quickly and more exactly. A wrought iron cylinder 12^{cm} in diameter, such as is used for the transportation of mercury, was cut off at a height of 27^{cm} and fitted with a cover 2^{cm} thick, which carried a turbine driven by an electric motor for stirring. The heating coil was of bare constantan wire 1.5^{mm} in diameter wound in two parallel coils upon the cylinder, the insulation being provided by a layer of asbestos board, and held in place by smearing with clay. The whole was enclosed in a larger fire-clay jacket and the space between closed in with asbestos wool, giving a layer of air a centimeter or more thick about the coil. This bath can be used up to 700°.

2.

$\frac{1}{8}$ Natural size.

For temperatures below 300° where insulating liquids may be used for the baths, an arrangement which did us exceedingly good service certainly deserves mention in passing. A

cylindrical glass vessel, with double walls enclosing a vacuum, such as is commonly used for liquid air (Prof. Dewar's design), was filled with olive oil. Into the oil dipped a porcelain tube with two spiral furrows upon the outer surface, carrying coils of bare constantan wire. Inside the tube a turbine was inserted and held in place above and below with brass clamping rings. The stirrer and heating coil were thus in one piece and could be introduced into any insulating bath at pleasure. A vessel with a vacuum jacket is preferable however, on account of the very small quantity of electrical energy required to heat it, even when the walls are left unsilvered for reading a completely immersed thermometer. With 1.2 l. of oil only 100 watts were necessary to maintain a temperature of 250° . Although in using this apparatus we did not have an accident from explosion of the vessel, still, as this now and then occurs with such vessels at low temperatures without any apparent cause, it is well to make provision against possible personal injury in such an event. Table XV contains the comparison of thermo-element and gas thermometer in the nitre bath. The bulb was filled with nitrogen under a pressure of 471.84^{mm} at 0° .

TABLE XV.
Observations in the Nitre Bath.

	t	e_2 (MV)	Obs.— Calcul.		t	e_2 (MV)	Obs.— Calcul.
Feb. 6	340.7°	2639	-0.8°	Feb. 8	395.8°	3153	-0.8°
	340.5	2635	-0.5		395.8	3151	-0.6
	387.5	3076	-0.9		492.6	4082	-0.7
	386.9	3071	-1.0		492.8	4084	-0.7
	439.8	3573	-1.0	March 29	359.6	2803	$+0.4$
	439.8	3572	-0.9		359.5	2802	$+0.4$
	501.3	4171	-1.3		400.5	3195	-0.6
	500.9	4168	-1.4		402.4	3217	-1.0
Feb. 8	267.4	1970	-0.6		498.5	4140	-1.0
	291.6	2191	-0.8		498.3	4139	-1.1
	291.7	2193	-0.9				

4. Formulae for Thermo-elements.

In a previous paper* we were able to show that the relation between the thermo-electric force and the temperature in metals of the platinum group together with gold and silver could be represented within wide limits with an accuracy of $\pm 1^{\circ}$ by a function of the second degree.

* Ludwig Holborn and Arthur L. Day, this Journal (IV), viii, 46, 1899.

The measurements made at that time were upon wires of pure rhodium, iridium, palladium, gold and silver together with alloys of platinum with palladium and ruthenium, whose thermo-electric force referred to pure platinum was measured up to 1300°. The elements with palladium or palladium alloys differed from the others in that the range within which the parabolic formula applies is smaller.

The formula for the normal element T_2 derived from the comparisons with the gas thermometer follows, together with certain of the others; those metals being chosen which are best suited to the measurement of high temperatures and which offer a basis for extrapolation.

These have been compared with the normal element from 50° to 50° approximately and the thermo-electric forces corresponding to the exact temperature intervals as contained in Table XVI, obtained from the observed data by graphical interpolation.

Since the publication of the earlier paper some observations above 1300° have been added with the aid of an oven equipped with a coil of platin-iridium wire.

Normal Element Pt-90 Pt, 10 Rh.—The thermo-electric force e_2 in microvolts of the platinum—platin-rhodium standard element T_2 is given by the following equation from 250° upwards

$$e_2 = -310 + 8.048t + 0.00172t^2$$

when the hot junction is maintained at the temperature t° and the cold junction at 0° . The formula is based upon the observations with the platin-iridium bulb above 500° and with the glass bulb and nitre bath below, as contained in Tables XIII, XIV and XV. In the columns "Obs.—Calcul." of these tables will be found the differences between the observed values and those obtained from the formula.

It will be recalled that the element T_1 was compared (first paper, Tables I to VII) above 500° with the gas thermometer equipped with porcelain bulbs. These observations differ among themselves somewhat, due in part to the behavior of the porcelain bulbs and in part to the less perfect conditions of measurement then obtaining. In the normal curve these observations are therefore not included, the curve being based entirely upon the temperatures measured with T_2 and the platin-iridium and glass bulbs. It is nevertheless not without interest to compare the temperatures obtained with T_1 and the porcelain bulbs, with the later ones.

This may be done by referring the normal values for T_1 (Table II former paper) to those of T_2 , by adding the differences $T_2 - T_1$ (Table XI, former paper) which were obtained by

direct comparison of the two elements, or in other words if T_2 be referred to the observations made with the gas thermometer as used with porcelain bulbs.

In Table XVI in the first column the values of the electromotive force for T_2 calculated from the formula are contained. The column Δ contains the differences between these values and those obtained from $T_1 + (T_2 - T_1)$ as suggested above. If now these values of Δ be compared with the earlier ones (Table XI, former paper) it will be seen that the differences have become very small now that the proper expansion coefficients of both porcelain and platinum-iridium have been applied.

From this the conclusion follows that the porcelain bulbs lead to substantially the same results as the platinum-iridium as long as the former are not used above 1100° . Under these conditions of course only bulbs glazed inside and out need be used, as the glazing does not melt up to that point.

Regarding the precautions necessary to be observed in the use of porcelain bulbs and the degree of accuracy obtained in temperature measurements with them, reference is made to the former communication.

Element Pt—90 Pt, 10 Ru.—The element platinum—platinum-ruthenium follows a curve very similar to that of the normal element. Its equation is

$$e_s = -359 + 9.260t + 0.00150t^2$$

Element Pt—Ir.—For the element platinum-iridium a formula has also been calculated which like the others holds from about 300° on. Like the following curves it is based on the thermoelectric force of two pure metals and possesses a much greater curvature than those of the alloys. It is—

$$e_s = -248 + 7.282t + 0.00554t^2$$

Element Pt—Rh.—For the combination platinum-rhodium two specimens of pure rhodium were at our disposal. The first was from Heräus, the second was especially prepared in the *Reichsanstalt*. The two formulae are

$$e_s = -228 + 7.230t + 0.00660t^2$$

$$e_s = -235 + 7.410t + 0.00660t^2$$

The second equation is derived under the assumption that the differences between the two curves e_s and e_n can be represented by a linear relation. The observed results between 300° and 1150° —the range of the gas thermometer—are made the basis for the derivation of this as well as of the other formulae.

Table XVI contains the observations upon these elements as well as the differences between them and the values calculated from the above formulae in microvolts and degrees.

TABLE XVI.

t	Pt - 90Pt, 10Rh.			Pt - 90Pt, 10Ru.			Pt - Ir			Pt - Rh ₁			Pt - Rh ₂			t
	e_2 Calcul. MV	Δ		e_3 Obs. MV	Obs. - Calcul.		e_4 Obs. MV	Obs. - Calcul.		e_5 Obs. MV	Obs. - Calcul.		e_6 Obs. MV	Obs. - Calcul.		
		MV	Degrees		MV	Degrees		MV	Degrees		MV	Degrees		MV	Degrees	
250°	1810	-10	-1.1°	2062	+12	+1.2°	1966	+47	+4.7°	2004	+12	+1.1°	2042	+12	+1.1°	250°
300	2260	+3	+0.3	2550	-4	-0.4	2474	+39	+3.7	2536	+1	+0.1	2580	-2	-0.2	300
350	2718	+9	+1.0	3056	-10	-1.0	3002	+23	+2.1	3112	+1	+0.1	3160	-7	-0.6	350
400	3185	+9	+1.0	3580	-5	-0.5	3550	-1	-0.1	3714	-6	-0.5	3780	-5	-0.4	400
450	3661	+11	+1.1	4112	+1	+0.1	4156	+5	+0.4	4362	0	0.0	4432	-4	-0.3	450
500	4145	+5	+0.5	4646	0	0.0	4778	0	0.0	5032	-5	-0.4	5118	-2	-0.2	500
550	4638	+4	+0.4	5184	-4	-0.4	5424	-9	-0.7	5744	-1	-0.1	5834	-3	-0.2	550
600	5139	+3	+0.3	5738	+1	+0.1	6102	-14	-1.0	6484	-2	-0.2	6582	-5	-0.3	600
650	5649	-1	-0.1	6290	-4	-0.4	6810	-16	-1.1	7260	0	0.0	7372	+2	+0.1	650
700	6168	-6	-0.6	6860	+2	+0.2	7564	0	0.0	8076	+9	+0.6	8192	+6	+0.4	700
750	6695	-9	-0.8	7430	0	0.0	8320	-10	-0.7	8906	-1	-0.1	9038	+3	+0.2	750
800	7231	-10	-0.9	8012	+3	+0.3	9116	-7	-0.4	9790	+10	+0.6	9928	+11	+0.6	800
850	7775	-11	-1.0	8596	0	0.0	9948	+4	+0.2	10688	+2	+0.1	10840	+8	+0.4	850
900	8328	-11	-1.0	9196	+6	+0.5	10798	+5	+0.3	11644	+19	+1.0	11802	+22	+1.1	900
950	8890	-9	-0.8	9804	+8	+0.7	11670	0	0.0	12614	+17	+0.9	12782	+21	+1.1	950
1000	9460	-8	-0.7	10410	+9	+0.7	12588	+14	+0.8	13600	-2	-0.1	13774	-1	-0.1	1000
1050	10039	0	0.0	11018	0	0.0	13518	+12	+0.6	14616	-24	-1.1	14800	-22	-1.0	1050
1100	10626	+13	+1.1	11646	+4	+0.4	14482	+16	+0.8	15692	-19	-0.9	15884	-18	-0.8	1100
1150	11222			12274	0	0.0	15462	+9	+0.5	16800	-15	-0.7	16976	-39	-1.7	1150
1200	11827			12918	+5	+0.4	16482	+21	+1.0	17946	-6	-0.3	18130	-31	-1.3	1200
1250	12440			13556	-4	-0.3	17498	-5	-0.2	19106	-17	-0.7	19280	-60	-2.5	1250
1300	13062			14208	-6	-0.5	18580	+7	+0.3	20314	-11	-0.5	20492	-60	-2.5	1300
1350	13692			14864	-12	-0.9	19662	-9	-0.4	21556	-5	-0.2	21728	-69	-2.7	1350
1400	14331			15528	-17	-1.3	20766	-20	-0.9	22800	-30	-1.2	22988	-87	-3.4	1400
1450	14979			16220	-2	-0.2	21904	-35	-1.5	24136	+4	+0.2	24276	-110	-4.1	1450
1500	15635			16914	+8	+0.6	23056	-74	-3.0	25486	+19	+0.7	25684	-46	-1.7	1500

Attention should perhaps be called to the fact that in the comparisons between these elements and the normal element, different sections of the same curve are separated in particular cases by considerable intervals of time so that the distribution of temperature from junction to junction was not always the same even through the observations of a single series. Small consistent differences between "Obs." and "Calcul." may be fairly attributed to this cause, though for the temperature range 300° to 1150° when the gas thermometer was used, the differences rarely exceed 1° ; above 1150° where the figures are based upon an extrapolation of the formula for T , they are sometimes larger, though nowhere exceeding 5° .

5. *Melting Points of Metals.*

To render the calibration of thermo elements independent of the gas thermometer we have determined the melting points of various metals lying between 300° and 1100° . Two methods were used: According to the first, a short wire (about 1 cm long) of the metal to be melted was introduced into the hot junction of the thermo-element itself, and the thermo-electric force at the moment of the melting and consequent interruption of the circuit, observed. This method is simple but leads easily to doubtful results if the melting point is at all affected by the surrounding atmosphere, as is the case with most of the metals which oxidize in air. The element also becomes considerably shortened by the continual cutting off of the drop of melted metal after the observations and renewing the junction.

By the second method a larger quantity of metal is melted in a crucible and the thermo-element, protected by light porcelain tubes, inserted. When the heating is properly regulated the beginning of the melting or freezing point is readily recognizable as the temperature remains stationary for a considerable length of time. In the following, the words "wire method" and "crucible method" may serve to distinguish the two processes.

For the latter method the apparatus was arranged as indicated in fig. 3. A porcelain or graphite crucible is contained within a short fire-clay tube carrying a coil of bare nickel wire whose separate turns were insulated by smearing with clay. The whole is protected against loss of heat by a layer of loose asbestos A and a thick protecting tube also of fire-clay. The wires of the thermo element are insulated from each other by means of thin porcelain tubes and from the molten metal by a somewhat thicker tube of the same material, 5 mm in inside diameter and 1.5 mm in thickness, which dipped at least 4 cm into

the melting metal (1^{cm} from the bottom of the crucible) and was clamped in position there.

The figure shows the oven with a graphite crucible in position and a second slightly smaller one with a hole bored in the bottom inverted over it as a cover.

The porcelain crucibles were similar in size and form, 1^{mm} thick and without cover.

Inasmuch as the electric heating furnished a much more uniform distribution of temperature than the gas oven and as no systematic differences between the melting and freezing temperatures were observed even with the most varied conditions of current and quantity of metal, we did not attempt to stir the metals in general. Only in one section of the observations with silver an effort was made to expose the melted metal more thoroughly to the air by stirring.

In the preliminary experiments the coil was wound directly upon a crucible of fire clay, but that was soon given up—first

because the clay was too porous to hold the melted metal in all cases (molten Cu for instance penetrated the wall and short-circuited a section of the coil), and second, the change from one crucible to another which happened nearly every day was much more convenient with the coil wound upon a separate tube. This oven consumed about 600 watts at 1000°

Some caution was necessary in heating up to the highest melting point (copper), otherwise the oven coil (1^{mm} in diameter) burned out—its renewal is a simple matter however.

For the temperature measurement thermo-elements were used which were cut from the same wire as T_2 and which have shown themselves to be perfectly identical with it in their results. Temperatures above 500° are derived from the normal curve (Table XVI) and below from the measurements in the nitre bath.

In each determination the thermo-electric force was observed from minute to minute and afterward plotted as a function of the time (mentioned hereafter as the "time curve"). A change of 10 microvolts could be compensated directly on the compensation apparatus by inserting 0.1 ohm. Smaller differences were interpolated from the galvanometer deflection, one scale division corresponding to from 0.5 to 1.4 microvolts according to the resistance in the branch circuit.

The accuracy of the crucible method is only limited by the accuracy with which it is possible to measure with the thermo-element, in regard to which more will be said further on. The wire method is less exact because the interruption of the circuit which indicates the melting point is not independent of any slight tension which may exist in the wires of the thermo-element, particularly the platin-rhodium wire—a factor which varies from one observation to another.

The highest temperatures observed for a particular metal by this method may therefore be expected to come nearest the truth. The inserted wire may even at times be seen to break just before the real melting takes place.

Gold.—The melting point of gold was determined by the wire method only. Two different specimens of gold had been placed at our disposal, one (I) from the *Gold und Silber Scheideanstalt* in Frankfurt-am-Main, the other (II) specially prepared and purified in the Reichsanstalt. No difference could be detected in their melting temperature.

The observations on the first two days (following table) were made in the gas thermometer oven, the others in the small oven used for the determinations by the crucible method (fig. 3) in which an empty crucible had been placed.

The arrangement of the thermo-element in the latter case was the same as above described for the crucible method with the omission of the porcelain protecting tube. The heating

was so regulated that the slowly rising temperature could be easily observed at any time. It was even possible to observe the stationary temperature at the melting point just before the interruption of the circuit. The observed melting temperatures in microvolts and in degrees follow:

	Microvolts.	Degrees.
Oct. 17 (I)	10209	1064.5°
	10209	1064.5
	10206	1064.2
	10208	1064.4
Oct. 18 (II)	10202	1063.9
	10201	1063.8
Nov. 15 (II)	10211	1064.6
	10211	1064.6
	10211	1064.6
Jan. 2 (II)	10190	1062.9
	10190	1062.9
	10200	1063.7
	10189	1062.8
Jan. 3 (II)	10203	1064.0
	10197	1063.5
	10213	1064.8

The mean is $1064.0^{\circ} \pm 0.6^{\circ}$.

Silver—Wire Method.—The melting point of silver was also first determined by the wire method and two specimens were used, both from the Frankfurt *Scheideanstalt*. One of these was in the form of wire 0.5^{mm} and 0.25^{mm} in diameter and the other a piece of sheet silver 0.25^{mm} in thickness, from which thin strips were cut and inserted in the junction of the element. Here again no difference in the melting temperature of the two specimens could be established. The same ovens were used as for the gold determination. The results follow:

	Microvolts.	Degrees.
Sept. 25	8928	953.3°
	8936	954.0
Oct. 16	8937	954.1
	8922	952.8
	8922	952.8
Oct. 18	8914	952.1
	8927	953.3
	8930	953.5
	8935	953.9
Nov. 15	8939	954.3
	8958	956.0
	8925	953.1
	8941	954.5
	8924	953.0

The mean is 953.6° with a mean error of $\pm 0.9^{\circ}$.

Callendar as well as Heycock and Neville* have called attention to the fact that silver in an oxidizing atmosphere melts and solidifies at a lower temperature than in a reducing atmosphere, the difference being caused by the fact that silver absorbs oxygen in melting which is given off again below the melting temperature with considerable violence ("spitting").

Silver—Crucible Method.—In order to ascertain whether the melting point as determined by the wire method differs from the normal melting temperature we made determinations of it by the crucible method also.

(1) *In an Oxidizing Atmosphere.*—At first the silver was melted in an open porcelain crucible without stirring. Under these conditions the results differed from those with other metals in that the silver showed no definite melting temperature. In melting as well as in solidifying the "time curve" takes the form A (fig. 4), i. e. throughout its length it contains

no horizontal section but falls or rises slowly over an interval of 6° to 8° , between which limits one point may be assumed as the melting point nearly as well as another. After substituting mica sheets for the clay oven-covers so as to be able to see the metal during the process, it was observed that it remained liquid through the greater part of this interval. The melting and solidifying occurred at about 954.5° (8940 microvolts). It may be added that the substitution of three mica covers separated by air layers, for the two clay covers, produced no essential change in the conditions within the oven.

If the thermo-element with its protecting tube were moved about or the liquid metal otherwise stirred, the form of the

* C. T. Heycock and F. H. Neville, Journ. Chem. Soc., 1895, 160 and 1024.

time curve remained in general the same except perhaps that the limits of the slow rise or fall of the temperature were moved closer together, and if the stirring was energetic, could be lowered some degrees.

Table XVII contains a number of results partly with stirring and partly without. *G* indicates the weight of the melted metal in grams, t_1 and t_2 the upper and lower limits of the slow change of temperature about the melting point, and $\bar{t}$ their arithmetical mean. The letters *F* and *M* distinguish freezing and melting points. The strength of the oven current i may serve to give an idea of the comparative expenditure of energy in the different determinations though only a rough one, as the resistance of the coil on different days was not always the same. The mean value of $\bar{t}$ for the observations where the metal was stirred is 954.9° and differs only 1.3° from the result

TABLE XVII.
Melting Point of Silver in Air.

1899. Novem'r.	<i>G</i> (gr.)	<i>i</i> (Amp.)		t_1		t_2		$\bar{t}$
				MV	Degrees.	MV	Degrees.	
Without stirring. 16	350	6.0	F	8940	954.4°	8983	958.2°	956.3°
		8.3	M	8960	956.1	9016	961.0	958.6
		0.0	F	8973	957.3	9000	959.6	958.5
		8.0	M	8970	957.0	9014	960.9	959.0
		6.5	F	8926	953.2	9006	960.2	956.7
		9.0	M	8970	957.0	9014	960.9	959.0
	17	5.0	F	8968	956.8	9001	959.7	958.3
		8.0	M	8963	956.4	9018	961.2	958.8
		5.5	F	8942	954.6	8995	959.2	956.9
		8.0	M	8950	955.3	9011	960.6	958.0
With stirring.	18	5.0	F	8931	953.6	8947	955.0	954.3
	20	6.0	F	8950	955.3	8967	956.7	956.0
		10.7	M	8931	953.6	9004	960.0	956.8
		8.0	F	8890	950.0	8943	954.6	952.3

obtained by the wire method. We assume therefore 955° as the mean melting point of silver in air, but at the same time we wish to emphasize the fact that the point is not well defined and, especially with the wire method, may suffer considerable variations with the nature of the surrounding atmosphere.

The "spitting" was also frequently observed through the mica covers. It took place between 933° and 940° , in the mean at about 936° , and was much more violent when the melted metal had been previously stirred.

The attempt to saturate the melted silver by allowing oxygen to bubble through it and thereby to reach a definite point of solidification for this condition led to no satisfactory result. The thermo-element showed considerable temperature oscillations throughout the solidification, but the mean, as was to be expected, lay much below the other determinations. Four observations gave the temperatures 939° , 938° , 942° and 938° — approximately the same temperature at which the absorbed oxygen is given off as noted above. Curve D (fig. 4) shows one of the time curves taken under these conditions, though it is by no means characteristic of all. In one case for instance with the temperature falling gradually, oxygen began to be given off at about 940° , whereupon the temperature began to rise, and reached 963° in the next five minutes, a violent spitting going on throughout the interval. At the latter temperature the metal became suddenly rigid and closed the porcelain tube through which the oxygen was entering.

(2) *In a Reducing Atmosphere.*—Higher results and better defined are obtained by preventing the access of oxygen. We sought to accomplish this first by melting the silver under a layer of common salt and afterward in a plumbago crucible over which a second crucible was inverted as a cover.

The time curves in both cases, for both melting and solidifying points, showed well defined horizontal segments, as may be seen from fig. 4, curves B (under NaCl) and C (in graphite).

Table XVIII contains a series of such observations from which 961.5° is obtained as the melting or solidifying tempera-

TABLE XVIII.
Melting Point of Silver in Absence of Oxygen.

Date.	G. (gr.)	i. (Amp.)		<i>t.</i>	
				MV.	Degrees.
In Porcelain Crucible under NaCl.					
Nov. 23	400	5.3	F	9023	961.7°
		10.7	M	9026	961.9
		6.7	F	9023	961.7
		11.3	M	9026	961.9
In Graphite Crucible.					
Dec. 8	352	6.7	F	9018	961.2
		9.5	M	9019	961.3
		6.0	F	9018	961.2
		9.3	M	9018	961.2

ture of pure silver. No spitting was observed under these conditions.

For the wire method neither of these courses is open for making determinations in the absence of oxygen. The bare junction cannot be placed in melted salt on account of its conductivity nor exposed to the reducing atmosphere of a plumbago crucible without danger of affecting the thermo-element.

Copper.—The melting point of copper was not determined by the wire method on account of the oxidation of the metal. In the crucible, the material used was pure copper in 100 gr. blocks from the *Haddernheim Kupferwerk* and determinations were made in both oxidizing and reducing atmospheres.

TABLE XIX.
Melting Point of Copper.

Date.	G. (gr.)	<i>i</i> . (Amp.)		<i>t</i> .	
				MV.	Degrees
In Oxidizing Atmosphere.					
Nov. 7	900	—	F	10216	1065·1°
29	330	7·5	F	10213	1064·8
		11·0	M	10215	1065·0
		7·5	F	10213	1064·8
		10·8	M	10214	1064·9
Dec. 5	350	10·3	M	10219	1065·3
		8·0	F	10210	1064·6
		10·5	M	10216	1065·1
6	350	7·5	F	10211	1064·7
		10·3	M	10220	1065·4
		7·0	F	10211	1064·7
		9·9	M	10219	1065·3
Mar. 19	370	6·8	F	10213	1064·8
		10·3	M	10213	1064·8
		6·8	F	10211	1064·7
		10·3	M	10211	1064·7
21	370	6·5	F	10212	1064·7
		8·5	M	10214	1064·9
		8·5	M	10216	1065·1
23	370	8·2	M	10216	1065·1
		8·2	M	10219	1065·3
In Reducing Atmosphere.					
Dec. 7	355	7·5	F	10442	1084·3
		10·2	M	10440	1084·2
		7·2	F	10440	1084·2
		10·4	M	10437	1083·9

(1) *In an Oxidizing Atmosphere.*—Copper differs distinctly from silver in that when melted in an open porcelain crucible it possesses perfectly definite and coincident melting and solid-

ifying points. This seems to indicate that the copper under these conditions becomes saturated with a definite quantity of oxygen or rather with a copper oxide.

To assure ourselves regarding the constancy of this point we have made a great many observations of it without being able to notice any essential variation.

It was also quite indifferent whether the copper was fresh or had been several times used for the same purpose before.

After many determinations with a particular mass of metal it seemed to melt with increasing difficulty, a phenomenon which points to a decrease in its conductivity for heat, but should receive rather more investigation. Table XIX contains the results of the observations, giving 1064.9° as the melting point of copper in air.

(2) *In a Reducing Atmosphere.*—If the same metal which has been repeatedly melted in air be heated in a plumbago crucible it gradually reduces and the melting point rises, ultimately reaching 1084° after the metal has remained for a long time in a molten condition and become thoroughly reduced.

Melting points obtained between 1065° and 1084° where the reduction is still incomplete give poorly defined curves.

At the close of Table XIX some observations with the pure metal are given. Fig. 5 shows time curves for observations in

porcelain crucibles (curves A and B) as well as in graphite (curves C and D).

If the melted copper contained oxygen, the unglazed porcelain tube which served to protect the thermo-element was

always colored black while pure copper had no noticeable effect upon it.

Antimony.—The antimony with which our determinations were made, as well as the following metals, were obtained from C. A. F. Kahlbaum, chemist, in Berlin; with the exception of aluminium they may be regarded as pure.

For melting the antimony only graphite crucibles were employed, and even then a slight superficial oxidation was observed after cooling. Reducing gases were not introduced on account of the thermo-elements.

In solidifying, the temperature first sank far below (as much as 20°) the melting point, to which it then rose suddenly (see fig. 6, curve A). The time curves are otherwise normal. The mean value for the melting temperature was 630.6° .

Aluminium.—Aluminium was melted in both porcelain and graphite crucibles. As has been noticed already by former observers, this metal shows no sharply defined melting point. Its time curves are similar in form to those obtained from silver in air. We give the melting point as 657.3° —the mean of the results obtained in the porcelain crucible. The melting temperatures observed in graphite were slightly lower to be sure, but the difference is more probably due to the smaller quantity of metal used.

The melting point of aluminium is not a sufficiently well-defined point for use in calibrating thermometrical apparatus;

should a temperature in this region be desired, the melting point of antimony is preferable.

Zinc.—The melting temperature of zinc can also be determined in an open porcelain crucible provided the same zinc be not too often used—with too much oxide present, the curves were less well-defined. In graphite the form of the time curve and the temperature are the same as in porcelain. The mean melting temperature may be given as 419.0° .

Lead.—The only noticeable feature in the determination of the melting point of lead is its small melting or “latent” heat, which makes some attention to the regulation of the oven temperature necessary. The mean melting point is 326.9° .

Cadmium.—The melting heat of cadmium is much greater and sharp curves are obtained with little trouble. Its mean value is 321.7° .

In Table XX are contained the determinations of the melting and freezing temperature of antimony, aluminium, zinc, lead and cadmium.

Tables XXI and XXII contain examples of the time curves as they were observed, the numbers representing the thermo-electric force in microvolts as observed from minute to minute.

Alloys.—In conclusion certain alloys remain to be mentioned whose melting points we investigated by the wire method only.

The metals were in thin strips cut from sheets of perhaps 0.2 to 0.3^{mm} thickness, prepared especially for the purpose by the Frankfurt *Scheideanstalt*.

As the investigation could only be undertaken in an oxidizing atmosphere, alloys of silver and copper gave no definite results whatever. The silver melts and separates out of the partly oxidized copper, leaving it to interrupt the circuit by breaking at a considerably higher temperature.

The two alloys 95Ag5Au and 90Ag10Au were especially prepared to ascertain whether the addition of a small quantity of gold would prevent the action of oxygen on the melting point of silver. The observed results seem to negative this assumption.

The temperature scale for the highest melting points is based upon extrapolation from the curve of the normal element T₂ (Table XVI).

6. Measurement with Thermo-elements.

Some ten years ago when the first platinum—platin-rhodium thermo-elements were obtained from the firm of Heräus for the measurement of high temperatures, both the platinum and the rhodium were so imperfectly purified chemically that the duplication of an element with approximately the same thermo-

TABLE XX.

Date.	G (gr.)	<i>i</i> (Amp.)		<i>t</i>		
				MV	Degrees	
Antimony.						
Dec. 14	260	0·0	F	5453	630·8°	In graphite.
		8·5	M	5449	630·4	
		5·0	F	5452	630·7	
		7·5	M	5448	630·3	
Aluminium.						
Dec. 4	180	0·0	F	5729	657·7°	In porcelain.
		8·5	M	5723	657·1	
		4·5	F	5727	657·5	
		7·5	M	5723	657·1	
Dec. 9	110	4·3	F	5725	657·3	In graphite.
		0·0	F	5717	656·6	
		8·0	M	5707	655·6	
		5·0	F	5718	656·6	
		7·5	M	5705	655·4	
Zinc.						
Dec. 2	389	4·2	F	3377	419·2°	In porcelain.
		7·9	M	3375	419·0	
		0·0	F	3376	419·1	
		7·0	M	3374	418·9	
Mar. 30	293	0·0	F	3376	419·1	In graphite.
		7·3	M	3375	419·0	
		0·0	F	3376	419·1	
		7·3	M	3373	418·8	
Lead.						
Dec. 15	500	0·0	F	2507	326·9°	In porcelain.
		7·0	M	2508	327·0	
		0·0	F	2505	326·7	
		6·0	M	2505	326·7	
Mar. 26	493	0·0	F	2505	326·7	In graphite.
		5·8	M	2508	327·0	
		4·2	M	2510	327·2	
		0·0	F	2510	327·2	
		4·2	M	2510	327·2	
Cadmium.						
Dec. 2	430	0·0	F	2461	321·9°	In porcelain.
		6·0	M	2460	321·8	
		0·0	F	2458	321·6	
		6·7	M	2459	321·7	
Mar. 27	430	0·0	F	2457	321·4	In graphite.
		6·5	M	2459	321·7	
		0·0	F	2459	321·7	
		4·3	M	2458	321·6	
		0·0	F	2461	321·9	
		4·3	M	2460	321·8	

electric force was impossible. The platinum was the first to be successfully purified, then, sometime after, the rhodium. Thermo-elements from different meltings now show variations of only 1 per cent, when formerly 10 per cent, and more was observed. The wires are also much more homogeneous now than formerly.

TABLE XXI.
"Time Curves" (MV).

Min.	Ag under NaCl	Ag under NaCl	Ag in Graphite	Ag in Graphite	Cu in Porcelain	Cu in Porcelain	Cu in Graphite	Cu in Graphite
1	9423	8513	9439	8766	10590	10003	10680	10081
2	9330	8599	9354	8861	10475	10106	10609	10179
3	9247	8684	9255	8956	10370	10183	10530	10268
4	9130	8775	9156	9016	10310	10201	10455	10353
5	9039	8857	9056	9018	10240	10207	10444	10409
6	9024	8937	9018	9018	10210	10210	10442	10426
7	9024	9017	9017	9019	10210	10210	10442	10431
8	9023	9023	9018	9019	10212	10211	10442	10433
9	9022	9024	9018	9019	10214	10213	10442	10436
10	9022	9024	9018	9019	10213	10213	10442	10437
11	9022	9025	9017	9022	10213	10213	10443	10438
12	9022	9026	9017	9033	10214	10213	10443	10439
13	9021	9026	9016	9043	10213	10214	10443	10440
14	9021	9026	9013	9055	10213	10214	10442	10440
15	9020	9026	9006	9064	10212	10215	10442	10441
16	9018	9026	8976	9074	10212	10215	10441	10444
17	9014	9027	8763	9121	10211	10216	10439	10456
18	9007	9028		9290	10210	10219	10437	10472
19	8990	9027			10210	10227	10433	10484
20	8800	9029			10208	10245	10427	10491
21	8600	9029			10203	10268	10410	10497
22		9029			10200	10300	10342	10503
23		9031			10193	10340	10195	10509
24		9034			10177	10460	10070	10516
25		9037			10097		9968	10564
26		9050			9900			10720
27		9069			9740			
28		9232						
29		9350						
30								

Since the platinum wire at temperatures above 1000° is considerably less stable than the platin-rhodium, much would be contributed in the direction of the durability of the elements if the platinum could be replaced by some related metal or alloy of greater stability.

Up to the present, however, no satisfactory substitute has been found. The alloys of platinum with iridium and ruthenium, in part also with palladium, differ little in their thermo-electric properties from platinum-rhodium.

Pure palladium does possess a higher thermo-electric force when combined with platinum-rhodium than platinum, but can-

TABLE XXII.
"Time Curves" (MV).

Min.	Sb in Graphite	Sb in Graphite	Zn in Porcelain	Zn in Porcelain	Pb in Porcelain	Pb in Porcelain	Cd in Graphite	Cd in Graphite
1	6216	5223	3551	3265	2718	2309	2852	2392
2	6080	5294	3500	3316	2671	2353	2809	2425
3	5960	5360	3449	3344	2621	2401	2767	2442
4	5840	5408	3400	3351	2574	2450	2726	2449
5	5720	5430	3376	3355	2529	2496	2685	2454
6	5600	5437	3376	3359	2506	2503	2646	2456
7	5495	5441	3376	3362	2506	2504	2607	2457
8	5390	5443	3376	3365	2505	2505	2570	2458
9	5280	5445	3376	3368	2505	2505	2533	2459
10	5190	5445	3376	3369	2505	2505	2496	2459
11	5450	5446	3376	3369	2505	2506	2462	2460
12	5454	5447	3375	3370	2504	2507	2460	2460
13	5454	5448	3375	3372	2503	2510	2459	2460
14	5453	5448	3375	3372	2502	2514	2459	2461
15	5454	5448	3375	3373	2501	2521	2459	2461
16	5452	5449	3375	3373	2497	2529	2459	2463
17	5452	5449	3374	3374	2488	2572	2459	2469
18	5451	5450	3373	3374	2473	2676	2459	2485
19	5451	5456	3374	3374	2444		2459	2499
20	5448	5468	3373	3374	2365		2458	2525
21	5438	5488	3373	3375			2458	
22	5310	5512	3372	3375			2457	
23	5060	5555	3370	3376			2456	
24		5655	3366	3389			2454	
25			3357	3404			2452	
26			3342	3433			2449	
27			3300				2422	
28							2367	
29								
30								

not be considered in this connection, for it is even less stable at high temperatures than platinum.

Thermo-elements made from different alloys of platinum-rhodium such as were formerly used by Holborn and Wien* for temperatures above 1000° are also unsuited for general use on account of their low sensitiveness.

* L. Holborn and W. Wien, loc. cit.

TABLE XXIII.
Melting Points of Alloys.

Alloy.	<i>t</i>		Mean.	Alloy.	<i>t</i>		Mean.
	MV	Degrees.			MV	Degrees.	
95 Ag, 5 Au	8989	958·7	958·5	95 Au, 5 Pt	10805	1115·0	1116·0
	8990	958·8			10799	1114·5	
	8980	957·9			10826	1116·8	
90 Ag, 10 Au					10827	1116·8	
	9067	965·5	90 Au, 10 Pt	11551	1177·2	1176·3	
	9070	965·8		11522	1174·9		
	9080	966·7		11533	1175·7		
	9060	964·9		11495	1173·6		
9070	965·8	11578		1179·7			
40 Ag, 60 Au	9753	1025·3	1025·1	85 Au, 15 Pt	11482	1171·5	1237·7
	9756	1025·5			11599	1181·2	
	9730	1023·3			12285	1237·4	
	9760	1025·9			12282	1237·1	
	9757	1025·6			12273	1236·4	
95 Au, 5 Pt	10821	1116·4			12317	1240·0	

Thermo-elements were first intended only for the measurement of temperatures from red heat upwards; afterwards it became evident that lower temperatures could be measured by this means as well. There is no advantage gained by going below 250°, however, as the errors due to the decrease in the sensitiveness at the lower temperatures begin to be more noticeable.

The accuracy of thermo-electric measurements in the earlier investigation of Holborn and Wien (*loc. cit.*) was stated to be 5°. The present results carry it further. It could fairly be said that, for temperatures up to 1150°, the present error would be about 1°; that is to say, for any distribution of temperature between the junctions, the temperature of the hot junction is defined by the thermo-electric force to within $\pm 1^\circ$.

This does not in the least mean however, that with constant conditions considerably more accurate relative measurements cannot be made. The determinations of the melting points of the metals contain many examples of this.

The chief reason for this progress lies in the facilities for electric heating whereby the whole investigation of high temperatures gains in accuracy and simplicity.

For the thermo-elements the change is especially important since the electric oven allows a definite temperature distribution to be exactly reproduced at any time, whence it becomes

possible even with inhomogeneous wires to carry out accurate temperature measurements by always working under the same conditions. It should be borne in mind however that this accuracy is only relative and that the same thermo-elements with a different temperature distribution between the junctions may show considerable variations.

To obtain the limits of absolute accuracy the fall in temperature along the wire must be varied as much as possible.

In the investigation here presented this was accomplished in two ways, either by measuring the temperature at a given point with two elements having a common hot junction and so arranged that the fall in temperature along the wire from the hot to the cold junctions could be varied; or secondly, by using as many different points of an element as possible successively, as junctions, and comparing them in a very short oven under exactly similar conditions of temperature distribution.

For example, by the first method the temperature near the end of a long electrically heated tube would be measured with two elements joined at their hot junctions, and the one passing out at the end near by, while the other extended through the middle of the tube which is hotter than near the ends, and out at the far end. It is clear that the distribution of temperature from hot to cold junction along the wires of the two elements would be very different and could be varied at will by simply moving the common junction to and fro.

Any lack of homogeneity in the wires would then become apparent at once in differences between the readings of the two elements.

We rather preferred the second method, the small melting-point oven (fig. 3) being well adapted to the purpose.

The wires of the elements are best simply bound together with a short platinum wire when it is desired to use several points provisionally as hot junctions. It has however no influence upon the thermo-electric force if the wire be cut in different places and afterward joined in the oxy-hydrogen flame.

Thick lumps along the wires are in the way to be sure, but with a little practice a junction can be made which can hardly be detected.

Thermo-elements as they are now prepared in a diameter of 0.8^{mm} are very homogeneous and over a length of several meters show no differences which could affect the temperature measurement 1° . Thin wires reduced from the above by drawing are often less uniform. Two wires, for example, which had been drawn down to 0.25^{mm} showed about double this variation, nor could this difference between the thin and thick wires be removed by glowing electrically.

Repeated heating to high temperatures may also under certain circumstances render the wires less homogeneous.

Attention has been called to this before, but now that the accuracy of thermo-electric measurements has been so materially increased it becomes necessary to go into the discussion of this matter in considerable detail.

The changes are such as Holborn and Wien observed in platinum and palladium due to the action of combustion gases or hydrogen in the presence of silicium, and which affect the resistance even more than the electromotive force. Even with electric heating where combustion gases should no longer be feared, the walls of an oven which has not been previously heated to a higher temperature than that to be measured, and kept there until burned through and through, develop gases which pass through platinum.

We have called attention to this in the discussion of a platinum bulb for the gas thermometer in our earlier communication. The thermo-elements are also affected by exposure to these gases but may usually be protected by the use of porcelain, which does not itself develop such gases and is very impervious to them even in its unglazed form. For temperatures below 1100° still further protection is afforded by glazing of course. Tubes of more refractory material intended for temperatures where porcelain can no longer be used and necessarily imperfectly burned we have found to be porous and when first heated to give off gases themselves at high temperatures which in the presence of silicium affect platinum strongly.

If the wires of a thermo-element which have been exposed in this way be afterward used for temperature measurement, there is often little or no change in the electromotive force from the normal values *so long as the temperature distribution along the wire remains unchanged*, but considerable variations always appear as soon as it is varied.

We made observations for example with such an element C which had been exposed in an imperfectly burned oven, the hot junction being combined with that of a second element A which had not been so exposed. At 550° the following differences (C-A) in microvolts were observed in an electric oven 40cm long in which the common junction of the two elements could be moved from the center toward either end as described elsewhere:

Hot Junction.		I.	II.
At the center (elements symmetrical)		7	7
6cm to the right	{ 2 wires heated	14 ^{cm}	- 73
6cm " left			
		26 ^{cm}	+ 36
			+ 126
			+ 3

In column I the elements were crossed while in II the two wires of each element passed out of the oven at the same end.

Originally the two elements had agreed for all positions to within 5 microvolts.

Further examples could be cited, but we will confine ourselves to two where efforts were made to restore the damaged elements.

The element C', cut from the same wire as T₂ was in use for a long time for high temperatures in a long oven and there exposed to these gases, after which the following differences were obtained by comparison with the normal elements G and H under *unchanged* conditions of temperature distribution.

<i>t</i>	H—C'	G—C'
200°	+ 5 MV	+ 5 MV
300	+ 5	+ 6
400	+ 4	+ 5
500	— 11	+ 6
600	— 13	+ 7
700	— 14	+ 7
800	— 13	+ 5
900	— 12	+ 7
1000	— 13	+ 7
1100	— 10	+ 8
1200	— 9	+ 8

When this same element C' was introduced into the short oven containing melted copper however, where the conditions of temperature distribution were very different, it gave 10,092 MV as the melting temperature while the two normal elements showed 10,212 microvolts.

C' was then taken out, glowed electrically at full white heat for several hours and again introduced into the copper crucible (with proper porcelain protection of course), when it gave 10,170 under the same conditions as before.

The same measurement was then a third time repeated after 5^{cm} had been cut from both wires at the hot junction—the electromotive force now proved to be 10,220 microvolts. In this condition further measurements were made of the melting points of lead, cadmium and zinc with results 2513, 2460 and 3371 microvolts respectively, all in good agreement with the normal values.

As has been said the glowing was done electrically, as much as 17 amperes being sent through the wires. Connected in series both wires glow with equal intensity at high temperatures, the smaller resistance of the platinum when cold being offset by its larger temperature coefficient.

An element B of the same group was used several times in an oven tube of a new material which was being tried for the first time, up to a temperature of 1600°.

The platinum wire became very brittle in the vicinity of the junction, broke in several places and was melted together in the oxy-hydrogen flame. Afterward when used for measurement at about 1000° in the long oven (unchanged temperature distribution) its reading was some 90 microvolts too low, but for the melting point of copper (different distribution) it gave only 9840 MV, i. e. some 400 MV too low. Sixteen centimeters were at once cut off at the hot junction, first from the platinum and afterward from the platin-rhodium wire, when the melting temperature of copper was given at 10,290 and 10,150 MV respectively. Further shortening did not serve to change these figures and the pieces cut out were again inserted. In this condition the element was glowed as in the previous case for some hours at white heat, when the melting point of copper was read at 10,216 MV—almost exactly the normal value.

The glowing also restores the bright surface to wires (platinum particularly) which have become dull after exposure to these gases.

It is probable that the standard element which represents the earlier temperature scale of Holborn and Wien and which has been used many times for comparisons up to 1600° has undergone similar changes.

Its indications at 500° are now 10° , and at 1000° , 18° too high, while the new determinations of the melting point of gold differ only 8° from the old. This melting point in particular was well determined at that time, the greatest variations from the mean in twenty-five determinations under varied conditions being $\pm 4^{\circ}$ while the corresponding variations for silver and copper amounted to $\pm 10^{\circ}$.

At the lower temperatures no fixed points were then determined so that no further comparison is possible.

We draw the conclusion from this that the temperature scale once established can be maintained with certainty only with the help of fixed temperatures such as the melting points given above. It is further advisable to divide a set of thermo-elements into two groups, one to be used only in porcelain tubes up to say 1200° and the other under other conditions or in higher temperatures.

For the latter, up to the present at least, the same accuracy is neither to be obtained nor expected until observations with the gas thermometer have been made and the technical resources much extended.

Especial attention ought again to be called to the fact that in the measurement of the fall in temperature in an extended space such as is necessary for the calculation of its mean temperature, the utmost care should be taken that the elements be

in perfect order. The best arrangement is always to measure with two elements having a common hot junction and entering the space in question from opposite sides, as has already been described in our former paper.

Furthermore, inasmuch as thermo-elements have come to be employed very generally for technical purposes during the past few years, we take this opportunity to say that it is impossible to give the limits to which the electromotive force can be affected by the breaking of the protecting tube or other accident through which the wires become exposed to combustion gases in the manner above described—the higher the temperature the greater the danger. In case of such an accident the element should at once be tested and restored as elsewhere indicated.

7. Conclusion.

By way of conclusion we will bring together the temperatures which we have obtained for the melting points of the metals based upon observations with the gas thermometer and some recent results of other observers employing other methods.

These include the measurements with platinum resistances as carried out by Callendar and by Heycock and Neville* which are also based upon the gas thermometer up to 445°, the boiling point of sulphur, and the higher temperatures extrapolated from a formula of the second degree.

The melting points of gold and silver have also been measured with thermo-elements by Berthelot,† using the wire method and determining the temperature optically from the decrease in density of an air column in an electrically heated, open, porcelain tube.

	Gas Thermometer.	Platinum Resistance.	Optical Method.
Cadmium	321.7°	320.7°	
Lead	326.9	327.7	
Zinc	419.0	419.0	
Antimony	630.6	629.5	
Aluminium	657.	654.5	
Silver, in air	955.	955.	962
Silver, pure	961.5	960.7	
Gold	1064.0	1061.7	1064
Copper, in air	1064.9		
Copper, pure	1084.1	1080.5	

Charlottenburg, May, 1900.

* Most of the figures are taken from Heycock and Neville's paper—loc. cit.; Callendar's values—Phil. Mag. V, xlviii, 519, 1899—differ in several cases 1°.

† D. Berthelot, C. R., cxxvi, p. 473, 1898.