ART. XLVII.—*The Present Status of High Temperature Research*; by CARL BARUS. With Plate X.

1. *Preliminary.*—Some time ago* I adduced reasons for supposing that the electromotive force, e , of a thermocouple, can be expressed by an equation of the form

$$e + e_0 = 10^{P+Q\theta} + 10^{P^1+Q^1\theta}, \dots\dots\dots (1)$$

where P , Q , P^1 , Q^1 , are constants, θ denotes temperature, and where e is zero, when $\theta = \theta_0$. I wish now to test this equation by the aid of data formerly found† in direct comparisons of the iridioplatinum thermocouple‡ with the porcelain air thermometer, and therewithal to exhibit the degree of accordance of known results in the region of high temperature.

Inasmuch as e must pass either through a maximum or a minimum, Q and Q^1 must have different signs; for θ_m , the temperature of this point, is

$$\frac{\log (-Q/Q^1) - (P^1 - P)}{Q^1 - Q}$$

when the sign connecting the two terms in (1) is positive.

2. *First extreme case.*—The simplest form which the above equation takes is the catenary, and it is interesting to note in what respect this curve falls short of reproducing the experimental results. Taking therefore the equation $y = k \cos \text{hyp } x/k$, it is necessary to shift the vertex to the position $(-a, -k^1)$ in order that the curve may pass through some fiducial point near the origin; or in other words, that the electromotive force may be zero when the hot junction has the stated temperature of the cold junction. The equation then becomes $e + k + k^1 = k \cos \text{hyp } (\theta + a)/k$, where e is the electromotive force for the temperature θ of the hot junction, k the constant of the catenary, and where $(-a, -k^1)$ are the coördinates of the vertex or the position of the thermoelectric minimum. In the absence of suitable tables it is then possible to find the constants involved by actually using a chain in connection with a carefully constructed and mounted chart of results. For if $e + k + k^1 = y$, then the length of the arc from the vertex to the end of the ordinate e is $s = \sqrt{y^2 - k^2}$; and therefore since a and k^1 are obtained by direct measurement, k can be computed from the measured length s of the arc or chain in question.

Constants so obtained are of course approximate and they must be improved by successive trials. Doing this I found for

* This Journal, xlvii, p. 366, 1894.

† See § 4.

‡ One metal containing about 20% of iridium, the other being soft platinum.

the 20% iridioplatinum-platinum couple, when electromotive forces are expressed in units of 10 microvolts,

$$\begin{aligned}a &= 2160, \\k^1 &= 985, \\k &= 2560,\end{aligned}$$

values which may be accepted for the time being, though they are by no means the best obtainable.

Above 500° this curve will then be found in remarkably good accord with the observations, § 4. Below 500° degrees, however, the agreement is less good, and the computed values lie as much as 10° above the observed values. Indeed to fully express the case one would have to use a string which grows successively heavier per unit of length towards the vertex; i. e. one would have to introduce another parameter conformably with the occurrence of two metals in the thermo-couple. It is difficult to reach this case practically.

Anticipating §§ 5 and 6, however, I may state that the catenary takes a mean course (above 500°) between the extreme curves there given.

3. *Second extreme case.*—Waiving the symmetrical method of finding suitable constants in equation (1), one may proceed by a process which is nearly the converse of this, and compute

$$e + e_0 = 10^{P + Q\theta} \dots \dots \dots (2)$$

first, and thereafter add the second term

$$10^{P^1 + Q^1\theta}$$

in accordance with the insufficiencies of equation (2). This may be done preferably with a table of Gaussian logarithms, by the aid of two pairs of observed data, when the thermal distance apart of each pair is the same. For in Gauss's tables pairs of values of A and B for two numbers a and b , are tabulated so that

$$\begin{aligned}B &= \log a - \log b, \\A &= \log (a - b) - \log b.\end{aligned}$$

If therefore for four temperatures $\theta, \theta', \theta_1, \theta'_1$, where $\theta - \theta' = \theta_1 - \theta'_1$, e_0 be eliminated from equation (2), the values B and A will take the form

$$\begin{aligned}B &= Q (\theta - \theta'), & B_1 &= Q (\theta_1 - \theta'_1), \\A &= \log (e - e') - (P + Q\theta), & A_1 &= \log (e_1 - e'_1) - (P + Q\theta'_1).\end{aligned}$$

But since $B = B_1$, $A = A_1$. Hence, as is otherwise evident,

$$Q = \log ((e - e') / (e_1 - e'_1)) / (\theta' - \theta'_1).$$

Q being given, B is given, and therefore A can be found from the tables so that P is known. Finally e_0 may be found from the equation (2).

Having found the constants of equation (2), the values of the second term of (1),

$$10^{P' + \theta' \theta},$$

which now merely expresses the shortcomings of (2), may be found by the same process. But in this case inspection will usually suffice.

From this point it would then be desirable to proceed in such a way as to give the two terms of equation (1) (second member) individual importance in their relation to the two metals of the couple; but as my present purposes are sufficiently met by the above constants I will not enter further into the work of finding characteristic parameters for each metal.

4. *Observations.*—To test the equations given I have made use of direct comparisons of the 20% iridioplatinum thermocouple and the porcelain air thermometer published in my Report on high temperature measurement,* and referring to an interval of temperature between about 350° and 1100°. Virtually the calibration is made determinate by observations of the boiling point of zinc† taken at 930°; for although the air thermometer is based wholly on independent volume measurements, and although the boiling points of both mercury and sulphur are well reproduced in the lower part of the curve, I do not derive much assurance from this without having quite eliminated the stem error in a way which I hope soon to describe.

A second series of measurements, made more recently, is contained in the following table. Here the electromotive force e_{20} in microvolts, while the cold junction is kept at 20° C., is given for a series of known melting and boiling points due to Regnault (Hg' and S') to Deville and Troost, (Zn'), to Troost (Se'), to Violle (Zn', Ag, Au, Cu, Pd, Pt) to LeChatelier (Al, Zn inferred), to Carnelley and Williams (Cd', Ni, Se' inferred). Accents denote boiling points. References will be found in the Bulletin cited.

MELTING POINTS.			BOILING POINTS.		
Substance.	Temperature.	e_{20} .	Substance.	Temperature.	e_{20} .
Zinc	415°	4260	Mercury	357°	3466
Aluminum	625°	7090	Sulphur	448°	4580
Silver	954°	11960	Selenium	{ 665°	7850
Gold	1045°	13520		{ 683°	
Copper	1054°	13585	Cadmium	{ 760°	9037
Nickel	1450°	19630		{ 775°	
Palladium	1500°	21430	Zinc	930°	11105
Platinum	1775°	24470	Bismuth	{ 1100°	18930?
				{ 1500°	
			Water	100°	680

* Barus: Bull. No. 54, U. S. Geolog. Survey, Washington, 1889, pp. 226–227.

† See § 6.

The platinum melting point merely refers to the fusion of the junction of the couple and is not very reliable. Metals whose boiling points show wide margins, like cadmium, are found by Carnelley's interpolation methods. Troost's Se' at 665° is probably too low.

5. *Constants*.—Applying the methods of § 3 to the air thermometer referred to in the preceding paragraph, the following mean results are available for the computation :

$$\begin{array}{ll} \theta = 400^\circ \text{ C.} & e = 3950 \text{ microvolts.} \\ \theta_1 = 600^\circ & e_1 = 6560 \\ \theta' = 800^\circ & e' = 9310 \\ \theta'_1 = 1000^\circ & e'_1 = 12200 \end{array}$$

and from low temperature work,

$$\begin{array}{ll} \theta = 0 & e_{20} = - 150 \\ 100 & + 680 \\ 200 & 1650 \\ 300 & 2760 \end{array}$$

The constants corresponding to these values as a whole are

$$(3) \dots e_{20} + 45680 = 10^{4.1515} + .0001106\theta + 10^{2.841} - .00331\theta.$$

Applying the same method to the data given in the above table, the following values are available in addition to the low temperature data just mentioned.

$$\begin{array}{ll} \theta = 357^\circ (\text{Hg}') & e = 3466 \text{ microvolts.} \\ \theta_1 = 457^\circ (\text{near S}') & e_1 = 4690 \\ \theta' = 954^\circ (\text{Ag}) & e' = 11960 \\ \theta'_1 = 1054^\circ (\text{Cu}) & e'_1 = 13585 \end{array}$$

The constants deduced are then

$$(4) \dots e_{20} + 23376 = 10^{3.3863} + .0002004\theta + 10^{2.7084} - .00301\theta.$$

Both equations (3) and (4) are given graphically in the accompanying chart, the former (the lower of the two curves), with all the observational data inserted. The abscissæ are temperatures in hundreds of degrees centigrade, and the ordinates electromotive forces, in thousands of microvolts. Horizontal lines drawn across the curves show the electromotive forces found by special experiments for the divers melting and boiling points of the metals marked on the line, the latter points being distinguished by accents. For points marked *R* see next paragraph.

6. *Conclusion*.—According as the one or the other of these curves is taken, the following sets of values are reached. Interpolations are made graphically with an accuracy of a few degrees.

MELTING POINTS.			BOILING POINTS.		
Substance.	Equation (4).	Equation (3).	Substance.	Equation (4).	Equation (3).
Zinc	420°	420°	Mercury ..	357°	357°
Aluminum. .	635°	638°	Sulphur ...	446°	446°
Silver	956°	986°	Selenium ..	687°	694°
Gold	1048°	1091°	Cadmium .	770°	782°
Copper	1054°	1096°	Zinc	905°	929°
Nickel	1382°	1476°	Bismuth ..	1346°	1435°
Palladium. .	1472°	1585°			
Platinum ..	1614°	1757°			

With regard to preferences in choosing between these two curves there is, at present, little opportunity for discretion. The lower temperatures are determined by the melting points of silver, gold and copper, systematically investigated by Violle; while the higher temperatures are in accordance with the boiling point of zinc as found by Deville and Troost, Violle, Mensching and Meyer, and in a measure by myself, some of the researches being remarkably elaborate. As is usual in such cases, the truth is to be sought somewhere between the extremes; and thus one finds in the recent work of Holborn and Wien* at the Reichsanstalt that silver, gold, and copper melt at 970°, 1082° and 1070° respectively; or at temperatures 16°, 25° and 28° higher than given by Violle. These points are indicated by the letter *R* in the chart and they lie quite within the limits indicated by the two curves. It will be seen too, that if I were to neglect outlying stragglers in my data at very high temperatures, where measurements are made under increasing difficulties, my results could be nearly reconciled with those of Holborn and Wien.

The purpose of this paper, however, is to show in a systematic way that to clear away the anomalies now existing in high temperature data either the boiling point of zinc must come down from 930° to 905°, or else the melting points of silver, gold and copper must move up 30° to 40°, or both must move towards each other by corresponding amounts. I hope myself to make some contributions toward a solution of these discrepancies.

I desire in conclusion to express my indebtedness to Prof. Alexander Graham Bell, by whose generosity I have in the past year, materially profited.

Washington, July, 1894.

* Holborn and Wien: Berl. Acad., June, 1892.