EXPERIMENTAL TEST OF THE WIEDEMANN-FRANZ RATIO THROUGH A CHANGE OF STATE.*

BY

EDWIN F. NORTHRUP, Ph.D.,
Palmer Physical Laboratory, Princeton, N. J.,
Member of the Institute,

AND

FRANK R. PRATT.

THE best conductors of electricity are, in general, the best conductors of heat. The ratio of the thermal to the electrical conductivity for all pure metals at the same temperature has nearly the same value when the temperature is in the neighborhood of 20° C. The value of this ratio is assumed to be proportional to the absolute temperature.

If we call k thermal conductivity, σ the electrical conductivity, α the universal gas-constant, e the electrical charge carried by a univalent electrolytic ion, and T the absolute temperature, then the law, which has long been known as the result of observations and generally called the Wiedemann-Franz law, states that

$$\frac{k}{\sigma} = \frac{4}{3}\left(\frac{a}{e}\right)^2 T = 0.715 \times 10^{-10} \text{ at } 18^\circ \text{ C.}$$ [1]

This law holds remarkably well for pure metals, less accurately for alloys, and not at all for poor conductors. How well it holds for the pure metals is exhibited in the table on page 68 of Campbell (see reference below). In this table the observed value given for silver is 0.76×10^{-10} and for bismuth 1.068×10^{-10} both at 18° C. Considering the large discrepancy in the resistance values for silver and bismuth, the closeness between these numerical values is very good, and the agreement between both values and the value obtained above for the ratio, obtained upon the basis of pure theory, is quite surprising.

The writers believe that any law which is based upon purely theoretical considerations can only be expected to hold over a comparatively limited range of variation of the magnitudes mutually related by the law. If the law can be shown experimentally to continue to hold when some one of the magnitudes,

---

* Communicated by Dr. Northrup.

[1] Consult Campbell, "Modern Electrical Theory," 1913 ed., pp. 66–68.

as the temperature, is varied through a wide range, then its usefulness and universality are both extended.

The object of the present investigation was to determine experimentally if the Wiedemann-Franz ratio continues to hold approximately true for two typical metals which change in resistance in opposite directions when these are carried from the solid into the molten condition. The two metals chosen for study were tin and bismuth, because both of these metals have low melting-points and both have been very carefully investigated by the first-named writer in respect to their resistivity characteristics.[2] Thus, the ratio of the electrical resistivity just after fusion (47.4 microhms) to its resistivity just before fusion (22.0 microhms) is 2.154 for the metal tin. Similar figures for the metal bismuth are 267 microhms just before fusion and 127.5 microhms just after fusion, the ratio of the latter to the former being 0.477. For the Wiedemann-Franz ratio to hold for these two metals, when carried from the solid into the molten state, their thermal resistivities or thermal conductivities must likewise change in an abrupt manner and in an opposite direction for each of the two metals.

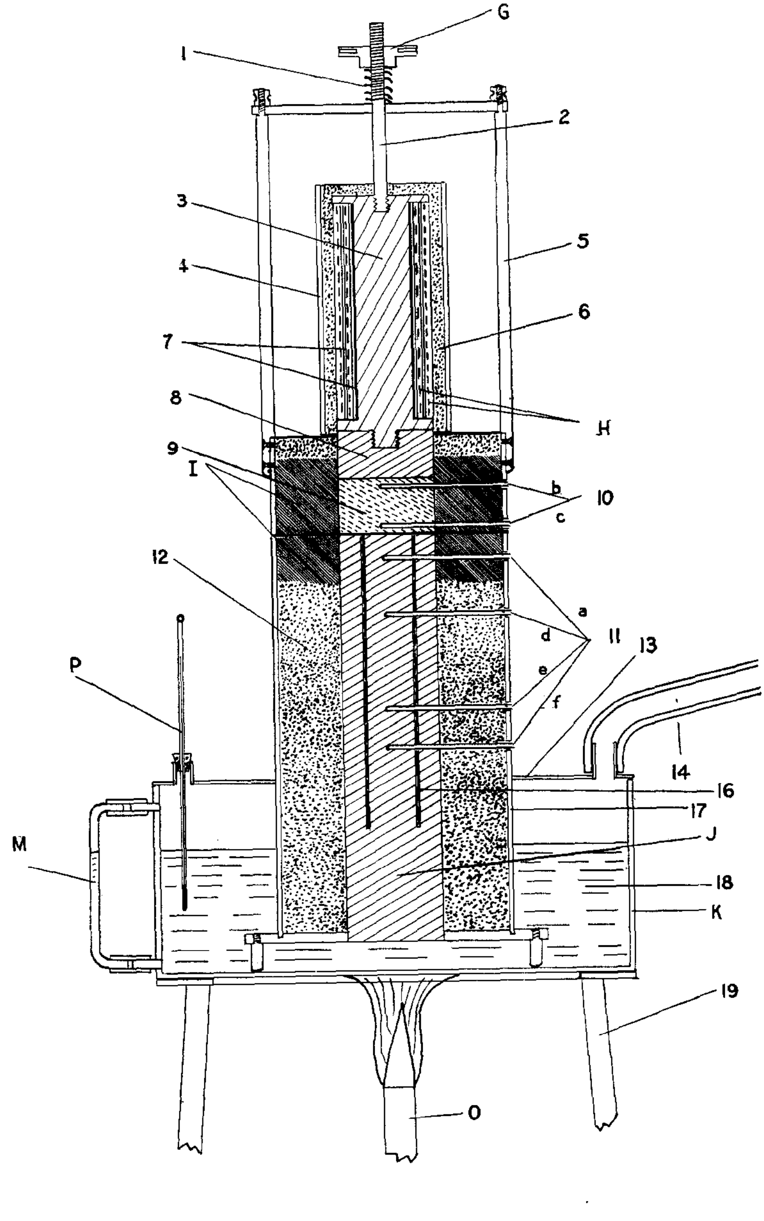
The investigation which we proceed to describe is not a first attempt to obtain information on this matter. After the present investigation was started an article was found in *The Physical Society of London Proceedings,* vol xxvii, part iv, June 15, 1915, p. 307, on "The Change in Thermal Conductivity of Metals on Fusion," by Alfred W. Porter, D.Sc., F.R.S., and F. Simeon, B.Sc., research scholar University College of London. Sodium and mercury were examined by these writers, using a method radically different from the one employed by us. Metals were placed in a glass tube, the portion in the upper half of the tube being maintained molten and the portion in the lower half of the tube being maintained solid. The ratio required was obtained by comparing the slopes of the tangents to the temperature gradient curves for the molten and the solid portions of each metal.

The results obtained seemed to indicate quite conclusively that the Wiedemann-Franz ratio holds over a change of state

---

[2] "Resistivity of a Few Metals Through a Wide Range of Temperature," by Edwin F. Northrup and V. A. Suydam, JOURNAL OF THE FRANKLIN INSTITUTE, February, 1913.

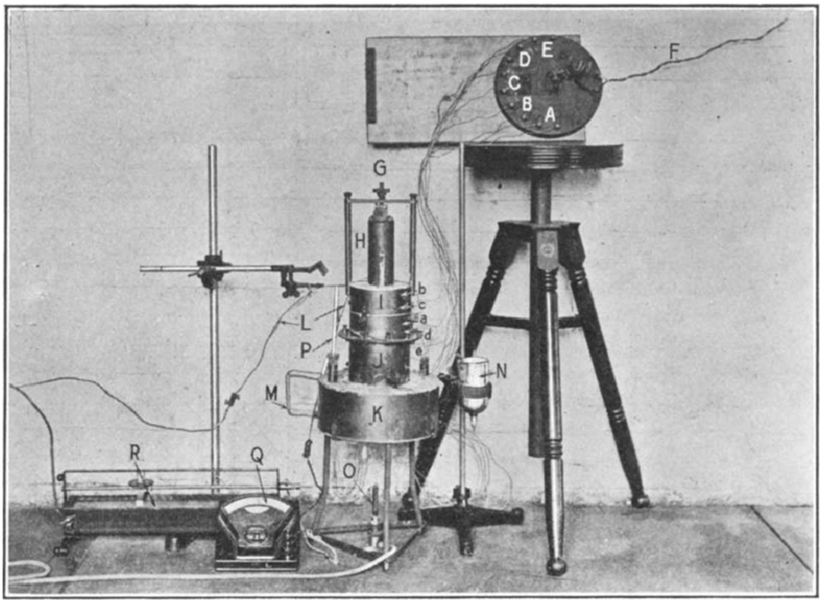
FIG. 1.



in the cases of these two metals. However, as sodium and mercury both *increase* in electrical resistance upon fusion, it seemed desirable to continue our investigation and extend the inquiry not only to other metals but to metals which change in resistance in opposite directions upon fusion. Furthermore, our method appears to us to be one which is not only more extensively applicable but also one which is capable of yielding more precise and certain results than the one above referred to.

While the method which we are about to describe is fully capable of giving the absolute values of the thermal resistivities before and after fusion, we only attempted, in the present investigation, to make an accurate determination of ratios for the reason that time was not available for anything more extensive.

FIG. 2.



DESCRIPTION OF METHOD AND APPARATUS EMPLOYED.

The method in general, which we employed, consists in comparing the temperature gradient between two points in a column of the metal under examination with the temperature gradient between two points of a cylinder of cold-rolled steel shafting. The arrangement provided gave assurance that the quantity of heat flowing per square centimetre between the two temperature-points in the metal being measured and between the two temperature-points in the steel cylinder was nearly the same, and that the heat flow was steady at the time of taking an observation. A full understanding of the method may be best obtained by a careful inspection of the cross-sectional view of the apparatus employed shown in Fig. 1 and the photographic view of the apparatus shown in Fig. 2.

Referring to Fig. 1, various parts which are lettered and numbered are as follows:

1. Spring which allows the metal to expand and contract.
2. Rod supporting heater.
3. Copper cylinder which conducts heat to the metal.
4. Brass casing surrounding heater.
5. Brass frame supporting heater.
6. Kieselguhr heat insulator.
7. Mica insulating sheets.
8. Upper steel cylinder.
9. Metal to be tested.
10. Thermo-elements in metal to be tested.
11. Thermo-elements in lower steel cylinder.
12. Kieselguhr heat insulator.
13. Cover to pan containing boiling water.
14. Rubber hose for conducting steam away from apparatus.
16. Fibrox heat insulator.
17. Brass casing surrounding lower steel cylinder and insulation.
18. Water at 100° C.
19. Supporting tripod.

G, H, I, J, K, M, O, P, a, b, c, d, e, see description of Fig. 2.

Referring to the photograph of the apparatus, Fig. 2, the various lettered parts are as described below.

A, B, C, D, E, a switch for shifting the lead wires *F* to any pair of wires coming from the several thermo-elements *a, b, c, d, e.* There are two binding posts near each letter. Lead wires *F* are connected to the two posts near *C* in the figure.

F, two lead wires running to the potentiometer which measures the potential of the several thermocouples.

G, screw with spring underneath, used to adjust the height of heater *H.* Spring allows heater to rise and fall as metal expands and contracts.

H, electric heater, insulated nichrome wire wound on copper cylinder and covered with brass case.

I, hollow alberene stone cylinder. Hollow part contains the metal to be tested, the upper steel cylinder and two thermocouples, *b* and *c.* Brass casing on the outside.

J contains the lower cylinder of steel. Between this cylinder and the outer brass casing is the kieselguhr heat insulator. This lower steel cylinder contains the thermocouples, *a* and *d*, for measuring the heat gradient in the steel; also an extra thermocouple, *e*, much lower down to test for loss of heat.

K, lower pan containing boiling water.
L, leads carrying direct electric current to heater *H*.
M, glass water gauge showing height of water in pan *K*.
N, Dewar bulb containing ice and thermocouples.
O, Bunsen burner for keeping water in *K* at the boiling-point.
P, thermometer for reading the temperature of water in *K*.
Q, Ammeter for measuring the current passing through heater *H*.
R, Rheostat for controlling current in heater *H*.

Dimensions of Heat-Resistance Apparatus.

Outside diameter of steel guard ring, *J*	5.08 cm.
Inside diameter of steel guard ring, *J*	2.54 cm.
Outside diameter of centre steel rod	1.80 cm.
Length of lower steel cylinder, *J*	21.59 cm.
Length of upper steel cylinder, 8	2.08 cm.
Length of copper heater, 3	12.70 cm.
Diameter of outside brass shell	12.70 cm.
Diameter of lower pan, *K*	25.40 cm.
Diameter of hole for thermocouple in guard ring	0.25 cm.
Diameter of hole for thermocouple in steel rod	0.19 cm.
Distance from top of lower cylinder to upper hole	1.00 cm.
Distance from upper hole to next hole	3.00 cm.
Distance between thermocouples in steel rod	3.00 cm.
Distance between thermocouples in metal used	2.00 cm.
Length of nichrome wire in heater, about	610.00 cm.
Width of nichrome wire in heater	.16 cm.
Thickness of wire in heater, No. 31 B. & S.	
Resistance of heating coil	12.95 ohms
Height of lower pan	10.16 cm.

DATA OBTAINED.

As the reliability and accuracy of the results obtained in this investigation are wholly determined by the consistency and reproducibility shown in the readings taken, we give below in tabulated form the various series of observations just as they were made.

Capital letters, *A, B, C, D,* refer to the lettered studs on the thermocouple switch (see Fig. 2). Small letters, *a, b, c, d,* refer to the corresponding thermocouples (see Fig. 1). Numerals refer to the number of the observation taken under a given set of conditions.

Results obtained for the metal tin follow below:

TIN (Solid).

May 16, 1915

Microvolts — Current, 4.5 ampères

No.	*A*	*B*	*C*	*D*
1	7618	9481	9205	638
2	7623	9497	9230	645
3	7650	9520	9247	645
4	7655	9533	9248	641

Temperatures computed from above data and thermal resistance compared to steel:

No.	*a*	*b*	*c*	*d*	Resistance
1	168.08	203.68	198.49	155.55	0.62
2	168.18	203.98	198.96	155.52	0.60
3	168.71	204.41	199.28	156.05	0.61
4	168.80	204.66	199.30	156.23	0.64

Average temperature of tin .... 202° C.
Average temperature of steel 162
Average resistance compared with steel...... 0.62

Microvolts — Current, 4.5 ampères

No.	*A*	*B*	*C*	*D*
1	7722	9616	9330	660
2	7729	9618	9330	658
3	7728	9618	9335	655
4	7730	9620	9333	653

Temperatures computed from above data and thermal resistance compared to steel.

No.	*a*	*b*	*c*	*d*	Resistance
1	170.11	206.21	200.84	157.17	0.62
2	170.24	206.25	200.84	157.35	0.63
3	170.22	206.25	200.94	157.39	0.64
4	170.26	206.28	200.90	157.47	0.65

Average temperature of tin .... 204° C.
Average temperature of steel 164
Average resistance compared with steel...... 0.63

Microvolts — Current, 4.7 ampères

No.	*A*	*B*	*C*	*D*
1	8137	10500	10034	783
2	8192	10538	10072	778
3	8230	10572	10091	783

Temperatures computed from above data and thermal resistance compared to steel.

No.	*a*	*b*	*c*	*d*	Resistance
1	178.13	222.59	213.99	162.92	.85
2	179.19	223.29	214.69	164.09	.86
3	179.94	223.91	215.04	164.80	.88

Average temperature of tin .... 219° C.
Average temperature of steel 172
Average resistance compared with steel...... 0.86

TIN (Solid)—*Continued.*

Microvolts			Current, 4.7 ampères	
No.	*A*	*B*	*C*	*D*
1	8443	10733	10197	810
2	8460	10748	10200	810
3	8470	10757	10205	805
4	8475	10751	10203	805
5	8480	10752	10204	805
6	8488	10759	10202	810

Temperatures computed from above data and thermal resistance compared to steel.

No.	*a*	*b*	*c*	*d*	Resistance
1	184.02	226.86	217.00	168.37	.94
2	184.35	227.14	217.06	168.71	.97
3	184.54	227.30	217.15	169.00	.98
4	184.63	227.19	217.12	169.10	.96
5	184.73	227.21	217.13	169.19	.97
6	184.88	227.34	217.10	169.23	.98

Average temperature of tin .... 222° C.
Average temperature of steel 177
Average resistance compared with steel...... 0.97

TIN (Molten).

Microvolts			Currents, 5 ampères	
No.	*A*	*B*	*C*	*D*
1	11628	14705	12680	1495
2	11937	14907	12903	1497
3	11991	15050	12962	1517
4	12026	15100	13022	1518
5	12103	15154	13092	1525
6	12134	15160	13140	1510
7	12152	15190	13146	1507
8	12185	15245	13196	1533
9	12210	15268	13205	1524
10	12226	15275	13218	1508
11	12228	15260	13222	1520
12	12227	15272	13212	1529
13	12238	15287	13223	1522

Temperatures computed from above data and thermal resistance compared to steel.

No.	*a*	*b*	*c*	*d*	Resistance
1	243.13	297.35	261.94	215.76	1.94
2	248.70	300.85	265.88	221.49	1.90
3	249.67	303.28	266.93	222.11	1.98
4	250.29	304.14	268.99	222.74	1.91
5	251.66	305.07	269.22	224.03	1.95
6	252.22	305.17	270.06	224.87	1.93
7	252.52	305.69	270.17	225.25	1.96
8	253.13	306.62	270.29	225.38	1.96

TIN (Molten)—*Continued.*

No.	*a*	*b*	*c*	*d*	Resistance
9	253.58	307.01	271.21	226.00	1.95
10	253.86	307.13	271.44	226.59	1.95
11	253.90	306.88	271.51	226.41	1.93
12	253.88	307.08	271.33	226.23	1.93
13	254.08	307.34	271.52	226.55	1.95

Average temperature of tin .... 285° C.
Average temperature of steel 235
Average resistance compared with steel...... 1.94

May 9, 1916
Current, 5.9 ampères

Microvolts

No.	*A*	*B*	*C*	*D*
1	12238	15305	13232	1527
2	12247	15310	13243	1512
3	12248	15303	13227	1530
4	12243	15330	13240	1520
5	12243	15284	13235	1532
Average	12243	15306	13239	1524

Computed temperatures in ° C. from above data.

a	*b*	*c*	*d*
254.17	307.66	271.81	226.61

Average temperature of tin .... 290° C.
Average temperature of steel 240
Average resistance compared with steel...... 1.95

May 16, 1916
Current, 6.5 ampères

Microvolts

No.	*A*	*B*	*C*	*D*
1	12937	16420	14212	1738
2	12968	16450	14248	1737
3	12990	16475	14293	1743

Computed temperatures and thermal resistances compared to steel.

Temperatures

No.	*a*	*b*	*c*	*d*	Resistance
1	266.52	326.60	288.82	235.36	1.82
2	267.10	327.11	289.46	235.94	1.81
3	267.51	327.53	289.90	236.24	1.81

Average temperature of tin .... 308° C.
Average temperature of steel 252
Average resistance compared with steel...... 1.81

Microvolts
Current, 6.5 ampères

No.	*A*	*B*	*C*	*D*
1	13032	16478	14309	1737
2	13040	16462	14305	1722
3	13044	16450	14314	1718
4	13050	16468	14323	1719

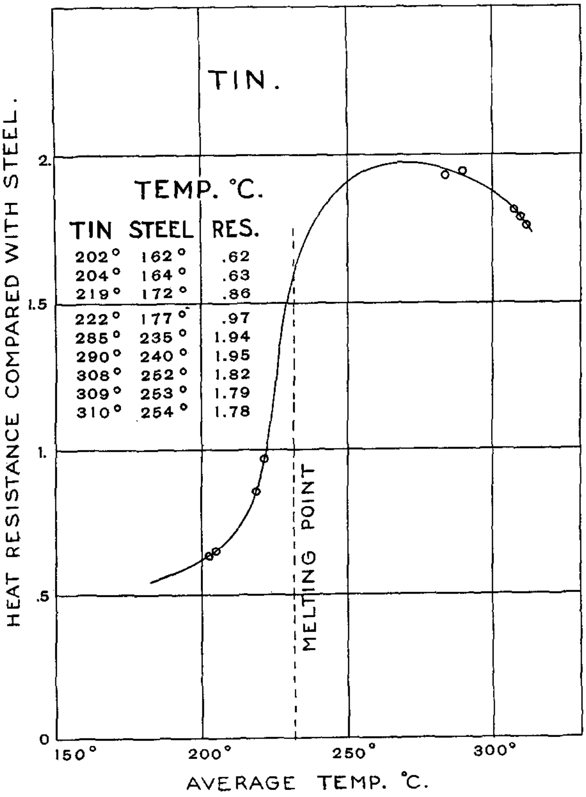
TIN (Molten)—*Continued.*

Temperatures				Thermal resistance	
No.	*a*	*b*	*c*	*d*	Resistance
1	268.16	327.58	290.51	237.11	1.79
2	268.30	327.31	290.44	237.53	1.80
3	268.37	327.11	290.59	237.67	1.79
4	268.47	327.41	290.75	237.76	1.79

Average temperature of tin .... 309° C.
Average temperature of steel 253
Average resistance compared with steel...... 1.79

Microvolts			Current, 6.5 ampères	
No.	*A*	*B*	*C*	*D*
1	13057	16482	14342	1727
2	13074	16480	14340	1720
3	13072	16470	14332	1720

FIG. 3.



Tin (Molten)—*Continued.*

	Temperatures			Thermal Resistance	
No.	*a*	*b*	*c*	*d*	Res.
1	268.60	327.65	291.08	237.74	1.78
2	268.90	327.61	291.04	238.18	1.78
3	268.87	327.44	290.90	238.14	1.78

Average temperature of tin............. 310° C.
Average temperature of steel............ 254
Average resistance compared with steel.. 1.78

The results of these observations are summarized and embodied in the curve for tin, Fig. 3.

A series of observations obtained for the metal bismuth are presented in the following tabulations:

Bismuth (Solid).

May 30, 1916

Microvolts by potentiometer			Current, 4 ampères	
No.	*A*	*B*	*C*	*D*
1	5923	9207	7325	327
2	5928	9220	7348	333
3	5940	9230	7350	332
4	5949	9230	7344	330
5	5950	9232	7350	332

Computed temperatures for each No. and resistance (thermal) compared with steel.

No.	*a*	*b*	*c*	*d*	Resistance
1	134.35	198.59	162.34	140.97	8.20
2	134.45	198.78	162.79	141.19	8.00
3	134.69	198.96	162.83	141.41	8.07
4	134.87	198.96	162.71	141.56	8.13
5	134.89	199.00	162.84	141.62	8.07

Average temperature of bismuth...... 180.69° C.
Average temperature of steel.......... 137.96
Average resistance compared with steel 8.09

Microvolts			Current, 4.5 ampères	
No.	*A*	*B*	*C*	*D*
1	6602	11537	8779	470
2	6618	11552	8813	470
3	6627	11567	8828	470
4	6634	11594	8827	475
5	6650	11614	8844	480

Computed temperatures in ° C. for each No. and thermal resistance compared with steel.

No.	*a*	*b*	*c*	*d*	Resistance
1	148.04	241.49	190.43	157.37	8.21
2	148.36	241.76	191.08	157.68	8.15
3	148.56	242.03	191.36	157.86	8.17
4	148.68	242.52	191.34	158.09	8.21
5	149.00	242.88	191.67	158.51	8.38

Average temperature of bismuth .... 216.62° C.
Average temperature of steel .... 153.23° C.
Average resistance compared with steel.. 8.22

BISMUTH (Molten)—*Continued.*

Microvolts No.	A	B	Current, 4.8 ampères C	D
1	7213	12873	9738	640
2	7227	12888	9743	644
3	7244	12883	9754	602
4	7257	12870	9767	603
5	7266	12875	9768	597

No.	a	b	c	d	Resistance
1	160.15	265.35	208.49	172.65	6.82
2	160.42	265.62	208.58	172.99	6.81
3	160.76	265.53	208.79	172.51	7.21
4	161.01	265.30	209.03	172.78	7.18
5	161.19	265.39	209.05	172.84	7.26

Average temperature of bismuth........ 237.13°C.
Average temperature of steel.......... 166.67
Average resistance compared with steel.. 7.06

May 23, 1916

Microvolts by potentiometer. Thermocouples	A	B	Current, 5.9 ampères C	D
	9685	17363	13326	1248
No. 1	9885	17395	13352	1260
	10075	17110	13258	1235
	11620	17097	13250	1230
Average	10316	17241	13297	1243
No. 2	10034	17067	13230	1215
	10040	17045	13210	1210
Average	10037	17056	13220	1212
No. 3	10392	17143	13307	1227
	10383	17116	13290	1220
	10389	17127	13285	1224
	10382	17132	13298	1225
	10390	17145	13292	1230
	10384	17156	13300	1228
	10400	17158	13300	1230
	10398	17155	13300	1230
Average	10390	17141	13297	1227

Computed temperatures in ° C., using average potential:

	a	b	c	d
No. 1	219.20	340.41	272.83	196.00
No. 2	214.04	337.30	271.47	191.30
No. 3	220.57	338.73	272.83	197.70

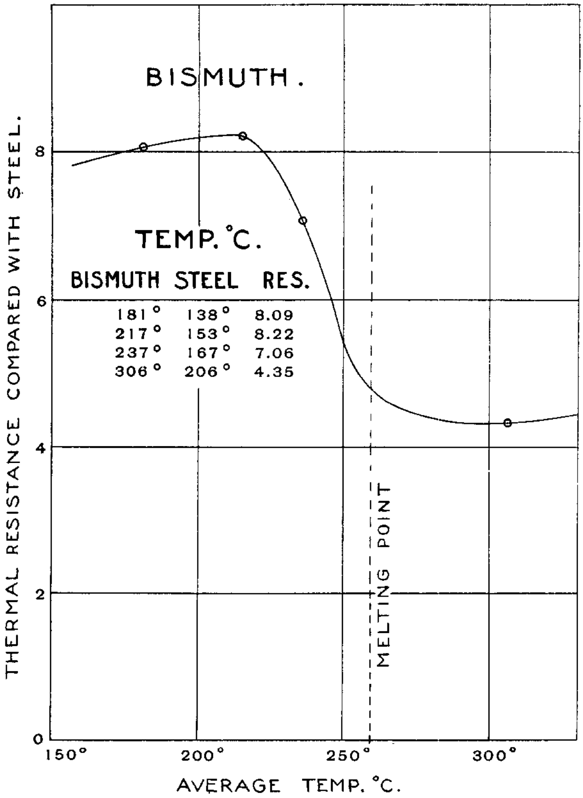
Average temperatures of the bismuth and steel between thermocouples. Thermal resistance compared to steel.

BISMUTH (Molten)—*Continued.*

	No. 1	No. 2	No. 3	Average
Bismuth temperature	306.62	304.36	305.78	305.59
Steel temperature	207.60	202.67	209.13	206.70
Resistance	4.37	4.35	4.33	4.35

These average values at the right give the only point found for molten bismuth. No point closer to the melting-point could have been found, because the melting-point of bismuth is 269° C., and the cooler thermocouple *c* registers only 272°, which shows that the cooler part of the bismuth was just above the melting-point. No point at a higher temperature could be found, because the nichrome wire used in the heater was at a bright red heat to obtain the above. Any higher temperature would have melted the wire.

FIG. 4.



TEMP. °C.

BISMUTH	STEEL	RES.
181°	138°	8.09
217°	153°	8.22
237°	167°	7.06
306°	206°	4.35

The curve for bismuth (Fig. 4) summarizes and embodies the observations given in the above tabulations.

A detailed description of the many precautions and arrangements employed to insure accuracy would be beyond the limits of our space for this article, but we can assure those interested that all the observations were taken with extreme care, and we feel certain that no errors of any considerable magnitude have crept into the observations. The conclusion, therefore, is inevitable that the thermal resistance characteristics for both tin and bismuth, when these metals pass from the solid into the molten state, are substantially the same as the electrical resistance characteristics, and therefore we can assert that the Wiedemann-Franz ratio holds, at least to a first approximation, when the metals tin and bismuth pass through a change of state. As the same was found to be true by other observers for the metals mercury and sodium, the presumption is strong that the same is true for other metals which have not yet been examined.

PALMER PHYSICAL LABORATORY,
PRINCETON, N. J.,
May, 1917.

The Air-cooled Automobile Engine. ANON. (*The Autocar*, vol. xxxix, No. 1145, p. 311, September 29, 1917.)—Whatever may be said about the heavier cars, air-cooling will always possess a special attraction for the designer of light cars. It diminishes weight, it reduces the cost of manufacture, and it simplifies upkeep. Air-cooling, as has been repeatedly pointed out, is making great strides, thanks to aviation; cylinder distortion is being eliminated; cooling is being improved by better material and sounder constructional methods, and weight is being reduced in an almost incredible ratio.

Of all types of air-cooled engine, the radial is possibly the most attractive. It can be mounted at the extreme nose of the chassis, where it will not be unsightly and where all of its cylinders will get an even cooling blast with a fan on the reverse side if necessary. Its short crank-shaft and other constructional details endow it with amazing power-to-weight ratios. Already we have a flat air-cooled twin engine at three pounds per horsepower. The radial engine is extremely shallow, and would allow the car builder an extra two feet of space along the chassis. There is no need for the large number of cylinders used in air propulsion to secure a satisfactory balance. A 20-horsepower, 800-pound vehicle is probably practicable. The type is perhaps suited only to comparatively low horsepowers, as the crank-shaft centre would come too high up if the cylinder were at all large.