On the Temperature Variation of the Electrical Resistances of Pure Metals, and Allied Matters

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obtain Chappuis' specimen of porcelain and repeat his experiments between 0° and 80° .

Mr. TUTTON, in reply to Dr. Shaw, said that the bands were perfectly distinct when using red hydrogen light. He did not use mercury light because of the necessity of constantly heating the tube.

XV. *On the Temperature Variation of the Electrical Resistances of Pure Metals, and Allied Matters.* By W. WILLIAMS, B.Sc., *Municipal Technical College, Swansea* *.

MANY of the physical properties of metals are periodic functions of their atomic weights. This is especially true of the valency and atomic volume. In a lesser degree it is also true of the melting-point and electric resistance. Now, the periodic variations of these four quantities for most of the metals can be very simply related to one another. For if σ is the specific resistance, at 0° C., m the maximum chemical valency, V the atomic volume, and T the absolute melting-point, to a first approximation $\sigma = \frac{KmV}{T}$, where K is a quantity which appears to have different values for different groups of metals. Dr. Fleming has already pointed out that the metals of large specific resistance are those having large atomic volumes and large valencies. For silver, copper, magnesium, zinc, cadmium, thallium, lead, mercury (in the solid state), and probably calcium, $K = 1.72 \times 10^2$ if σ is measured in microhms for a centimetre cube, and V is the quotient of the atomic weight by the density. For gold, indium, tin, and aluminium, however, K has only half this value. For sodium and potassium also its value appears to be half that given above; while for arsenic, antimony, and bismuth it is about double.

In the table that follows, σ is the value calculated for the specific resistance at 0° C. from $\frac{KmV}{T}$, while σ' is the value obtained by observation. The maximum chemical valency is as given by the Periodic Law, except in the case of gold and copper, where the values 3 and 2 are taken as being

* Read March 14, 1902.

more consistent with the chemical characteristics of the metals.

	<i>m.</i>	<i>V.</i>	<i>T.*</i>	σ .	σ' .	Diff.
Silver.....	1	10.2	1173	1.5	1.5	0 p. cent.
Copper	2	7.1	1333	1.82	1.7	7 "
Magnesium	2	13.9	1023	4.6	4.1	12 "
Zinc	2	9.1	676	4.65	5.8	20 "
Cadmium	2	12.9	593	7.5	7.5	0 "
Thallium	3	17.2	561	15.9	17.6	9.6 "
Lead	4	18.1	605	20.6	20.0	3 "

* The melting-points are as given in Nernst's '*Chemistry*.'

The resistance of a metal is approximately proportional to the absolute temperature. Hence $\sigma = \frac{K}{273} \cdot \frac{mV\theta}{T}$, where θ is the absolute temperature, so that the specific resistance in the solid state at the temperature of fusion is $\frac{KmV}{273}$. Now, the resistance of pure mercury in the solid state has been very carefully investigated by Dr. Fleming (Proc. Royal Society, vol. lx. No. 359, p. 79). According to his results, the process of fusion appears to set in at -50°C. , and is not properly completed until -36°C. is reached, the value of σ' at -50°C. just before fusion begins being 21. By calculation, taking m to be 2, and $V=14.1$, we get 17.8. Again, at -95°C. (-100°C. on the *pt* scale), the calculated value is 14.4, Dr. Fleming's value being 15.5.

The melting-point of calcium is not definitely given. The metal, however, is said to melt at "red heat," and will therefore have a melting-point between 500°C. and 600°C. , so that T is about 853. Hence, m being 2 and V 25.4, $\sigma=10.6$, Matthiessen's value being 7.5 †.

Taken as a whole, the accordance between σ and σ' is not unsatisfactory, being about the same as the accordance observed in the case of the law of Dulong and Petit as to atomic heat. Thus, taking 6.3 for the constant of that law, the value is 15 per cent. above it in the case of calcium, and 20 per cent. below it in the case of sulphur. Also, considering the wide variations that occur in the values of m , V , T , and σ , the accordance cannot be regarded as a matter of

† The melting-point of calcium is probably underestimated, 800°C. , or 1073 absolute being perhaps more nearly correct.

accident, but must be taken as an indication of a definite physical law.

Certain metals, however, fail to conform with the relation for σ although they are closely related, both physically and chemically, to those that do. Thus gold, indium, tin, and aluminium fail, although the first is allied to copper and silver, the second to thallium, and the third to lead. Thus:—

	<i>m.</i>	V.	T.	σ .	σ' .
Gold	3	10.1	1310	3.99	2.0
Indium	3	15.3	449	17.64	8.4
Tin.....	4	16.3	503	22.05	10.5
Aluminium	3	10.6	923	5.94	2.9

The metals of the alkali and arsenic groups also fail. Thus:—

	<i>m.</i>	V.	T.	σ .	σ' .
Potassium	1	45.4	335	23.4	8.4
Sodium	1	23.7	369	11.1	5.1
Arsenic	5	13.2	773	14.8	35.1
Antimony	5	17.9	710	21.7	43.1*
Bismuth	5	21.1	538	33.9	108.0

According to Pictet, if α is the coefficient of thermal expansibility, $V\frac{1}{2}\alpha T$ is a constant for metals. Calling this constant c , we get the following for its values in the case of the metals discussed above:—

	V.	α .	T.	c .
Silver.....	10.2	.0000194	1173	.0486
Copper	7.1	.0000170	1333	.0436
Gold	10.1	.0000147	1310	.0417
Magnesium	13.9	.0000270	1023	.0664
Zinc	9.1	.0000298	676	.0421
Cadmium	12.9	.0000316	593	.0440
Tin.....	16.3	.0000230	503	.0293
Thallium	17.2	.0000302	561	.0437
Aluminium	10.6	.0000222	923	.0450
Indium	15.3	.0000417	449	.0465
Lead	18.1	.0000290	605	.0461

* For antimony, $\sigma' = 45.8$ according to Lorenz, and 40.3 according to Berget.

Excluding magnesium and tin, the probable value of the constant is $\cdot 045$.

The alkali metals appear to constitute a separate group having a different value for c , thus,

	V.	α .	T.	c .
Sodium	23.7	$\cdot 000072$	369	$\cdot 0763$
Potassium	45.4	$\cdot 000083$	335	$\cdot 0992$

The mean value for c being $\cdot 088$, or about double its value for copper, &c. The arsenic metals, or at least bismuth and antimony, also appear to constitute a separate group, having $c = \cdot 021$ or half its value for copper, &c. Thus,

	V.	α .	T.	c .
Antimony	17.9	$\cdot 0000116$	710	$\cdot 0215$
Bismuth	21.1	$\cdot 0000137$	538	$\cdot 0204$

On account of the irregularities of the metal, the result in the case of arsenic cannot be taken as definite*.

Now, the groups that are thus characterized by different values for c are also characterized by corresponding values for K . Thus, where $c = \cdot 045$, K is 1.72×10^2 . Where c is approximately ($\frac{1}{2} \times \cdot 045$), K is approximately $2 \times 1.72 \times 10^2$, and where c is approximately ($2 \times \cdot 045$), K is approximately ($\frac{1}{2} \times 1.72 \times 10^2$). This suggests that the relation for σ can be rendered more comprehensive if written

$\sigma = \frac{A}{273} \cdot \frac{mV\theta}{cT}$, where A is a constant. Thus modified, the relation gives the following values for σ :—

	Observed.	Calculated.
Silver	1.5	1.5
Copper	1.7	2.0
Magnesium	4.1	3.4
Sodium	5.1	7.1
Zinc	5.8	5.36
Cadmium	7.5	7.95
Potassium	8.4	11.5
Thallium	17.6	17.7
Lead	20.0	21.7
Arsenic	35.1	34.3
Antimony	43.1	50.2
Bismuth	108.0	80.1

* The metal sublimes when heated and has a definite melting-point only under pressure.

Except in the case of sodium, the order in which the metals stand is the same as regards the observed and calculated values of σ ; and although the differences are great in the case of some of the metals, the values are throughout of the proper order of magnitude. The modified relation fails to hold, however, for gold, indium, tin, and aluminium, so that these metals, as before, are exceptional. Whether it holds for calcium and mercury cannot be ascertained until the value of c can be obtained for those metals. If they follow Pictet's law, so that c lies between $\cdot 04$ and $\cdot 05$, they will conform with the relation in its modified form to the same degree of approximation as they do in the case of the original one.

If m , in the relation for σ , is to be the maximum valency according to the Periodic Law, the relation will approximately hold for platinum and palladium. Thus :

	V.	m .	T.	c .	σ .	σ' .	Diff.
Palladium.....	9.2	8	1775	$\cdot 0411$	8.44	10.2	17 p. cent.
Platinum	9.1	8	2050	$\cdot 0379$	7.82	9.0	13 „

The metals of the platinum and palladium groups have a valency of 4 in their sesqui- and tetra-chlorides. Ruthenium and osmium, however, form potassium compounds analogous to chromates, manganates, and ferrates, in which the valency must be 6. In addition, they form tetroxides RuO_4 and OsO_4 , indicating a valency of 8 in accordance with the Periodic Law, a valency that also accords with the potassium compounds K_2PtCl_6 , and K_2PdCl_6 . It therefore appears that a maximum valency of 8 is not incompatible with the chemical characteristics of the metals.

The metals of the Iron Group do not conform with the relation for σ , a matter to be fully dealt with on a future occasion.

According to the law of Dulong and Petit, s is approximately $\frac{6.3}{w}$, where s is the specific heat and w the atomic weight. Also, $V = \frac{w}{d}$, where d is the density. Hence $V = \frac{6.3}{sd}$. Again, if α is the coefficient of thermal expansibility, supposed to be constant, and if $\lambda = V^{\frac{1}{2}}\alpha\theta$ and $c = V^{\frac{1}{2}}\alpha T$,

we get

$$\sigma = \frac{A}{273} \cdot \frac{nV\theta}{cT} = \frac{Bm\lambda}{c^2sd} = \frac{Bm\lambda}{c^2n\rho} = \frac{Bm\lambda\theta}{c^2nh}.$$

where B is a constant, n the average number of atoms per unit volume, ρ the atomic specific heat, and h or $(\rho\theta)$ the average thermal energy of an atom at temperature θ . Now, V is proportional to the average space assigned to an atom at the absolute zero. Hence λ or $V^{\frac{1}{3}}\alpha\theta$ will be proportional to the average relative displacement of the centres of two neighbouring atoms between absolute zero and the temperature θ , which we may call the average atomic displacement at temperature θ .

If α is constant, so that λ for any metal is proportional to θ , and if ρ is also constant, σ must be proportional to θ , so that $\frac{\sigma}{\sigma_0} = \frac{\theta}{273} = 1 + \epsilon t$, where σ and σ_0 are the values at $t^\circ \text{C}$. and 0°C . respectively, and $\epsilon = .003665$. According to this, the temperature resistance-coefficients of all pure metals must be the same, namely $\frac{1}{273}$, and the resistance must vanish at the absolute zero. The investigations of Fleming and Dewar, however, have shown that while the resistance tends to vanish at the absolute zero, the temperature-coefficient is usually higher than $\frac{1}{273}$, its average value being about .004. Now we know that α and ρ are not constant, but slowly increase with rise of temperature. Hence the view suggests itself that the deviation of the temperature-coefficients from the simple value $\frac{1}{273}$ may be due to the temperature-variations of α and ρ .

Since the relation $\sigma = \sigma_0(1 + \epsilon t)$ is true to a first approximation for all pure metals, we can put

$$\frac{\sigma}{\sigma_0} = \frac{\theta}{273} \phi(\theta) = (1 + \epsilon t)(1 + \gamma t + \eta t^2 + \dots),$$

which suggests that temperature enters into the relation for σ in two ways essentially different, namely :

(1) Directly, as an essential factor, and represented above by $\frac{\theta}{273}$; and

(2) Indirectly, and represented above by $\phi(\theta)$, as the temperature-variation of one or more of the other essential factors.

We have then to inquire whether these essential factors can be α and ρ , and whether $\phi(\theta)$ can be built up from their temperature-variations.

According to Prof. J. J. Thomson ('Nature,' May 10th, 1900), the specific resistance of a metal on the electronic theory is given by

$$\sigma = \frac{2\mu n^2}{qe^2l^2},$$

where q is the average number of electrons dissociated in unit volume per unit time, μ is the mass of an electron, e its electrical charge, u its average velocity of translation, and l the length of its mean free path. Hence, since μ , e , and l are constant as regards temperature, the temperature-variation of σ must depend upon the temperature-variations of u and q . On this matter, Prof. J. J. Thomson makes the following observation:—"If we suppose that u , the mean velocity of translation of the corpuscles, varies with the temperature in the same way as the velocity of translation of the molecules of a gas, μu^2 would be proportional to the absolute temperature, and the specific resistance would, considered as a function of the absolute temperature θ , vary as $\frac{\theta}{q}$; if q , the amount of ionization, increases as the temperature increases, the resistance will vary more slowly than the absolute temperature; if q diminishes as the temperature increases, the resistance will vary more rapidly than the temperature." Hence, according to Prof. J. J. Thomson, in the temperature relation $\frac{\sigma}{\sigma_0} = \frac{\theta}{273} \phi(\theta)$, the factor $\frac{\theta}{273}$ enters in the determination of the average velocity of translation of the moving electrons, while $\phi(\theta)$ enters as the temperature-variation of the electronization-coefficient q .

But $\sigma \propto \frac{m\lambda\theta}{e^2nh}$. Hence $\frac{\sigma}{\sigma_0} = \frac{\theta}{273} \cdot \frac{\lambda h_0}{\lambda_0 h}$, so that $\phi(\theta) = \frac{\lambda h_0}{\lambda_0 h}$, and therefore, since according to Prof. J. J. Thomson $\phi(\theta) = \frac{q_0}{q}$, we must have $q \propto \frac{h}{\lambda}$. This result, taken in conjunction with $\sigma \propto \frac{m\lambda\theta}{e^2nh}$, suggests that $q \propto \frac{nh}{m\lambda}$. That is, that for the metals that conform with the relation for σ , the electronization per unit volume increases with the average thermal energy of the

atom and the number of atoms per unit volume, and decreases with the average relative displacements of the atoms and their maximum chemical valency.

The investigations of Fleming and Dewar have shown that $\phi(\theta)$ is not a linear function of θ . If, however, we confine ourselves to a limited range, say from 0° C. to 100° C., we may consider it to be approximately linear, and so considerably simplify the matter. In that case we get $\sigma = \sigma_0(1 + \epsilon t)(1 + \gamma t) = \sigma_0(1 + at + bt^2)$, where $a = (\epsilon + \gamma)$, and $b = \epsilon\gamma$. As might be expected, this temperature-factor fails to hold both at very high and at very low temperatures, but may be taken to hold with a considerable degree of accuracy between 0° and 100° , the only range within which the temperature-variations of α and ρ can be said to be fairly accurately known.

Let α and s be linear functions of the temperature, which is sufficiently accurate for our present purpose, and let $\alpha = \alpha_0(1 + \beta t)$ and $s = s_0(1 + \delta t)$, where α and s are the values at t° C., α_0 and s_0 at 0° C., and β and δ the temperature-variations. Then

$$\lambda = V^{\frac{1}{2}} \alpha_0 \left[\left(1 - \frac{273\beta}{2} \right) + \frac{1}{2}\beta t \right] (273 + t),$$

$$h = \rho_0 \left[\left(1 - \frac{273\delta}{2} \right) + \frac{1}{2}\delta t \right] (273 + t);$$

and therefore,

$$\begin{aligned} \phi(\theta) &= \frac{h_0 \lambda}{h \lambda_0} = \frac{1 + \frac{1}{2}\beta' t}{1 + \frac{1}{2}\delta' t} \\ &= 1 + \frac{1}{2}(\beta' - \delta')t - \frac{1}{4}\delta'(\beta' - \delta')t^2 + \&c., \end{aligned}$$

$$\text{where } \beta' = \frac{\beta}{1 - \frac{273\beta}{2}}, \text{ and } \delta' = \frac{\delta}{1 - \frac{273\delta}{2}}.$$

Thus $\gamma = \frac{1}{2}(\beta' - \delta')$, $\eta = -\frac{1}{4}\delta'(\beta' - \delta')$, &c., and in the approximate temperature-factor $\frac{\sigma}{\sigma_0} = 1 + at + bt^2$, which holds between 0° and 100° , $a = \epsilon + \frac{1}{2}(\beta' - \delta')$ and $b = \frac{1}{2}\epsilon(\beta' - \delta')$.

This result, however, cannot at present be subjected to any reliable and decisive test. For the accurate investigation of the temperature-variation of α over wide ranges of temperature has not been made for pure metals, while, though various observers have investigated the temperature-variations of s , there is a considerable want of accordance between the

results obtained. The accurate determination of both thermal expansibility and specific heat are matters of very great difficulty, trifling differences in the values of either quantity producing very serious differences in the values of the temperature-variations deduced from them. Thus, according to Naccari, the specific heat of copper at 100° C. is $\cdot 09422$, and $\cdot 09634$ at 200° C. Assuming the latter value to be only $\frac{1}{2}$ per cent. too high, the value at 200° C. would be $\cdot 09586$. In the former case the temperature-variation is $\cdot 0000212$, in the latter $\cdot 000016$; so that a difference of only $\frac{1}{2}$ per cent. per 100° in the value of s produces a difference of 30 per cent. in the value of the temperature-variation. Now, apart altogether from experimental difficulties, which are certainly very considerable, differences greater than this can arise in the values of s at the same temperature of different specimens of the same metal from differences in mechanical qualities alone. Unless, therefore, the value of σ , α , and s are accurately determined *for the same specimen and over a considerable range of temperature*, we cannot expect a close and definite relation to exist between their temperature-variations. Hence, as the experimental information has to be collected from different observers for different specimens, probably in different mechanical conditions, we must be satisfied if the relation $\gamma = \frac{1}{2}(\beta' - \delta')$ yields values of the proper order of magnitude, differing from those obtained experimentally by no more than those values for the same metals according to different observers differ from one another.

In spite, however, of the imperfections of the experimental data available to test the matter, enough appears to be known to show that $\phi(\theta)$, for many of the metals, is *mainly* determined by β and δ , that the probable form of the function is $\frac{1 + \frac{1}{2}\beta't}{1 + \frac{1}{2}\delta't}$, and that $\gamma = \frac{1}{2}(\beta' - \delta')$, as the following results will show.

In selecting experimental data respecting β and δ , the results of Fizeau by the interferometer method have been taken for α between 0° and 100° ; these being taken because they depend upon measurements susceptible of more accurate determination than those of other methods.

As regards specific heats, the results of Naccari (1888) have principally been followed.

Naccari's values for s are as follows—the values at 0°C . being calculated from the values given at 100°C ., 200°C ., and 300°C . :—

	0° .	100° .	200° .	300° .	δ .
Copper	·0921	·09422	·09634	·09846	·0002302
Silver.....	·05449	·05663	·05877	·06091	·0003927
Cadmium	·0546	·0570	·0594	·0617	·0004385
Lead	·02972	·03103	·03244	·03380	·0004575
Zinc	·0906	·0951	·0996	·1040	·0004967
Aluminium	·2116	·2211	·2306	·2409	·0004489

Naccari's results for copper are not in accord with those of Bedè and Trowbridge. Thus, according to Bedè, the mean value of s between 15° and 100° is ·09331 ; ·09483 between 16° and 172° ; and ·09680 between 17° and 247° . Hence, the average value of δ is ·000516. Again, according to Trowbridge ('Science Abstracts,' Dec. 1898), the mean value of s between -181° and 13° is ·0868, and ·094 between 23° and 100° . Hence the average value of δ is ·000546.

Naccari gives no results in the case of tin. Lorenz gives the following : s at $0^\circ = \cdot 05368$; at $50^\circ = \cdot 05534$; at $75^\circ = \cdot 05643$. Hence the average value of δ is ·00064.

Naccari's results for aluminium are confirmed by those of Richards. Thus, according to Richards, the mean value of s between 0° and 100° is ·2270 ; ·2370 between 0° and 300° ; and ·2520 between 0° and 600° . Hence the average value of δ is ·000463.

Fizeau's values for α are as follows— α_{40} denoting the value at 40°C ., and α_{50} that at 50°C . :—

	α_{40} .	α_{50} .	β .
	·0000	·0000	
Copper	1678	1698	·001251
Silver.....	1921	1936	·000806
Cadmium	2069	3102	·001124
Lead	2924	2948	·000848
Zinc	2918	2915	
Aluminium	2313	2336	·001036
Tin.....	2234	2269	·001671

According to Fizeau, zinc behaves in an anomalous manner as regards its thermal expansibility, the value of α being

greater at 40° than at 50° C. This, however, is not in accord with the observations of Matthiessen, according to whose results for zinc, $l = l_0[1 + \cdot 00002741t + \cdot 0000000234t^2]$, where l and l_0 are the lengths of the same bar at t° and 0° respectively. Hence $\beta = \cdot 00172$. For most of the metals, however, for which both Matthiessen and Fizeau give values, Fizeau's values for β are about half those deduced from Matthiessen's observations. Thus :

	Matthiessen.	Fizeau.	Ratio.
Copper	$\cdot 0025$	$\cdot 00125$	2·0
Silver.....	$\cdot 00149$	$\cdot 000806$	1·85
Cadmium	$\cdot 00354$	$\cdot 001124$	3·15
Tin.....	$\cdot 00259$	$\cdot 001671$	1·55
Lead	$\cdot 000543$	$\cdot 000348$	$\cdot 64$
Palladium.....	$\cdot 00184$	$\cdot 00088$	2·09
Gold	$\cdot 00165$	$\cdot 000567$	2·91
Platinum	$\cdot 000823$	$\cdot 000923$	$\cdot 89$

Mean = 1·89

Fizeau's values for copper and aluminium are confirmed by those of Dulong and Petit, and Mr. Tutton. Thus, according to Dulong and Petit, the mean value of α for copper between 0° and 100° C. is $\cdot 00001718$, and $\cdot 00001883$ between 0° and 300° . Hence $\beta = \cdot 00101$. Again, according to Mr. Tutton (Proc. Royal Society, lxiii. p. 208), the value of α for pure aluminium is 10^{-8} [$2204 + 2\cdot 12 t$], so that $\beta = \cdot 000962$. Hence, perhaps, until more decisive determinations are made in the case of pure zinc, by Mr. Tutton's improved interferometer method for instance, and as the molecular constitution of the metal is simple like that of copper and silver, we may take for β half the value deduced from Matthiessen's observations as in the case of most of the metals tabulated above.

From the values of β and δ given above, we get the following results :

	β' . ·00	δ' . ·000	$\frac{1}{2}(\beta' - \delta')$. ·000	a . ·00	b . ·00000
Copper	1509	590	460	4125	167
Silver.....	0906	393	245	3910	090
Tin.....	2163	700	731	4396	270
Cadmium	1327	468	431	4096	158
Lead	0959	488	236	3901	087
Zinc	0966	533	217	3882	080
Aluminium	1206	478	364	4029	133

For magnesium β appears to be abnormally high. Thus, according to Fizeau, the value of α at 40° is $\cdot 00002694$, and $\cdot 00002762$ at 50° , so that $\beta = \cdot 00281$. We must therefore conclude, either that magnesium does not conform with the relation for γ , or that Fizeau's value for β is not characteristic of the metal itself, but of a particular specimen only. For the remaining metals, with the exception of those afterwards to be mentioned, data cannot be obtained respecting δ and β .

According to the temperature relation $\frac{\sigma}{\sigma_0} = 1 + [\epsilon + \frac{1}{2}(\beta' - \delta')]t + \frac{1}{2}\epsilon(\beta' - \delta')t^2$, since in the case of the metals tabulated above δ' is less than β' , the locus of α or $\frac{\sigma}{\sigma_0}$ must be concave upwards, and the value of $\frac{d\alpha}{dt}$ must increase as the temperature rises. This is in accord with the results of observation as the following table will show, where $\frac{d\alpha}{dt}$ and its mean value between 0° and 100° are tabulated. For comparison, the

		$\frac{d\alpha}{dt}$	Mean.
Tin	T	$\cdot 00440 + \cdot 0000054 t$	$\cdot 00467$
	F	$\cdot 00425 + \cdot 0000040 t$	$\cdot 00445$
	B	$\cdot 00403 + \cdot 0000117 t$	$\cdot 00461$
Copper	T	$\cdot 00413 + \cdot 0000033 t$	$\cdot 00429$
	F	$\cdot 00412 + \cdot 0000033 t$	$\cdot 00428$
	E	$\cdot 00412 + \cdot 0000060 t$	$\cdot 00442$
Cadmium	T	$\cdot 00410 + \cdot 0000032 t$	$\cdot 00425$
	F	$\cdot 00405 + \cdot 0000028 t$	$\cdot 00419$
	V	$\cdot 00402 + \cdot 0000018 t$	$\cdot 00412$
Lead	T	$\cdot 00390 + \cdot 0000017 t$	$\cdot 00399$
	F	$\cdot 00399 + \cdot 0000028 t$	$\cdot 00411$
	B	$\cdot 00395 + \cdot 0000028 t$	$\cdot 00409$
Zinc	T	$\cdot 00388 + \cdot 0000016 t$	$\cdot 00396$
	F	$\cdot 00395 + \cdot 0000020 t$	$\cdot 00405$
Silver	T	$\cdot 00391 + \cdot 0000018 t$	$\cdot 00400$
	F	$\cdot 00391 + \cdot 0000018 t$	$\cdot 00400$
	B	$\cdot 00397 + \cdot 0000014 t$	$\cdot 00404$
Aluminium	T	$\cdot 00403 + \cdot 0000027 t$	$\cdot 00416$
	F	$\cdot 00408 + \cdot 0000030 t$	$\cdot 00423$
	B	$\cdot 00388 + \cdot 0000026 t$	$\cdot 00401$

values deduced from Fleming and Dewar's observations, denoted by F, those given by Benoit denoted by B, and those given by Vicentini and Omadei denoted by V, have also been inserted. The values calculated from Fleming and Dewar's observations have been obtained by applying to them the approximate relation $\frac{\sigma}{\sigma_0} = (1 + \epsilon t)(1 + \gamma t)$ between 0° and 100° .

T denotes the values obtained from thermal data, δ and β , while E, in the case of copper, denotes the values given by Elmore.

In the case of the metals tabulated above, it will be found that not only is γ approximately $\frac{1}{2}(\beta' - \delta)$ and α approximately $\epsilon + \frac{1}{2}(\beta' - \delta)$, but that γ is also approximately $\frac{1}{3}\beta$ or $\frac{1}{3}\beta'$, and α approximately $\epsilon + \frac{1}{3}\beta'$, or $\epsilon + \frac{1}{3}\beta$, as the table opposite (p. 209) will show.

In the table the column headed γ contains the values calculated for that constant from Fleming and Dewar's observations; the third column headed Diff. indicates the percentage difference of $\frac{3\gamma}{\beta}$ from its mean value 1.046, while the second is the percentage difference of $\frac{3\gamma}{\beta'}$ from its mean value .896.

From the table it will be seen that the order in which the metals stand as regards the values of γ is, with the exception of aluminium, the same as that as regards the values of $\frac{1}{3}\beta$ and $\frac{1}{3}\beta'$; that the ratios $\frac{3\gamma}{\beta}$ and $\frac{3\gamma}{\beta'}$ are approximately constant; and that the values deduced for α from γ , namely $\epsilon + \gamma$, are practically the same as those deduced from β and β' , namely $\epsilon + \frac{1}{3}\beta$, and $\epsilon + \frac{1}{3}\beta'$.

Hence, since for these metals γ is approximately $\frac{1}{2}(\beta' - \delta)$, and also approximately $\frac{1}{3}\beta$ or $\frac{1}{3}\beta'$, it follows that δ' must be approximately $\frac{1}{3}\beta'$, and δ approximately $\frac{1}{3}\beta$. That is, that the temperature-variation of the specific heat must depend upon that of the thermal expansibility, or, more correctly perhaps, that *the temperature-variation of the specific heat and that of the thermal expansibility must depend upon the temperature-variation of the same physical property of the metal.* This result, again, on account of uncertainties respecting the

<i>Metal.</i>	γ . ·000	$\frac{1}{3}\beta$. ·000	$\frac{1}{3}\beta'$. ·000	$\frac{3\gamma}{\beta}$.	Diff. Per cent.	$\frac{3\gamma}{\beta'}$.	Diff. Per cent.	$e+\gamma$. ·00	$e+\frac{1}{3}\beta$. ·00	$e+\frac{1}{3}\beta'$. ·00
Tin	538	557	721	·97	7·3	·75	16·3	4203	4222	4386
Copper	450	417	503	1·08	3·2	·9	·5	4115	4082	4168
Cadmium ..	384	375	443	1·02	2·5	·87	2·8	4049	4040	4108
Lead	326	283	320	1·15	10·0	1·02	13·8	3991	3948	3985
Zinc	289	283	320	1·02	2·5	·9	·5	3954	3948	3985
Silver	245	269	302	·89	14·5	·81	9·6	3910	3934	3967
Aluminium ..	412	345	403	1·19	13·8	1·02	13·8	4077	4010	4070

experimental data bearing upon it, cannot be accepted without considerable doubt and hesitation. I have only ventured to put it forward because it appears to have enough probability in its favour, and to be sufficiently interesting and suggestive to deserve a fuller consideration, and to have a special investigation into the experimental facts bearing upon it made by competent observers.

If ϵ is the average increase of s per unit rise of temperature, and if $\delta = \frac{1}{3}\beta$, as suggested above, then, approximately, $\epsilon = \frac{1}{3}(s_0\beta) = \frac{2 \cdot 1\beta}{w}$, where w is the atomic weight. The following are some of the results obtained for ϵ from this relation:—

	β . ·00	w .	ϵ (calc.) ·0000	ϵ (obs.) ·0000	
Aluminium	1036	27	800	950	Naccari.
Copper	1251	63·3	410	1000	Richards.
				460	Bède.
				490	Trowbridge.
Tin	1671	119	295	341	Lorenz.
Cadmium	1124	112	210	240	Naccari.
Palladium	0880	106	175	210	Violle.
Silver	0806	108	160	210	Naccari.
Iridium	1198	192·5	131	151	Violle.
Platinum	0923	195	100	112	Violle.

The relation does not hold for the metals of the Iron group. Also, for many of the metals experimental results cannot be obtained to test the matter, while for metals like lead, magnesium, and zinc, the results available are not conclusive.

According to the relation $\sigma \propto \frac{\theta}{q}$, since θ is constant during fusion, the change of resistance that accompanies fusion must depend upon the change in the value of q *. Hence, if σ_s is the value of σ in the solid state just before fusion has begun, and σ_l its value in the liquid state just when fusion is completed, and if q_s and q_l be the corresponding values of q ,

* Which implies that the average velocity of translation u of the moving electrons is not affected by the act of fusion, but remains unaltered like the temperature.

$\frac{\sigma_e}{\sigma_s} = \frac{q_e}{q_s}$. For copper, silver, magnesium, zinc, cadmium, calcium, thallium, lead, and mercury, $q \propto \frac{nh}{m\lambda}$. If we assume that h in this relation is to stand for the *internal*, and not for the *total* energy of the atom, it will be the same in the solid and liquid states at the temperature of fusion. Hence, if λ_e, λ_s be the values of λ corresponding to σ_e, σ_s , $\frac{\sigma_e}{\sigma_s} = \frac{\lambda_e}{\lambda_s}$ *.

The ratio $\frac{\lambda_e}{\lambda_s}$ can be calculated from the increase of volume that accompanies the fusion. Thus, if d is the average distance between the centres of two neighbouring atoms at the absolute zero, $d + \lambda_e$ and $d + \lambda_s$ will be its values in the liquid and solid states respectively at the temperature of fusion. Also, if ρ_e and ρ_s be the corresponding densities, and if $\left(\frac{\rho_e}{\rho_s}\right)^{\frac{1}{3}}$ or $\frac{d + \lambda_e}{d + \lambda_s}$ be denoted by x , we get

$$\lambda_e = (d + \lambda_s)x - d.$$

Now the only cases where reliable information respecting ρ_s, ρ_e, σ_s , and σ_e can at present be obtained, are those of lead, cadmium, tin, and zinc, and in the case of these metals, since the melting-point is low, the average value of α between 0° and 100° is probably not far from its value between absolute zero and the melting-point T , so that very approximately $\lambda_e = d\alpha T$. Hence

$$\frac{\lambda_e}{\lambda_s} = \frac{(1 + \alpha T)x - 1}{\alpha T},$$

the ratio being thus independent of the actual value of d . In order, however, to compare the value of λ_e with the constant of Pictet's law, namely $V^{\frac{1}{3}}\alpha T$, we shall put $d = V^{\frac{1}{3}}$.

The increase of volume that accompanies fusion has been specially investigated for several metals by Vicentini and Omadei, their results being taken in the table that follows except in the case of zinc.

* This assumption implies that the electronization per unit volume, so far as it depends upon temperature, is determined:—

(1) By the kinetic energy of an atom considered as a system of electrons in orbital motion,—this being unaffected by fusion, since the temperature of the atom is not altered.

(2) By the average distance apart of the atomic centres,—which is directly affected by fusion.

	ρ_s	ρ_l	λ_s	λ_l	$\frac{\lambda_l}{\lambda_s}$	$\frac{\sigma_l}{\sigma_s}$	Diff.
Lead	11.005	10.645	.076	.046	1.65	1.9	+12 p. cent.
Cadmium ...	8.366	7.989	.085	.044	1.93	2.3	+16 „
Tin	7.183	6.988	.054	.029	1.86	2.1	+12 „
Zinc		6.480	.087	.042	2.07	2.0	- 4 „

Vassura's values for $\frac{\sigma_l}{\sigma_s}$ have been taken in the case of cadmium and tin, and De la Rive's in the case of lead and zinc.

Omadei gives no values for ρ_s and ρ_l in the case of zinc. According to Roberts-Austen, however, the density of zinc just when fusion is completed is 6.480, from which value $\frac{\lambda_l}{\lambda_s}$ can be calculated.

Taking the results in the table as experimentally valid, it is seen that to a rough approximation $\frac{\sigma_l}{\sigma_s} = \frac{\lambda_l}{\lambda_s}$. The determination of $\frac{\lambda_l}{\lambda_s}$, however, is a matter of difficulty, the results obtained above from $\frac{\rho_l}{\rho_s}$ being undoubtedly imperfect and unreliable. Thus, Omadei's value for the percentage increase of volume of thallium in the act of fusion is 4.32, whereas, according to Toepler, it ought to be 3.22. The former of these values gives $\lambda_s = .081$ and $\frac{\lambda_l}{\lambda_s} = 1.84$, whereas the latter gives $\lambda_s = .072$, and $\frac{\lambda_l}{\lambda_s} = 1.64$. Moreover, it is not probable that the increase of resistance that accompanies fusion is determined by the increase in λ alone, though possibly λ may be the most important factor concerned in the matter. At any rate it is worthy of note that, whereas in the case of metals which expand on melting the specific resistance is greater in the liquid than in the solid state at the temperature of fusion, in the case of bismuth and antimony, which contract on melting, it is less.

Platinum and palladium differ from the metals already discussed, as regards their temperature-coefficients, in the fact that for them the value of α is less than $\frac{1}{273}$, and the locus

of σ concave towards the axis of temperature, whereas, in the case of the other and apparently simpler metals, σ is greater than $\frac{1}{273}$ and the locus of σ convex towards that axis. This anomaly indicates that for platinum and palladium, the temperature-variation of the electronization-coefficient q cannot be accounted for by the temperature-variations of λ and h , as in the case of the simpler metals. Some other factor has to be superposed upon these in order to convert into an increase the decrease that would arise in q from them alone. The thermoelectric curves of platinum and palladium are also exceptional as compared to those of the simpler metals. For whereas the curves, as given by Fleming and Dewar, have a positive curvature for the simpler metals, for platinum and palladium the curvature is decidedly negative. These exceptional characteristics are probably closely related, since on the electronic theory both the electrical resistance and the thermoelectric properties of a metal depend upon the electronization-coefficient q .

As might be expected from their ferro-magnetic properties, iron, nickel, and cobalt, as regards their temperature-coefficients, constitute an exceptional and highly characteristic group, the discussion of which must be reserved for a future occasion.

The results discussed in the paper may be summarized thus :—

(1) A relation $\sigma = \frac{KmV\theta}{cT}$ which roughly holds for

Silver,	Platinum,
Copper,	Palladium,
Magnesium,	Thallium,
Sodium,	Lead,
Zinc,	Mercury,
Cadmium,	Arsenic,
Calcium,	Antimony,
Potassium,	Bismuth ;

but fails for gold, indium, tin, and aluminium. It also fails, as we should expect, for iron, nickel, and cobalt—while in the case of the remaining metals data cannot be obtained to test the matter.

(2) A temperature factor

$$\frac{\sigma}{\sigma_0} = (1 + \epsilon t) \left[1 + \frac{1}{2} (\beta' - \delta') t + \dots \right]$$

obtained from the relation $q \propto \frac{nh}{m\lambda}$, approximately true for tin, copper, cadmium, lead, zinc, silver, and aluminium, but not for platinum and palladium, and of course the metals of the Iron group.

(3) A specific heat relation $\epsilon = \frac{2.1\beta}{w}$, approximately true for

Aluminium,
Copper,
Tin,
Cadmium,
Palladium,
Silver,
Iridium,
Platinum ;

but not, of course, for the metals of the Iron group. The results are uncertain in the case of lead, magnesium, and zinc; while in the case of the remaining metals, the relation cannot at present be tested.

(4) A relation $\frac{\sigma_e}{\sigma_s} = \frac{\lambda_e}{\lambda_s}$ at the temperature of fusion, roughly true for lead, cadmium, tin, and zinc, the only metals for which, at present, it can be tested.

The results, however, in many respects are incomplete and unsatisfactory, as of course is to be expected from the imperfect character of their experimental basis. Perhaps, however, the paper—in spite of its imperfections, may prove useful as a statement of what may be done to correlate expansion-coefficients, specific heats, and electrical resistances, and that it may do good by calling attention to the matter, and stimulating experienced observers to take up its systematic investigation.