Chemistry. — *The Exact Measurement of the Specific Heats of Iridium and Ruthenium between 0° and 1604° C. and a Comparison of the Calorimetrical Results obtained with the Elements of the Eighth Group of the Periodical System.* By F. M. JAEGER and E. ROSENBOHM.

§ 1. In the present paper the results are published of our measurements of the specific heats of *iridium* and *ruthenium* in their dependence on the temperature. They form a completion of the data previously obtained[1]) in the case of the four other metals of the *platinum*-group, so that now a complete comparison becomes possible between the behaviour of all metals of the 8th group of the periodical system of the elements.

Iridium. This metal has a melting point[2]) of 2360° C.; its density in literature is given by values[3]) ranging from 22.4 to 22.8. From X-ray-measurements[4]) it follows, that *iridium* crystallizes in the cubic system, its lattice being the face-centred one, with $a_0 = 3.823$ Å, and with 4 atoms within its elementary cell. From this its true density is calculated to be $d = 22.81$.

About its specific heat (mean values) a series of data were given by VIOLLE[5]) in 1879; however, these values appear to be too high and the slope of his c_p-t-curve is too steep.

§ 2. *Apparatus; thermocouples.* In our measurements we used the new and much improved form of our calorimeter. By these improvements the apparatus, in the determination of its capacity, now yields results which do not differ more than 1 : 15000 of its value. A higher sensivity is unnecessary, as the temperature-measurements in the furnace are less accurate than this.

If t_B is the temperature (in degrees) of the waterbath surrounding the calorimeter, and if E is the electromotive force of the total series of 60 thermocouples, — then: $(t-t_B) = 4.1325 . 10^{-4} . E - 1.375 . 10^{-10} . E^2$. This equation is valid, when t_B is at least 19° C. and does not surpass 25° C.

[1]) F. M. JAEGER and E. ROSENBOHM, Proceed. R. Acad. Amsterdam, **33**, (1930), 462: **34**, (1931), 85; Recueil des Trav. d. Chim. Pays-Bas. **47**, (1928), 513.

[2]) F. MYLIUS and R. DIETZ, Ber. d. d. chem. Ges., **31**, (1899), 3188; H. VON WARTENBERG, Ber. d. phys. Ges., **12**, (1910), 121.

[3]) Conf.: LANDOLT-BÖRNSTEIN's *Tabellen*, 5e Aufl., (1923), 287; Erg. Bnd., (1927), 169; *Int. Crit. Tables*, 1 (1926), 104.

[4]) R. W. G. WYCKHOFF, Zeits. f. Kryst., **59**, (1923), 55; T. BARTH and G. LUNDE, Zeits. f. phys. Chem., **121**, (1926), 83, 99, 100.

[5]) J. VIOLLE, Compt. rend. Paris, **89**, (1879), 702.

§ 3. The material used was the purest *iridium* from HERAEUS; it had the shape of small globulets of pea-size, evidently obtained by melting the metal and suddenly quenching the drops in water. Also here, — just as in a lesser degree in the case of *osmium*, — it appeared necessary to heat the metal within the evacuated crucible beforehand to a high temperature, so as to obtain really constant and reproducible results: perhaps the complete and perfect crystallisation is, hindered by the preliminary quenching, and, therefore, gives rise to abnormal heat-effects caused by the recrystallisation of the metal at temperatures between 400° and 1000° C. As an example of this effect, the following data may be mentioned: at 630° C. the first experiment gave: $\overline{c_p} = 0.03239$; on repeating this measurement, we found: $\overline{c_p} = 0.03283$; but after heating the crucible for a sufficiently long time at 1000° C., the measurement yielded the value: $\overline{c_p} = 0.03312$, and *this value remained absolutely constant in all later experiments*. If the recrystallisation is, however, once completed, perfectly reproducible results are obtained in consecutive experiments at the same temperatures [1]).

The data obtained in these measurements are collected in Table I., the mean specific heat $\overline{c_p}$ between 22° and 0° C. was calculated at: 0.03073. (See Table I, following page.)

From these measurements the values of c_p, as indicated in the last column, are calculated for a series of temperatures between 0° and 1700° C.

§ 4. Although the data in literature are scarce, it appeared possible in this case to determine, at least approximately, the values of c_v of *iridium* by using the well-known thermodynamical formula: $c_p - c_v = \dfrac{0.02345 \cdot T \cdot (3a)^2}{\varkappa \cdot d}$.

The coefficient of linear thermal expansion a has been determined by several observers within limited ranges of temperature. As the dependence of a on the temperature is only slightly different from a linear one, we have made use for the calculation of $3a$ at different temperatures, of the formula given by HOLBORN and VALENTINER [2]):

$$l_t = l_0 \left(1 + 0.0000066967 \cdot t + 0.000000001158 \cdot t^2\right).$$

As to the compressibility $\varkappa$ (in KG/cM²), — this has been determined by BRIDGMAN [3]), but only at 30° and 75° C.: at 30° C. he finds:

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[1]) We recently found another very striking example of this behaviour in the case of *gold*, which at the same time seems to make it probable, that these divergencies in the values of $\overline{c_p}$ are caused *by the original distortion of the lattice by the preliminary treatment of the metal*. Purest, 100 °/₀ *gold*, obtained from the Royal Mint, was used in the form of plated sheets. and cut in small pieces before brought into the vacuum-crucible. At 419° we found in the 1st experiment: $\overline{c_p} = 0.0304$; in the 2nd: $\overline{c_p} = 0.0309$. At 801° C. in the 1st experiment: $\overline{c_p} = 0.0321$, in the 2nd: $\overline{c_p} = 0.0324$. At 1000° C., however, the values remained constant in repeating the experiment: $\overline{c_p} = 0.334$.

[2]) L. HOLBORN and S. VALENTINER, Ann. der Physik, **22**, (1907), 1.

[3]) P. W. BRIDGMAN, Proceed. Amer. Acad. of Sciences, Washington, **59**, (1923), 111.

TABLE I.

The Specific Heats under Constant Pressure c_p of *Iridium* at Different Temperatures between 0° and 1600° C.

Temperature t in °C. :	Final temperature t' of calorimeter :	Increase to temperature Δt of calorimeter in Microvolts :	Weight of the Substance used :	Weight of Platinum :	Total amount of heat Q delivered between t and t' in calories by 1 Gr.:	Total amount of heat Q_0 delivered between $t°$ and 0° in calories by 1 Gr. :	Total amount of heat Q'_0 in calories as calculated from the formula :	True specific heat c_p at t^0 :	
								t :	c_p :
327°.21	20°.33	949.19	29.5717	27.8250	9.824	10.449	10.449	0°	0.0307
420.10	20.55	1248.46	29.5717	27.8250	12.929	13.560	13.560	100	0.0315
630.53	20.88	1945.74	29.5717	27.8250	20.189	20.831	20.843	200	0.0322
801.61	21.14	2535.53	29.5717	27.8210	26.358	27.007	27.007	300	0.0329
996.29	21.34	3229.59	29.5717	27.8270	33.622	34.278	34.283	400	0.0337
1201.0	21.90	3988.77	29.5717	27.8250	41.586	42.259	42.237	500	0.0344
1392.4	21.94	4725.27	29.5717	27.8270	49.292	49.966	49.955	600	0.0352
1535.9	22.51	5289.98	29.5717	27.8280	55.226	55.918	55.918	700	0.0359
								800	0.0366
								900	0.0374
								1000	0.0381
								1100	0.0389
								1200	0.0396
								1300	0.0403
								1400	0.0411
								1500	0.0418
								1600	0.0426
								1700 (extr.)	0.0433

The total amount of heat Q'_0 delivered by 1 Gr. of the substance between 0° and t^0 C. can be calculated from the formula :

$$Q'_0 = 0.030725 \cdot t + 0.0000037002 \cdot t^2.$$

The true specific heat c_p at t^0 C. can, therefore, be found from the formula :

$$c_p = \frac{d Q'_0}{d t} = 0.030725 + 0.0000074004 \cdot t.$$

The atomic heat C_p is expressed by : $C_p = 5.933 + 0.001429 \cdot t.$

$\varkappa . 10^6 = 0.268 - 1.3 . 10^{-6} p$; at 75° C.: $\varkappa . 10^6 = 0.281 - 2.2 . 10^{-6} p$. In our calculations we have supposed a linear dependence of $\varkappa$ on the temperature; although this is uncertain, there seems to be more probability, that the values of $(c_p - c_v)$ thus calculated will appear rather greater than the real ones, so that most probably the $c_p - t$-, and the $c_v - t$-curves will be closer to each other, than they are at the present moment. In every case, the differences of $(c_p - c_v)$ are only small, although they increase with increasing temperatures.

In the following Table II the values of c_p, c_v and of the corresponding atomic heats C_p and C_v thus obtained, are collected :

TABLE II.				
True Specific and Atomic Heats of Iridium at Constant Pressure and at Constant Volume (approximately), between 0° and 1700° C.				
Temperature in °C.:	c_p :	c_v :	C_p :	C_v :
0°	0.0307	0.0303	5.928	5.851
100	0.0315	0.0310	6.083	5.986
200	0.0322	0.0316	6.218	6.102
300	0.0329	0.0322	6.353	6.218
400	0.0337	0.0329	6.508	6.353
500	0.0344	0.0335	6.643	6.469
600	0.0352	0.0342	6.797	6.604
700	0.0359	0.0348	6.932	6.720
800	0.0366	0.0355	7.067	6.855
900	0.0374	0.0362	7.222	6.990
1000	0.0381	0.0368	7.357	7.106
1100	0.0389	0.0375	7.512	7.241
1200	0.0396	0.0381	7.647	7.357
1300	0.0403	0.0388	7.782	7.492
1400	0.0411	0.0395	7.936	7.628
1500	0.0418	0.0401	8.072	7.743
1600	0.0426	0.0406	8.226	7.840
1700	0.0433	0.0413	8.361	7.975

These values are graphically represented in Fig. 1 and 3B.

It is, therefore, evident, that the value of $3 R$ calories is, in the case of *iridium*, already surpassed at as low a temperature as 40° C. for C_p and at

$105°$ C. for C_v, — which is in accordance with the results formerly obtained in the case of the other metals of this group. The values of C_p and even these of C_v, gradually increase to 8 calories and more, at temperatures still far below the meltingpoint of the metal.

§ 5. *Ruthenium.* In exactly the same way, the specific heats c_p of *ruthenium* were determined. Also this metal was obtained from HERAEUS in a perfectly pure state and, in the form of small spheres, placed into an evacuated platinum crucible. Soon already it became evident, that several allotropic changes take place in the metal at higher temperatures, and the extreme sensitiveness of our experimental device allowed us to fix some of the corresponding temperatures sufficiently well. Indeed, also the values given in literature for the density of the metal vary considerably: they oscillate between 8.06 (CLAUS) and 12.063 [1]), — which fact beforehand gives some indication in the direction of the occurrence of allotropism.

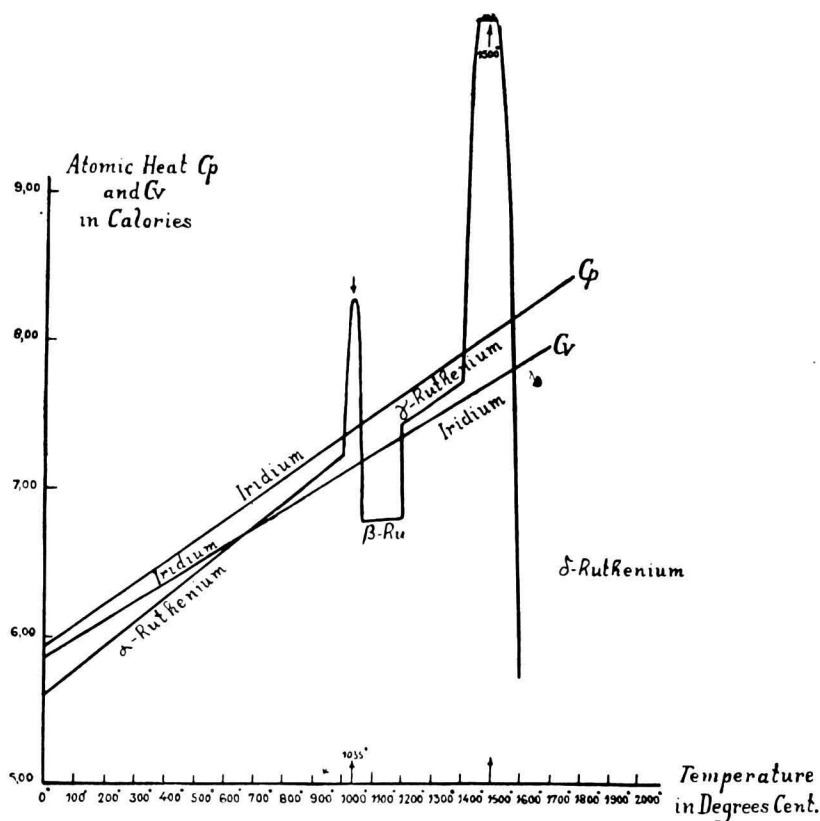Perhaps another indication of an allotropic change taking place in this

Fig. 1. The Atomic Heats C_p and C_v of Iridium and Ruthenium in their Dependance on the Temperature.

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[1]) A. JOLY, Compt. rend. Paris, **116**, (1893), 430.

metal might be deduced from the abnormal increase of its magnetism with the temperature between 1000° and 1100° C., as observed by HONDA [1]). But other data about the said phenomenon are not found in the literature.

The values of c_p obtained are tabulated in Table III:

					Total amount of heat Q delivered between t and t' in calories by 1 Gr.	Total amount of heat Q_0 delivered between $t°$ and $0°$ in calories by 1 Gr.	Total amount of heat Q'_0 in calories as calculated from the formula :	True specific heat c_p at t^0:	

T A B L E III.
The Specific Heats under Constant Pressure c_p of *Ruthenium* at Different Temperatures between 0° and 1604° C.

Temperature t in °C.:	Final temperature t' of calorimeter:	Increase of temperature $\varDelta t$ of calorimeter in Microvolts:	Weight of the Substance used:	Weight of Platinum:	Total amount of heat Q delivered between t and t' in calories by 1 Gr.	Total amount of heat Q_0 delivered between $t°$ and $0°$ in calories by 1 Gr.	Total amount of heat Q'_0 in calories as calculated from the formula :	True specific heat c_p at t^0: t:	c_p
385.92	20.484	1169.13	17.4157	27.4917	21.330	22.462	22.462	0°	0.0551
389.67	20.418	1181.38	17.4157	27.4855	21 5525	22.681	22.681	100	0.0567
629.94	20.918	2004.89	17.4157	27.4918	36.7475	37.904	37.897	200	0.0583
801.93	21.240	2620.60	17.4157	27.4919	48.183	49.357	49.358	300	0.0599
1001.0	21.656	3361.68	17.4157	27.4963	62.028	63.224	63.222		
1051.1	21.455	3564.64	17.4157	27.4964	65.991	67.177	67.177	400	0.0615
1062.7	21.445	3610.52	17.4157	27.4997	66.865	68.050	} 68.049	500	0.0631
1062.8	21.505	3609.83	17.4157	27.4917	66.858	68.047	{	600	0.0648
1063.5	21.747	3616.89	17.4157	27.5029	67.049	68.251	68.303	700	0.0664
1070.3	21.808	3643.10	17.4157	27.4988	67.550	68.755	68.753	800	0.0680
1201.3	22.171	4130.57	17.4157	27.5005	76.284	77.509	77.509	900	0.0696
1202.3	22.006	4133.12	17.4157	27.4939	76.318	77.534	77.534	1000	0.0712
								1060	0.0781
1301.2	22.180	4525.73	17.4157	27.4967	83.630	84.855	84.855	1070	0.0664
1392.6	22.007	4895.36	17.4157	27.4943	90.505	91.721	91.721	1100	0.0665
								1200	0.0730
1535.9	22.609	5542.73	17.4157	27.4938	103.562	104.812	104.812	1300	0.0745
1603.7	22.662	5819.94	17.4157	27.4964	108.609	109.862	109.862	1400	0.0745
								1450	0.0940
								1500	0.1075
								1550	0.0850
								1600	0.0566

[1]) K. HONDA, Tohoku Imp. Univ. Science Rep., 1, (1912), 37, 42.

The corresponding values in the neighbourhood of the transition-temperatures were determined with particular care, for the purpose of fixing these temperatures more accurately and of getting some estimation of the heat-effects involved in these transitions. In general, the effects are only small, so that the temperatures could only be determined w:th a fair approximation. These results are graphically represented in Fig. 1 and in Fig. 3A.

At least *four* such transitions occur, — exactly as it is the case with *iron*, — corresponding to four different modifications a, β, γ and δ of the metal. The first transformation $a \rightleftarrows \beta\text{-}ruthenium$ occurs at about 1030°—1040° C.; the accompanying heat-absorption is only small and amounts to about 0.69 calories per gramme of the metal at 1035°. The second transformation takes place at a temperature somewhat lower than 1200° C., and here $\gamma\text{-}ruthenium$ is formed, — which, in its turn, is changed into $\delta\text{-}ruthenium$ at a temperature, which must be localised somewhere in the vicinity of 1500° C., —as can be seen from the much more rapid increase of the specific heat of this new phase with the temperature. The only well determined modification of the metal at this moment is $a\text{-}ruthenium$, which crystallises in a hexagonal, closest-packed arrangement, with $a_0 = 2.695$ Å, $c_0 = 4.273$ Å, and $a : c = 1 : 1.586$; the calculated density is: 12.71. As the metal cannot be drawn out into wires of a constant diameter, an *X*-ray-analysis at temperatures of 1100°, 1200° and 1400° C. appears practically impossible, and the same is the case with respect to a number of other physical properties.

The total amount of heat Q_0 delivered can be calculated from the following formulae:

Between 0° and 1000° C.: $Q'_0 = 0.0550657 \cdot t + 0.0000080838 \cdot t^2$.

Between 1000° and 1070° C.: $Q'_0 = 0.070641 (t - 1000) +$
$+ 0.00028953 \cdot (t - 1000)^2 - 0.0000025245 \cdot (t - 1000)^3$.

Between 1070° and 1200° C.: $Q'_0 = 0.062078 \cdot t + 0.00000201895 \cdot t^2$.

Between 1200° and 1400° C.: $Q'_0 = 0.0559489 \cdot t + 0.000007119 \cdot t^2$.

Between 1400° and 1604° C.: $Q'_0 = 0.074615 \cdot (t - 1400) +$
$+ 0.00027376 \cdot (t - 1400)^2 - 0.0000010624 \cdot (t - 1400)^3$.

From this, the true specific heats c_p can be calculated from the equations:

Between 0° and 1000° C.: $c_p^a = 0.0550657 + 0.0000161676 \cdot t$. ($a$-Mod.); the corresponding values are given in Table III.

Between 1000° and 1070° C.: $c_p = 0.070641 + 0.00057905 (t - 1000) - 0.0000075736 \cdot (t - 1000)^2$.

The values of c_p and C_p in this interval of temperature are:

t:	c_p:	C_p:
1000°	(0.0706[4]); 0.0712	—
1010	0.0757	7.696
1020	0.0792	8.059
1030	0.0812	8.258
1040	0.0817	8.309
1050	0.0806	8.201
1060	0.0781	7.943
1070	(0.0741); 0.0664	—

The values at 1000° and 1070°, being the very limits of the temperature-interval considered, cannot be identical, without applying a formula with much more constants.

The *maximum* in this curve is situated at about 1035° C.

Between 1070° and 1200° C.: $c_p = 0.062078 + 0.0000040379 \cdot t$. ($\beta$-Mod.); also some of these values can be found in Table III.

Between 1200° and 1400° C.: $c_p^\gamma = 0.0559489 + 0.000014238 \cdot t$. ($\gamma$-Mod.); see Table III.

Finally, for the δ-phase of *ruthenium*, c_p can be calculated from the formula:

$$c_p^\delta = 0.074615 + 0.00054752 \cdot (t - 1400) - 0.000003187 \cdot (t - 1400)^2.$$

Some values calculated for *δ-ruthenium* within this temperature-interval are here mentioned:

t:	c_p:	C_p:
1400°	0.0746	7.588
1450	0.0940	9.553
1500	0.1075	10.932
1550	0.0850	8.647
1600	0.0566	5.760

The maximum value is situated almost exactly at 1500° C.

For the atomic heats C_p the corresponding formulae are:

$0° - 1000°$ C.: $C_p^\alpha = 5.6002 + 0.001644 \cdot t.$

$1000° - 1070°$ C.: $C_p = 7.1842 + 0.5889 \cdot (t - 1000) -$
$$- 0.00077 \cdot (t - 1000)^2.$$

$1070° - 1200°$ C.: $C_p^\beta = 6.3133 + 0.0004107 \cdot t.$

$1200° - 1400°$ C.: $C_p^\gamma = 5.6900 + 0.0014517 \cdot t.$

Between $1400°$ and $1604°$ C., the atomic heat of δ-*ruthenium* can be expressed by:

$$C_p^\delta = 7.5884 + 0.055682 \cdot (t - 1400) - 0.000324116 \cdot (t - 1400)^2.$$

Exactly as in the case of *iron*, the β-modification has the smallest temperature-coefficient of its specific heat. The values of C_p for the different modifications of *ruthenium* are graphically represented in Fig. 1 and Fig. 3A; the evident analogy in the behaviour of *ruthenium* and of *iron*, — as far as their allotropism is concerned, — is highly interesting indeed.

§ 6. It is of interest to compare the results obtained in the case of the six *platinum*-metals here studied, with those of the three other elements: *Fe*, *Co* and *Ni* of the eighth group of the periodical system of the elements. All nine elements of this group, — which form three different "triplets", — are those, which are situated at the very bottom of the periodical branches on LOTHAR MEYER's curve for the atomic volumes in their dependence on the atomic number. Indeed, the atomic volumes in $\overset{\circ}{\text{A}}{}^3$, as deduced from their mean atomic radii [1]), appear all to be *minimum* values:

	Fe (26)	*Co* (27)	*Ni* (28)
At. W.	55.84	58.97	58.68
Mean At. Vol.	11.7 $\overset{\circ}{\text{A}}{}^3$.	11.2 $\overset{\circ}{\text{A}}{}^3$.	10.9 $\overset{\circ}{\text{A}}{}^3$.
	Ru (44)	*Rho* (45)	*Pd* (46)
At. W.	101.7	102.9	106.7
Mean At. Vol.	13.4 $\overset{\circ}{\text{A}}{}^3$.	13.7 $\overset{\circ}{\text{A}}{}^3$.	14.8 $\overset{\circ}{\text{A}}{}^3$.
	Os (76)	*Ir* (77)	*Pt* (78)
At. W.	190.9	193.1	195.2
Mean At. Vol.	13.6 $\overset{\circ}{\text{A}}{}^3$.	14.0 $\overset{\circ}{\text{A}}{}^3$.	14.9 $\overset{\circ}{\text{A}}{}^3$.

[1]) J. D. BERNAL, *Fortschritte d. Roentgenforschung*, **II**, (1931), 236.

The first triplet (*Fe, Co, Ni*) shows, however, a decrease of the atomic volumes with increasing atomic number, while the opposite occurs in the case of the six platinum-metals. The special place, occupied by the *iron*-triplet within this 8th group, also becomes more evident when the arrangement of the outer electrons of these nine elements, according to BOHR—STONER is considered:

	K	L	M	N	O	O	P
Fe :	2	2 2 4	2 2 4 3 3	(2)			
Co :	2	2 2 4	2 2 4 3 4	(2)			
Ni :	2	2 2 4	2 2 4 3 5	(2)			
Ru :	2	2 2 4	2 2 4 4 6	2 2 4 4 2	(2)		
Rho :	2	2 2 4	2 2 4 4 6	2 2 4 4 3	(2)		
Pd :	2	2 2 4	2 2 4 4 6	2 2 4 4 4	(2)		
Os :	2	2 2 4	2 2 4 4 6	2 2 4 4 6 (6, 8)		2 2 4 4 2	(2)
Ir :	2	2 2 4	2 2 4 4 6	2 2 4 4 6 (6, 8)		2 2 4 4 3	(2)
Pt :	2	2 2 4	2 2 4 4 6	2 2 4 4 6 (6, 8)		2 2 4 4 4	(2)

§ 7. The three *iron*-metals all show the phenomenon of true allotropism, and their different modifications are separately known in the pure state (static allotropism).

1. *α-Iron* is ferromagnetic and has a bodily-centred cubic structure, with $a_0 = 2.860$ Å between —190° and 16° C. At 768° C. it changes, — without any alteration of its crystalline structure, but under a heat-absorption of 6.56 calories [1]) per gramme, — into paramagnetic *β-iron*, the parameter a_0 having a value of 2.90 Å. No considerable change of volume [2]) accompanies this transition.

The magnetic behaviour is evidently an atomic property and not immediately connected with the crystalline structure. At 919° C. this *β*-modification is, — again with an absorption of heat of 6.67 calories per gramme, — transformed into the face-centred cubic *γ-iron*, with $a_0 = 3.63$ Å. At 1404°.5 C. this modification is finally, — with a heat-absorption of 1.94 calories per gramme, — transformed into the bodily-centred cubic *δ-iron*: its parameter: $a_0 = 2.93$ Å makes it probable, that this *δ-iron* represents the same phase as the *β*-modification. This was

[1]) R. DURRER, Diss. Aachen, (1915).
[2]) H. LE CHATELIER, Comp. rend. Paris, **128**. (1899), 331; G. CHARPY and L. GRENET, Bull. Soc. d'Encour., **104**, (1903), 464.

afterwards confirmed by the study of several *iron*-alloys [1]). Later-on we will consider the specific heats of these modifications more in detail.

2. *α-Cobaltum* is the low-temperature form of this metal; it has a hexagonal closest-packing of its atoms, with: $a_0 = 2.51$ Å and $c_0 = 4.09$ Å, *a : c being* $= 1 : 1.63$. Above or at 114° C. a cubic *α'-cobaltum* exists, with a face-centred lattice and with $a_0 = 3.533$ Å; as a wire-shaped cathode the *α*-form can be easily evaporated, while the *α'*-modification is not volatile under these circumstances. Electrolytically deposited *cobaltum* is a mixture of both the *α*- and *α'*-forms.

The ferromagnetic *α-*(or *α'-*)-*cobaltum* completely loses its magnetism at a temperature, which is 985° C. according to SHUKOW (Journ. russ. phys. chem. Ges., **40**, (1909), 1748), or 1150° C., according to GUERTLER and TAMMANN (Zeits. anorg. Chem., **42**, (1904), 353).

At this temperature it is, with a slight heat-effect, transformed into *β-cobaltum*.

3. *α-Nickel* is ferromagnetic and possesses a bodily-centred cubic lattice, the parameter a_0 of which seems to be somewhat variable between 3.49 and 3.54 Å; there is, however, another *α'*-form, between 357° and 363° C., which probably is hexagonal (BREDIG) with $a_0 = 2.684$ Å and $c_0 = 4.382$ Å, and a density of 7.04. Between 357° and 363° C. it changes into a feebly paramagnetic *β*-modification.

The heat of transformation [2]) at this transition-temperature is only small and was determined at: 0.013 calories per gramme.

§ 8. The specific heats of *iron* and *nickel* have been determined by several authors, i.a. by WEISS, PICCARD and CARRARD [3]), by DURRER [4]) and by SCHÜBEL [5]).

I. *Iron*. From DURRER's data the following values of the true specific and atomic heats of *iron* are deduced : (See table following page)

The colossal values for the atomic heat of *iron*, — eventually running up to almost 21 calories. — are highly remarkable. The corresponding C_p—*t*-curve is represented in the graph of Fig. 2.

II. *Nickel*. The values for c_p and C_p in the case of *α*- and *β-Nickel* are determined by SCHÜBEL [6]); the curves constructed by means of these data (See table 820) are reproduced in the same Figure 2.

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[1]) Conf.: F. WEVER, *Fortschritte der Roentgenforschung*, **II**, (1931), 241.

[2]) M. WERNER, Zeits. f. anorg. Chem., **83**, (1913), 313.

[3]) P. WEISS, A. PICCARD and A. CARRARD, Arch. des Sciences phys. et nat. Genève, **42**, (1916), 378; **43**, (1917), 22, 113, 199.

[4]) R. DURRER, loco cit.

[5]) P. SCHÜBEL, Zeits. f. anorg. Chem. **87**, 91, 100.

[6]) P. SCHÜBEL, loco cit., 108.

$t°$ (in degrees C.)	c_p :	C_p :
0	0.10545	5.889
100	0.1168	6.522
200	0.1282	7.159
300	0.1396	7.795
400	0.1509	8.426
500	0.1623	9.063
600	0.1737	9.699
700	0.1850	10.331
720	0.1873	10.459
725	0.1879	10.492
735	0.2830	15.803
745	0.3080	17.200
755	0.3760	20.996
765	0.3440	19.210
775	0.2676	14.942
785	0.1592	8.890
790 ↓ 919 ↓ 1200	0.1592 ↓ 0.1448 ↓ 0.1448	8.890 ↓ 8.086 ↓ 8.086
1300 ↓ 1404.5 ↓ 1528 ↓ 1600	0.1449 ↓ 0.2142 ↓ 0.1501 ↓ 0.1501	8.091 ↓ 11.961 ↓ 8.382 ↓ 8.382

III. *Cobaltum.* Finally, SCHÜBEL has also given [1]) a series of numbers for the specific heats of *cobaltum* up to 600° C. It is, however, impossible to conclude from his data, whether and where a discontinuity in the curve of this metal appears, because the transition-temperature of $a \rightleftarrows \beta$-*cobaltum* lies much higher than 600° C. The curve of Fig. 2 has, up to 600° C., been constructed from the mean values of SCHÜBEL and PIONCHON, and above this temperature, up to 1150° C., from the data calculated by means

[1]) Ibidem, p. 108; J. PIONCHON, Compt. rend. Paris, **103**, (1886), 1122. His values are 3 or 4 % higher than those of SCHÜBEL.

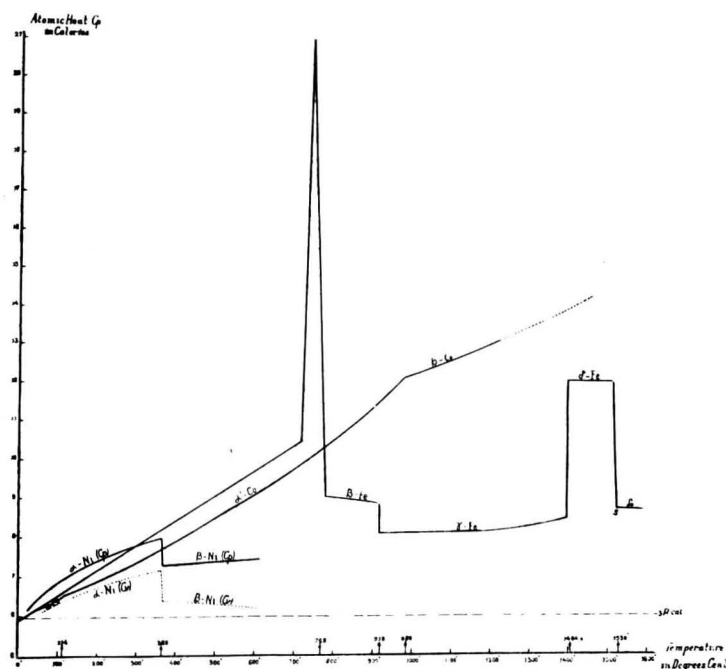| $t^°$ (in degrees C.)	c_p :	C_p :	C_v :
50	0.1080	6.34	—
100	0.1133	6.65	6.30
200	0.1237	7.26	6.72
300	0.1320	7.75	6.99
365	—	7.95	7.13
400	0.1245	7.30	6.38
500	0.1255	7.37	6.30
600	0.1260	7.40	6.18

Fig. 2. The Specific Heats of Iron, Cobaltum and Nickel in their
Dependance on the Temperature.

of PIONCHON's formulae, which are valid between 0°—890° C., and
between 890°—1150° C. respectively.

It seems, that there is a slight difference present between the inclinations
of the curves for α- and of α'-cobaltum.

In general, it can be remarked, that the values of the atomic heat C_p
between 365° and 768° are greatest for *iron* and smallest for *nickel*; but

t° (in degrees C.)	c_p :	C_p :
0	0.1055	6.22
100	0.1094	6.45
· 200	0.1160	6.84
300	0.1228	7.24
400	0.1318	7.77
500	0.1416	8.35
600	0.1534	9.05
700	0.1653	9.75
800	0.1781	10.50
900	0.1945	11.47
1000	0.2040	12.03
1100	0.2120	12.50
1200	0.2190	12.91

above 768° they are greater for *cobaltum* than for *iron*. All the values, however, are already at 0° C. appreciably greater than the limit of 3 R calories, and in the cases of *iron* and *cobaltum* they even increase to quite colossal values.

§ 9. If we now compare the results obtained with the nine metals of the eighth group of the periodical system, a remarkable dependence on the special positions of these metals within this group is brought about : while the C_p-t-curves for the first triplet of elements (fig. 2) are highly irre-gular, because of the many allotropic changes occurring in them, the C_p-t-curves for the metals of the last triplet : *Os, Ir* and *Pt*, are practically straight lines, giving no indication whatsoever of any allotropic trans-formation occurring. Evidently, however, the second triplet : *Ru, Rho* and *Pd* forms a truly *transitional* series between these two extreme cases : *ruthenium,* — being the nearest homologue of *iron,* — still shows the phenomenon of a true static allotropism, which, in many respects, is very analogous to that observed in the case of *iron*. The curve for *rhodium,* and, — to less a degree, — also that for *palladium,* with their typical *maxima,* prove the existence of at least *one* allotropic change ; but this time it is of a more *dynamical* nature, — a state of mobile equilibrium between the different modifications here being evidently established at each temperature. Thus, these nine elements, with an increasing complexity of their atomic structure, clearly show a decreasing tendency for such

kind of allotropic transformations, as are leading to the existence of *separate* phases.
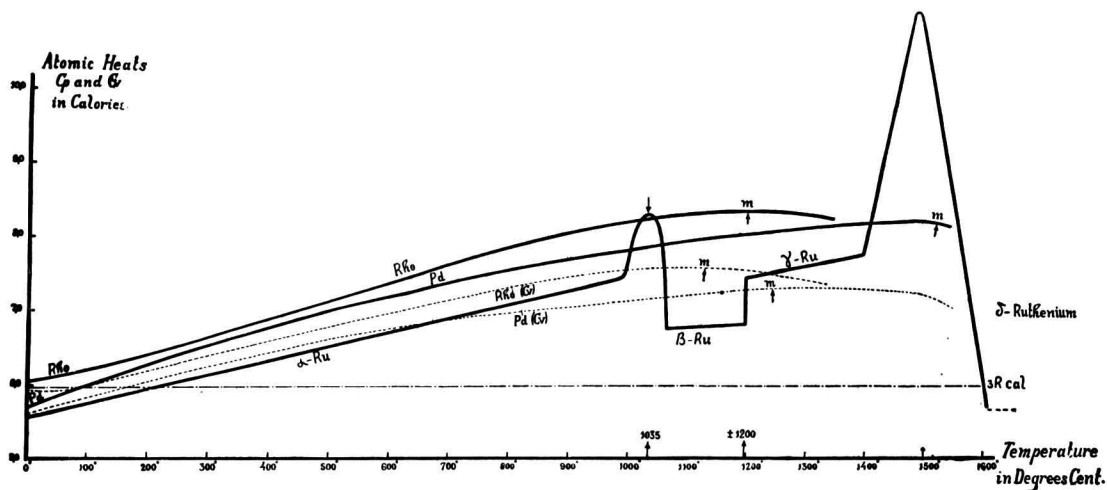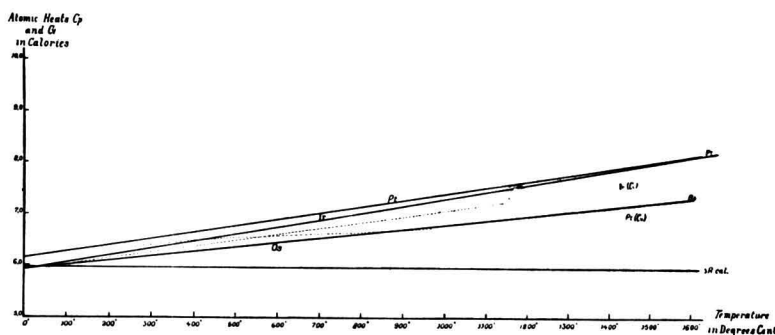

Fig. 3A.

Fig. 3B.

Fig. 3. The Atomic Heats C_p and C_v of Ruthenium, Rhodium and Palladium (3A) and those of Osmium, Iridium and Platinum (3B), in their Dependance on the Temperature.

This fact is the principal conclusion to be drawn from these measurements; on the other hand, they simultaneously indicate, that *no* limiting value of $3R$ calories for the atomic heat seems to exist, as soon as the temperature sensibly surpasses those between 0° and 100° C. More particularly in the cases of *iron* and *cobaltum*, it must become evident, that no theory at this moment can fully explain the enormous values which the specific heats here can obtain; nor can the significance of allotropic changes in this respect be elucidated by such theoretical views.

These investigations are being continued with other groups of high-melting elements.

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