

**Chemistry.** — *On reversible phase-transitions in solid refractory metals.*  
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§ 1. During the last twenty years a great number of systematical investigations have been made in the Laboratory of Inorganic and Physical Chemistry of the Groningen University, concerning the phase-transitions occurring in refractory metals at temperatures between 0° C. and about 1650° C., whilst the accompanying phenomena were studied in detail. The metals here considered all belong to the 4th till 8th group of the periodic table: more especially they bear the atomic numbers: 22 to 28, 40 to 46

4th Group	5th Group	6th Group	7th Group	8th Group				
22	23	24	25	Atomic Number	26	27	28	
<i>Ti</i>	<i>V</i>	<i>Cr</i>	<i>Mn</i>	Element	<i>Fe</i>	<i>Co</i>	<i>Ni</i>	
47.9 (5 isot.)	50.95 (1 isot.)	52.01 (4 isot.)	54.93 (1 isot.)	Atomic Weight	55.84 (4 isot.)	58.94 (2 isot.)	58.69 (5 isot.)	IV th per.
1730°C.	1715°C.	1765°C.	ca. 1245°C.	Meltingpoint	1530°C.	1490°C.	1455°C.	
2 (3)	1	2 (3)	3	Number of Solid States	4 (2)	3 (2)	3 (2)	
40	41	42	43	Atomic Number	44	45	46	
<i>Zr</i>	<i>Nb</i>	<i>Mo</i>	<i>Ma</i>	Element	<i>Ru</i>	<i>Rh</i>	<i>Pd</i>	
91.2 (5 isot.)	92.91 (1 isot.)	95.95 (7 isot.)	(ca. 99) (—)	Atomic Weight	101.7 (6 isot.)	102.91 (2 isot.)	106.7 (6 isot.)	Vth per.
2130°C.	1950°C.	2625°C.	—	Meltingpoint	2450°C.	1966°C.	1554.5° C.	
2 (3)	1	1	—	Number of Solid States	4	2	1	
72	73	74	75	Atomic Number	76	77	78	
<i>Hf</i>	<i>Ta</i>	<i>W</i>	<i>Re</i>	Element	<i>Os</i>	<i>Ir</i>	<i>Pt</i>	
178.4 (5 isot.)	180.88 (1 isot.)	183.92 (4 isot.)	186.31 (2 isot.)	Atomic Weight	191.5 (6 isot.)	193.1 (2 isot.)	195.23 (5 isot.)	VIth per.
2230°C.	3030°C.	3370°C.	3440°C.	Meltingpoint	2700°C.	2454°C.	1773.5° C.	
2	1	1	1	Number of Solid States	1	1	1	

and 72 to 78, including the three series of elements ranging from *titanium* to *nickel*, from *zirconium* to *palladium* and from *hafnium* to *platinum*. Their meltingpoints (under the pressure of 1 atm.) all lie between about 1500° and 3500° C.; many of them belong to the technically most important materials, either in the pure or in the alloyed state.

After the recently <sup>1)</sup> finished investigation of *cobaltum* in this respect, the work which had to be done concerning the 8<sup>th</sup> group can now be considered as accomplished; so that, therefore, a summarizing review of the results obtained in the latter group, seems not to be out of place here.

§ 2. A few additional remarks may be made here about the methods applied in these investigations. As the purpose was to collect not only the necessary data about the accurate situation of the characteristic transition-temperatures, but also to make sure that no phase-transitions in the solid state could be overlooked, — it appeared from the beginning advisable to determine those data by *several different* experimental methods in such a way, that the values obtained could be controlled by mutual comparison; moreover, that these values should preferentially not be gained by *separate* observations at *arbitrarily selected* temperatures, but by an experimental device which would allow us to acquire a record of the dependence of the studied properties on *all intermediate* temperatures. For this reason the method of the optically-coupled double-galvanometer, as first designed by SALADIN and LE CHATELIER, in combination with a photographic registration of the curves obtained, was modified in several directions; so that now it allows the direct record on the photographic plate of the curves for the *relative heat-capacity*, the *thermal expansion*, the *electric resistance* and the *thermo-electrical* behaviour of the metals studied in function of the temperature (as abscissa). As soon as in this way the true situation of the remarkable points on the curves is sufficiently ascertained, the accurate measurements of the absolute specific heats by means of the metalblock-calorimeter at carefully selected intervals of the temperature are made in the way that has already often been described <sup>2)</sup>. In these experiments

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<sup>1)</sup> F. M. JAEGER, E. ROSENBOHM and A. J. ZUITHOFF, Rec. d. trav. d. Chim. d. Pays-Bas, **59**, 831 (1940); conf. also: F. M. JAEGER and A. J. ZUITHOFF, these Proceed., **43**, 815 (1940).

<sup>2)</sup> For these methods, compare e.g.: F. M. JAEGER, E. ROSENBOHM and J. A. BOTTEMA, Rec. Trav. chim. d. Pays-Bas, **52**, 61 (1933); F. M. JAEGER and W. A. VEENSTRA, *ibid.*, **53**, 677 (1934); F. M. JAEGER, E. ROSENBOHM and R. FONTEYNE, *ibid.*, **55**, 615 (1936); E. ROSENBOHM, *Physica*, **5**, 385 (1938); F. M. JAEGER, E. ROSENBOHM and J. A. BOTTEMA, Rec. d. Trav. d. Chim. d. Pays-Bas, **57**, 1137 (1938); F. M. JAEGER and E. ROSENBOHM, Rec. trav. chim., **47**, 513 (1928); *id.* *Physica* **6**, 1123 (1939); F. M. JAEGER and E. ROSENBOHM, Rec. trav. chim. **51**, 1 (1932); F. M. JAEGER and W. A. VEENSTRA, Proc. Kon. Akad. v. Wetensch., Amsterdam, **37**, 280 (1934); M. EWERT, Proc. Kon. Akad. v. Wetensch., Amsterdam, **39**, 833 (1936); F. M. JAEGER, E. ROSENBOHM and A. J. ZUITHOFF, Rec. trav. chim. **57**, 1313 (1938); A. J. ZUITHOFF, Rec. trav. chim. **58**, 131 (1939); etc.

the metals were always studied either enclosed in the usual evacuated platinum crucibles of special construction, or within an electrically heated high-vacuum furnace; the metals must beforehand be freed as completely as possible from adherent or absorbed gases.

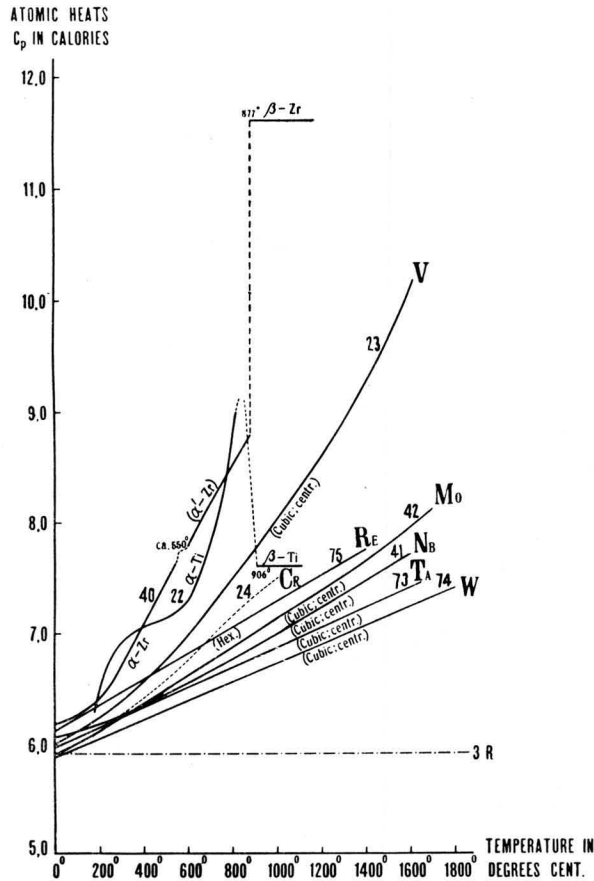


Fig. 1. The atomic heats  $C_p$  of some elements of the 4th, 5th, 6th and 7th group.

§ 3. With the exception of some elements of groups IV to VII, like *chromium*, *manganese*, *masurium* and *hafnium*, — which were not available either in sufficient quantities or in the necessary degree of purity, — the numerical data for all the other metals were finally obtained. It can here be remarked, that the metals of the 5th, 6th and 7th groups, in general proved *not* to occur in more than a *single* crystalline state; thus e.g. in the case of *vanadium*, *niobium*, *tantalum*, *molybdenum*, *tungsten*, *rhenium*, etc. (Fig. 1). This fact is contrary to the behaviour of the metals of the 4th group, which all very conspicuously manifest the phenomenon of multiple states. But *all* these elements, — just as is the case with most other metals, — prove to have values for their atomic heats  $C_p$ , which, — even at the

lower temperatures ( $50^{\circ}$ — $100^{\circ}$  C.), — are far superior to the theoretical limiting value of  $3R$  ( $= 5,965$ ) calories. —

§ 4. If the elements of the 8th group now are considered here more in detail, — then the general aspect is quite a different one. In the first place it can be stated, that here only the *last tetrad* of elements of this group: *platinum, iridium, osmium and palladium*, do not manifest the *phenomenon of multiple states*. Indeed, they show *no trace whatsoever* of a change of their internal condition between  $0^{\circ}$  and  $1650^{\circ}$  C.; they preserve their original structure even at the highest temperatures considered, — as may be seen (Fig. 2) from the perfectly smooth and uninterrupted shape of all curves representing the numerical values of their physical properties in their dependence on the temperature, e.g. of their specific heats, electrical resistance, etc. Especially in the case of *platinum*, — the mean specific heats of which are now known with an accuracy of 0,1 % of their values, — this fact is of the utmost practical importance, because this indispensable metal is used in *all* high-temperature investigations as a *standard-material* for all comparative and absolute measurements; and its different physical properties in function of the temperature must, therefore, everywhere be

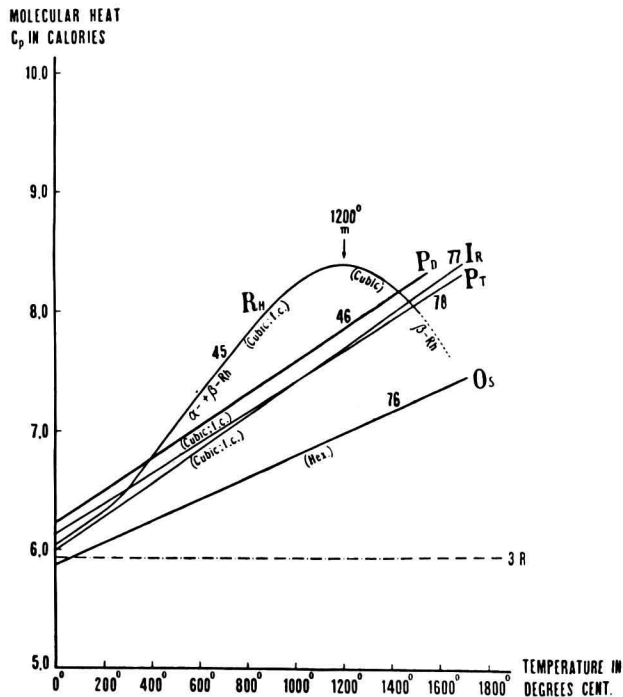


Fig. 2. The atomic heats  $C_p$  of five elements of the 8th group.

taken into account. The certitude, that up to the highest temperatures below the meltingpoint all physical properties of *platinum* remain *continuously*

variable with the temperature, is, therefore, of essential interest to the practice of high-temperature experiments.

An apparent, small discrepancy in the  $c_p$ - $t$ -curve of palladium, — originally found as a weak maximum — was afterwards proved as *non-existent*, — it only being caused by the adoption of an erroneous figure for the meltingpoint of the metal by DAY and SOSMAN in their work on the nitrogengasthermometer: a redetermination of the meltingpoint of *palladium* in this laboratory yielded the value: 1554°,5 C. instead of the old value: 1549°,2 C. After the corresponding corrections for the indications of our thermocouples had been applied, the deviations of the  $c_p$ - $t$ -curve of *palladium* proved to have completely disappeared: *palladium*, up to its meltingpoint, therefore, exhibits a *quite normal* behaviour, — just like the three other platinummetals here considered.

§ 5. In rigorous contradistinction now to the behaviour of the four *latter* elements of the 8<sup>th</sup> group, is that of the *first tetrad*: *iron*, *cobaltum*, *nickel* and *ruthenium*. For these metals all show the phenomenon of multiple phase-transitions in the solid state in a most conspicuous way. Thus *iron* shows four, *cobaltum* three, *nickel* two (or three) and *ruthenium* no less than four, perhaps even five, of such successive reversible changes in the solid state; the field of stability of each of them is, according to the rules of thermodynamical equilibrium, always limited by as many sharply defined temperature-boundaries. In the cases of *iron*, *cobaltum* and *nickel* there are, in the first place, their "CURIE-points", — i.e. the temperatures at which their *ferromagnetic states* suddenly disappear and make place for weakly-paramagnetic phases; which, in their turn, may at other temperatures be substituted by still different ones. Whilst in the case of *iron* the CURIE-point (760° C.) is, however, *first* reached and *then* the other transformations afterwards occur at 906° C. and 1401° C. successively, — the sequence of these phenomena in *cobaltum* (and probably in *nickel*) is exactly *the reverse*: with *cobaltum* e.g. *ferromagnetic  $\alpha$ -cobaltum* proves at 445° C. *first* to be transformed into equally *ferromagnetic  $\beta$ -cobaltum*, with an accompanying change of crystalline structure; subsequently the CURIE-point of the latter is reached at 1125° C., where  *$\beta$ -cobaltum* is changed into paramagnetic  *$\gamma$ -cobaltum*. In all three cases, however, *the transitions at the CURIE-point appear never to be accompanied by a change of the crystalline architecture* of the original phase. In the case of *cobaltum* the change at 445° C. (with *nickel* perhaps also at 345°; CURIE-point at 355°—360° C.) is accompanied by a typical hysteresis-effect, — the details of which have been discussed in detail in our paper in the *Recueil* <sup>1)</sup>.

Most remarkable with respect to its phase-transitions is *ruthenium*, —

<sup>1)</sup> F. M. JAEGER, E. ROSENBOHM and A. J. ZUITHOFF, Rec. d. trav. d. Chim. d. Pays-Bas, **59**, 831 (1940); conf. also: F. M. JAEGER and A. J. ZUITHOFF, Proc. Ned. Akad. v. Wetensch., Amsterdam, **33**, 815 (1940).

which in its general points appears to behave in a similar way as *iron*. But *ruthenium* is *paramagnetic* and, therefore, does *not* possess a CURIE-temperature. The metal has three or four transition-points at 310°, 1035°, 1200° and 1500° C. respectively; the nature of the transition-point at 310° C., deduced from the recent measurements of the temperature-coefficient of the electrical resistance, still remains problematic <sup>1)</sup>. The corre-

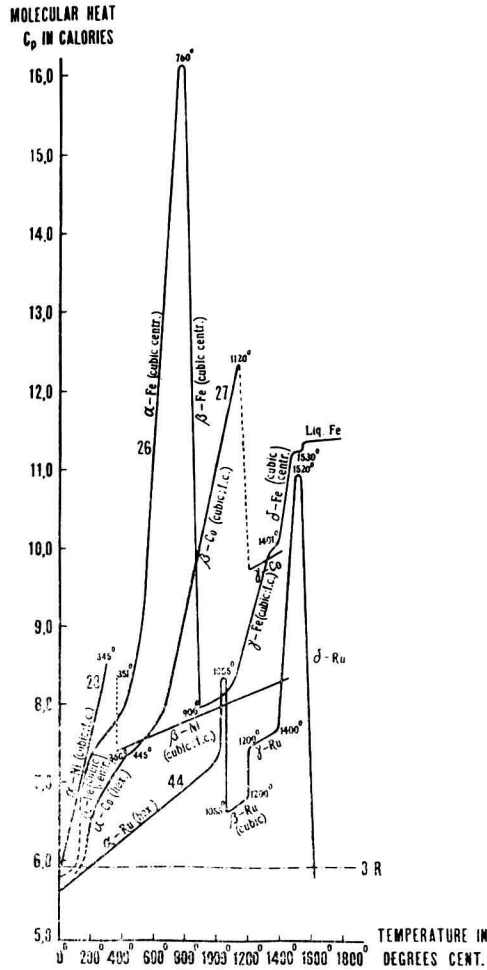


Fig. 3. The atomic heat of the four first elements of the 8th group.

sponding transformations at these different temperatures, — as well on heating as on cooling, — all occur *rather rapidly*, without retardation-phenomena of any appreciable significance. Recently this fact was once more qualitatively corroborated by us during a study of the electrical

<sup>1)</sup> There seems *not* to occur a change of the crystalline structure of the metal at this temperature.

resistance of the metal in its dependence on the temperature, which will be published later.

§ 6. Thus it becomes evident, that the *first* tetrad of metals of the 8th group manifests the phenomenon of enantiotropous phase-transitions to a high degree, whilst the *latter* tetrad of this group, does *not* show it at all. Between these two tetrads, however, the element *rhodium* is placed, — like a central link between the two groups. Now *rhodium* shows a  $c_p$ - $t$ -curve of an entirely different character, as it consists of a *single, steeply rising, smooth curve* with an unmistakable *maximum* at about  $1204^\circ \text{C.}$ ; then subsequently the curve at higher temperatures falls-off rather rapidly. As a consequence of a number of experimental facts, earlier investigators have already come to the conclusion, that the internal condition of *rhodium* *gradually* changes to an appreciable degree, when the metal is heated between  $1200^\circ$  and  $1300^\circ \text{C.}$  Thus already in 1908 MENDENHALL and INGERSOLL drew attention to the fact, that at about  $1200^\circ \text{C.}$  an abnormal increase in the radiation of the glowing metal is observed; and in 1931 DIXON stated a similar behaviour with respect to the photo-electrical and the thermo-ionic phenomena. In this laboratory an analogous fact was observed in connection with the temperature-coefficient of the electrical resistance, measured in a high vacuum, which also has a maximum between  $1200^\circ$  and  $1300^\circ \text{C.}$

Although the fact, that the inner condition of *rhodium* changes on heating can hardly any longer be doubted, — this change appears to be a *gradual* one. There is nowhere observed any discontinuity in the curves representing the measured properties in function of the temperature. *X*-ray examinations of heated *rhodium*-wires in a vacuum, however, seem to indicate with much more probability, that metallic *rhodium* at each temperature consists of a *homogeneous mixture* of *two different cubic forms* of the metal in variable proportions, — their ratio being characteristic for each temperature. The quantity of the face-centred, cubic  $\alpha$ -form of the metal predominates at the *lower*, the cubic  $\beta$ -form (with a simple cubic elementary cell), on the contrary, prevails at the *higher* temperatures. On the other hand it proves not to be possible to isolate either of the two forms in a completely pure state. At each temperature the metal is a homogeneous mixture of  $\alpha\text{-Rh} + \beta\text{-Rh}$ , in which the two forms are in *dynamical equilibrium* with each other at each temperature; so that, when the latter is more or less completely established, the composition of the phase must appear to be continually-variable with the temperature; — in the same way as this seems also to have been observed in the case of the equally cubic  $\alpha$ - and  $\beta$ -forms of *manganese*.

In this way, therefore, the metal *rhodium*, with its "dynamic allotropism", evidently represents *the natural transition-term* between the *first* tetrad of elements in the 8th group, — with its conspicuous "static" allotropism —,

and the *latter* one with its complete lack of reversible changes in the solid state.

From all this, it thus becomes evident, that also with respect to the phenomena here studied, the eighth group of the periodic system in its present form really constitutes *an entity*, with the rigorous character of true systematical uniformity.

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