

# The Platinum Metals in the Periodic System

## A COMPARATIVE STUDY OF THE TRANSITION METALS

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*The characteristics of the six platinum metals provide an interesting study in their variations with atomic number and position in the periodic table. This article discusses the inter-relationships of the physical and chemical properties of these elements and of those of their neighbouring transition metals.*

It was in 1860 that the platinum metals were first recognised as a distinct group of elements. Sixteen years earlier Carl Ernst Claus, while Professor of Chemistry at the University of Kazan in Russia, had discovered the sixth member of the group and named it ruthenium in honour of his adopted country. During the intervening period Claus published fourteen papers describing the compounds of the six metals and their

inter-relationships, finally announcing (1) his view that the platinum metals formed "an isolated metallic group, inseparable, and solidly constituted", having a number of properties in common, that could be arranged in two superimposed groups of three, the "Nebenreihe" or secondary series—ruthenium, rhodium and palladium—and the "Hauptreihe" or principal series—osmium, iridium and platinum.

	Группа I.	Группа II.	Группа III.	Группа IV.	Группа V.	Группа VI.	Группа VII.	Группа VIII. Переходная к групп. I.
Типичные элементы.	H=1							
Первая серия.	Ряды 1-8	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19
	— 2-8	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5
Вторая серия.	— 3-8	K=39	Ca=40	—44	Ti=50?	V=51	Cr=52	Mn=55
	— 4-8	(Cu=63)	Zn=65	—68	—72	As=75	Se=78	Br=80
Третья серия.	— 5-8	Rb=85	Sr=87	(?Yt=88?)	Zr=90	Nb=94	Mo=96	—100
	— 6-8	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=128?	J=127
Четвертая серия.	— 7-8	Cs=132	Ba=137	—137	Ce=138?	—	—	—
	— 8-8	—	—	—	—	Ta=182	W=184	—
Пятая серия.	— 9-8	(Au=197)	Hg=200	Tl=204	Pb=207	Bi=208	—	—
	— 10-8	—	—	—	Th=232	—	U=240	—
Высшая соевая окисл.	RO	RO <sup>2</sup> или RO	RO <sup>3</sup>	RO <sup>4</sup> или RO <sup>3</sup>	RO <sup>5</sup>	RO <sup>6</sup> или RO <sup>5</sup>	RO <sup>7</sup>	RO <sup>8</sup> или RO <sup>7</sup>
Высшее водородное соединение.			(RH <sup>3</sup> )	RH <sup>4</sup>	RH <sup>5</sup>	RH <sup>6</sup>	RH	—

Mendeléev's revised Periodic Table, published in 1871

## The Platinum Metals and their Neighbours in the Periodic Table

	Group VIA	Group VIIA	Group VIII			Group IB
First long period	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29
Second long period	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47
Third long period	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79

Although Döbereiner had described his triads some thirty years before this, Claus was some years ahead of the famous Newland octaves, while the broader generalisations of Lothar Meyer and Mendeléev were still ten years away.

Curiously, it was also in 1860 that Cannizzaro addressed the gathering of over a hundred chemists convened at Karlsruhe by Kekulé, Welzien and Wurtz in an attempt to clear up some of the muddle into which chemical formulation had fallen. Cannizzaro, by reaffirming the disregarded views of Avogadro, succeeded in bringing order into the many conflicting opinions on the relationship of the atomic and molecular weights, and in so doing laid the foundations of a common system on which Lothar Meyer and Mendeléev were to build.

Meyer's well-known curve of atomic volumes, published in 1870, clearly showed the existence of a periodicity in the characteristics of the elements. A year earlier Mendeléev had published his first periodic table in the course of a paper to the Russian Chemical Society, "On the Correlation of the Properties and Atomic Weights of the Elements", but further study of the problem caused him to revise the table considerably and to publish it in its new form in 1871.

It will be seen in the reproduction on the

opposite page that the two platinum metal triads described by Claus, together with the triad iron, cobalt and nickel, were placed in Group VIII by Mendeléev, but that the elements copper, silver and gold also appeared in the same group although alternative positions were left for them in Group I. Unfortunately, and probably owing to a misunderstanding of the true nature of the rare earth elements, Mendeléev had now inserted an extra series in the table, so leaving a gap between the two platinum metal triads. This had the inevitable result of prompting the re-examination of platinum ores for these apparently missing elements, and a number of "discoveries" were claimed, including Guyard's Uralium and Kern's Davyum.

With the development of the electronic theory and the recognition that the periodic classification of the elements was dependent on atomic number and not on atomic weight this anomaly disappeared, and with the allocation of the rare earth elements to a single space in the table the apparent gap in the platinum metal sequence vanished.

The portion of the modern periodic table in which the platinum metals occur is shown above. This of course includes rhenium, discovered by Noddack and his co-workers in 1925, and technetium—formerly known as masurium—predicted by Mendeléev as eka-

manganese, and discovered only in 1937 among the products of nuclear fission.

### Physical and Mechanical Properties

In general the platinum metals are characterised by high melting points and small atomic diameters. As Claus pointed out, the two triads show certain marked differences; in the upper triad comprising ruthenium, rhodium and palladium the atomic weights are of the order of 100 and the densities around 12 g/cc, while in the heavy or lower triad, osmium, iridium and platinum, the atomic weights are around 190 and the densities around 22 g/cc. The specific heats of the elements in the upper triad are about twice those of the elements in the lower triad.

Nevertheless, as is general in the periodic system, the greatest similarity in properties is found in the vertical groups; this is well illustrated by comparing the physical and chemical properties of the metals in the second long period with those of the metal immediately below in the third long period; there is a strong resemblance between ruthenium and osmium, between rhodium and iridium, and between palladium and platinum. There is a much less marked

similarity in properties between each of these pairs of metals and the metals above them in the first long period, but none the less certain similarities do exist between iron, cobalt and nickel and the platinum metals below them.

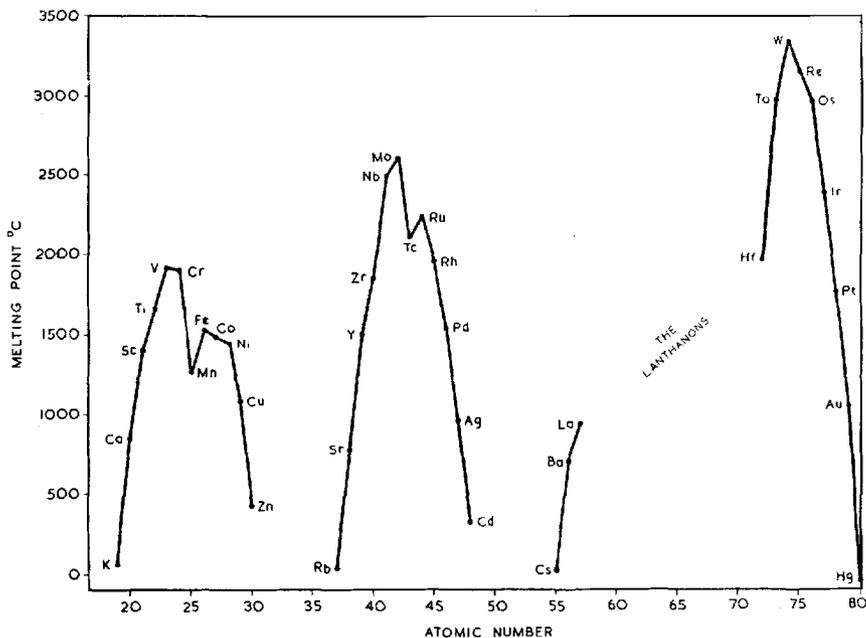
The crystal structure of the metals in the second and third long periods changes, as shown in the table below, from b.c.c. in Group VIA to c.p.h. in Groups VIIA and VIII(a) and then to f.c.c. in Groups VIII(b) and (c) and Group I. The metals of the first long period in Groups VIA, VIIA and VIII differ from those below them in the same group in exhibiting allotropy.

In the graph on page 147 the melting points of the metallic elements are plotted against the atomic number; it will be seen that they form three fairly smooth curves, the maximum point of each being occupied by a Group VIA element and the elements of the following groups all being placed on the descending side of the peak.

When the atomic diameter is plotted against the atomic number the transition elements are grouped closely together along the troughs of the curves, indicating strong inter-atomic bonding in these metals. In both cases the position of manganese is

Crystal Structure of the Transition Metals					
Group VIA	Group VIIA	Group VIII			Group IB
Cr α b.c.c. β c.p.h.	Mn* α β γ δ	Fe α b.c.c. γ f.c.c. δ b.c.c.	Co α c.p.h. β f.c.c.	Ni α c.p.h. β f.c.c.	Cu f.c.c.
Mo b.c.c.	Tc c.p.h.	Ru c.p.h.	Rh f.c.c.	Pd f.c.c.	Ag f.c.c.
W α b.c.c. β*	Re c.p.h.	Os c.p.h.	Ir f.c.c.	Pt f.c.c.	Au f.c.c.

\* Mn and β-W have complicated structures



The melting points of the metallic elements plotted against atomic number

anomalous, probably owing to its peculiar lattice structure.

The greatest hardness and the highest mechanical strengths are generally exhibited by the metals at the peak of the melting point curves, the values of both these properties generally decreasing with increasing distance of the metal from the peak. Thus in the two platinum metal triads the hardness and strength decrease from left to right and are greater in the second triad than they are in the first.

This same periodicity was observed at high temperatures in a study of the creep strengths in compression of a number of metals at 1000°C carried out by Allen and Carrington (2); these authors reported, among other examples of periodicity, a marked fall of strength between rhodium and palladium in the second long period, and between iridium and platinum in the third, this fall being continued to silver and gold respectively.

The metals of the iron group triad differ from those in the two platinum group triads in that their melting points, hardnesses and strengths are much closer to one another

than is the case with the platinum metals.

The workability of the metals in this portion of the periodic table depends on their crystal structure, those with a f.c.c. structure being much more easily worked than those with a b.c.c. structure while these, in turn, are more easily worked than those with a c.p.h. structure. Ruthenium and osmium are brittle, but can be worked—although only with difficulty—at high temperatures if protected from oxidation; manganese is brittle and unworkable owing to its complex structure, and the b.c.c. metals require in general to be hot-worked in the initial stages. On the other hand the metals in the third column of Group VIII and those in Group IB are relatively soft and can be easily worked in the cold.

An interpretation of these facts based on the electronic structure of the metals has been attempted by Pauling (3) and by Hume-Rothery and his collaborators (4), who have attributed the observed differences in behaviour to hybridisation of the *spd* orbitals and to a stabilising effect due to resonance between the various possible structures.

## Chemical Properties

In MendeléeV's table the iron triad was placed above the two platinum metal triads to form Group VIII but, in considering the chemical properties of the group, greater similarities in behaviour are observed in the vertical columns than in the horizontal. All the metals in the first vertical column exhibit a principal valency of 3; iron has a secondary valency of 2 whereas the main secondary valency of ruthenium and osmium is 8. Ferric chloride and bromide form anionic complexes of the type  $\text{HFeX}_4$  analogous to the corresponding gold compounds and like them extractable into ether. Ruthenium and osmium halides on the other hand form anionic complexes of the type  $\text{H}_2\text{MX}_5$  and  $\text{H}_2\text{MX}_6$ , the latter being analogous to the corresponding iridium, palladium and platinum compounds and yielding ammonium and potassium salts of relatively low solubility; quadrivalent rhenium and technetium also form this type of compound.

Iron, ruthenium, and osmium resemble one another in forming compounds of the type  $\text{K}_2\text{MO}_4$  and stable complex cyanides with the formula  $\text{R}_4\text{M}(\text{CN})_6, 3\text{H}_2\text{O}$ .

An interesting point of resemblance between the two higher members of Groups VIA, VIIA and VIII(a) is the comparatively high volatility of the highest oxide. Molybdenum trioxide volatilises above about  $600^\circ\text{C}$ , tungsten trioxide above  $1200^\circ\text{C}$ , rhenium heptoxide above  $250^\circ\text{C}$ , and ruthenium and osmium tetroxides volatilise at around  $100^\circ\text{C}$ ; the first three oxides are acid anhydrides whereas the last two behave neither as acids nor as bases. Like manganese, technetium, and rhenium, ruthenium forms salts of the type  $\text{KMO}_4$  in which it is heptavalent. The compounds  $\text{K}_2\text{FeO}_4$ ,  $\text{K}_2\text{RuO}_4 \cdot \text{H}_2\text{O}$ , and  $\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$  have a similar composition to the chromates, molybdates, tungstates and rhenates, but are much less stable, and differ in their water of crystallisation and crystal structure.

In the absence of air ferrous salts give with ammonium halides in strongly ammoniacal

solutions crystalline precipitates of the type  $[\text{Fe}(\text{NH}_3)_6]\text{X}_2$ . Analogous compounds of bivalent ruthenium have recently been prepared by reducing ruthenium compounds with zinc dust in ammoniacal ammonium halide solutions (5). There is evidence (6) that reduction of rhodium trichloride in the same way yields  $[\text{Rh}^{\text{II}}(\text{NH}_3)_6]\text{Cl}_2$ .

Turning now to the metals in the second vertical column of Group VIII, the chief compounds that are common to all three metals are the double nitrites  $\text{R}_3\text{M}(\text{NO}_2)_6$ , the amines, e.g.  $[\text{M}(\text{NH}_3)_6]\text{X}_3$ ,  $[\text{M}(\text{NH}_3)_5\text{X}]\text{X}_2$ , the alums  $\text{RM}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , and the double cyanides  $\text{R}_3\text{M}(\text{CN})_6$ . The only analogous purely inorganic compounds of the bivalent metals are the amines  $[\text{M}^{\text{II}}(\text{NH}_3)_6]\text{X}_2$  where M is Co or Rh; although no amines of bivalent Ir have yet been isolated some evidence has been obtained of their existence (6). Analogous compounds of all three metals in the bivalent state with organic ligands have, however, been prepared within recent years.

The metals of the third vertical column of Group VIII show analogies only in the composition of the oxides and anhydrous halides, in which they are bivalent. The chemical behaviour of these compounds differs markedly, however;  $\text{NiCl}_2$  is readily soluble in water from which it crystallises as the hexahydrate, whereas  $\text{PdCl}_2$  and  $\text{PtCl}_2$  are insoluble in water and dissolve only in solutions of other chlorides forming the anions  $\text{PdCl}_4^{--}$  and  $\text{PtCl}_4^{--}$  respectively. In forming anionic halogen complexes palladium and platinum resemble gold. Nickel forms amines of the type  $[\text{Ni}(\text{NH}_3)_3]\text{X}_2$ , whereas the bivalent palladium and platinum amines have the formula  $[\text{M}(\text{NH}_3)_4]\text{X}_2$  and the chemical behaviour of these tetramines is quite different from that of the nickel hexammines. The two platinum metals form double nitrites of the type  $\text{K}_2\text{M}(\text{NO}_2)_4$ , whereas the nickel compound has the formula  $\text{K}_4\text{M}(\text{NO}_2)_6$ , but the three metals resemble one another in yielding double cyanides of the type  $\text{R}_2\text{M}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$ , the nickel compound being, however, immediately decom-

posed by mineral acid, whereas the platinum metal compounds are stable.

In the metallic state there are obvious analogies between palladium and silver, and between platinum and gold. The former pair of metals dissolve readily in nitric acid and in boiling concentrated sulphuric acid, and react superficially with iodine at room temperature. Platinum and gold resist all acids except aqua regia and are not oxidised on heating, or affected by iodine. Rhodium dissolves slowly in boiling concentrated sulphuric acid, in which respect it resembles palladium, but otherwise is unaffected, like iridium and

ruthenium, by all acids or mixtures of acids. Osmium is slowly converted by boiling nitric acid or aqua regia into the volatile tetroxide except when in the massive form.

To sum up, it will be seen that in their physical and chemical properties, ruthenium and osmium more closely resemble technetium and rhenium, or in certain respects molybdenum and tungsten, than they do iron. Rhodium and iridium are more closely allied to cobalt than to any other metal, while palladium and platinum have close analogies both with nickel and with the precious metals of Group I.

### References

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## Improved Stainless Steel Reactor Material

### RESISTANCE TO CORROSION INCREASED BY PLATINUM ADDITION

The corrosion resistance in uranyl sulphate and uranyl nitrate solutions of 304 stainless steel alloyed with small amounts of platinum or copper has been investigated as part of the reactor materials research programme of the Oak Ridge National Laboratory. Preliminary results reported by J. C. Griess *et al* in three recent Homogeneous Reactor Project Progress Reports (ORNL-2743, 2879 and 2920) show that the resistance to corrosion of the 18-8 steel is increased by the addition of small amounts of either element. Of the alloys investigated, 304 stainless steel containing 0.5 per cent platinum had the lowest corrosion rate.

Working at 250°C and at a solution velocity of 17 ft/sec with a heavy water solution containing uranyl sulphate and copper sulphate, it was found that the corrosion rate for 304 stainless steel was reduced from

35-36 mil/year to 15 mil/year by the addition of 0.5 per cent platinum. No significant improvement was observed at a higher solution velocity of 68 ft/sec. In a heavy water solution containing uranyl nitrate and copper nitrate, however, the corrosion resistance at 250°C of the steel was increased by the addition of 0.5 per cent platinum at both low and high solution velocities. At a velocity of 17 ft/sec the corrosion rates for the unalloyed and alloyed material were 10 and 1.6 mil/year respectively. With the same uranyl nitrate solution and a velocity of 70 ft/sec an even more significant decrease from 300 to 14 mil/year is reported. Further corrosion tests on the 0.5 per cent platinum-alloyed 304 stainless steel are to be undertaken in view of its possible applications in homogeneous reactors in which uranyl sulphate and nitrate solutions may be used as fuels.