

A Chemist's View of the Platinum Metals

CORRELATIONS BETWEEN THEIR PROPERTIES AND THEIR FUNDAMENTAL ATOMIC PARAMETERS

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In his Presidential Address to the Chemistry Section of the British Association in 1966 Professor Sir Ronald Nyholm took as his theme "Metals and Interatomic Bonding in Chemical Compounds" and began by reminding us that metals mean different things to investigators in different fields (1). The engineer, who uses them for fabrication purposes, is particularly interested in their malleability and ductility, in their ability to conduct heat and electricity and, if alloyed with other metals, in their ability to provide materials of great strength. The metallurgist is concerned more with their extraction, their bulk physical properties and how these may be changed by heat treatment and by alloying with other elements. The physicist seeks to correlate their physical properties with fundamental atomic parameters. At that time, however, with few notable exceptions, any correlation between the structure and chemical properties of metals had been neglected by the chemist. In general, it was assumed that he was interested in metals only as catalysts, as reducing agents in chemical reactions or for the formation of their chemical compounds. This is no longer true, and since 1966 considerable progress has been made. The subject of metal-metal bonding has been developed in some detail, our understanding of the structures and properties containing groups or clusters of metals has advanced considerably, and bonding theories of metals are much more reliable—although still not especially good in predicting chemical as opposed to physical properties.

In this account we shall take as our basis some of the views and ideas put forward by

Nyholm and seek correlations between the properties of the platinum metals and some of their fundamental atomic parameters.

The Metallic State

The number of atoms required to describe "the metallic state" depends on which properties of the metal we wish to describe. Groups, or clusters, of metal atoms M_m with values of m in the range of 40 to 60 would be quite valuable for the assessment of the nature and energy distribution of orbitals, as well as in discussion of local bonding arrangements. In contrast, such values would be quite inadequate for any consideration of effects associated with the Fermi surface of a metal. Recent calculations have been taken to suggest that metal aggregates containing as few as four noble metal atoms have gross electronic structures that can be related to the bulk metal electronic structures. Against this other calculations would indicate that, in the ground state, the equilibrium bond-lengths of molecules (M_2) at the beginning and end of the 3d transition series are less than nearest neighbour distances in bulk metals especially at the right-hand side of the series where

$$r_e = R_{\text{bulk}} - 0.4 \text{ \AA}$$

From a structural point of view the relative numbers of edge and face atoms vary widely for metal particles with sizes in the range 10 to 50 Å. Below 10 Å the crystallites have only edge atoms. Beyond 50 Å more than 90 per cent of the surface atoms are regular face atoms. This effect is demonstrated for rhodium metal clusters in Table I. The chemist, who rightly associates changes in reactivity with changes in

co-ordination number, orbital vacancies and electron distribution, will expect the greatest change in reactivity within this range of particle sizes. Such effects will tend to level out beyond that region. It is for particle sizes falling between 10 and 50 Å that the chemist, who is specially interested in the catalytic behaviour of the platinum metals, has been able to obtain considerable information about the interaction

of commercially important molecules such as olefins, alkynes, carbon monoxide and hydrogen with small metal aggregates from studies of the co-ordination chemistry of metal clusters $M_m L_n$ ($m \geq 3$); $L = \text{ligand}$.

In general two questions are being asked:

- (1) What does the chemist (as distinct from the physicist, for example) mean by a metal, and
- (2) At what stage in the construction of a metallic lattice (from one metal atom to an infinite number) do metallic properties emerge?

Here we define a metal, as did Nyholm, as an element which, in one or more of its forms, is a good conductor of electricity and whose specific resistance (ρ) is proportioned to the absolute temperature, $T^\circ\text{K}$.

The second question is not so easily answered. In the past there has been a tendency among chemists to assume that when a stable metal aggregate is under construction atom by atom the growth sequence will follow a path to either a hexagonal close-packed (h.c.p.) or a cubic close-packed form (c.c.p.). In the main, work on transition-metal clusters has tended to support this view, most clusters forming fragments of these common close-packed arrangements. The Rh_{13} skeleton in $[\text{Rh}_{13}(\text{CO})_{24}\text{H}_{5-n}]^{n-}$ ($n = 2, 3$ or 4) forms a piece of regular h.c.p. lattice and the Rh_{14} skeleton in $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ possesses essentially a body centred cubic (b.c.c.) type of structure. Of special interest is the Rh_{15} cluster $[\text{Rh}_{15}(\text{CO})_{27}]^{3-}$ which possesses a

Table I
A Comparison of the Total Number and the Number of Surface Atoms for Polyhedra of Rhodium Atoms (After Chini (2))

Polyhedron	Number of M_m atoms	
	Total	Surface
Tetrahedron	4	4
Octahedron	6	6
Square antiprism	8	8
Cuboctahedron	13	12
2 Layer of cuboctahedra	55	42
18 Layers of cuboctahedra	3,242	2,117

structure that is an intermediate structure between the h.c.p. and the b.c.c. forms. The structural relationship between these three structures may be seen in Figure 1.

Another point of interest in connection with the structures of transition metal clusters is the sequence of structures adopted by the osmium compounds $[\text{Os}_6(\text{CO})_{18}]^{2-}$, $[\text{Os}_7(\text{CO})_{21}]^{2-}$, $[\text{Os}_8(\text{CO})_{22}]^{2-}$ and $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$. These progress from the O_h -octahedron, through the mono- and bicapped forms until at $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ a tetracapped octahedral arrangement of metal atoms is observed. The latter is clearly a fragment of c.c.p. (Figure 2). Of further interest, the carbido-atom in this dianion resides in an octahedral interstitial site.

Cluster compounds, exemplified by these osmium and rhodium compounds, which, in contrast to the metals themselves, are easily studied by the usual physico-chemical techniques, would appear to fill the gap between simple molecular compounds and infinite metallic lattices—at least from a structural point of view.

However, as may be seen from Table II the structures of these small clusters are different from those of the pure metals. Polymorphism is common to the transition metals and structural changes which are sensitive to external influences (for example, ligands such as CO) are not, therefore, too surprising. This is apparent from the work carried out on the Rh_{13} , Rh_{14} and Rh_{15} clusters referred to earlier in the text.

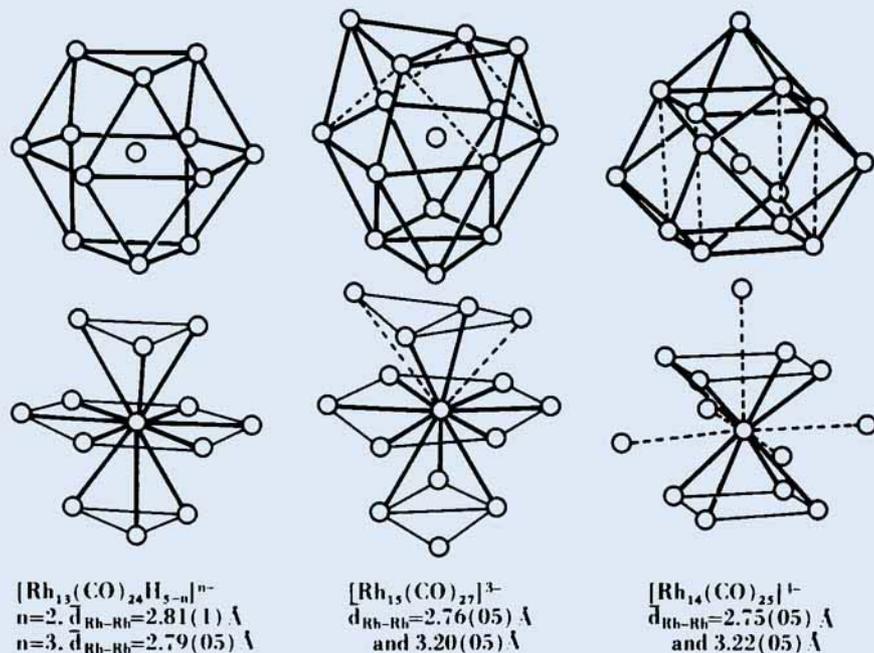
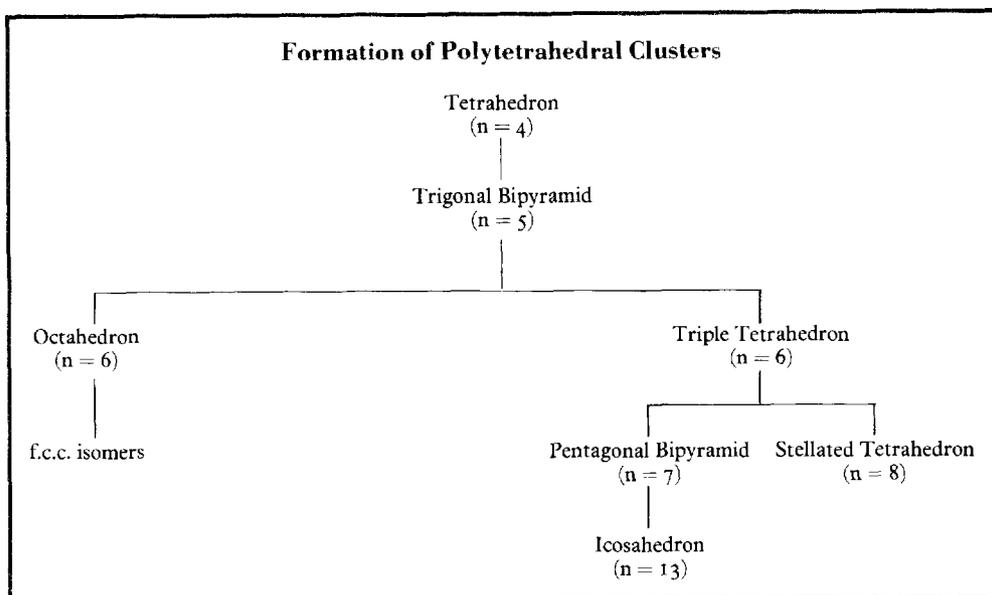


Fig. 1 The structural changes observed for the rhodium cluster unit in Rh_{13} , Rh_{14} , and Rh_{15} carbonyl clusters. Of special interest is the change from the h.c.p. arrangement in the Rh_{13} unit through to the c.c.p. arrangement in the Rh_{15} unit

Recent calculations on the stability of small aggregates of platinum metals, using both the Lennard-Jones and the Morse potential, showed

that polytetrahedral aggregates are more stable than the face centred cubic (f.c.c.) or h.c.p. types. Polytetrahedral packing may be carried



out atom by atom according to three different growth sequences as shown in the Scheme, opposite. It would appear that for clusters with more than 70 atoms ($\sim 10\text{\AA}$) the more stable aggregates are expected to form regular f.c.c. types. Examples of tetrahedral growth patterns have been found in cluster co-ordination chemistry. Commonly found for gold, such icosahedral forms are not related to the more common close-packed arrangements. Again, cluster chemistry provides examples of pentagonal symmetries in, for example, the $\text{Pt}_{19}(\text{CO})_{22}^{4-}$ anion, which provides an especially attractive example (Figure 3) and in $\text{Os}_6(\text{CO})_{18}$ which has the triple tetrahedron structure (Figure 4).

We should note that the ductility, malleability and softness of pure metals depend at least to some extent, on the ease with which adjacent planes and rows of atoms can glide over one another. This in turn depends upon the ability of the metal atom to reorganise its bonding requirements. In a cubic close-packed crystal there is a greater possibility of gliding because there are four equivalent sets of parallel close-packed planes whereas in hexagonal close-packed crystal there is only one such plane. Thus palladium and platinum are ductile and

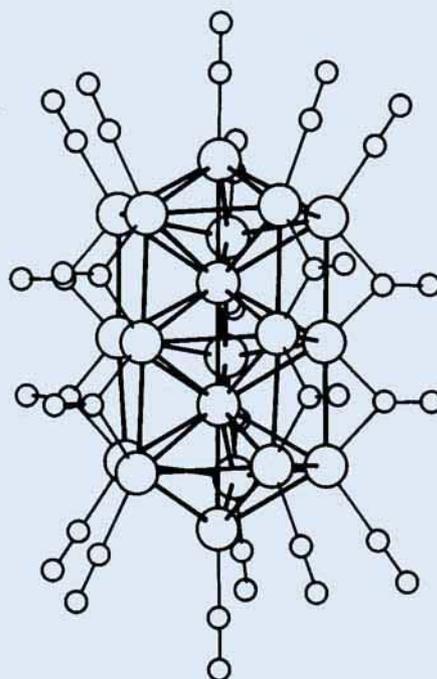


Fig. 3 The molecular structure of the $[\text{Pt}_{19}(\text{CO})_{22}]^{4-}$ tetraanion illustrating the pentagonal growth pattern of platinum atoms with an overall symmetry D_{3h}

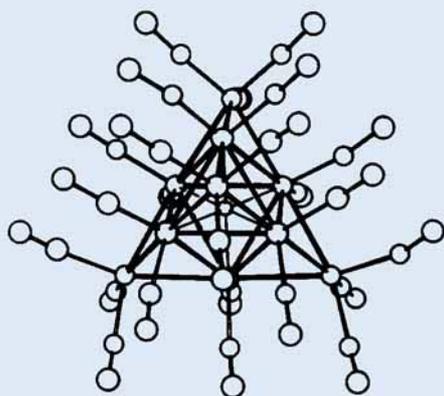


Fig. 2 The molecular structure of the dianion $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$. The ten osmium atoms define a tetracapped octahedron and the carbido-atom occupies the octahedral interstitial site

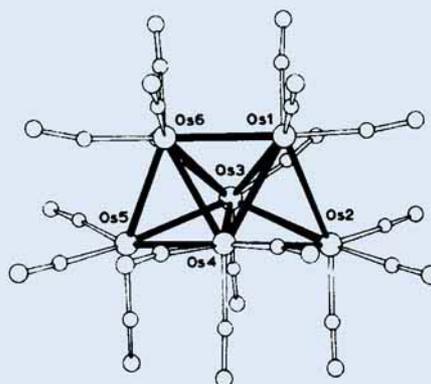


Fig. 4 The molecular structure of $\text{Os}_6(\text{CO})_{18}$ illustrating the bicapped tetrahedral arrangement of the Os_6 unit which forms part of the tetrahedral growth pattern ($n=6$) in the scheme

Ruthenium h.c.p.	Rhodium c.c.p.	Palladium c.c.p.
Osmium h.c.p.	Iridium c.c.p.	Platinum c.c.p.
Less malleable		
←		
Less ductile		

malleable by comparison with ruthenium and osmium, see Table II. Crystals with pentagonal symmetries (D_{5h} etc.) might be expected to be quite hard and brittle, similar to boron in fact.

Bonding

Put simply, the properties of metals—good conductors whose specific resistance (ρ) is proportional to the absolute temperature $T^\circ\text{K}$ —arise because metals have a (relatively) small number of available valence electrons in comparison with the larger number of low-lying (molecular) bonding orbitals. Thus, metals display multicentre, electron-deficient bonding. The view that the bonding in metals may be described as involving “positive metal ions in a sea of electrons” is misleading, emphasising as it does an ionic nature within the metal. Metals are best regarded as covalent with bonding delocalised throughout the metal lattice, allowing the easy movement of electrons through the lattice.

This easy movement of valence electrons between the atoms of the metallic lattice is responsible essentially—although not exclusively—for the transport of electric current. A small part of the current may be due to the motion of metallic ions. It is worth remembering, however, that at high current densities it is often possible with alloys to observe a change in the concentration of alloy components as a consequence of the passage of current. This effect may be correlated with large differences in the coefficient of electronegativities. It can also be shown that the

geometric arrangement of metal atoms within limits does not unduly affect orbital overlap, thus allowing easy movement of metal atoms with respect to each other without breaking the lattice. The activation energy for such movement is small (~ 0.5 kJ/mol) compared to usual chemical processes (80 to 160 kJ/mol) or fluxional behaviour (20 to 80 kJ/mol). Metal atoms may, therefore, be displaced very easily. This explains, at least to some extent, their malleability and ductility and the ease of polishing of, for example, palladium and platinum. To some degree it may also account for their catalytic properties.

The ability of the metallic surface to undergo structural rearrangement to accommodate the incoming substrate is clearly of importance. It has also been argued that the catalytic activity of the platinum metals is related to the anomalous co-ordination numbers and site deficiencies exhibited by the surface even within regular lattice types. However, it is significant that the importance of the so-called non-lattice symmetries (as in the tetrahedral growth patterns outlined in the scheme and often found for microcrystallites of the platinum metals) in catalysis has been recognised, and it is interesting to record that such geometries are observed with platinum metal cluster compounds, for example Os_6 and Pt_{19} .

However, this description of bonding is far too simple. The chemical bond in metals is far less well defined than in simple molecular species. Unlike simple molecules, the atomic orbitals within a metal do not so easily form a sound basis for discussing the electronic properties of metals. Within the metal the density of orbitals is so high that atomic orbital overlap occurs far beyond the first co-ordination sphere, (next nearest neighbours). It is, therefore, difficult to assign any special chemical significance to the overlap of atomic orbitals on nearest neighbours though it is just this overlap which is used to give a quantum mechanical meaning to the idea of the chemical bond.

Apart from the advantages stemming from high co-ordination numbers and close-packing,

little is known of the basis of geometric arrangement as a source of structural stability—apart from transition metal cluster compounds with up to about six metal atoms. It appears that close-packed structures occur when the concentration of electrons is low (~ 2 electrons per atom) whereas for higher concentrations (~ 2 to 4) directed chemical bonds play a role in the structural arrangement—hence more success with molecular cluster compounds—and structures are no longer close-packed. A major problem in assessing the importance of geometric effects is the lack of any precise knowledge of the suitable sizes of metal atoms. This point is clearly emphasised by the range of metal-metal distances found in cluster compounds. In metals the atoms frequently have vacant orbitals in addition to those containing electrons; in addition they are generally surrounded by far more neighbours than can be bonded by simple electron pair bonds. As a consequence atoms are generally separated by distances considerably greater than those expected for a bond order of one. It follows that there is a considerable latitude in how closely any particular pair of atoms may approach each other without generating a strongly repulsive interaction. For this reason many different interatomic distances are found in the structures of metals, alloys and cluster compounds. Any relationship between bond length and bond order is thus not readily developed for such systems. The compression of atoms may occur in order to produce high coordination numbers, the total summation of bond energies outweighing any energy penalty created. A bond shortening should not, therefore be necessarily interpreted as the result of increased bonding in these directions, since it may arise merely in order to allow more effective contacts between atoms in other directions. In the case of metals it is for this reason that the concept of atomic volume is more meaningful than that of interatomic distance. It follows from these arguments that the more strongly electronegative ligands such as Cl^- cause a contraction in interatomic distance, whereas more strongly electron donating ligands such as CO

cause interatomic expansion in metallic clusters such as $\text{Pt}_5\text{Cl}_{12}$ and $\text{Os}_8(\text{CO})_{18}$, respectively.

Properties of Metals

A chemist's role is to seek general relationship covering a group of elements or compounds and then to look for an explanation of similarities and differences. We will adopt this attitude and seek correlations between the properties of the metal and platinum fundamental atomic parameters. Given that metals are essentially covalent, it is not unreasonable to ask how far one can go in correlating the properties of solid metals with a simple model based on a diatomic molecule.

Physical Properties

For a diatomic molecule (M_2), the vibration frequency (ν) and the force constant (k') are related by the expression

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k'}{\mu}}$$

where μ is reduced mass given by the equation

$$\mu = \frac{M_1 M_2}{M_1 + M_2} \quad \left(\text{or } \frac{M}{2} \right)$$

Physical properties which are dependent on the stretching of M–M bonds should be dependent on k' and hence proportional to $M\nu^2$.

Using this very simple model most of the physical properties may be understood in terms of:

- (a) Multicentre bonding and structure
- (b) The atomic weight (M) of the metal atom
- (c) The mean vibration frequency of the metal atoms in the lattice, or the restoring force constant (k') for the metal atom for a small displacement.

The metal is regarded as an assembly of n metal atoms, each of mass m , oscillating in simple harmonic motion with a range of frequencies which at low temperatures range from ν_0 , ν_1 , ν_2 up to ν_{max} . As the temperature is raised the mean frequency (and amplitude) of vibration of individual atoms increases. At temperatures near to, or above, θ (the so-called Debye temperature) it is assumed that most

Table III			
Physical Properties of Metals at Room Temperature as a Function of the Simple Fundamental Properties of a Metal Atom			
Fundamental property	Bulk physical property		
Multicentre bonding and structure	Electrical conductivity Malleability Ductility Ease of polishing Polymorphism	Elasticity Coefficient of expansion Hardness	Melting point Electrical conductivity Thermal conductivity
Mass M , ν_{\max}			
Mass M , ν_{\max} , $\langle \bar{x}^2 \rangle$			

Table IV			
Ionisation Energies, ΔU_0 (kJ/mol)			
[Ionisation Potentials, I (eV)], from (3)			
	1st	2nd	3rd
Iron	762 (7.90)	1561 (16.18)	2956 (30.64)
Ruthenium	710.6 (7.364)	1617 (16.76)	2746 (28.46)
Osmium	840 (8.7)	1640 (17.0)	
Cobalt	758 (7.86)	1644 (17.05)	3231 (33.49)
Rhodium	720 (7.46)	1744 (18.07)	2996 (31.05)
Iridium	900 (9)		
Nickel	736.5 (7.633)	1752 (18.15)	3489 (36.16)
Palladium	804 (8.33)	1874 (19.42)	3177 (32.92)
Platinum	870 (9.0)	1791 (18.56)	
Copper	745.2 (7.724)	1958 (20.29)	3545 (36.83)
Silver	730.8 (7.574)	2072 (21.48)	3360 (34.82)
Gold	889 (9.22)	1980 (20.5)	

atoms are vibrating with a frequency ν_{\max} provided that θ is not too large compared with room temperature, and the expression

$$h\nu_{\max} = k\theta$$

may be used.

(d) The mean amplitude of vibration of the metal atoms.

For a particle of mass m vibrating in simple harmonic motion the kinetic energy is given by $\frac{1}{2}k'\bar{x}^2$ ($\bar{x}^2 =$ mean square of the amplitude of vibration), which may be rewritten as $CM\theta^2\langle \bar{x}^2 \rangle$ ($C =$ constant), and since the energy is proportional to $T^\circ K$ then

$$\bar{x}^2 \propto \frac{T}{M\theta^2}$$

Thus, properties dependent on \bar{x}^2 should be

proportional to $T^\circ K$. Within this class fall melting point, electrical conductivity and thermal conductivity.

This information is classified in Table III.

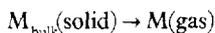
Properties dependent on (a), namely multicentre bonding and the ability to undergo structural rearrangement, will be electrical conductivity, malleability, ductility, ease of polishing, and polymorphism. Those properties which will also be dependent on (b) and (c), the mass of the metal atom (M) and the vibration frequency (ν_{\max}) will include elasticity, the thermal coefficient of expansion and hardness. Finally there are those properties which will depend not only on (a), (b) and (c) but also on (d), the amplitude of vibration (\bar{x}^2). Since \bar{x}^2 is

proportional to $T^\circ\text{K}$ these will include melting point, electrical conductivity and thermal conductivity.

Chemical Properties

For an understanding of the chemical properties of metals knowledge of four further parameters is necessary. These parameters are:

- (i) The heat of atomisation of the metal ($\Delta H_{\text{at}}^\circ$), that is the heat absorbed during the process:



at 298°K and one atmosphere pressure.

Essentially it may be taken as a measure of the M-M bond strength ($E_{\text{M-M}}$). The manner in which $\Delta H_{\text{at}}^\circ$ (and thus $E_{\text{M-M}}$) varies within the transition metal block is shown in Figure 5. Some of the highest values are found for the platinum metals although the values for palladium, silver, and gold are smaller than those for several first row elements. A plot of the boiling points against $\Delta H_{\text{at}}^\circ$ values is

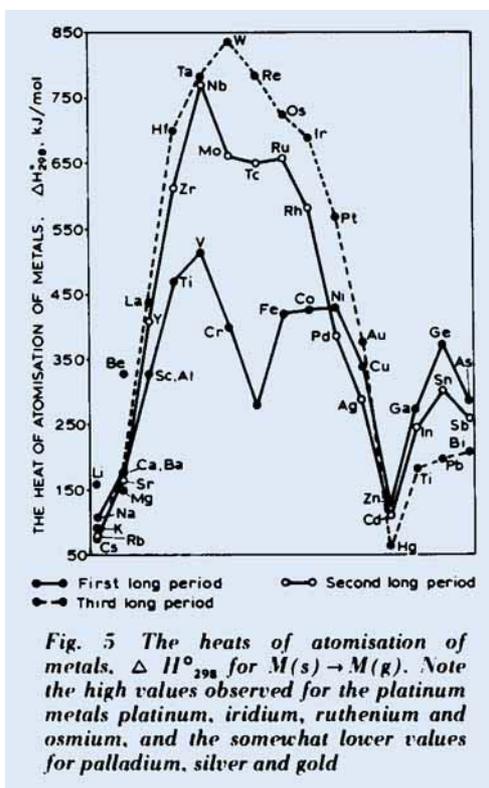
Iron	Cobalt	Copper	Potassium
1.8	1.8	1.9	0.8
Ruthenium	Rhodium	Silver	Rubidium
2.2	2.2	1.9	0.8
Osmium	Iridium	Gold	Caesium
2.2	2.2	2.4	0.7

roughly linear, suggesting that the boiling point of a metal is largely dependent on $E_{\text{M-M}}$. It would appear that there is very little disruption of the metallic bonding when the crystal melts, and nearly all metallic bond strength is conserved until the metal boils.

- (ii) The ionisation energy for the formation of the appropriate ion M^{n+} (I.P.).

The ionisation energies (and potentials) for the platinum metals are given in Table IV.

Among the platinum metals the third row elements, osmium, iridium and platinum, exhibit very high first ionisation energies. However, as elsewhere in the transition metal block, values for some members of the second row are less than those of the first row, for example $\text{Ru} < \text{Fe} < \text{Os}$, $\text{Rh} < \text{Co} < \text{Ir}$ and $\text{Ag} < \text{Cu} < \text{Au}$, but a revision occurs in the nickel triad $\text{Ni} < \text{Pd} < \text{Pt}$. The very high values of $\Delta H_{\text{at}}^\circ$ and ionisation energies for the members of the third row are clearly responsible for the relative inertness of these metals. The high values of $\Delta H_{\text{at}}^\circ$ for osmium, iridium and platinum must also be largely responsible for the tendency that these metals have to form cluster compounds. It may be argued that by forming such clusters the energy required is a fraction of that necessary to produce individual atoms. Furthermore, one of the consequences of the multicentre bonding approach—or broadening of the energy levels containing the valence electrons into an energy band—is that the minimum energy required to remove an electron from the bulk metal is much



less than the ionisation energy of the free atoms. This so-called work function may be determined from photoelectric measurements. It follows that the energy required to remove an electron from a small cluster of atoms will also be less than the ionisation energy, although certainly more than the work function. Hence both ΔH_{at}° and ionisation energies favour cluster formation as opposed to the formation of simple monometal compounds.

(iii) The electron affinity (E.A.) of the metal atom—for which few reliable data have been obtained—and

(iv) The electronegativity (χ) of the metal atom.

Values of electronegativity coefficients, as derived by Pauling, are given in Table V. Metals with the largest electronegativity values include the noble metals with coefficients in the range 1.9 (silver) to 2.4 (gold). These values may be compared to those of the more electropositive metals rubidium (0.8) and caesium (0.7). As listed above a pure metal has essentially covalent multicentre bonding and replacement of one metal by another of a similar kind produces an alloy with similar bonding. In con-

trast, if two metals of widely differing electronegativities are employed then an ionic compound results. Such is the case with caesium and gold giving Cs^+Au^- . As such, gold may be regarded as a *quasi* halide. It is worth remembering in any discussion of this sort that electronegativity values are dependent on their source. The Pauling values, derived from bond energies of chemical compounds, tend to be larger than those of Mulliken given by $(I.P. + E.A.)/2$.

Conclusion

Any simplistic approach such as that offered here can at best offer only a limited guide to the behaviour, both physical and chemical, of the platinum metals. Nevertheless, such a simple model is not without its attractions. Certainly it can act as a useful guide and can offer some understanding of the multitude of factors responsible for the so-called metallic properties.

References

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- 3 W. E. Dasent, "Inorganic Energetics", Penguin Books, 1970

Progress by Rustenburg Platinum Mines

Rustenburg Platinum Mines has recently reported progress in a number of important areas. Prospecting operations around Potgietersrust, reported here a year ago, are now nearing completion, although it will be some time before metallurgical and feasibility studies are concluded. Expansion at the Amandelbult Section, to provide capacity for a previously announced contract, has been completed, as has the sinking and commissioning of a new shaft at the Rustenburg Section of the mine.

At the Union Section a second electric smelting furnace, shown here, is now fully operational. The rectangular furnace is of the submerged arc type and has six large consumable electrodes. Electric smelting is highly efficient and permits more economical production than the traditional blast furnace. Molten matte, consisting of the platinum metals together with very much larger amounts of iron, copper and nickel sulphides, is periodically

tapped from the furnace and fed into the two large refractory-lined steel ladles, each with a capacity of 15 tonnes, for transport by overhead crane to the casting area.

