

																1	2																
																H	He																
3	4															5	6	7	8	9	10												
Li	Be															B	C	N	O	F	Ne												
11	12															13	14	15	16	17	18												
Na	Mg															Al	Si	P	S	Cl	Ar												
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36																
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54																
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																
55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72																
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																
87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102																		
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub																						
73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90																
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu																				
91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108																
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr																				

# 27

## Nickel, Palladium and Platinum

### 27.1 Introduction

An alloy of nickel was known in China over 2000 years ago, and Saxon miners were familiar with the reddish-coloured ore, NiAs, which superficially resembles Cu<sub>2</sub>O. These miners attributed their inability to extract copper from this source to the work of the devil and named the ore “Kupfernickel” (Old Nick’s copper). In 1751 A. F. Cronstedt isolated an impure metal from some Swedish ores and, identifying it with the metallic component of Kupfernickel, named the new metal “nickel”. In 1804 J. B. Richter produced a much purer sample and so was able to determine its physical properties more accurately.

Impure, native platinum seems to have been used unwittingly by ancient Egyptian craftsmen in place of silver, and was certainly used to make small items of jewellery by the Indians of Ecuador before the Spanish conquest. The introduction of the metal to Europe is a complex and intriguing story.<sup>(1)</sup> In 1736 A. de Ulloa, a Spanish astronomer and naval officer, observed an unworkable metal, *platina* (Spanish, little

silver), in the gold mines of what is now Colombia. Returning home in 1745 his ship was attacked by privateers and finally captured by the British navy. He was brought to London and his papers confiscated, but was fortunately befriended by members of the Royal Society and was indeed elected to that body in 1746 when his papers were returned. Meanwhile, in 1741, C. Wood brought to England the first samples of the metal and, following the eventual publication of de Ulloa’s report in 1748, investigation of its properties began in England and Sweden. It became known as “white gold” (a term now used to describe an Au/Pd alloy) and the “eighth metal” (the seven metals Au, Ag, Hg, Cu, Fe, Sn and Pb having been known since ancient times). Great difficulty was experienced in working it because of its high mp and brittle nature (due to impurities of Fe and Cu). Powder metallurgical techniques of fabrication were developed<sup>†</sup> in great secrecy in Spain by the

<sup>†</sup> Precedence must in fact be given to the South American Indians to whom platinum was available only in the form of fine, hand-separated grains which must have been fabricated by ingenious, if crude, powder metallurgy.

<sup>1</sup> L. B. HUNT, *Platinum Metals Rev.* **24**, 31–9 (1980).

Frenchman P. F. Chabeneau, and subsequently in London by W. H. Wollaston,<sup>(2)</sup> who in the years 1800–21 produced well over 1 tonne of malleable platinum. These techniques were developed because the chemical methods used to isolate the metal produced an easily powdered spongy precipitate. Not until the availability, half a century later, of furnaces capable of sustaining sufficiently high temperatures was easily workable, fused platinum commercially available.

In 1803, in the course of his study of platinum, Wollaston isolated and identified palladium from the mother liquor remaining after platinum had been precipitated as  $(\text{NH}_4)_2\text{PtCl}_6$  from its solution in aqua regia. He named it after the newly discovered asteroid, Pallas, itself named after the Greek goddess of wisdom ( $\pi\alpha\lambda\lambda\acute{\alpha}\delta\iota\omicron\nu$ , palladion, of Pallas).

## 27.2 The Elements

### 27.2.1 Terrestrial abundance and distribution

Nickel is the seventh most abundant transition metal and the twenty-second most abundant element in the earth's crust (99 ppm). Its commercially important ores are of two types:

- (1) *Laterites*, which are oxide/silicate ores such as garnierite,  $(\text{Ni,Mg})_6\text{Si}_4\text{O}_{10}(\text{OH})_8$ , and nickeliferous limonite,  $(\text{Fe,Ni})\text{O}(\text{OH})\cdot n\text{H}_2\text{O}$ , which have been concentrated by weathering in tropical rainbelt areas such as New Caledonia, Cuba and Queensland.
- (2) *Sulfides* such as pentlandite,  $(\text{Ni,Fe})_9\text{S}_8$ , associated with copper, cobalt and precious metals so that the ores typically contain about  $1\frac{1}{2}\%$  Ni. These are found in more temperate regions such as Canada, the former Soviet Union and South Africa.

Arsenide ores such as niccolite ( $\text{Kupfernickel}$  ( $\text{NiAs}$ ), smaltite  $(\text{Ni,Co,Fe})\text{As}_2$ ) and nickel glance ( $\text{NiAsS}$ ) are no longer of importance.

The most important single deposit of nickel is at Sudbury Basin, Canada. It was discovered in 1883 during the building of the Canadian Pacific Railway and consists of sulfide outcrops situated around the rim of a huge basin 17 miles wide and 37 miles long (possibly a meteoritic crater). Fifteen elements are currently extracted from this region (Ni, Cu, Co, Fe, S, Te, Se, Au, Ag and the six platinum metals).

Although estimates of their abundances vary considerably, Pd and Pt (approximately 0.015 and 0.01 ppm respectively) are much rarer than Ni. They are generally associated with the other platinum metals and occur either native in placer (i.e. alluvial) deposits or as sulfides or arsenides in Ni, Cu and Fe sulfide ores. Until the 1820s all platinum metals came from South America, but in 1819 the first of a series of rich placer deposits which were to make Russia the chief source of the metals for the next century, was discovered in the Urals. More recently however, the copper-nickel ores in South Africa and Russia (where the Noril'sk-Talnakh deposits are well inside the Arctic Circle) have become the major sources, supplemented by supplies from Sudbury.

### 27.2.2 Preparation and uses of the elements<sup>(3,3a,4)</sup>

Production methods for all three elements are complicated and dependent on the particular ore involved; they will therefore only be sketched in outline. In the case of nickel the oxide ores are not generally amenable to concentration by normal physical separations and so the whole ore has to be treated. By contrast the sulfide ores

<sup>3</sup> J. HILL in D. THOMPSON (ed.), *Insights into Speciality Inorganic Chemicals*, pp. 5–34, R.S.C., Cambridge, 1995.

<sup>3a</sup> Kirk–Othmer *Encyclopedia of Chemical Technology*, 4th edn., Interscience, New York: Ni, 17, 1–47 (1996); Pt metals, 19, 347–407 (1996).

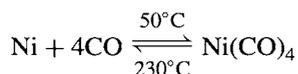
<sup>4</sup> F. R. HARTLEY (ed.) *Chemistry of the Platinum Group Metals*, Elsevier, Amsterdam, 1991, 642 pp.

<sup>2</sup> J. C. CHASTON, *Platinum Metals Rev.* 24, 70–9 (1980).

can be concentrated by flotation and magnetic separations, and for this reason they provide the major part of the world's nickel, though the use of laterite ores is appreciable.

A quarter of the world's nickel comes from Sudbury and there silica is added to the nickel/copper concentrates which are then subjected to a series of roasting and smelting operations. This reduces the sulfide and iron contents by converting the iron sulfide first to the oxide and then to the silicate which is removed as a slag. The resulting "matte" of nickel and copper sulfides is allowed to cool over a period of days, when  $\text{Ni}_3\text{S}_2$ ,  $\text{Cu}_2\text{S}$  and Ni/Cu metal<sup>†</sup> form distinct phases which can be mechanically separated. (In the older, Orford, process the matte was heated with  $\text{NaHSO}_4$  and coke, producing molten  $\text{Na}_2\text{S}$  which dissolved the copper sulfide and formed an upper layer, leaving the nickel sulfide below; on solidification the silvery upper layer was cut from the black lower layer — hence the process was commonly called the "tops and bottoms" process.) The matte may be cast directly as anode with pure nickel sheet as cathode and electrolysed using an aqueous  $\text{NiSO}_4$ ,  $\text{NiCl}_2$  electrolyte. Alternatively, the matte may be leached with hydrochloric acid, nickel chloride crystallized and converted to the oxide by high temperature oxidation with air, and finally the oxide reduced to the metal by  $\text{H}_2$  at  $600^\circ\text{C}$ .

The carbonyl process developed in 1899 by L. Mond is still used, though it is mainly of historic interest. In this the heated oxide is first reduced by the hydrogen in water gas ( $\text{H}_2 + \text{CO}$ ). At atmospheric pressure and a temperature around  $50^\circ\text{C}$ , the impure nickel is then reacted with the residual CO to give the volatile  $\text{Ni}(\text{CO})_4$ . This is passed over nucleating pellets of pure nickel at a temperature of  $230^\circ\text{C}$  when it decomposes, depositing nickel of 99.95% purity and leaving CO to be recycled.



<sup>†</sup> This metallic phase is worked for precious metals which are preferentially dissolved in it.

Somewhat higher pressures and temperatures (e.g. 20 atm and  $150^\circ\text{C}$ ) are used to form the carbonyl in modern Canadian plant, but the essential principle of the Mond process is retained.

Total world production of nickel is in the region of 1.0 million tonnes pa of which (1995) 25% comes from the former Soviet Union, 18% from Canada, 12% from New Caledonia and 10% from Australia. The bulk of this is used in the production of alloys both ferrous and non-ferrous. In 1889 J. Riley of Glasgow published a report on the effect of adding nickel to steel. This was noticed by the US Navy who initiated the use of nickel steels in armour plating. Stainless steels contain up to 8% Ni and the use of "Alnico" steel for permanent magnets has already been mentioned (p. 1114).

The non-ferrous alloys include the misleadingly named nickel silver (or German silver) which contains 10–30% Ni, 55–65% Cu and the rest Zn; when electroplated with silver (electroplated nickel silver) it is familiar as EPNS tableware. *Monel* (68% Ni, 32% Cu, traces of Mn and Fe) is used in apparatus for handling corrosive materials such as  $\text{F}_2$ ; cupro-nickels (up to 80% Cu) are used for "silver" coinage; *Nichrome* (60% Ni, 40% Cr), which has a very small temperature coefficient of electrical resistance, and *Invar*, which has a very small coefficient of expansion are other well-known Ni alloys. Electroplated nickel is an ideal undercoat for electroplated chromium, and smaller amounts of nickel are used as catalysts in the hydrogenation of unsaturated vegetable oils and in storage batteries such as the Ni/Fe batteries.

Ninety-eight per cent of the world's supply of platinum metals comes from three countries — the former Soviet Union (49%), the Republic of South Africa (43%), and Canada (6%). Because of the different proportions of Pt and Pd in their deposits, the Republic of South Africa is the major source of Pt and the former USSR of Pd. Only in the RSA (where the Bushveld complex contains over 70% of the world's reserves of the platinum metals at concentrations of 8–9 grams per tonne) are the

platinum metals the primary products. Elsewhere, with concentrations of a mere fraction of a gramme per tonne, millions of tonnes of ore must be mined, milled and smelted each year. Precious metal concentrates are obtained either from the metallic phase of the sulfide matte (see above) or as anode slimes in the electrolytic refinement of the baser metals. From these, all six platinum metals as well as Ag and Au are obtained by a composite process. Traditional methods were based on selective precipitation and developed to suit the composition of the

concentrate. Although these methods are still in use the efficiency of the separations is not high and costly recycling is required. Solvent extraction and ion exchange techniques offer superior efficiency and are increasingly replacing the classical processes. Fig. 27.1 outlines a typical solvent extraction process (see also p. 1073 and p. 1114).

Current annual world production of all platinum metals is around 380 tonnes of which perhaps 150 tonnes is platinum and 210 tonnes is palladium. 35-40% of Pt and about half as

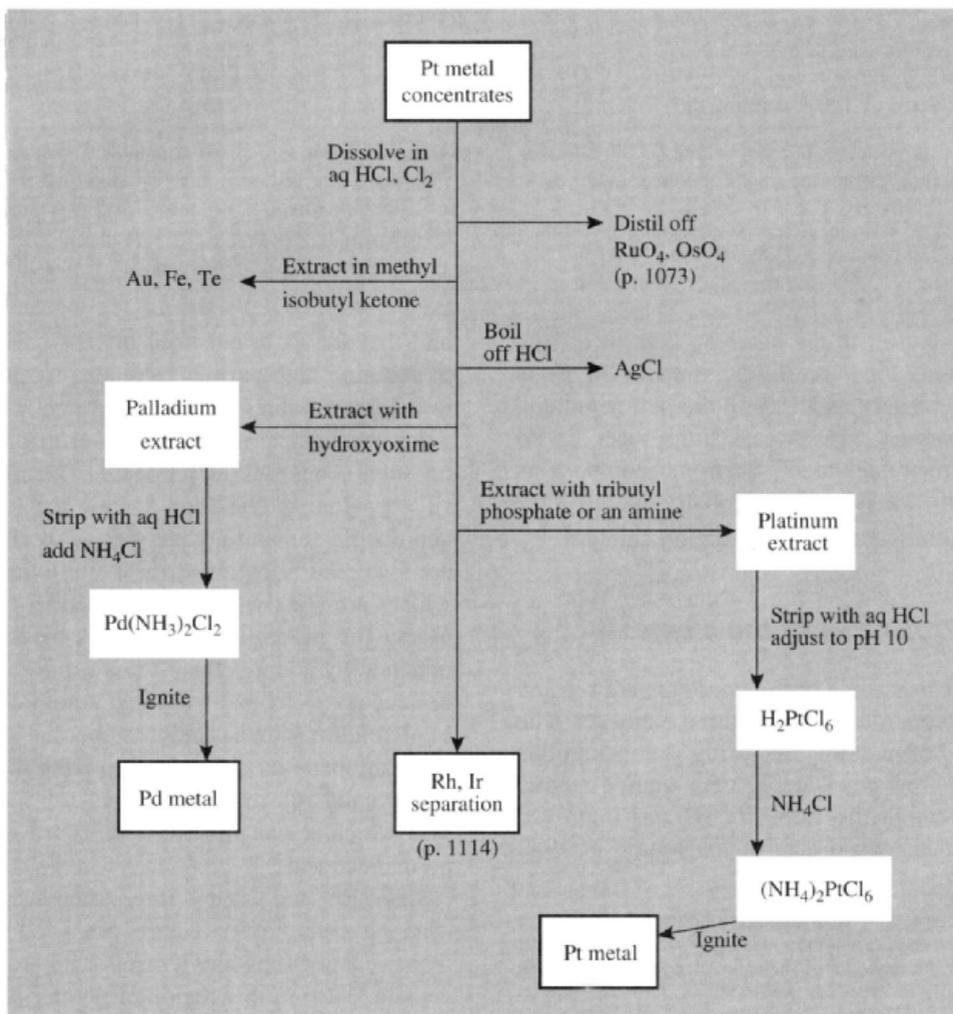


Figure 27.1 Flow diagram for refining palladium and platinum by solvent extraction.

Table 27.1 Some properties of the elements nickel, palladium and platinum

Property	Ni	Pd	Pt
Atomic number	28	46	78
Number of naturally occurring isotopes	5	6	6 <sup>(a)</sup>
Atomic weight	58.6934(2)	106.42(1)	195.078(2)
Electronic configuration	[Ar]3d <sup>8</sup> 4s <sup>2</sup>	[Kr]4d <sup>10</sup>	[Xe]4f <sup>14</sup> 5d <sup>9</sup> 6s <sup>1</sup>
Electronegativity	1.8	2.2	2.2
Metal radius (12-coordinate)/pm	124	137	138.5
Effective ionic radius (6-coordinate)/pm	—	—	57
	IV	61.5	62.5
	III	76	—
	II	86	80
MP/°C	1455	1552	1769
BP/°C	2920	2940	4170
$\Delta H_{\text{fus}}/\text{kJ mol}^{-1}$	17.2(±0.3)	17.6(±2.1)	19.7(±2.1)
$\Delta H_{\text{vap}}/\text{kJ mol}^{-1}$	375(±17)	362(±11)	469(±25)
$\Delta H_{\text{f}}(\text{monatomic gas})/\text{kJ mol}^{-1}$	429(±13)	377(±3)	545(±21)
Density (20°C)/g cm <sup>-3</sup>	8.908	11.99	21.45
Electrical resistivity (20°C)/μohm cm	6.84	9.93	9.85

<sup>(a)</sup>All have zero nuclear spin except <sup>195</sup>Pt (33.8% abundance) which has a nuclear spin quantum number  $\frac{1}{2}$ : this isotope finds much use in nmr spectroscopy both via direct observation of the <sup>195</sup>Pt resonance and even more by the observation of <sup>195</sup>Pt “satellites”. Thus, a given nucleus coupled to <sup>195</sup>Pt will be split into a doublet symmetrically placed about the central unsplit resonance arising from those species containing any of the other 5 isotopes of Pt. The relative intensity of the three resonances will be  $(\frac{1}{2} \times 33.8):66.2:(\frac{1}{2} \times 33.8)$ , i.e. 1:4:1.

much Pd is used in the catalytic control of car-exhaust emissions. A similar amount of Pt is used for jewellery and 18% in the petroleum and glass industries. The largest single use for Pd is in the manufacture of electronic components (46%), but 25% is used in dentistry and 10% for hydrogenation and dehydrogenation catalysis.<sup>†</sup>

### 27.2.3 Properties of the elements

Table 27.1 lists some of the important atomic and physical properties of these three elements. The prevalence of naturally occurring isotopes in this triad limits the precision of their quoted atomic weights, though the value for Ni was improved by more than two orders of magnitude in 1989

<sup>†</sup> It should not be overlooked that platinum has played a crucial role in the development of many branches of science even though the amounts of metal involved may have been small. Reliable Pt crucibles were vital in classical analysis on which the foundations of chemistry were laid. It was also widely used in the development of the electric telegraph, incandescent lamps, and thermionic valves.

and that for Pt fifteen fold in 1995. Difficulties in attaining high purities have also frequently led to disparate values for some physical properties, while mechanical history has considerable effect on such properties as hardness. The metals are silvery-white and lustrous, and are both malleable and ductile so that they are readily worked. They are also readily obtained in finely divided forms which are catalytically very active. *Platinum black*, for instance, is a velvety-black powder obtained by adding ethanol to a solution of PtCl<sub>2</sub> in aqueous KOH and warming. Another property of platinum which has led to numerous laboratory applications is its coefficient of expansion which is virtually the same as that of soda glass into which it can therefore be fused to give a permanent seal.

Like Rh and Ir, all three members of this triad have the fcc structure predicted by band theory calculations for elements with nearly filled d shells. Also in this region of the periodic table, densities and mps are decreasing with increase in Z across the table: thus, although by comparison

with the generality of members of the d block these elements are in each case to be considered as dense refractory metals, they are somewhat less so than their immediate predecessors, and palladium has the lowest density and melting point of any platinum metal.

Nickel is ferromagnetic, but less markedly so than either iron or cobalt and its Curie point (375°C) is also lower.

### 27.2.4 Chemical reactivity and trends

In the massive state none of these elements is particularly reactive and they are indeed very resistant to atmospheric corrosion at normal temperatures. However, nickel tarnishes when heated in air and is actually pyrophoric if very finely divided (finely divided Ni catalysts should therefore be handled with care). Palladium will also form a film of oxide if heated in air.

Nickel reacts on heating with B, Si, P, S and the halogens, though more slowly with F<sub>2</sub> than most metals do. It is oxidized at red heat by steam, and will dissolve in dilute mineral acids: slowly in most but quite rapidly in dil HNO<sub>3</sub>. Conc HNO<sub>3</sub>, on the other hand, renders it passive and dry hydrogen halides have little effect. It has a notable resistance to attack by aqueous caustic alkalis and therefore finds used in apparatus for producing NaOH.

Palladium is oxidized by O<sub>2</sub>, F<sub>2</sub> and Cl<sub>2</sub> at red heat and dissolves slowly in oxidizing acids. Platinum is generally more resistant to attack than Pd and is, for instance, barely affected by mineral acids except aqua regia. However, both metals dissolve in fused alkali metal oxides and peroxides. It is also wise to avoid heating compounds containing B, Si, Pb, P, As, Sb or Bi in platinum crucibles under reducing conditions (e.g. the blue flame of a bunsen burner) since these elements form low-melting eutectics with Pt which cause the metal to collapse. All three elements absorb molecular hydrogen to an extent which depends on their physical state, but palladium does so to an extent which is unequalled by any other metal (section 27.3.1).

A list of typical compounds of these elements is given in Table 27.2 and it is noticeable that the reduction in the range of oxidation states compared to that in previous groups is continuing and differences between the two heavier elements are becoming increasingly evident. The maximum oxidation state is +6 but this is attained only by the heaviest element, platinum, in PtF<sub>6</sub>; nickel and palladium only reach +4. At the other extreme, palladium and platinum provide no oxidation state below zero. The changes down the triad implied by these facts are also evidenced by those oxidation states which are the most stable for each element. For nickel, +2 is undoubtedly the most common and provides that element's most extensive aqueous chemistry. For palladium, +2 is again the most common, and [Pd(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> like [Pt(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> occurs in aqueous solutions from which potential ligands are excluded. For platinum, however, both +2 and +4 are prolific and form a vital part of early as well as more recent coordination chemistry.

Table 27.2 also reveals the reluctance of these elements to form compounds with high coordination numbers, a coordination number of 6 being rarely exceeded. In the divalent state nickel exhibits a wide and interesting variety of coordination numbers and stereochemistries which often exist simultaneously in equilibrium with each other, whereas palladium and platinum have a strong preference for the square planar geometry. The kinetic inertness of Pt<sup>II</sup> complexes has led to their extensive use in studies of geometrical isomerism and reaction mechanisms. As will be seen presently, these differences between the lightest and heaviest members of the triad can be largely rationalized by reference to their CFSEs.

Also in the divalent state, Pd and Pt show the class-b characteristic of preferring CN<sup>-</sup> and ligands with nitrogen or heavy donor atoms rather than oxygen or fluorine. Platinum(IV) by contrast is more nearly class-a in character and is frequently reduced to Pt<sup>II</sup> by *P*- and *As*-donor ligands. The organometallic chemistry of these metals is rich and varied and that involving unsaturated hydrocarbons is the most familiar of its type.

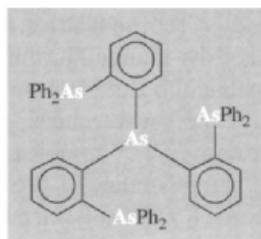
**Table 27.2** Oxidation states and stereochemistries of compounds of nickel, palladium and platinum

Oxidation state	Coordination number	Stereochemistry	Ni	Pd/Pt
-1	4	?	$[\text{Ni}_2(\text{CO})_6]^{2-}$	
0 ( $d^{10}$ )	3	Planar	$[\text{Ni}\{\text{P}(\text{OC}_6\text{H}_4\text{-2-Me})_3\}_3]$	$[\text{M}(\text{PPh}_3)_3]$
	4	Tetrahedral	$[\text{Ni}(\text{CO})_4]$	$[\text{M}(\text{PF}_3)_4]$
1 ( $d^9$ )	4	Tetrahedral	$[\text{NiBr}(\text{PPh}_3)_3]$	
	3	Trigonal planar	$[\text{Ni}(\text{NPh}_2)_3]^-$	
2 ( $d^8$ )	4	Tetrahedral	$[\text{NiCl}_4]^{2-}$	
		Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$	$[\text{MCl}_4]^{2-}$
	5	Trigonal bipyramidal	$[\text{Ni}(\text{PPhMe}_2)_3(\text{CN})_2]$	$[\text{M}(\text{qas})\text{I}]^{+(a)}$
		Square pyramidal	$[\text{Ni}(\text{CN})_5]^{3-}$	$[\text{Pd}(\text{tpas})\text{Cl}]^{+(b)}$
	6	Octahedral	$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	$[\text{Pd}(\text{diars})_2\text{I}_2]$
		Trigonal prismatic	NiAs	
	7	Pentagonal bipyramidal	$[\text{Ni}(\text{dapbH})_2(\text{H}_2\text{O})_2]^{2+(c)}$	
3 ( $d^7$ )	4	Square planar	—	$[\text{Pt}(\text{C}_6\text{Cl}_5)_4]^-$
	5	Trigonal bipyramidal	$[\text{NiBr}_3(\text{PET}_3)_2]$	
	6	Octahedral	$[\text{NiF}_6]^{3-}$	$[\text{PdF}_6]^{3-}$
4 ( $d^6$ )	6	Octahedral	$[\text{NiF}_6]^{2-}$	$[\text{MCl}_6]^{2-}$
	8	“Piano-stool”	—	$[\text{Pt}(\eta^5\text{-C}_5\text{H}_5)\text{Me}_3]$
5 ( $d^5$ )	6	Octahedral	—	$[\text{PtF}_6]^-$
6 ( $d^4$ )	6	Octahedral	—	$\text{PtF}_6$

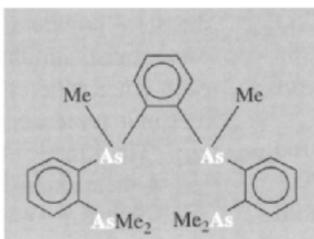
<sup>(a)</sup>qas, tris-(2-diphenylarsinophenyl)arsine,  $\text{As}(\text{C}_6\text{H}_4\text{-2-AsPh}_2)_3$ .

<sup>(b)</sup>tpas, 1,2-phenylenebis((2-dimethylarsinophenyl)-methylarsine).

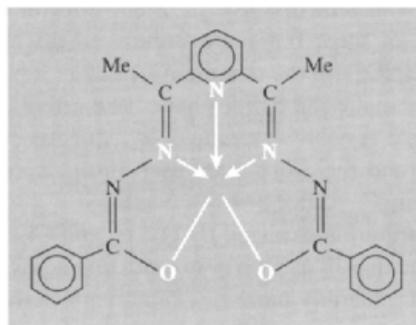
<sup>(c)</sup>dapbH, 2,6-diacetylpyridinebis(benzoic acid hydrazone).



(a)



(b)



(c)

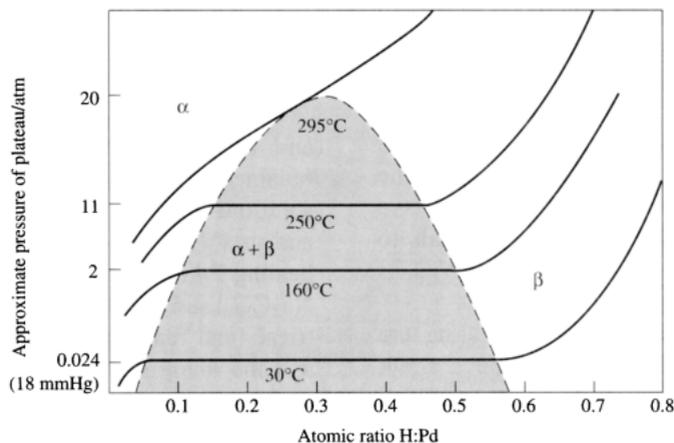
## 27.3 Compounds of Nickel, Palladium and Platinum

Such binary borides (p. 145), carbides (p. 297) and nitrides (p. 417) as are formed have been referred to already. The ability of the metals to absorb molecular hydrogen has also been alluded to above. While the existence of definite hydrides of nickel and platinum is in doubt the

existence of definite palladium hydride phases is not.

### 27.3.1 The Pd/H<sub>2</sub> system

The absorption of molecular hydrogen by metallic palladium has been the subject of theoretical and practical interest ever since 1866 when T. Graham reported that, on being cooled from red heat, Pd can absorb (or “occlude” as



**Figure 27.2** Pressure-concentration isotherms for the Pd/H<sub>2</sub> system: the biphasic region (in which the  $\alpha$ - and  $\beta$ -phases coexist) is shaded. (From A. G. Knapton, *Plat. Met. Revs.* **21**, 44 (1977). See also F. A. LEWIS, *ibid.* **38**, 112–18 (1994))

he called it) up to 935 times its own volume of H<sub>2</sub>.<sup>†</sup> The gas is given off again on heating and this provides a convenient means of weighing H<sub>2</sub> — a fact utilized by E. W. Morley in his classic work on the composition of water (1895).

As hydrogen is absorbed, the metallic conductivity falls until the material becomes a semiconductor at a composition of about PdH<sub>0.5</sub>. Palladium is unique in that it does not lose its ductility until large amounts of H<sub>2</sub> have been absorbed. The hydrogen is first chemisorbed at the surface of the metal but at increased pressures it enters the metal lattice and the so-called  $\alpha$ - and  $\beta$ -phase hydrides are formed (Fig. 27.2). The basic lattice structure is not altered but, whereas the  $\alpha$ -phase causes only a slight expansion, the  $\beta$ -phase causes an expansion of up to 10% by volume. The precise nature of the metal–hydrogen interaction is still unclear<sup>‡</sup> but the hydrogen has a high

mobility within the lattice and diffuses rapidly through the metal. This process is highly specific to H<sub>2</sub> and D<sub>2</sub>, palladium being virtually impervious to all other gases, even He, a fact which is utilized in the separation of hydrogen from mixed gases. Industrial installations with outputs of up to 9 million ft<sup>3</sup>/day (255 million litres/day) are operated and it is of great importance in these that formation of the  $\beta$ -phase hydride is avoided, since the gross distortions and hardening which accompany it may result in splitting of the diffusion membrane. This can be done by maintaining the temperature above 300°C (Fig. 27.2), or alternatively by alloying the Pd with about 20% Ag which has the additional advantage of actually increasing the permeability of the Pd to hydrogen (p. 39).

### 27.3.2 Oxides and chalcogenides

The elements of this group form only one reasonably well-characterized oxide each, namely NiO, PdO and PtO<sub>2</sub>, although claims for the existence of many others have been made. Formation of NiO by heating the metal in oxygen

<sup>†</sup> This approximates to a composition of Pd<sub>4</sub>H<sub>3</sub> and represents a concentration of hydrogen approaching that in liquid hydrogen!

<sup>‡</sup> In March 1989 S. Pons and M. Fleischmann reported the production of excess heat from heavy water electrolysis using Pd cathode and Pt anode, and postulated nuclear fusion (“cold fusion”) as the reason. In spite of widespread scepticism, work in many laboratories was quickly initiated and focused on: (a) measuring the excess heat effect, and (b) identifying any nuclear particles produced. Emissions of <sup>4</sup>He, <sup>3</sup>H and <sup>1</sup>n have been variously reported and it appears that production of

excess heat is associated with very heavy deuterium loading of Pd in the  $\beta$ -phase. Reproducibility is, however, poor and it seems probable that more than one effect is involved. The current consensus is against a “cold-fusion” explanation of the effects.

is difficult to achieve and incomplete conversion may well account for some of the claims for other nickel oxides, while grey to black colours probably arise from slight nonstoichiometry. It is best prepared as a green powder with the rock-salt structure (p. 242) by heating the hydroxide, carbonate or nitrate.  $\text{Ni}(\text{OH})_2$  is a green precipitate obtained by adding alkali to aqueous solutions of  $\text{Ni}^{\text{II}}$  salts and, like  $\text{NiO}$ , is entirely basic, dissolving easily in acids.

Black  $\text{PdO}$  can be produced by heating the metal in oxygen but it dissociates above about  $900^\circ\text{C}$ . It is insoluble in acids. However, addition of alkali to aqueous solutions of  $\text{Pd}(\text{NO}_3)_2$  produces a gelatinous dark-yellow precipitate of the hydrous oxide which is soluble in acids but cannot be fully dehydrated without loss of oxygen. No other palladium oxide has been characterized although the addition of alkali to aqueous solutions of  $\text{Pd}^{\text{IV}}$  produces a strongly oxidizing, dark-red precipitate which slowly loses oxygen and, at  $200^\circ\text{C}$ , forms  $\text{PdO}$ .

Addition of alkali to aqueous solutions of  $[\text{Pt}(\text{H}_2\text{O})_4](\text{ClO}_4)_2$  under an atmosphere of argon gives a white amphoteric hydroxide of  $\text{Pt}^{\text{II}}$  at pH 4 which redissolves at pH 10.<sup>(5)</sup> The precipitate slowly turns black at room temperature (more rapidly when dried at  $100^\circ\text{C}$ ) and has been formulated as  $\text{PtO}_x \cdot \text{H}_2\text{O}$ , but it is too unstable to be properly characterized. The stable oxide of platinum is found, instead, in the higher oxidation state. Addition of alkali to aqueous solutions of  $\text{PtCl}_4$  yields a yellow amphoteric precipitate of the hydrated dioxide which redissolves on being boiled with an excess of strong alkali to give solutions of  $[\text{Pt}(\text{OH})_6]^{2-}$ ; it also dissolves in acids. Dehydration by heating produces almost black  $\text{PtO}_2$  but this decomposes to the elements above  $650^\circ\text{C}$  and cannot be completely dehydrated without some loss of oxygen.

Nickel sulfides are very similar to those of cobalt, consisting of  $\text{NiS}_2$  (pyrites structure, p. 680),  $\text{Ni}_3\text{S}_4$  (spinel structure, p. 247), and the black, nickel-deficient  $\text{Ni}_{1-x}\text{S}$  (NiAs structure, p. 555), which is precipitated from aqueous

solutions of  $\text{Ni}^{\text{II}}$  by passing  $\text{H}_2\text{S}$ . There are also numerous metallic phases having compositions between  $\text{NiS}$  and  $\text{Ni}_3\text{S}_2$ .

Palladium and platinum both form a mono- and a di-sulfide. Brown  $\text{PdS}$  and black  $\text{PtS}_2$  are obtained when  $\text{H}_2\text{S}$  is passed through aqueous solutions of  $\text{Pd}^{\text{II}}$  and  $\text{Pt}^{\text{IV}}$  respectively. Grey  $\text{PdS}_2$  and green  $\text{PtS}$  are best obtained by respectively heating  $\text{PdS}$  with excess S and by heating  $\text{PtCl}_2$ ,  $\text{Na}_2\text{CO}_3$  and S. The crystal chemistry and electrical (and magnetic) properties of these phases and the many selenides and tellurides of Ni, Pd and Pt are complex.

### 27.3.3 Halides

The known halides of this group are listed in Table 27.3. This list differs from that of the halides of Co, Rh and Ir (Table 26.3) most obviously in that the +2 rather than the +3 oxidation state is now well represented for the heavier elements as well as for the lightest. The only hexa- and penta-halides are the dark-red  $\text{PtF}_6$  and  $(\text{PtF}_5)_4$  which are both obtained by controlled heating of Pt and  $\text{F}_2$ . The former is a volatile solid and, after  $\text{RhF}_6$ , is the least-stable platinum-metal hexafluoride. It is one of the strongest oxidizing agents known, oxidizing both  $\text{O}_2$  (to  $\text{O}_2^+[\text{PtF}_6]^-$ ) and Xe (to  $\text{XePtF}_6$ ) (p. 892). The pentafluoride is also very reactive and has the same tetrameric structure as the pentafluorides of Ru, Os, Rh and Ir (Fig. 25.3). It readily disproportionates into the hexa- and tetra-fluorides.

Platinum alone forms all 4 tetrahalides and these vary in colour from the light-brown  $\text{PtF}_4$  to the very dark-brown  $\text{PtI}_4$ .  $\text{PtF}_4$  is obtained by the action of  $\text{BrF}_3$  on  $\text{PtCl}_2$  at  $200^\circ\text{C}$  and is violently hydrolysed by water. The others are obtained directly from the elements, the chloride being recrystallizable from water but the bromide and iodide being more soluble in alcohol and in ether. The only other tetrahalide is the red  $\text{PdF}_4$  which is similar to its platinum analogue.

The most stable product of the action of fluorine on metallic palladium is actually  $\text{Pd}^{\text{II}}[\text{Pd}^{\text{IV}}\text{F}_6]$ , and true trihalides of Pd do not occur. Similarly, the diamagnetic "trichloride" and "tribromide" of Pt

<sup>5</sup> L. J. ELDING, *Inorg. Chim. Acta* **20**, 65-9 (1976).

Table 27.3 Halides of nickel, palladium and platinum (mp/°C)

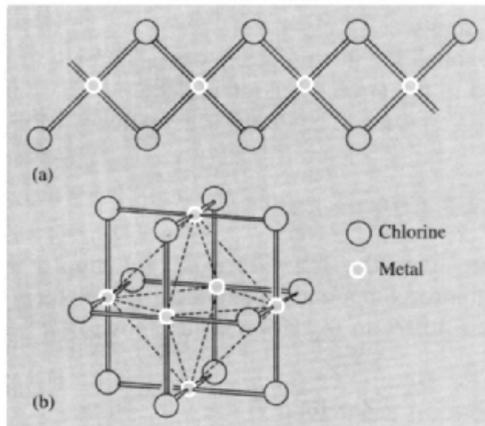
Oxidation State	Fluorides	Chlorides	Bromides	Iodides
+6	PtF <sub>6</sub> <sup>(a)</sup> dark red (61.3°)			
+5	[PtF <sub>5</sub> ] <sub>4</sub> deep red (80°)			
+4	PdF <sub>4</sub> brick-red	PtCl <sub>4</sub> red-brown (d 370°)	PtBr <sub>4</sub> brown-black (d 180°)	PtI <sub>4</sub> brown-black (d 130°)
“+3”	Pd[PdF <sub>6</sub> ] —	PtCl <sub>3</sub> green-black (d 400°)	PtBr <sub>3</sub> green-black (d 200°)	PtI <sub>3</sub> black (d 310°)
+2	NiF <sub>2</sub> yellow (1450°)	NiCl <sub>2</sub> yellow (1001°)	NiBr <sub>2</sub> yellow (965°)	NiI <sub>2</sub> black (780°)
	PdF <sub>2</sub> pale violet	α-PdCl <sub>2</sub> <sup>(b)</sup> dark red (d 600°)	PdBr <sub>2</sub> red-black	PdI <sub>2</sub> black
	—	α-PtCl <sub>2</sub> <sup>(b)</sup> olive-green (d 581°)	PtBr <sub>2</sub> brown (d 250°)	PtI <sub>2</sub> black (d 360°)

<sup>(a)</sup>PtF<sub>6</sub> boils at 69.1°. <sup>(b)</sup>β-PdCl<sub>2</sub> and β-PtCl<sub>2</sub> (reddish-black) contain M<sub>6</sub>Cl<sub>12</sub> clusters (Fig. 27.3b).

contain Pt<sup>II</sup> and Pt<sup>IV</sup> and the triiodide probably does also. Trihalides of nickel are confined to impure specimens of NiF<sub>3</sub>.

All the dihalides, except PtF<sub>2</sub>, are known, fluorine perhaps being too strongly oxidizing to be readily compatible with the metal in the lower of its two major oxidation states. Except for NiF<sub>2</sub>, the yellow to dark-brown dihalides of nickel can be obtained directly from the elements; they dissolve in water from which hexahydrates containing the [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> ion can be crystallized. These solutions may also be prepared more conveniently by dissolving Ni(OH)<sub>2</sub> in the appropriate hydrohalic acid. NiF<sub>2</sub> is best formed by the reaction of F<sub>2</sub> on NiCl<sub>2</sub> at 350°C and is only slightly soluble in water, from which the trihydrate crystallizes.

Violet, easily hydrolysed, PdF<sub>2</sub> is produced when Pd<sup>II</sup>[Pd<sup>IV</sup>F<sub>6</sub>] is refluxed with SeF<sub>4</sub> and is notable as one of the very few paramagnetic compounds of Pd<sup>II</sup>. The paramagnetism arises from the *t*<sub>2g</sub><sup>6</sup>*e*<sub>g</sub><sup>2</sup> configuration of Pd<sup>II</sup> which is consequent on its octahedral coordination in the rutile-type structure (p. 961). The dichlorides of both Pd and Pt are obtained from the elements and exist in two isomeric forms: which form is produced depends on the exact experimental conditions used. The more usual α-form of PdCl<sub>2</sub> is a red material with



**Figure 27.3** (a) The chain structure of α-PdCl<sub>2</sub>, and (b) the M<sub>6</sub>Cl<sub>12</sub> structural unit of β-PdCl<sub>2</sub> and β-PtCl<sub>2</sub>. (Note its broad similarity with the [M<sub>6</sub>X<sub>12</sub>]<sup>n+</sup> unit of the lower halides of Nb and Ta shown in Fig. 22.6 and to the unit cell of the three-dimensional structure of NbO.)

a chain structure (Fig. 27.3a) in which each Pd has a square planar geometry. It is hygroscopic and its aqueous solution provides a useful starting point for studying the coordination chemistry of Pd<sup>II</sup>. β-PdCl<sub>2</sub> is also known and its structure is based on Pd<sub>6</sub>Cl<sub>12</sub> units in which, nevertheless, the preferred square-planar coordination of the Pd<sup>II</sup> is still