Aspects of the platinum group metals (PGM)

The PGM iridium, osmium, palladium, platinum, rhodium, and ruthenium are commonly found together in ores, along with silver, gold and base metals. To understand how they are separated from each other and purified, it is necessary to to know something of their chemistry.

The PGM are found in the second and third row of the transition metals in the Periodic Table, see below.

d-block									
45.0 Sc Scandium 21	47.9 Ti Titanium 22	50.9 V Vanadium 23	52.0 Cr Chromium 24	54.9 Mn Manganese 25	55.8 Fe Iron 26	58.9 Co Cobalt 27	58.7 NI Nickel 28	63.5 Cu Copper 29	65.4 Zn Zinc 30
88.9 Y Yttrium 39	91.2 Zr Zirconium 40	92.9 Nb Niobium 41	95.9 Mo Molybdenum 42	(99) Tc Technetium 43	101.1 Ru Ruthenium 44	102.9 Rh Rhodium 45	106.4 Pd Palladium 46	107.9 Ag Silver 47	112.4 Cd Cadmium 48
138.9 La Lanthanum 57	178.5 Hf Hafnium 72	181.0 Ta Tantalum 73	183.9 W Tungsten 74	186.2 Re Rhenium 75	190.2 Os Osmium 76	192.2 Ir Iridium 77	195.1 Pt Platinum 78	197.0 Au Gold 79	200.6 Hg Mercury 80

The PGM plus gold and silver make up the Precious Metals.

They have very similar chemical behaviour which makes separation difficult. However, like the other d-block elements the PGM are able to form complexes with a wide variety of ligands. From a practical view the most important are the chloro-complexes, *eg* $[PtCl_6]^{2-}$, because in the final stage of processing the ore, the PGM concentrate is treated with 6 mol dm^{-3} hydrochloric acid to dissolve all the precious metals. The result is a mixture of complexes in which the elements can have several different oxidation states. These are summarised overleaf.

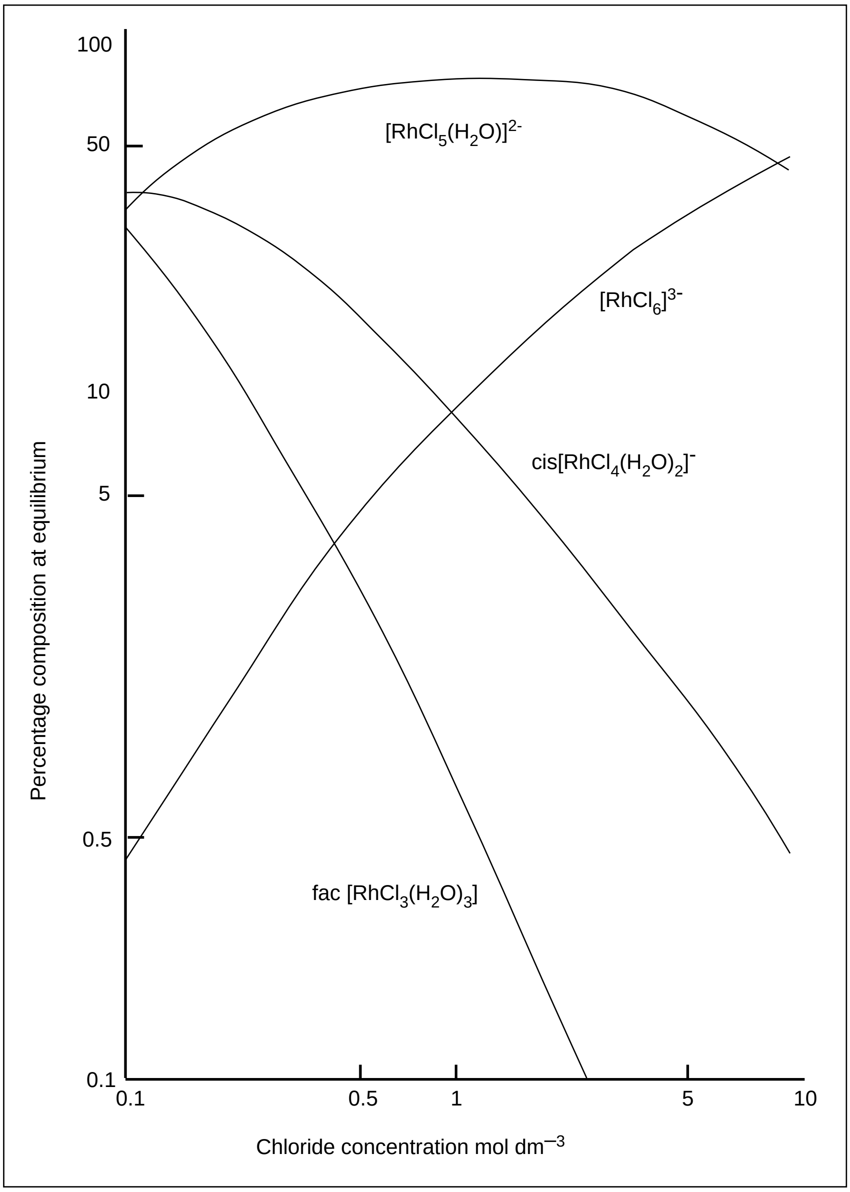
Ruthenium	**Rhodium**	**Palladium**	**Silver**
Ru(III) $[RuCl_6]^{3-}$ $[RuCl_5(H_2O)]^{2-}$ $[RuCl_4(H_2O)_2]^{-}$ $[RuCl_3(H_2O)_3]$ Ru(IV) $[RuCl_6]^{2-}$ $[Ru_2OCl_{10}]^{4-}$ $[Ru_2OCl_8(H_2O)_2]^{2-}$	Rh(III) $[RhCl_6]^{3-}$ $[RhCl_5(H_2O)]^{2-}$ $[RhCl_4(H_2O)_2]^{-}$	Pd(II) $[PdCl_4]^{2-}$ Pd(IV) $[PdCl_6]^{2-}$	Ag(I) AgCl
Osmium	**Iridium**	**Platinum**	**Gold**
Os(III) $[OsCl_6]^{3-}$ $[OsCl_5(H_2O)]^{2-}$ $[OsCl_4(H_2O)_2]^{-}$ Os(IV) $[OsCl_6]^{2-}$	Ir(III) $[IrCl_6]^{3-}$ $[IrCl_5(H_2O)]^{2-}$ $[IrCl_4(H_2O)_2]^{-}$ Ir(IV) $[IrCl_6]^{2-}$	Pt(II) $[PtCl_4]^{2-}$ Pt(IV) $[PtCl_6]^{2-}$	Au(III) $[AuCl_4]^{-}$

The precious metals and their oxidation states in hydrochloric acid

a) Apart from gold, the elements form a series of aquated chloro-complexes when in oxidation state +III.

b) Ruthenium is unique among the PGM in that it also forms a series of oxo-bridged dimers in oxidation state +IV.

c) The chloro-aquocomplexes of an element exist in equilibrium with each other. For example, the equilibrium distribution diagram for rhodium(III) shows how the relative concentrations of the complexes change with increasing concentration of the chloride ion.



Equilibrium distribution diagram for Rh(III)
(note the non-linear scales on the axes)

This has important practical implications, because the PGM present in concentrated hydrochloric acid are separated from each other on the basis of the different solubilities of their complexes in organic solvents. In general the following order of solubility is seen in the organic phase:

$[MCl_4]^- > [MCl_6]^{2-} > [MCl_6]^{3-}$

This is thought to be for steric reasons. It is harder to pack three bulky organic monocations around $[MCl_6]^{3-}$ than it is to place two around $[MCl_6]^{2-}$ or one around $[MCl_4]^-$.

PGM chloro-complexes can be extracted in one of two ways.

1 Ligand exchange

2 Anion exchange

Ligand exchange

The PGM are generally much less reactive than the base metals. With base metal complexes one ligand can easily be substituted for another,*eg*

$$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightarrow [Cu\,Cl_4]^{2-}(aq) + 6H_2O(l)$$

This reaction occurs rapidly, but equivalent reactions amongst the PGM can take hours, days or even months under standard conditions. The kinetics are summarised below.

Ruthenium	**Rhodium**	**Palladium**	**Silver**
Ru(III) 10^{-3}–10^{-4}	Rh(III) 10^{-3}–10^{-4}	Pd(II) 1	Ag(I) 10^{4}–10^{6}
Ru(IV) 10^{-5}–10^{-6}			
Osmium	**Iridium**	**Platinum**	**Gold**
Os(III) 10^{-7}–10^{-9}	Ir(III) 10^{-4}–10^{-6}	Pt(II) 10^{-3}–10^{-5}	Au(III) 10^{1}–10^{-1}
Os(IV) 10^{-10}–10^{-12}	Ir(IV) 10^{-8}–10^{-10}	Pt(IV) 10^{-10}–10^{-12}	

Relative substitution kinetics of the precious metal chloro-complexes (palladium = 1) Note: The smaller the substitution constant the more stable the complex

There is a wide variation between the different PGM and their oxidation states. Silver(I) has a reactivity approaching that of the base metals, gold(III) is relatively reactive but osmium(IV) is inert. In practice only palladium(II) is extracted into the organic layer via ligand substitution as gold has been removed previously.

Anion exchange

The remaining PGMs are mostly extracted by anion exchange in which their complexes replace chloride ions,*eg*

$$2[R_2NH_2^+\,Cl^-] + [PtCl_6]^{2-}(aq) \rightleftharpoons (R_2NH_2^+)_2\,[PtCl_6]^{2-} + 2Cl^- \quad (R_2NH = \text{amine})$$

The PGM, like all transition metals, have variable oxidation numbers and therefore can participate in redox reactions. For example, during the separation process, iridium(III) is first oxidised to iridium(IV), extracted, then reduced back again in the organic phase. The redox behaviour of the PGM in acidic chloride media is summarised overleaf.

Ruthenium	**Rhodium**	**Palladium**	**Silver**
Ru(III) $[RuCl_5(H_2O)]^{2-}$ $\rightleftharpoons$ 0.83 V Ru(IV) $[Ru_2OCl_{10}]^{4-}$ $\rightleftharpoons$ >1.4 V Ru(VIII) RuO_4	Rh(III) $[RhCl_6]^{3-}$ $\rightleftharpoons$ >1.4 V Rh(IV) $[RhCl_6]^{2-}$	Pd(II) $[PdCl_4]^{2-}$ $\rightleftharpoons$ 1.29 V Pd(IV) $[PdCl_6]^{2-}$	Ag(I) AgCl
Osmium	**Iridium**	**Platinum**	**Gold**
Os(III) $[OsCl_6]^{3-}$ $\rightleftharpoons$ 0.42 V Os(IV) $[OsCl_6]^{2-}$ $\rightleftharpoons$ 1.0 V Os(VIII) OsO_4	Ir(III) $[IrCl_6]^{3-}$ $\rightleftharpoons$ 0.96 V Ir(IV) $[IrCl_6]^{2-}$	Pt(II) $[PtCl_4]^{2-}$ $\rightleftharpoons$ 0.74 V Pt(IV) $[PtCl_6]^{2-}$	Au(I)* $[AuCl_2]^-$ $\rightleftharpoons$ 0.93 V Au(III) $[AuCl_4]^-$

* Au(I) slowly disproportionates $3[AuCl_2]^- \longrightarrow [AuCl_4]^- + 2Au + 2Cl^-$

Redox behaviour of precious metals in acidic chloride media

Note

The more positive E^θ, the more oxidising the conditions must be for a reaction to take place.

The stability of the higher oxidation states tends to decrease from left to right across the precious metals. For example, silver usually only forms stable complexes with an oxidation number of +I, while ruthenium and osmium form stable tetroxides with an oxidation number of +VIII under highly oxidising conditions. This enables these elements to be separated from the other PGM, as their tetroxides are volatile.

Questions

1. Explain the following terms, giving examples from the text where possible.

   a) Ligand.

   b) Complex.

   c) Coordination number.

   d) Oxo-bridged dimer.

   Suggest a structure for an oxo-bridged dimer.

2. From the figure listing the precious metals and their oxidation states in hydrochloric acid, give an example of a complex in which a PGM has the oxidation number:

   a) +II

   b) +III

   c) +IV

3. a) Predict the shapes of the following complexes:

      (i) $[PtCl_6]^{2-}$

      (ii) $[Ru_2OCl_{10}]^{4-}$

   b) What isomers are possible for the following complexes (a set of molecular models might help): $[PtCl_2(H_2O)_2]$ (this is square planar), $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$

4. The graph shows the equilibrium distribution of rhodium(III) chlor-aquo-species at 25 °C. List the complexes in order of relative abundance at

   a) $[Cl^-] = 0.3$ mol dm^{-3}

   b) $[Cl^-] = 5$ mol dm^{-3}

5. For each pair of complexes, say which you think is more soluble in organic solvents compared with the aqueous phase. Explain your reasons for the answer you choose.

   a) $[MCl_6]^{2-}$ or $[MCl_4]^-$

   b) $[MCl_6]^{2-}$ or $[MCl_5(H_2O)]^{2-}$