

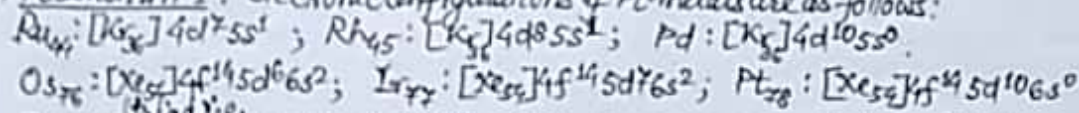
⇒ Platinum metals?

The members of the second and the third triads of Group VIII (Mendeleev's PT) / Group-8, 9 & 10 (Modern PT) namely Ruthenium (Ru), Rhodium (Rh) & Palladium (Pd) and Osmium (Os), Iridium (Ir) & Platinum (Pt) are together known as Platinum metals since they chemically resemble Platinum in several respects. The first three elements (Ru, Rh & Pd) however, have only <sup>about</sup> half the density of Pt. These are so called light platinum metals. The other three metals (Os, Ir & Pt) are called as heavy platinum metals.

Platinum metals are all rare elements, their sum total abundance in the earth's crust is  $2 \times 10^{-5}\%$ . They are chemically inert at ordinary conditions. The platinum metals occur in nature in uncombined state, together with other noble metals such as Cu, Ag & Au alloys. So, Platinum metals are noble metals.

⇒ General chemistry of Pt-metals

\* Position in PT: Electronic configurations of Pt-metals are as follows:



First three (Ru, Rh & Pd) metals belong to Groups 8, 9 & 10 respectively and fifth period while, other <sup>triad</sup> i.e. three metals (Os, Ir & Pt) belong to Groups 8, 9 & 10 respectively <sup>some</sup> sixth period in the modern P.T.

We have, the members of Group VIII (8 to 10) as three triads, in fact a vertical relation is more realistic. Again these vertical relations are stronger between corresponding members of the

Period	Group		
4	Fe	Co	Ni
5	Ru	Rh	Pd
6	Os	Ir	Pt

Second and the third triads than it is between the members of the first triad and the second triad. Thus, the pairs Ru & Os, Rh & Ir and Pd & Pt are quite close in their chemistries. All the six elements have almost the identical atomic size. This is one reason for the Pt-metals showing comparable chemical behaviour, and so placed together in PT.

\* Oxidation states: There are wide variations in their chemistries due to varying stabilities of the different oxidation states. Very many oxidation states are known with the Platinum metals. These are given below: Table-1

Element	Oxidation States
Ru	+8, +7, +6, +5, (+4), (+3), (+2), 0
Os	+8, +7, +6, (+5), (+4), +3, +2, 0
Rh	+6, +4, (+3), +2, 0
Ir	+6, (+4), (+3), +1, 0
Pd	+4, (+2), 0
Pt	(+4), (+2), 0

The circled oxidation states are most stable & best known. The compounds of Pt-metals are more easily spin paired than those of 1st triad (Fe, Co & Ni).

\* Physical characteristics: Platinum metals have high melting points, boiling points and also have very high heats of vaporisation (heat of atomisation). All these properties

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indicate great stability of the metallic lattice which is largely responsible for the non-reactive (noble) nature of these metals. Their ionisation energies are also very high which also explain the noble nature of the metals. Their oxidation potentials ( $E^{\circ}$ ) are negative and hence they are not able to displace hydrogen from dilute acids and are poor reducing agents. Some physical properties data of Pt metals shown below:

Table-2.

Property	Ru	Rh	Pd	Os	Ir	Pt
Melting point ( $^{\circ}\text{C}$ )	2500	1968	1552	2700	2454	1769
Boiling point ( $^{\circ}\text{C}$ )	4900	4500	3980	5500	5300	4530
Heat of Vaporisation (kcal/mol)	144	133	91	165	155	135
Ionisation energy (kcal/mol)	173	178	192	201	212	207
Oxidation pot <sup>l</sup> (volt)	-0.5	-0.6	-1.2	-0.9	-1.0	-1.2

\* Chemical reactivity: Pt-metals are noble (non-reactive) nature due to <sup>their</sup> very high ionisation energies. They do not displace hydrogen from dilute mineral acids (e.g. HCl,  $\text{H}_2\text{SO}_4$ , etc.). They are poor reducing agents and so they cannot oxidised. All these metals form a large number of binary compounds namely oxides, sulphides & halides.

\* Complex formation: Pt-metals have small atomic sizes and particularly the very small ionic size lead expectedly to a dominant complex chemistry. Besides forming the usual  $\sigma$ -bonded complexes with common ligands, viz.  $\text{H}_2\text{O}$ ,  $\text{X}^-$ ,  $\text{NH}_3$ ,  $\text{en}$ ,  $\text{EDTA}$  etc. They are also quite capable of forming an extensive series of  $\pi$ -complexes. With the exception of Pd & Pt they all form binary carbonyls. All the Pt-metals, however, form carbonyl halides, and other  $\pi$ -bonded complexes with isocyanides ( $-\text{NC}$ ), mixed complexes with  $\pi$ -bonding ligand etc. Ru forms a number of nitrosyl complexes. A molecular nitrogen complex of Ru,  $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$  is known. Complexes with  $\text{R}_2\text{S}$ ,  $\text{R}_3\text{P}$  &  $\text{R}_3\text{As}$  ligands are also known. Finally, Pt forms interesting complexes with acetylene, ethylene and also forms a Pt-C bonded acetylacetonate complex.

⇒ Occurrence of Pt-metals

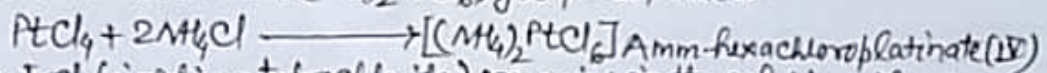
Palladium (Pd): It occurs alloyed with other metals (e.g. Au, Cu, Fe & Ni) and more abundant than any other Pt-metals (10-6%). The chief ore of Pd is 'Sudbury nickel ore', which contains Pt as well as Pd in equal amounts mixed with sulphides of Cu, Ni & Fe.

Platinum (Pt): It occurs only to the extent of  $5 \times 10^{-4}\%$  in the earth's crust. It occurs mostly in the native state mixed with other <sup>Pt-</sup>metals as with Cu, Fe & Au. The chief ore of Pt are Ural, contains about 76% Pt, 11.7% Fe, 4.3% Ir, 4.1% Cu, 1.4% Pd, 0.5% Os, 0.3% Pb etc. mixed with sand, (ii) Platinum deposits (Alluvial sand or gravel)

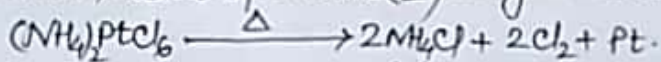
⇒ Extraction of Platinum metal: Platinum metal is extracted from platinum deposits (Alluvial sand or gravel). Alluvial sand or gravel is first washed, when heavier

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 metallic particles are separated. Gold, if present, is removed by the amalgamation process. The rest of the ore is digested with aqua regia which dissolves all the Pt-metals forming chlorides except Os, which is separated thereby. The solution containing Pt-metals chlorides is evaporated to dryness and the residue heated to  $175^{\circ}\text{C}$ . Pd & Rh-tetrachlorides are thus converted into the lower chlorides,  $\text{PdCl}_2$  &  $\text{RhCl}_3$ . On adding water,  $\text{PtCl}_4$  together with  $\text{IrCl}_3$  pass into solution while the lower chlorides of Pd & Rh remain as the residue.

The solution is acidified and ammonium chloride is added when the sparingly soluble double salt,  $(\text{NH}_4)_2\text{PtCl}_6$ , gets precipitated.



The  $\text{IrCl}_3$  (iridium tetrachloride) remains in the solution. The precipitate of ammonium hexachloroplatinate(IV) is ignited when it decomposes to give spongy Pt.



It is heated to redness and hammered to get the metal in the form of coherent sheets.

#### Extraction of Pd

Palladium (Pd) metal is extracted generally from the Sudbury nickel ore. The ore is first concentrated by froth floatation method to separate the metal sulphide and then digested with dilute aqua regia under pressure. The solution containing the chlorides of Pt & Pd is treated with  $\text{NH}_4\text{Cl}$  when a yellow precipitate of ammonium chloroplatinate,  $(\text{NH}_4)_2\text{PtCl}_6$ , is obtained. The precipitate is separated and ignited when spongy platinum is left behind. The solution now contains mostly  $\text{PdCl}_2$ . It is mixed with ammonia and concentrated by heating. On cooling, crystals of tetraammine palladium(II) chloride,  $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$  separate out. These are redissolved in water and a small amount of  $\text{HCl}$  is added to extract a yellow precipitate of diamminedichloropalladium(II). On heating, it converts into Pd metal.

