Greenwood & Earnshaw

2nd Edition

Chapter 27

Group 10

Nickel, Palladium & Platinum

Nickel, Palladium & Platinum

•**Nickel (99 ppm) is 22nd most abundant element & 7th most abundant transition metal. World production 1,000,000 tonnes/y most recovered in association with platinum group metals. Richest single source: Sudbury Basin, Canada, possibly of meteoric origin, 18%, next former USSR 25%. Used iron alloys, stainless steels, armor plating, Alnico permanent magnets, German Silver (Ni,Cu,Zn); Monel (Ni 68%/Cu 32%), Nichrome (Ni 60%/Cr 40%), Nickel-Cadmium batteries, Alkaline dry cells, catalysts (Reppe synthesis).**

•**Palladium (0.015 ppm) and platinum (0.01 ppm) are much rarer most coming from South Africa (3rd major source of Ni also Ag, Au). Palladium used hydrogenation catalysts, Pd - $H_2/D_2/T_2$ separations/purifications, Wacker process. Platinum has extensive use as catalysts (HNO_3 production, oxidation catalysts, petroleum reforming, hydrogenations, etc.), jewelry (“*platina*”). ^{195}Pt I = ½.**

Nickel, Palladium & Platinum

•**Note the diversity in electron configurations of elements:**
Ni d^8s^2 Pd d^{10} Pt $f^{14}d^9s^1$.

•**Electronegativities mirror Groups 8 & 9.**

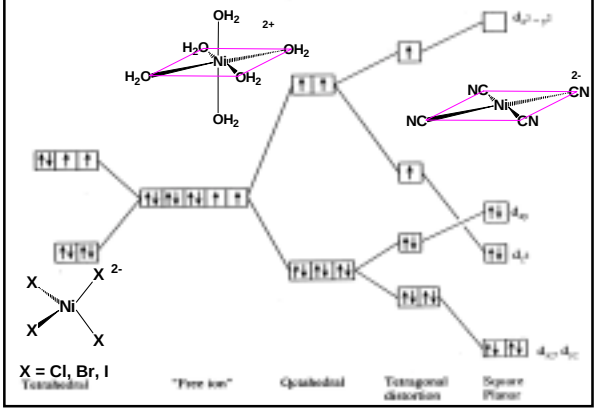
•**Limited oxidation states at both ends: Pt(V) to M(II).**

•**All three metals have *fcc* metal structure, all resist atmospheric oxidation; all dissolve in molten alkali meetal oxides. Platinum very prone to B, Si, Pb, P, As, Sb, Bi melts under reducing conditions.**

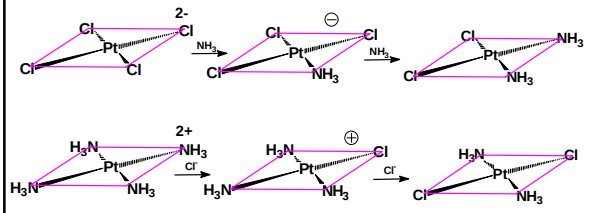
•**Metals all have high melting points but are nor refractory, showing a decrease in all periods. Enthalpy of atomizations show a parallel decrease: Ni ~ Co > Fe > Mn.**

•**Most stable oxidation states: Ni(II), Pd(II), Pt(II), Pt(IV), latter two are kinetically inert, Pt(IV) is class “a” Pd(II) & Pt(II) class “b” all have an extensive aqueous complex chemistry.**

Ni(II) Coordination Chemistry



Pd(II) & Pt(II) Coordination Chemistry



Weakest trans labelizing effect

F^-, OH^-, H_2O, NH_3, py < Cl^- < Br^- < I^- ~ SCN^-, NO_2^-, $C_6H_5^-$ <

$S{=}C(NH_2)_2$, CH_3^-, < H^- , PR_3, AsR_3 < CN^-, CO, C_2H_4

Strongest trans labelizing effect

Pd(II) & Pt(II) Coordination Chemistry

Trans Effect

- **"Trans effect" – Kinetic - Strong π-acceptor character drains electron density from the metal and from the trans-ligand's π orbitals thus encouraging nucleophilic attack.**
- **"Trans influence" – Thermodynamic – Strong σ-donor ligands produce an axial polarization of the metal and ligand lone pair inducing a positive charge on the near-side of the metal and a negative charge on the far-side which weakens the trans-ligand attachment to the metal.**
- **Pt(II) and Pd(II) bromides and iodides are insoluble. Most common compounds are the $[MX_4]^{2-}$ complexes.**

Pd(IV) & Pt(IV) Coordination Chemistry

- **Virtually all are octahedral, kinetically inert, and diamagnetic, t_{2g}^6.**
- **K_2PtCl_6 is the most common compound of Pt.**

Other Coordination Chemistry

- **Ni(III) is rather well represented. K_3NiF_6 is another octahedron with an axial elongation due to a Jahn-Teller distortion caused by the $t_{2g}^6 . e_g^1$ electron configuration.**
- **The M(III) oxidation state is rather poorly represented in Pd & Pt.**
- **Some compounds claimed to be Pt(III) such as Wolffram's red salt have been shown to be mixed valent.**