Greenwood & Earnshaw

2nd Edition

Chapter 26

Group 9

Cobalt, Rhodium & Iridium

Properties of Co, Rh, Ir

•Cobalt is appreciably rarer (29 ppm) than other elements of the first transition series except Sc. Usually recovered from copper and nickel manufacture. Used in steel alloys, ceramics (deep blue) usually to get white (countering iron yellow). Appreciably harder than iron, important as catalyst (OXO process), used in magnetic alloys "Alnico". Cobalt is, like iron, ferromagnetic. World production (1995) was ~ 20,000 tonnes. Only one natural isotope, can be converted to Co-60 ($t_{1/2}$ 5.27 y) a β and intense γ emittor with medical and food preservation uses.

•Rhodium (0.0001ppm) & Iridium (0.001 ppm) are exceedingly rare. 1996 consumption was 14.2 and 3.8 tonnes respectively. Both have fcc structures, the first transition metals to have this structure. Rh is like Co monoisotopic, Ir has 2 naturally occurring isotopes; 191-Ir (37.3%) and 193-Ir (62.7%).

Properties of Co, Rh, Ir

- **The electronegativities of the elements mirror those in Group 8 with the lower two of higher electronegativity.**
- **The mp, bp & enthalpies of atomization are lower than the preceding group.**
- **The range of oxidation states has been appreciably curtailed for all members of the group. This is usually attributed to the increasing stability of the (n-1)d electrons.**
- **The most important aqueous oxidation state for all three metals is the M(III), where almost all are low spin, having the t_{2g}^{6} electron configuration with the highest CFSE.**
- **Lower oxidation states occur principally with π-acid ligands. M(I) tend to be square planar, undergo oxidative addition and are important catalytically.**

Properties of Cobalt

- **Most simple salts of Cobalt are limited to the M(II) state since Co(III) is strongly oxidizing.**
- **Co(II) complexes may be O_h or T_d, are kinetically labile, susceptible to oxidation with π-acid and other strong-field ligands. Both Co(II) and Co(III) important to development of CFT/LFT.**
- **$Co(H_2O)_6$ - Low spin, highly oxidizing, aqueous solutions are unstable.**
- **The Co(II)/Co(III) redox couple is strongly dependent of ligand:**

$$[Co(H_2O)_6]^{3+} \rightarrow [Co(H_2O)_6]^{2+} \quad 1.83\ V \text{ cf } 1.23\ V\ O_2/H_2O$$

$$[Co(NH_3)_6]^{3+} \rightarrow [Co(NH_3)_6]^{2+} \quad 0.108\ V$$

$$[Co(CN)_6]^{3-} \rightarrow [Co(CN)_6]^{4-} \quad -0.8\ V$$