

Manganese

Occurrence –

Very common. Silicates. Also more useful as oxides.

Extraction –

- Reduce MnO_2 in blast furnace with Carbon).
- Alternatively, electrolysis for pure sample.

Structure –

- 4 allotropes known, most common in BCC. Hard and brittle.
- Metal-metal bonding is weak because 3d electrons are held tightly in inert electron core.
- Hence lower mp (1244°C) and enthalpy of atomisation.
- Change in the common trend for radii, where Mn is large compared to the expected drop
- across the period. This is due to the stability of the free d^5 configuration, and also explains the
- further loss of metal-metal bonding that is seen.

Trends in Oxidation States –

- Most stable is +2 (high spin d^5). This great stability explains why the redox potential in moving from higher oxidation states is so large.
- +7 is Group Oxidation state, and is extremely oxidising (3d electrons held tightly by nucleus).
- Wide range of states possible because the d-orbitals have not yet dropped in energy into the inert electron core, so the number of electrons available for bonding is maximised.

Redox –

- Highly electropositive compared to its neighbours in Periodic Table. More reactive.

- Will oxidise in air but not on a large scale. Burns in air if finely divided.
- Dissolves in acid to form Mn(II) salts.
- Not particularly reactive at room temperature, but will react with most things after heating.
- +2 state very stable (high spin d^5 – symmetrical). This breaks the trend – more resistant to oxidation than either Cr or Fe.

Structure of Oxides –

- Mn_2O_7 requires prior oxidation to +7 state.
- MnO_2 most useful. Corner-sharing MnO_4 tetrahedra with Mn-O-Mn bridging. Not the most stable though, it will decompose to Mn_2O_3 .
- Mn_3O_4 has spinel structure with some Jahn-Teller distortion (Mn(III)).
- MnO can be made by reduction of any of the above with H_2 . Basic oxide. Rock salt structure.

Structure of Halides –

- MnF_4 is highest halide for Manganese (note that this shows Mn is less able to reach high oxidation states than Chromium).
- MnF_3 forms octahedra which distort due to Jahn-Teller (d^4).
- Oxohalides are explosively unstable.

Complexing –

- Many d-electrons available for back-donation from metal to ligand, stabilising low oxidation states.
- Oxidation State VII, VI & V – not really any. Oxidation State IV highest for stable complexes.
- Mostly dimeric or polymeric (as in oxygen evolving complex of photosynthesis).
- Oxidation State III – high spin d^4 . Small Jahn-Teller distortions also observed. Mn(III) is strongly oxidising and

tends to disproportionate, but is stabilised by O-donor ligands.

- $[\text{Mn}(\text{CN})_6]^{3-}$ is low spin however (good ligand – π bonding, covalency. Easily oxidised).
- Oxidation State II – MnSO_4 very important complex. Surprising thermal stability (compared to Fe, Co and Ni which all decompose quite easily under heat).
- In water this forms the aquated ion with high spin ($t_{2g}^3 e_g^2$) d^5 configuration - gives no CFSE so stability constants are low compared to other 1st row M(II) ions.
- Also indicates why a wide range of stereochemistry is observed for these complexes (no real advantage to any of them if no CFSE).

Organometallics –

Limited to low Oxidation States. Carbonyl is quite stable, and dimerises (M-M bond).

Iron

Occurrence –

- Very stable nucleus, hence great abundance. Many oxides and carbonates.

Extraction –

- Blast furnace. Reduction over C / CO.

Structure –

- Soft metal. BCC. Turns to FCC at higher temperatures (and eventually back to BCC at really high temperatures).
- $[\text{Ar}]3d^64s^2$.
- Magnetic (lots of unpaired electrons aligned).
- (n-1)d electrons are contributing less to metallic bonding than in previous groups, although Mn is anomalous.

Trends in Oxidation States –

- First element in 1st row that does not reach its group oxidation state of +8. Highest known is +6 but this is very easily reduced.
- Most common states are +2 and +3.

Redox –

- Iron much more reactive than Ru or Os. Oxide film formed by oxidising acids protects it from further reaction. Also, iron rusts. Reacts with air / water.
- Iron has the widest range of spin states: every integer and half-integer from 0 to 5/2.

Structure of Oxides –

- FeO is unstable with respect to $\text{Fe} + \text{Fe}_3\text{O}_4$.
- Fe_3O_4 is a mixture of Fe(II) and Fe(III). Inverse spinel. Conducts electricity due to transfer of electrons between Fe(II) and Fe(III). Fe_2O_3 is the Fe(III) state and is quite stable. They all interconvert quite easily though due to

similar structures, except the stable form of Fe_2O_3 which has a HCP lattice.

Structure of Halides –

- Iron forms only trihalides and dihalides
- Iron (III) iodide not stable due to Fe(III) being oxidising and I^- being reducing.

Complexing –

- Fe has extensive aqueous chemistry in lower oxidation states.
- Oxidation State III complexes can be either high or low spin, and are usually (but not always) octahedral. The aquo ion is too easily hydrolysed to be common. Iron in this state greatly prefers O-donors to N-donors (ammines very unstable, even chelating ones are) (unlike Cr(III) which is otherwise similar).
- Down the halide group, the complexes with iron become much less stable such that Br and I are unknown since they readily reduce iron to Fe(II).
- Fe(III) is d^5 and thus there is no great advantage to any particular stereochemistry, so a range is observed. Usually high spin is preferred unless ligand is very strong.
- Oxidation State II will bind to almost any anion. Aquated ion is stable now. Fe(II) is however susceptible to oxidation to Fe(III). The complexes are often less stable than with Fe(III) due to lower charge of central metal ion.
- Most are octahedral and high spin, again unless the ligand is very strong, in which case low spin octahedral is preferred.
- Lower oxidation state complexes can be achieved with carbonyls and phosphines.

Organometallics –

d^8 configuration allows for 18 electron rule to be satisfied – $\text{M}(\text{CO})_5$.