Iron, Ruthenium & Osmium

- Iron bears greater similarities to Cobalt & Nickel than to Ru & Os.
- Ru/Os bear greater similarities to Rh-Pd/Ir-Pt than to iron.
- Electronegativities – large increase in 5th & 6th periods.
- Burning in O₂ yields Fe(III); Ru(IV) and Os(VIII) oxides.
- MPs Iron higher than Mn; Ru ~ Tc; Os ~ Re.
- Enthalpies of atomization Fe higher than Mn; Os greater than Re.
- Density of Osmium highest of all elements.
- Iron is the first transition element to not attain its group oxidation state. The highest is [FeO₄]²⁻ or Fe(VI).
- Trends in the d-block are smooth if the anomalous behavior of the Group 7 elements are neglected, a consequence of their d⁵ e config. A factor also seen in the metal electrical resistivities.

Iron is technologically very important. The control of carbon content is extremely important to the properties of iron & steel. Steel < 2% carbon < cast iron. Heat and mechanical history play crucial roles in malleability, hardness, strength and corrosion resistance. Iron is electropositive, pyrophoric as a fine powder and burns in air if fine threads. Bulk iron oxidizes readily in air especially if moisture is present, reacts readily with dilute acids but is rendered passive by concentrated oxidizing acids such as nitric. Fe₂O₃ is used as a pigment (RR red) and abrasive (jewelers rouge).

- Ru and Os are stable to atmospheric attack, but are susceptible to halogen oxidation. Finely divided Os however gives of the characteristic odor of OsO₄. They react with strong alkali when air is present but are un affected by non-oxidizing acids. Ru & Os have no oxides below M(IV).
Oxides of Ruthenium & Osmium

(VIII) RuO₄

OsO₄

H₂O → [OsO₄(OH)₂]⁻²

Os

O

O

N

NH₃

KOH(aq)

HX(aq)

X = Cl, Br

OsCl₃

Cl

Cl

Cl

Cl

Cl

Cl

[OsO₂(OH)₄]⁰

Perosmate, deep red, octahedral, trans O's.

This bond much longer and is labile, 293 pm.

Osmate, octahedral purple, diamagnetic.

RuO₄

HCl

KCl K₄[RuCl₅ORuCl₅]

Deep red, diamagnetic Ru(V), linear Ru-O-Ru.

M(IV) ordinarily the most stable oxidation state of Os, Ru easily reduced to M(III). The [OsX₆]⁻² and [RuX₆]⁻² are most well known.

Aqueous complexes of 5th and 6th period transition elements, but especially the platinum group, tend to be low spin. Spin Orbit Coupling is much stronger in these groups, nuclear charges much larger than 4th period, ligands are more strongly held, magnetic moments fall with decreasing temperature due to SOC.

Metal Carbonyls