DESCRIPTIVE TRANSITION METAL CHEMISTRY

Titanium

Occurrence –

This element occurs mainly as oxides, TiO_2 (rutile) and Perovskite ($CaTiO_3$). In these, the Ti occupies octahedral holes.

Extraction –

Add Cl_2 over Carbon with TiO_2 to get $TiCl_4$.
Ti metal can be obtained from $TiCl_4$ by adding Mg with a lack of air (both N_2 and O_2 will react by reduction).

The Element –

Radius = 147pm. Silver metal with high melting point, indicative of some metal-metal bonding (1667^oC).
$[Ar]3d^24s^2$.
Reacts with non-metals after heating.

Ti(II) is a strong reducing agent, and the low ionisation energy here typifies this. As anticipated, the M/H_2 couple will get more and more oxidising across the period, as the ionisation energy increases.

Compounds –

Oxidation State of +4 is the most pronounced, which indicates covalent character (a +4 ion would be unstable). It can have lower oxidation states though, but these are readily oxidised.

Ti has a high affinity for Oxygen (sulphide ores are rare, unlike other TM's).
Ti-O bonds are short and strong, which implies $d(\pi)$-$p(\pi)$ bonding (vacant d orbitals on Ti). As a result, the metal often has an oxide film (so resists corrosion).
TiO_2 is a white pigment and fairly unreactive. It occupies the rutile structure predominantly (distorted HCP with half Octahedral holes occupied by Ti). However, other oxides can be formed, e.g. Ti_2O_3 and TiO.
$TiCl_4$ forms adducts with ethers, esters, ketones, etc.

All tetrahalides are known. As the halide changes the colour changes, i.e. the charge-transfer band is moved to steadily lower energies (more absorption in the visible region).
Note that the tetrahalide is most stable (as in the extraction process). There is now highly covalent bonding.
All trihalides are known. Hard to make since tetrahalides so stable, which are difficult to reduce.
Also, TiX_2 can be formed by reduction of TiX_4 with Ti. There is extensive Metal-Metal bonding here (as shown by a low magnetic dipole moment). These are strongly reducing.

Compounds with oxoanions are not really favoured, due to high ratio of ionic charge to radius of Ti(IV).

Metal-Metal Bonding will occur. It is favoured due to large d-orbital overlap (it is relative to other TM's a large metal ion). There is only 1 d electron present in Ti^{3+} though.
Due to the small M-M distance, anions must be small to interact, therefore ions of O, X. The consequence of this is higher enthalpies (e.g. of atomization).

Examples:
β-$TiCl_3$ has an unusual structure and dark colour, with Ti-Ti bonds. Low magnetism for a d^1 ion.
$[Ti^{III}(acac)_2Cl]_2$, d^1 diamagnet.
TiO metallic conductor, black. Compare other transition metal oxides.

Complexing –

Titanium is just about large enough to reach coordinate 8 ligands, but this is rare.
Octahedral is the most common arrangement with halides and water, while tetrahedral is adopted by halides. Basically there is a wide range of stereochemistry due to the d^0

configuration which is spherically symmetrical. Hence, Square Planar only for bulky ligands with strong π-effects, e.g. $N(SiMe_3)_2$.

Complexes hydrolyse in water easily, particularly octahedral ones. Results in OH and O bridging between the Ti.

Oxidation State IV (d=0) gives diamagnetic complexes.

Oxygen affinity again seen:
- Ammines hydrolyse.
- Potential for TiO double bonds, e.g. $[TiOCl_4]^{2-}$ and $KTiOPO_4$ (KTP – non-linear optic material, doubles laser frequencies).
- Stable peroxides – Ti(IV) + H_2O_2 to form TiO_2^{2+} (yellow).

High coordination number:
$Ti(NO_3)_4$ has 8 coordinate O.
$TiCl_4(diars)_2$ has 4Cl+4As.

Organometallics –
M-C σ bonds are weak due to few d electrons to strengthen it.
Ti often electron deficient. This is because 6 ligands is still not enough to attain 18e. This is important in polymerisation catalysis (C=C electron rich). Ziegler-Natta catalysts – industrial, very crystalline, high RMM, stereospecific – polyethene and polypropene.

Uses –
Properties of $BaTiO_3$ – ferroelectricity and applications (transducers, capacitors).

Zirconium + Hafnium
Occurrence –
As oxides and silicates.

Extraction –
Difficult to extract due to affinity for oxygen. Use the iodide decomposition process and then reduction with sodium. The two elements are separated by the sodium, i.e. an ion exchange resin – otherwise difficult.

Structure –
These elements have virtually identical radii. Only things that differ are densities, transition temperatures and neutron-absorbing abilities.
Zr = $[Kr]4d^25s^2$. Hf = $[Xe]4f^{14}5d^26s^2$. There melting points are 1857°C & 2222°C respectively, showing that increased metal-metal bonding is observed down the Group due to the increase in size (overlap) such that transition temperatures and enthalpies of atomisation increase.
Their size also explains why they occur as more basic oxides (more aqueous chemistry).

Trends in Oxidation States –
More stable in higher states. Lower states tend to be reducing, and are not stable in water (no aquocation complexes).
+4 tends to dominate.

Structure of Oxides –
Only stable oxides are MO_2. These are 7-coordinate.

Structure of Halides –
Zr & Hf halides are all white (they are less polarizing to the halide compared to Ti).
They are typically tetrahedral, although this can vary in the solid state, where octahedral coordination can occur to give zigzag polymer chains which edge-share.
All tetrahalides are known, and also all trihalides except HfF_3.
Any lower halides will form clusters.

Complexing –

Will favour much higher coordination numbers such as 7 & 8, e.g. ZrF_8^{4-}, ZrF_7^{3-}, etc. Zr tends to favour 8.
There size allows them to coordinate more ligands without steric repulsions, and this is advantageous electrostatically. Lower oxidation states are usually hydrolysed, as these element favour O-donor ligands strongly like Titanium.

Uses –
Zr is a useful structural metal (like Ti). Low neutron capture cross-section, use for nuclear fuel cans. Must separate Hf fully for this.
ZrO_2 is as hard as diamond – used as a cutting tool. Reacts with steam to form H_2, as at Chernobyl!

Summary –

- High oxidation states predominate.
- Very electropositive elements, difficult to extract.
- Empty d-orbitals encourages oxygen ligands.
- High charge, extensive hydrolysis and polymerisation in water.
- High charge, and size, several examples of coordination number > 6.
- Lower oxidation states with large d-orbital radius, many examples of M-M bonds.

Vanadium
Occurrence –
VO_4 and VS_4 compounds.

Extraction –
Add NaCl or Na_2CO_3 at high temperatures to give $NaVO_3$. Leached out with water. Al used as reductant.
VCl_5 reduced with H_2 or Mg.

Structure –
Metallic BCC. Shiny silver metals.
Additive to steel – V_4C_3 formed with any carbon present, which disperses to make the steel more resistant to wear and stronger.

Properties –
Radius has contracted compared to Ti, showing that the extra d electron does not compensate sufficiently for the extra nuclear charge (higher Z_{eff}).
Highest melting point of the 1st row (1915°C) since Vanadium is the last element before some of the (n-1)d electrons begin to enter the inert electron core of the atom (hence not available for bonding).
For the same reason, it is also last element that is not strongly oxidising in the Group oxidation state.

Trends in Oxidation States –
+4 state is most stable, but +3 and +2 are stable (although reducing).
Vanadium is the most stable Transition Metal in lower oxidation states.
Only pentahalide is with fluoride (since it is so oxidising), otherwise Vanadium(V) forms pentoxides and oxohalides.
VO^{2+} is a very stable ion (vanadyl).

Coordination Numbers –
+4 state can reach 8 (which would be good with low steric repulsions, because M-L bonds maximise the energy of the complex), but not +5 unless bidentate ligands, because the metal is too small, and steric effects become limiting.
Tends to form octahedral complexes (typical of 1st row TM's).

Structure of Oxides –
Most stable oxide is V_2O_5. Complicated arrangement of trigonal bipyramids.
It dissolves in acid to produce the pale yellow VO_2^+ ion.
In alkali it forms VO_4^{3-}

Intermediate pHs give hydrolysis / polymerisation reactions to form isopolyvanadates.
This oxide can also be reduced to VO_2 (deep blue, rutile distorted by M-M bonding).
Magneli phases (see later metals) can be formed by reduction with H_2, CO or C.
V_2O_3 is highly basic (V(III) ions formed) and is conductive above 170K but insulating below this.
VO can also be formed (grey).
Thus, wide range of oxides possible.

Structure of Halides –
Vanadium V forms only the fluoride. This forms a polymer chain.
Vanadium IV does not form the iodide.
All halides of V(III) and V(II) are known.
Hydrolysis of VCl_4 gives oxovanadium(IV) chloride (similarly for VBr_4).
Dihalides have simplistic structure.

In Aqueous –
VO_5 gives polymerised vanadates.

Complexing –
Vanadium(V) binds to oxygen very strongly, like titanium. Means that complexes not containing V-O bonds are susceptible to hydrolysis.
Tetrahalides of oxidation state +4 are Lewis acids, and end up coordinating 6.
VO_2^+ stable, vanadium(IV). Is *type a* (hard), binds very strongly to F in particular. Usually 5-coordinate square pyramidal.
Vanadium(III) is similar to Titanium(III) and favours octahedral coordination (d^2).
M-C sigma bond is very weak – limited chemistry, but more stable than Titanium version. Will form a hexacarbonyl, for example.
Mostly octahedral and tetrahedral compounds (since low spin always, no reason for Square Planar).

Niobium + Tantalum
Occurrence –
$(Fe,Mn)M_2O_6$

Extraction –
Dissolve in acid, then separate by solvent extraction (one more soluble than the other), then reduce with Na or C.

Structure –
Metallic BCC. Shiny silver metals. Nb used with Zr in superconductors.
Ta very resistant to corrosion – tough oxide layer. Also is an insulator.

Properties –
Unlike V, the entry of (n-1)d electrons does not occur, and they are not of the highest melting points. However, they are higher than V, indicating more metal-metal bonding is occurring.
Tend to oxidise, as for Vanadium.
The two elements are virtually identical in size (due to Lanthanide Contraction – addition f-electron shell is weakly shielding and allows d-electrons to penetrate just as well for Ta as for Nb).

Trends in Oxidation States –
Mostly +5. Note that highest oxidation state of V is the most favoured of the triad below. Other oxidation states rarely found. This is because the 4d and 5d orbitals are less influenced by the formal charge of the metal as they penetrate further into the core.

Coordination Numbers –
+5 state gives coordination number of 8 even with monodentate ligands. This is due to these elements being larger than V, so they can coordinate more ligands without the interference of steric repulsion between them.

+3/+2 chemistry not known. Instead, form cluster compounds based on octahedral M_6X_{12} units. This indicates strong metal-metal bonding due to greater overlap of orbitals (as shown by high enthalpies of atomisation).

Structure of Oxides –

Pentoxides are much more stable for Nb and Ta than for V, so hard to reduce. Hence there is less of a range of oxides found. Nb more easily forms lower oxides than Ta.
More extensive metal-metal bonding is observed here due to greater overlap.

Structure of Halides –

All halides known for Nb and Ta in the high oxidation state (unique in this respect).
MF_3 and TaF_4 not known. Clustering occurs in lower oxidation states.
MF_5 are tetramers, MCl_5 and MBr_5 are dimers (contrast VF_5 polymers).
Tetrahalides are easily hydrolysed.
Structures reflect increased metal-metal bonding tendencies.
Dihalides do not exist. Instead forms clusters. These are diamagnetic, indicating metal-metal bonding.

Complexing –

Nb(V) and Ta(V) are often pentahalides. Concentrations of HF can be varied to increase coordination to 6, 7 and 8 (more easily for Ta).
In aqueous solutions, X=Cl, Br will give oxochloro- or oxobromo- complexes instead.
Forms octahedral and tetrahedral complexes on the whole. Can coordinate more ligands than V though, due to size (sterics).
Nb and Ta are generally classed as *type a* (hard, O & N) but will bind to S readily, as well as P.
Nb(III) and Ta(III) chemistry does exist, particularly with S and P donor ligands. Not very stable though.

Chromium

Occurrence –

Ore is chromite, $Fe^{(II)}Cr^{(II)}{}_2O_4$, a normal spinel.

Extraction –

Add NaOH + O_2 to oxidise, then add C to give Cr_2O_3.
Cr_2O_3 can be converted to Cr by adding Al.

Structure –

Metallic BCC, silver, fairly soft. $[Ar]3d^5 4s^2$.
Metal-Metal bonding can occur.
Lower melting point and enthalpy of atomisation than Vanadium (1900^oC), due to more electrons entering the inert electron core (less readily delocalised by metal-metal bonds).
Ionisation Energy has also increased, and successive ionisation energies are difficult because (as for all 1st row TM's) the 3d orbital is sensitive to charge.

Trends in Oxidation States –

+6 is highly oxidising, so can only support O and F ligands, e.g. $Cr_2O_4^{2-}$.
+5 is unstable.
+3 is the dominant oxidation state (d=3). It forms very stable complexes, which do not substitute ligands easily. Drop from +4 being most stable in Vanadium because of more electrons in inert core.
+2 is Jahn-Teller distorted. It is strongly reducing. The ethanoate can be isolated and dimerises, indicating metal-metal bonding occurs. This compound is also diamagnetic.
Cr(0) is stable, e.g. $Cr(CO)_6$. This fulfils the 18e rule. There is a wide range of low oxidation state organometallic compounds.

Coordination Numbers –

As typifies most 1st row transition metals, octahedral is favoured for most complexes.

Structure of Oxides –

CrO_3 has low melting point, since it has a high degree of covalency. Forms corner sharing tetrahedra. Also strongly acidic.
This converts to Cr_2O_3 under heating – stable.
CrO_2 – rutile. Intermediate of CrO_3 decomposition.
Has a less wide range of poly oxoanions, unlike Vanadium and Molybdenum.

Structure of Halides –
+6 oxidation state can support Fluoride only. Iodides not stable in +5/+4. Halides implies fluorides for stable chemistry in higher oxidation states.
Lower oxidation states – all known. Trihalides have octahedral coordination.
Hexahalides easily hydrolysed.
Dihalides are Jahn-Teller distorted (d^4).

Complexing –
Oxidation State VI tends to involve oxohalides not halides.
Oxidation State V not stable, hydrolyse with disproportionation to Cr(III) and Cr(VI).
Oxidation State III easily the most common, and almost always octahedral (d^3).
Oxidation State II can be high spin ($t_{2g}^3e_g^1$) or low spin (t_{2g}^4). Jahn-Teller also occurs. Tends to form dinuclear compounds with multiple metal-metal bonds + bridging groups. Also prefers N-donor ligands.

Organometallics –
6 ligands will satisfy the 18e rule, so there is plenty of scope for organometallic Cr compounds, particularly with carbonyl ligands.

Molybdenum + Tungsten

Occurrence –
$Mo^{(IV)}S_2$.
$CaW^{(VI)}O_4$

Extraction –
Mo extracted by adding O_2, then NH_4OH to give MoO_3. $Mo_{(s)}$ by adding H_2.
W extracted by adding NaOH then HCl, then H_2.

Structure –
Metallic BCC, silver, fairly soft.
Metal-Metal bonding is more prolific in these elements because the d-orbital overlap is larger and the electron-electron repulsions are smaller. In fact, Tungsten is the last element in the 3rd row to have all 5d electrons in metal bonding (i.e. it forms metal-metal bonds to the greatest degree of all TM's).

The M-M bonds do not occur in higher oxidation states (e.g. not in Mo_2Cl_{10} – paramagnetic). This is due to orbital contraction reducing its effectiveness.

Trends in Oxidation States –
Higher oxidation states are more stabilised here than for Cr, as expected for 2nd/3rd row.

Redox –
Mo(III) is reducing (as opposed to Cr(III) being neither). This is due to stability of higher oxidation state.

Coordination Numbers –
Both can reach high coordination numbers.

Structure of Oxides –
No lower oxides unlike Cr. MoO_2 and MoO_3 common, as are Magneli phases, e.g. Mo_8O_{23} (mixed valence). This is where rows of oxygen atoms have been removed from MO_3, and M(VI) and M(V) are present.
WO_3 is a typical ionic structure with WO_6 octahedra.
Trioxides are insoluble in water and not particularly oxidising. Heating gives MO_2.

Structure of Halides –

Dihalides not very stable. Tend to form clusters to maximise metal-metal bonding.
Hexahalides easily hydrolysed.
Structure of Mo & W trihalides often distorts to increase metal-metal contribution, and form classic cluster compounds.

Complexing –

Oxidation State V is more stable for these metals than Cr.
Oxidation State III few and far between, especially for W (metal-metal triple bonds mostly).
Oxidation State II shows a difference between Mo and W, Mo behaves like Cr in that it tends to form dinuclear metal-metal bonded compounds, while W does not.

Organometallics –

Mo is important in nitrogen fixation (N_2 isoelectronic to CO).
As for Cr, 18e rule easily satisfied, so many organometallic compounds possible.

Manganese

Occurrence –

Very common. Silicates. Also more useful as oxides.

Extraction –

Reduce MnO_2 in blast furnace with C.
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^{o}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) and follows the trend V→Cr→Mn). 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 of 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 chlorophyll, 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. $[Mn(CN)_6]^{3-}$ 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 ($t_{2g}{}^3e_g{}^2$). 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 really advantage to any of them if no CFSE).

Organometallics –

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

Technetium + Rhenium

Occurrence –

Technetium is an artificial element.

Rhenium concentrations extremely low (last natural element found). Part of molybdenites.

Extraction –

Tc can be acquired from Uranium fission in nuclear power plants.

Re collects as Re_2O_7 after roasting molybdenites. Reduced by H_2.

Structure –

HCP. Typical metallic appearance.

Re has very high melting point (2nd only to W).

Trends in Oxidation States –

Do not tend to decrease below +4 state.

Redox –

Less reactive than Mn. Resist oxidation in air.

Lower oxidation states less favoured, particularly Re, where +2 state is ignored in preference of Re(III) clusters.

Tc easily converts from one oxidation state to another (low gradient on Frost Diagram).

+7 state less oxidising for these two elements – more stable here.

Structure of Oxides –

Re_2O_7 is most stable product on burning in oxygen.

Re compound has a different structure – higher mp – polymeric double layers.

Only Re forms stable trioxide (reduction of Re_2O_7 with CO). Octahedral. Will disproportionate if boiled in alkali.

Re_2O_5 not very stable, but known. Also disproportionates.

TcO_2 is its most stable oxide (+4 state). ReO_2 also known, and both are rutile.

Structure of Halides –

ReF_7 is only stable heptahalide of a transition metal. $ReCl_4$ forms face-sharing pairs which then link in chains, indicating metal-metal bonding factors (face sharing = close metal nuclei).

TcF_6 is the highest for Technetium. $TcCl_4$ only stable chloride – edge-sharing octahedra.

Halides tend to form mixtures and convert to oxohalides easily, so hard to separate and study.

Re(III) forms clusters, e.g. Re_3Cl_9. Dissolves in water then hydrolyses to give Re_2O_3.

These elements do not form dihalides.

Oxohalides here are more stable than for Mn, but do hydrolyse and disproportionate easily.

Metal-Metal bonding especially important for low to mid oxidation states. This is observed for many of these type of metals, e.g. Nb, Ta, Mo, W, (Tc), Re.

Complexing –
Oxidation State VII – limited to oxohalides of Re, easily hydrolysed.
Oxidation State VI – fluoro/oxo complexes dominate.
Oxidation State V – mainly oxo complexes still. Tc forms many in this state of importance biologically. Can be 8-coordinate.
Oxidation State IV – not that many since metal-metal bonding not most effective and oxo-compounds not as favoured as in higher states.
Oxidation State III – Tc complexes known and stabilised by back-bonding ligands. Usually 6 coordinate. Re(III) needs to be stabilised by extensive metal-metal bonding or it will oxidise to IV or VII easily.
Oxidation State II – very limited – P/As donors only.

Organometallics –
Re has wide range of organometallic compounds possible. It can extend these compounds right up to VII Oxidation State. Carbonyls are less stable than for Mn in low oxidation states.

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).
$[Ar]3d^6 4s^2$.
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 wrt Fe + Fe_3O_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 – $M(CO)_5$.

Ruthenium + Osmium

Occurrence –
Metallic state.

Extraction –
Distillation of tetroxide.

Structure –
Osmium is the most dense element.
HCP, not very malleable.

Trends in Oxidation States –
Both these metals will reach the group oxidation state of +8. This is the highest oxidation state for any element. Ru(VIII) not very stable though, unlike Os. Thus, 2nd row and 3rd row not quite so alike as earlier in transition series.
Most common states are +3 for Ru and +4 for Os.

Redox –
Virtually unaffected by non-oxidising acids, unlike iron. Hard to get them to react with non-metals as well unless powerful oxidising agents.
Resist atmospheric attack.

Structure of Oxides –
Do not compare to Iron at all. Lowest oxidation state of oxides is +4. RuO_2 & OsO_2 – rutile.
Tetroxides are volatile. Tetrahedral molecules. OsO_4 dissolves in alkali and oxidises HCl to Cl_2. Oxidises C=C bonds to diols. Very volatile and very toxic.
RuO_4 not as stable and can explode at 100°C or if brought into contact with oxidisable organic solvents.

Structure of Halides –
Heptafluoride of Os exists, but very unstable. OsF_6 is comparatively stable next to other hexafluorides.
Ru doesn't form Chlorides above +3 state, which is surprising when compared to Os.

Complexing –
Ru has some aqueous chemistry, while Os has none.
Osmium can form complexes based on OsO_4 in the Oxidation State of VIII.
Fluorides of Ru and Os exist in VII state.
Oxidation State IV (d^4) most stable for Osmium. Ruthenium complexes tend to reduce to Ru(III).
They are always low spin octahedral with 2 unpaired electrons.
Oxidation State III gives octahedral low spin again here with now 1 unpaired electron. Best state for Ru to be in. Os(III) rarely found, since it is either oxidised to IV, or if strong pi-acceptor ligands are present, reduced to Os(II).

Cobalt

Occurrence & Extraction –

Arsenides and sulphides. By-product of nickel extraction.

Structure –

Lustrous and silvery with bluish tinge. Less hard than others in triad, but harder than iron. HCP unless heated (FCC). Melting point and enthalpy of atomisation lower than previous group due to more d electrons in the inert core.

Trends in Oxidation States –

Lower range of oxidation states here due to stability of (n-1)d electrons – attraction to nucleus is now sufficient to prevent the elements attaining the highest oxidation states. No Group Oxidation State.
+5 is highest oxidation state, but rare, as is +4.
+2 and +3 most common. +3 is a strong oxidising agent, and will oxidise water with evolution of oxygen. Thus, Co(III) produces few simple salts, and they are unstable. Is a very good complexing metal though – low spin t_{2g}^6 produces very high CFSE.

Redox –

Less reactive than iron.
Stable to atmospheric oxygen unless heated. Dissolves to give Co(II). Unreactive to H_2 and N_2. Reacts with C, P, S, X on heating.
Oxoanion compounds are rare since binding oxygen will donate pi-electrons, and the Co shell is already rather full.

Coordination Numbers –

Rarely above 6, reflecting trend to decrease in coordination across period.

Structure of Oxides –

Only two forms – CoO and Co_3O_4.
CoO is stable in air up to 600-700°C.
$Co(II)Co(III)_2O_4$ has normal spinel structure. Expected since d^6 favours octahedral sites – low spin implies favourable CFSE.

Structure of Halides –

Co forms dihalides predominantly, and also CoF_3 (highly oxidising). Co is always octahedrally coordinated.

Complexing –

Oxidation State III – large range of complexes, due to low spin octahedral arrangement giving large CFSE with t_{2g}^6 ($^{12}/_5\Delta_o$). Binds very strong to N-donors.
Co(III) complexes are kinetically inert, so are made by oxidising Co(II) in presence of ligands.
O-donor ligands are less stable than N-donors.
Forms bridged superoxide states though (dimer).
Class a metal – doesn't bind to heavier atoms of Groups 15 & 16.
Oxidation State II – one of the most stable oxidation states. Not nearly as common as Co(III) since no longer t_{2g}^6 stable. Most commonly high spin octahedral, unless CN^- or similar ligand. Tetrahedral geometry is very favoured here compared to other transition metals (CFSE reasoning – d^7).
$[Co(H_2O)_6]^{2+}$ is stable now.
Oxidation State I – requires π-accepting stabilisation – organic ligands.

Organometallics –

M-M bonds required to satisfy 18e rule, so less common. $Co(CO)_4^-$ (Co^{-1}) is known (18e compound).

Rhodium + Iridium

Occurrence –

Metallic state.

Structure –
Lustrous and silvery. Both are hard metals. FCC – more stable than BCC/HCP when outer d orbitals are nearly full (first elements to do so).
Melting points and enthalpy of atomisation lower than previous group due to more d electrons in the inert core.

Trends in Oxidation States –
Lower range of oxidation states here due to stability of (n-1)d electrons – attraction to nucleus is now sufficient to prevent the elements attaining the highest oxidation states. No Group Oxidation State.
Effect of CFSE for Co is greater for heavier elements because field splittings are much greater. +3 is the most important state for Rh and Ir and only forms $[M(H_2O)_6]^{3+}$ aquo cation.
With strong π-accepting ligands, +1 oxidation state is known.
Significant differences however between Rh and Ir (e.g. +4 state for Ir), unlike most of the earlier triads. Trend as you move across 2nd row.

Redox –
React slowly on heating with oxygen. Very resistant to acids.
Oxoanion complexes are rare since binding oxygen will donate pi-electrons, and the M shell is already rather full.

Coordination Numbers –
Rarely above 6, reflecting trend to decrease in coordination across period.

Structure of Oxides –
Rh forms only Rh_2O_3 (the stable one) and RhO_2 (rutile), while Ir forms only IrO_2 (rutile).

Structure of Halides –
Ir and Rh can form higher fluorides, but mostly form the stable trihalides. RhF_6 is very unstable. Dihalides not known conclusively.

Complexing –
Ir(IV) is the only element in this triad capable of forming stable complexes in this oxidation state.
Rh(III) and Ir(III) are low spin and diamagnetic. Mostly octahedral. Similarly to Co(III), they bind to N-donors preferentially.
M-C bond strength increases in the order Co < Rh < Ir.
Rh will form bridged superoxides like Co.
Class b metals, unlike Co. Bind to P, As and S donor ligands. Transition from hard to soft occurs at Rhodium.
Oxidation State II – not stable, unlike Co(II).

Organometallics –
M-M bonds required to satisfy 18e rule – no mononuclear carbonyl complexes.

Nickel
Occurrence –
NiS. Note sulphide not oxide, reflects high covalency of metal-sulphide bond. This is because as Z_{eff} increases across the period, the energy of the accepting orbitals is lowered. Thus, sulphides are less soluble. Also, Ni-Ni bond length is as short as possible.

Extraction –
Heat in air. $NiO + C \rightarrow Ni$. Purified by adding carbonyl.

Structure –
Silvery-white, lustrous. Malleable and ductile. FCC – nearly filled d-shells predicts this.

Ionisation Energy –
+2 has high ionisation energy, hence small heat of formation (easily reduced to metal). Ni = 737 kJ mol^{-1}.

Trends in Oxidation States –
+2 is the most stable state, with 0 and +4 also known. +4 has low thermal stability. +3 is very rare, and needs highly stabilising ligands.
Note decrease in maximum oxidation state trend starting with Mn.

Redox –
Not particularly reactive, though will tarnish when heated in air. React with P, S more readily, so “soft”.

Coordination Numbers –
Octahedral with small uncharged ligands.
Tetrahedral with large charged ligands.
Square Planar with strong field ligands (normally π-acceptors).
More reluctant to form compounds with high coordination numbers (rarely above 6).

Structure of Oxides –
Only really forms NiO. Greater range of nickel sulphides possible, with the NiAs structure.

Structure of Halides –
Trihalides not really known – impure mixtures of oxidation states.
Dihalides dissolve in water to give the aquated ion easily.

Complexing –
Oxidation State IV – Octahedral, diamagnetic. Low spin t_{2g}^6 configuration.
Oxidation State III – more numerous for Ni than for Pd/Pt. Jahn-Teller distortion will occur here ($t_{2g}^6e_g^1$).
Oxidation State II – easily the most stable state. Thus, resists redox reactions. Ni(II) will bind to a wide range of ligands. Mostly octahedral and square planar, except $[NiX_4]^{2-}$ which are tetrahedral (ligand not strong enough to support Square Planar arrangement).
d^8 configuration favours octahedral over tetrahedral. Also, for square planar, all 8 electrons can be in 4 lower orbitals, thus low symmetry or strong ligands split the d-orbitals enough to offset the energy required to pair up 2 electrons. Favoured for strong field ligands.

Organometallics –
$[Ni(CO)_4]$ conforms to 18 electron rule.

Palladium + Platinum
Occurrence –
As metals.

Extraction –
Dissolve in aqua regia (conc. HNO_3 for oxidation, conc. HCl for chloride complexing, aquo complexes unstable wrt metal ➔ as metals).

Structure –
Silvery-white, lustrous. Malleable and ductile.
FCC

Ionisation Energy –
Pd = 804 kJ mol^{-1} and Pt = 965 kJ mol^{-1}.

Trends in Oxidation States –
Only even numbered oxidation states dominant. Can reach +6 (PtF_6).

Redox –
Fairly unreactive.
Strongly prefer class-b type ligands (“soft”).

Coordination Numbers –

All complexes in the (II) state are square planar, as in halides.
Anything not 4-coordinate form chains or clusters (apart from PtF_2 – rutile. Loss of LE is largest with small anion. Poor ligand doesn't yield much gain from LFSE).
Reasons for this – ligand field splitting effect increases with increased d-orbital radius, steric factors are reduced as metal gets bigger, as is electron-electron repulsion.

Structure of Oxides –
Only PdO and PtO_2 formed.
Note that chemistry of Pd and Pt is varied, showing breaking of trend of 2nd = 3rd row as the period continues.

Structure of Halides –
No PtF_2. Pt is only element that reaches hexa- and pentahalides. Not too stable though – one of the most potent oxidising agents.
All Tetrahalides known for Pt.
Pd doesn't even form trihalides convincingly, they tend to be impure mixtures like Nickel. Dihalides adopt chains which involve square planar geometry, which is always preferred by these two metals.

Complexing –
Oxidation State IV – Octahedral, diamagnetic. Low spin t_{2g}^6 configuration. Pd less common than Pt in this state.
Oxidation State II ligand binding causes very large splitting of these orbitals – planar and diamagnetic.
In lower oxidation states, phosphines are required to stabilise carbonyl ligands. Something to do with sigma bonding role and ionisation energies of Pd/Pt being higher.
Pt(IV) complexes stable and inert. Tends to favour harder ligands, while soft ligands prefer Pt(II).
No aquated ion, $Pt(H_2O)_4^{2+}$.
Sulphur and Phosphorus donors are preferred to O and N donors – "type b" or "soft" metals. Reason – M-O bond is weak. Unlike the Ti-O bond where π-bonding helped strengthen this bond, now the d orbitals are filled with electrons so putting more electrons in destabilises the bond (this also explains why not PtF_2). Bonding dominated by sigma-bonds.

Organometallics –
π-acceptor ligands can bind to Pd and Pt, e.g. ethane. Extensive chemistry due to them being "soft".

Copper

Occurrence –
Common. Ores of sulphide, oxide and carbonate.

Extraction –
Can reduce oxides with carbon, but usually start with sulphides in blast furnace.

Structure –
Low mp, soft and very malleable. FCC.
Conduct electricity and heat extremely well due to $d^{10}s^1$ configuration.

Ionisation Energy –
1st ionisation energies are far higher than Group 1 alkali metals due to d electrons being very poor shielders.
However, 2nd and 3rd ionisation energies are much lower because a filled d shell is more easily disrupted than a p shell. Thus, they can reach oxidation states above +1.

Trends in Radii –
Ionic radii are far smaller than Group 1 alkali metals due to d electrons being very poor shielders.

Trends in Oxidation States –

IV can be reached only very rarely.

Favoured oxidation state is +2 (lowest total of IE1+IE2 of the 3 metals). Exists in aqueous in this state.

Redox –

Will react with air under heating, and sulphur and halides at room temp.

Coordination Numbers –

Rarely above 6. 2 is surprisingly well favoured for transition metals.

Cu(II) favours 4, 5 and 6. Geometry is hard to establish due to Jahn-Teller effect – distorted octahedral or square planar.

Structure of Oxides –

Cu_2O and CuO exist. Cu_2O is favoured by high temperatures.

Structure of Halides –

Cu will form dihalides but not trihalides.

CuF_2 has distorted rutile structure.

$CuBr_2$ tends to be more of a polymeric chain structure, reflecting the increased covalency with larger halides.

CuI_2 does not exist, as Iodide reduces the Cu(II) to Cu(I). CuF not stable – F too electronegative.

Complexing –

In water, Cu(II) more stable than Cu(I). Reason – smaller ion with higher charge interacts more strongly with solvent water. Difference here outweighs the 2nd IE and is in spite of Cu(I) d^{10} configuration being very stable.

Oxidation State III – low spin, square planar, diamagnetic (d^8).

Oxidation State II – most common for Cu, and most ligands bind in this state (except CN- and I-, which reduce it to Cu(I)). Strong Jahn-Teller effect of d^9.

Oxidation State I – diamagnetic. Colourless unless easily polarised ligand. Forms stable complexes with low solubility or strong π-accepting character. Usually tetrahedral.

Organometallics –

Compounds in neutral oxidation state are not very stable.

Cu(I) will form complexes with alkenes etc.

Silver + Gold

Occurrence –

Fairly common. Silver sulphides. Gold often elemental.

Structure –

Conduct electricity and heat extremely well due to $d^{10}s^1$ configuration.

Low mp, soft and very malleable. FCC.

Form a range of alloys.

Ionisation Energy –

1st ionisation energies are far higher than Group 1 alkali metals due to d electrons being very poor shielders.

However, 2nd and 3rd ionisation energies are much lower because a filled d shell is more easily disrupted than a p shell. Thus, they can reach oxidation states above +1.

Trends in Radii –

Ionic radii are far smaller than Group 1 alkali metals due to d electrons being very poor shielders.

Trends in Oxidation States –

Au(V) is known for fluorides, but also rare.

Ag favours +1 (due to having lowest ionisation energy of the 3 metals), Au favours +3 (lowest total of IE1+IE2+IE3). Indicative of the fact that the three metals are not very closely related in properties.

Redox –
Gold is the most electronegative metal. Can be reacted with group 1 metals and behave like a salt.
Near the bottom of the electrochemical series (unlike Group 1).
Very stable to reaction with air (close to platinum in their inertness). Silver tarnishes due to sulphide reaction. Gold does not.

Coordination Numbers –
Rarely above 6. 2 is surprisingly well favoured for transition metals.

Structure of Oxides –
Ag and Au do not bind to O as strongly as Cu, so they are less thermally stable.
AgO is not Ag(II), but in fact Ag(I)Ag(III)O_2 – diamagnetic. Reason is that it prefers the square planar arrangement with Ag(III). Will also form Ag_2O_3 and Ag_3O_4 for similar reasons.
Gold readily forms stable Tellurides.

Structure of Halides –
Only pentahalide is AuF_5. Not too stable. AuF_3 more stable.
Only dihalide is AgF_2.
Silver(I) forms all four monohalides with rock salt structure. Insolubility. Covalency.

Complexing –
For Silver, Ag(I) is more stable than Ag(II). Silver is much larger than Cu so difference in hydration energies is reduced, does not outweigh the d^{10} / +1 factors.
Au is stable +3 because of the CFSE associated with square planar d^8 configuration.
Au(V) exists with Fluoride ligand, octahedral anions.
Ag(III) is quite stable with periodates and tellurate complexes.
Au(III) is most stable for gold, and isoelectronic to Pt(II). Usually square planar (orbitals easily split).
Au(II) rare – usually a mix of Au(I) and Au(III).
Ag(II) are usually square planar and paramagnetic. High CFSE with 4d electrons.
Ag(I) is favoured. Doesn't bind well to oxygen (insoluble compounds) therefore soft (type b) metal. Prefers 2 coordinate linear complexes in this state as opposed to tetrahedra like Cu(I). This effect is also true for Au(I).
Au will form a range of cluster compounds in preference to polymeric complexes. M-M bonding favoured.

Organometallics –
Ag-C bond is very weak – highest stretching frequency of any metal carbonyl.
Compounds in neutral oxidation state are not very stable.
Ag(I) will form complexes with alkenes etc.