
d-Block chemistry

28.1 The *d*-block elements

- The atomic radii of the first row *d*-block elements do not decrease smoothly across the row as might be expected. This is because the increase in electron–electron repulsions across the series counteracts the effect of the increase in Z_{eff} .
- The first, second, and third ionization enthalpies increase across the first row *d*-block elements with increasing Z_{eff} , though there are some anomalies. These are due to the greater electron–electron repulsions between paired electrons than between unpaired electrons, and also losses in exchange energy.
- In a particular triad, the atoms of the second and third row *d*-block elements are larger than the atoms of the first row element, though of similar size to each other. The similarity in sizes of the second and third row atoms is caused by the lanthanide contraction.
- Metals on the left of the *d* block exist naturally as oxides and are obtained from the ores by reduction. Metals on the right of the *d* block occur naturally as sulfides, and are obtained by conversion to the oxide followed by reduction.

28.2 Chemistry of the first row *d*-block elements

- Although most *d*-block elements contain *s* electrons in addition to *d* electrons, in both ions and compounds the *s* orbital is of higher energy than the *d* orbitals. This means that the electronic configuration of a *d*-block element in a compound is *always* d^n and *never* $d^{n-2} s^2$.
- With the exceptions of Groups 3 and 12, *d*-block elements have more than one possible oxidation state, and this is reflected by the different oxides and halides the elements form.

- For the first row *d*-block elements the +3 oxidation state is more stable than the +2 oxidation state on the left-hand side, but the +2 oxidation state is more stable than the +3 oxidation state on the right-hand side.
- The availability of different oxidation states is a factor in the catalytic activity of many *d*-block compounds.

28.3 Coordination chemistry

- In a coordination complex, ligands are generally coordinated to a metal centre through electron pairs on their donor atoms.
- Monodentate ligands coordinate through one donor atom, whereas polydentate ligands coordinate through more than one donor atom, giving rise to chelate rings.
- The total number of donor atoms coordinated to a metal ion is known as the coordination number. For a first row *d*-block complex, this can vary from 2 to 8, but 4 and 6 are the most common.
- 4-coordinate complexes can be tetrahedral or square planar, and 6-coordinate complexes are almost always octahedral.
- Structural isomers and stereoisomers are possible for coordination complexes. Ionization isomers, hydrate isomers, coordination isomers, and linkage isomers are types of structural isomers. Geometric isomers and configurational isomers are both types of stereoisomers.
- Metal ions and ligands can be divided into hard and soft classes. Hard metals have high charges or high charge densities, whereas soft metals are larger, with lower charges, and more polarizable. Hard ligands have small electronegative donor atoms such as N, O, or F, whereas soft ligands have larger, more polarizable donor atoms. Hard metals form more stable complexes with hard ligands and soft metals form more stable complexes with soft ligands.

28.4 Crystal field theory

- Crystal field theory is an electrostatic model of bonding in coordination complexes that considers the ligands as point charges. Electrostatic attraction between the metal ion and the point charges holds a complex together. Electrostatic repulsion between the ligands and the metal *d* orbitals causes the *d* orbitals to lose their degeneracy and split into sets of different energies.

- In an octahedral complex, the d orbitals are split into two sets, with three orbitals stabilized (the t_{2g} set) and two orbitals destabilized (the e_g set). The crystal field splitting energy is the gap between these sets, and in an octahedral complex it is given the symbol Δ_o .
- In a tetrahedral complex, the d orbitals are split into two sets, with two orbitals stabilized (the e set) and three orbitals destabilized (the t_2 set). The crystal field splitting energy is Δ_t .
- The crystal field splitting energies Δ_o and Δ_t are related by the expression $\Delta_t = \frac{4}{9}\Delta_o$.
- The d -orbital splitting diagram for a square planar complex is obtained from that for an octahedral complex by stabilizing all of the orbitals with a z -component and destabilizing those without a z -component.

28.5 Filling the d orbitals

- Uneven occupation of the d orbitals means that the electrons in a transition metal complex are generally at a lower energy than in the free ion in a spherical field. The difference is called the crystal field stabilization energy.
- Octahedral complexes with the electronic configurations d^4 – d^7 have two possible arrangements, and the one that is adopted depends on the values of Δ_o and P , the pairing energy. If $\Delta_o > P$, a high spin complex is formed and, if $\Delta_o < P$, a low spin complex is formed.
- The ranking of ligands in order of decreasing Δ is called the spectrochemical series. Ligands with large values of Δ are called strong field ligands, and those with small values of Δ are called weak field ligands.
- Low spin complexes are favoured by a high charge on the metal ion and the presence of strong field ligands. Low spin complexes are more prevalent for second and third row d -block metals.
- Jahn–Teller distortions occur when there is a degenerate ground state. This is particularly significant for octahedral complexes in which the e_g orbitals are unevenly filled, which occurs in d^4 and d^9 configurations.

28.6 Colour in coordination compounds

- Many d -block complexes are coloured because photons of visible light give rise to electronic transitions between the two sets of d orbitals.

- The colour observed for a complex ion is complementary to the colour of the light absorbed.
- The intensity of an absorption is affected by three selection rules—the Laporte, parity, and spin selection rules. The more selection rules that are broken, the less intense the absorption.
- Charge-transfer absorptions do not involve $d-d$ transitions, so they generally give rise to intense colours.
- As a result of the parity selection rule, tetrahedral complexes are generally more intensely coloured than octahedral complexes.

28.7 Magnetic properties

- The magnetic moment of a first row transition metal complex is related to the number of unpaired electrons through the spin-only formula.
- By comparing the measured magnetic moment with the value calculated using the spin-only formula you can determine whether an octahedral complex is high spin or low spin and whether a 4-coordinate complex is tetrahedral or square planar.

28.8 Aqueous chemistry of the first row d -block ions

- Ligand substitution reactions occur when one ligand replaces another. This happens stepwise, and each ligand replacement reaction has an equilibrium constant known as a stability constant.
- The values of stepwise equilibrium constants decrease with increasing substitution for statistical reasons.
- Equilibrium constants are always higher for complexes of polydentate ligands than those of monodentate ligands. This is called the chelate effect and it is caused by greater changes in entropy.
- Redox reactions are common in aqueous solution, and the nature of the ligands affects the value of the reduction potential.
- Ions with a charge of +3 or more undergo hydrolysis, giving acidic solutions.

Learning outcomes

By the end of this chapter you should be able to do the following.

- Work out the valence electronic configuration for any *d*-block ion.
- Describe the trends in atomic radii, ionic radii, and ionization enthalpies across the first row of the *d* block and account for these.
- Explain why the second and third row elements in a *d*-block triad have similar chemistries, but are rather different from the first row element.
- Describe the general trend in the most stable oxidation states of the first row *d*-block elements, and explain its origin.
- Know the important geometries for coordination numbers between 2 and 8.
- Give the name of a coordination compound from its formula, and the formula of a coordination compound from its name.
- Work out the oxidation state of the metal in a coordination compound, its valence electronic configuration, and its coordination number.
- Work out if isomers are possible for a coordination compound and, if they are, describe the type of isomerism.
- Use the concept of hard and soft acids and bases to predict what type of ligands a particular ion will form the strongest complexes with.
- Work out the *d*-orbital splitting for octahedral, tetrahedral, and square planar complexes.
- Work out the crystal field stabilization energy (CFSE) for an octahedral or tetrahedral complex.
- Predict whether a complex is high spin or low spin from values of the crystal field splitting energy, Δ , and the pairing energy, P .
- Predict whether a complex will undergo a Jahn–Teller distortion.
- Explain the basis of colour in coordination compounds.
- Calculate the spin-only magnetic moment, μ_{so} , for a *d*-block complex.
- Understand the origin of the chelate effect.