

Transition metals



Transition Metals 1a) The d-orbitals of a free transition metal atom or ion are degenerate (all have the same energy.) However, when transition metals form coordination complexes, the d-orbitals of the metal interact with the electron cloud of the ligands in such a manner that the d-orbitals become non-degenerate (not all having the same energy.) The way in which the orbitals are split into different energy levels is dependent on the geometry of the complex. Crystal field theory can be used to predict the energies of the different d-orbitals, and how the d-electrons of a transition metal are distributed among them.

When the d-level is not completely filled, it is possible to promote an electron from a lower energy d-orbital to a higher energy d-orbital by absorption of a photon of electromagnetic radiation having an appropriate energy. Electromagnetic radiations in the visible region of the spectrum often possess the appropriate energy for such transitions. The magnitude of the splitting of the d-orbitals in a transition metal complex depends on three things: * the geometry of the complex * the oxidation state of the metal * the nature of the ligands(Kotz, J.

C 1987) Kotz, J. C. ; Purcell, K. F. Chemical and Chemical ReactivitySaunders: New York, 1987, Chapter 25. Rodgers, G. E. Introduction to Coordination, Solid State, and Descriptive Inorganic ChemistryMcGraw -Hill: New York, 1994, Chapter 4. b. The origin of colour in complex ions containing transition metals Complex ions containing transition metals are usually coloured, whereas the similar ions from non-transition metals aren't. That suggests that the partly filled d orbitals must be involved in generating the colour in some way.

Remember that transition metals are defined as having partly filled d orbitals. Octahedral complexes For simplicity we are going to look at the octahedral complexes which have six simple ligands arranged around the central metal ion. The argument isn't really any different if you have multidentate ligands - it's just slightly more difficult to imagine! | When the ligands bond with the transition metal ion, there is repulsion between the electrons in the ligands and the electrons in the d orbitals of the metal ion.

That raises the energy of the d orbitals. However, because of the way the d orbitals are arranged in space, it doesn't raise all their energies by the same amount. Instead, it splits them into two groups. The diagram shows the arrangement of the d electrons in a Cu^{2+} ion before and after six water molecules bond with it. Whenever 6 ligands are arranged around a transition metal ion, the d orbitals are always split into 2 groups in this way - 2 with a higher energy than the other 3.

The size of the energy gap between them (shown by the blue arrows on the diagram) varies with the nature of the transition metal ion, its oxidation state (whether it is $3+$ or $2+$, for example), and the nature of the ligands. When white light is passed through a solution of this ion, some of the energy in the light is used to promote an electron from the lower set of orbitals into a space in the upper set. Each wavelength of light has a particular energy associated with it. Red light has the lowest energy in the visible region.

Violet light has the greatest energy. Suppose that the energy gap in the d orbitals of the complex ion corresponded to the energy of yellow light. The yellow light would be absorbed because its energy would be used in promoting the electron. That leaves the other colours. Your eye would see

the light passing through as a dark blue, because blue is the complementary colour of yellow. | | | Examples: <http://www.chemguide.co.uk/inorganic/complexions/colour.html#top> 2. Transition metal compounds are paramagnetic when they have one or more unpaired d electrons. 15] In octahedral complexes with between four and seven d electrons both high spin and low spin states are possible. Tetrahedral transition metal complexes such as $[\text{FeCl}_4]^{2-}$ are high spin because the crystal field splitting is small so that the energy to be gained by virtue of the electrons being in lower energy orbitals is always less than the energy needed to pair up the spins. Some compounds are diamagnetic. These include octahedral, low-spin, d^6 and square-planar d^8 complexes. In these cases, crystal field splitting is such that all the electrons are paired up.

Ferromagnetism occurs when individual atoms are paramagnetic and the spin vectors are aligned parallel to each other in a crystalline material. Metallic iron and the alloy alnico are examples of ferromagnetic materials involving transition metals. Anti-ferromagnetism is another example of a magnetic property arising from a particular alignment of individual spins in the solid state (. adapted from "Transition Metalsa," 2012, from http://en.wikipedia.org/wiki/Transition_metal#Coloured_compounds) http://en.wikipedia.org/wiki/Transition_metal#Coloured_compounds) 3.

Catalytic properties The transition metals and their compounds are known for their homogeneous and heterogeneous catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states and to form complexes. Vanadium(V) oxide (in the contact process), finely divided iron (in the Haber process), and nickel (in Catalytic hydrogenation)

are some of the examples. Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first row transition metals utilize 3d and 4s electrons for bonding).

This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowering). (http://en.wikipedia.org/wiki/Transition_metal#Coloured_compounds). The d orbitals are what give transition metals their special properties. In transition metal ions the outermost d orbitals are incompletely filled with electrons so they can easily give and take electrons. This makes transition metals prime candidates for catalysis.

Transition metal catalysts can be very useful for oxidation/reduction reactions because their outer electrons are especially susceptible to oxidation and reduction. If an oxidized transition metal runs into a molecule it can take electrons from that molecule, thereby oxidizing the molecule. If a reduced transition metal runs into a molecule it can give the molecule electrons and reduce it. Because transition metals are easier to oxidize and reduce than other elements, this process goes faster!

Transition metals can both lend electrons to and take electrons from other molecules. By giving and taking electrons so easily, transition metal catalysts speed up reactions. (<http://www.chemeddl.org/resources/TSTS/Stahl/Stahl9-12/Transitionorbitals9to12.html>) Transition metals as catalysts Iron in the Haber Process The Haber Process combines hydrogen and nitrogen to make ammonia using an iron catalyst. Nickel in the

hydrogenation of C=C bonds This reaction is at the heart of the manufacture of margarine from vegetable oils.

However, the simplest example is the reaction between ethene and hydrogen in the presence of a nickel catalyst. Transition metal compounds as catalysts Vanadium(V) oxide in the Contact Process At the heart of the Contact Process is a reaction which converts sulphur dioxide into sulphur trioxide. Sulphur dioxide gas is passed together with air (as a source of oxygen) over a solid vanadium(V) oxide catalyst. Iron ions in the reaction between persulphate ions and iodide ions Persulphate ions (peroxodisulphate ions), $S_2O_8^{2-}$, are very powerful oxidising agents.

Iodide ions are very easily oxidised to iodine. And yet the reaction between them in solution in water is very slow. The reaction is catalysed by the presence of either iron(II) or iron(III) ions. * <http://www.chemguide.co.uk/inorganic/transition/features.html#top> 4. Test For Gases & Ions : <http://www.pearsonschoolsandcolleges.co.uk/Secondary/Science/14-16forEdexcel/EdexcelGCSEBiologyChemistryPhysics/Samples/ChemistryRevisionGuide/ChemistryRevisionGuideChapter16.pdf> Also Refer to Slide !