First row d-block

electronic structure

Table 18.1
The electron structures of atoms and ions of the elements K to Zn ((Ar) ≡ electron structure of argon)

Element	Symbol	Electron structure of atom	Common ion	Electron structure of ion
potassium	K	$(Ar)4s^1$	K^+	(Ar)
calcium	Ca	$(Ar)4s^2$	Ca^{2+}	(Ar)
scandium	Sc	$(Ar)3d^14s^2$	Sc^{3+}	(Ar)
titanium	Ti	$(Ar)3d^24s^2$	Ti^{4+}	(Ar)
vanadium	V	$(Ar)3d^34s^2$	V^{3+}	$(Ar)3d^2$
chromium	Cr	$(Ar)3d^54s^1$	Cr^{3+}	$(Ar)3d^3$
manganese	Mn	$(Ar)3d^54s^2$	Mn^{2+}	$(Ar)3d^5$
iron	Fe	$(Ar)3d^64s^2$	Fe^{2+}	$(Ar)3d^6$
			Fe^{3+}	$(Ar)3d^5$
cobalt	Co	$(Ar)3d^74s^2$	Co^{2+}	$(Ar)3d^7$
nickel	Ni	$(Ar)3d^84s^2$	Ni^{2+}	$(Ar)3d^8$
copper	Cu	$(Ar)3d^{10}4s^1$	Cu^+	$(Ar)3d^{10}$
			Cu^{2+}	$(Ar)3d^9$
zinc	Zn	$(Ar)3d^{10}4s^2$	Zn^{2+}	$(Ar)3d^{10}$

physical properties K to Zn

	s-block metals			transition metals								
Element	**K**	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
Atomic radius/nm	0.24	0.20	0.16	0.15	0.14	0.13	0.14	0.13	0.13	0.13	0.13	0.13
Melting point/°C	64	850	1540	1680	1900	1890	1240	1540	1500	1450	1080	420
Boiling point/°C	770	1490	2730	3260	3400	2480	2100	3000	2900	2730	2600	910
Density/g cm^{-3}	0.86	1.54	3.0	4.5	6.1	7.2	7.4	7.9	8.9	8.9	8.9	7.1
Ionic radius/nm												
M^+	0.130											
M^{2+}		0.094		0.090	0.088	0.084	0.080	0.076	0.074	0.072	0.070	0.074
M^{3+}			0.081	0.076	0.074	0.069	0.066	0.064	0.063	0.062		

Table 18.3
Physical properties of the elements K to Zn

electronic structure

Element		3d					4s
		Electron structure					
Scandium	(Ar)	↑					↑↓
Titanium	(Ar)	↑	↑				↑↓
Chromium	(Ar)	↑	↑	↑	↑	↑	↑
Iron	(Ar)	↑↓	↑	↑	↑	↑	↑↓
Copper	(Ar)	↑↓	↑↓	↑↓	↑↓	↑↓	↑

Figure 18.2
The 'electrons-in-boxes' representation of the electron structures of certain transition metals.

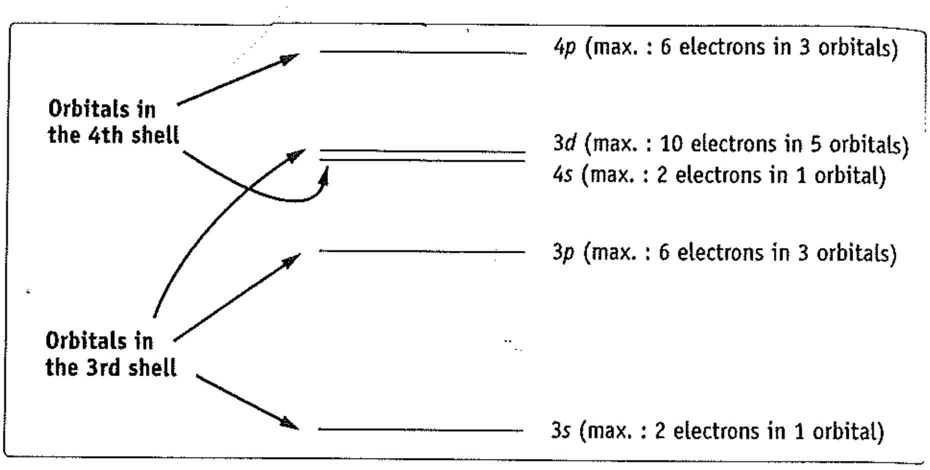


Figure 18.1
Relative energy levels of the 3*s*, 3*p*, 3*d*, 4*s* and 4*p* orbitals.

Atom/Ion		3d					4s
		Electron structure					
Mn	(Ar)	↑	↑	↑	↑	↑	↑↓
Mn^{2+}	(Ar)	↑	↑	↑	↑	↑	
Mn^{3+}	(Ar)	↑	↑	↑	↑		
Fe	(Ar)	↑↓	↑	↑	↑	↑	↑↓
Fe^{2+}	(Ar)	↑↓	↑	↑	↑	↑	
Fe^{3+}	(Ar)	↑	↑	↑	↑	↑	

Figure 18.8
Electron structures of manganese, iron and some of their respective ions.

variable oxidation states

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Common oxides	Sc_2O_3	Ti_2O_3	V_2O_3	Cr_2O_3	MnO	FeO	CoO	NiO	Cu_2O	ZnO
		TiO_2	V_2O_5	CrO_3	MnO_2	Fe_2O_3	Co_2O_3		CuO	
					Mn_2O_7					
Common chlorides	$ScCl_3$	$TiCl_3$	VCl_3	$CrCl_2$	$MnCl_2$	$FeCl_2$	$CoCl_2$	$NiCl_2$	$CuCl$	$ZnCl_2$
		$TiCl_4$		$CrCl_3$	$MnCl_3$	Fe_2Cl_6			$CuCl_2$	

Oxidation numbers that occur in compounds	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
					7					
				6	6	6				
			5	5	5	5	5			
		4	4	4	**4**	4	4	4		
	3	**3**	**3**	**3**	3	**3**	**3**	3	3	
		2	2	2	**2**	**2**	**2**	**2**	**2**	**2**
		1	1	1	1	1	1	1	**1**	

Figure 18.5
Oxidation states of the elements Sc to Zn. (Common oxidation numbers are in bold print.)

ionization energies

Table 18.2
Electronegativities, ionisation energies and electrode potentials for the elements Sc to Zn

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Metallic (atomic) radius/nm	0.16	0.15	0.14	0.13	0.14	0.13	0.13	0.13	0.13	0.13
Electronegativity	1.2	1.3	1.45	1.55	1.6	1.65	1.7	1.75	1.75	1.6
First ionisation energy/kJ mol^{-1}	+630	+660	+650	+650	+720	+760	+760	+740	+750	+910
Second ionisation energy/kJ mol^{-1}	+1240	+1310	+1410	+1590	+1510	+1560	+1640	+1750	+1960	+1700
Third ionisation energy/kJ mol^{-1}	+2390	+2650	+2870	+2990	+3260	+2960	+3230	+3390	+3560	+3800
Electrode potential for $M^{2+}(aq) + 2e^- \rightarrow M(s)$/V			−1.20	−0.91	−1.19	−0.44	−0.28	−0.25	+0.34	−0.76
Electrode potential for $M^{3+}(aq) + 3e^- \rightarrow M(s)$/V	−2.1	−1.2	−0.86	−0.74	−0.28	−0.04	+0.40			

ionization energies

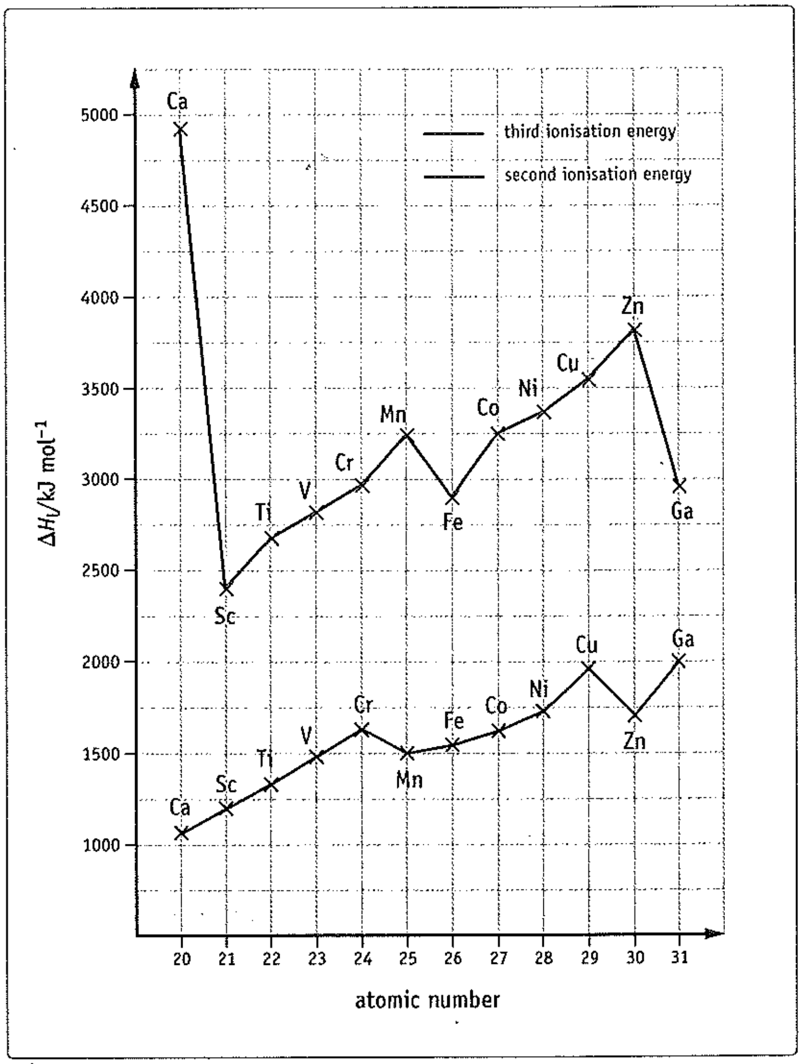


Figure 18.4
Graphs of the second and third ionisation energies of the elements from calcium to gallium.

coloured compounds: field splitting

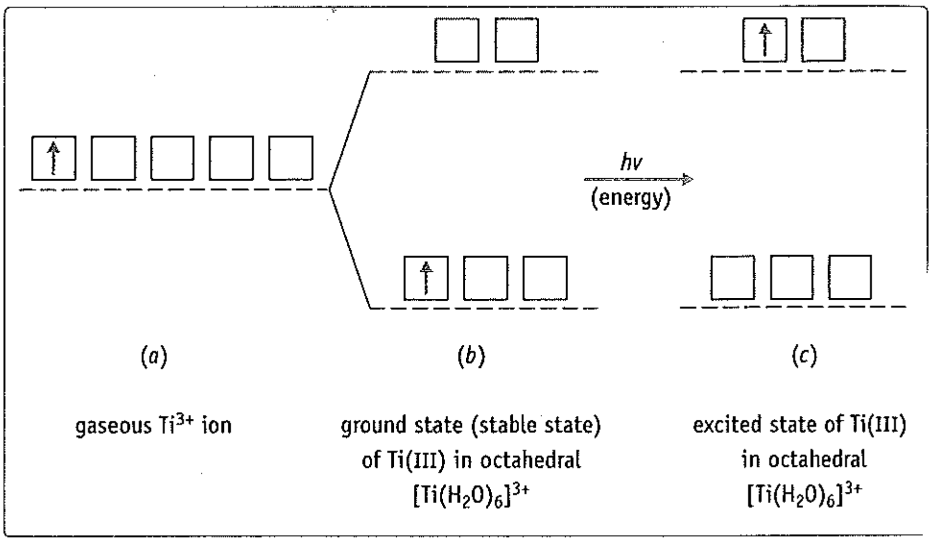
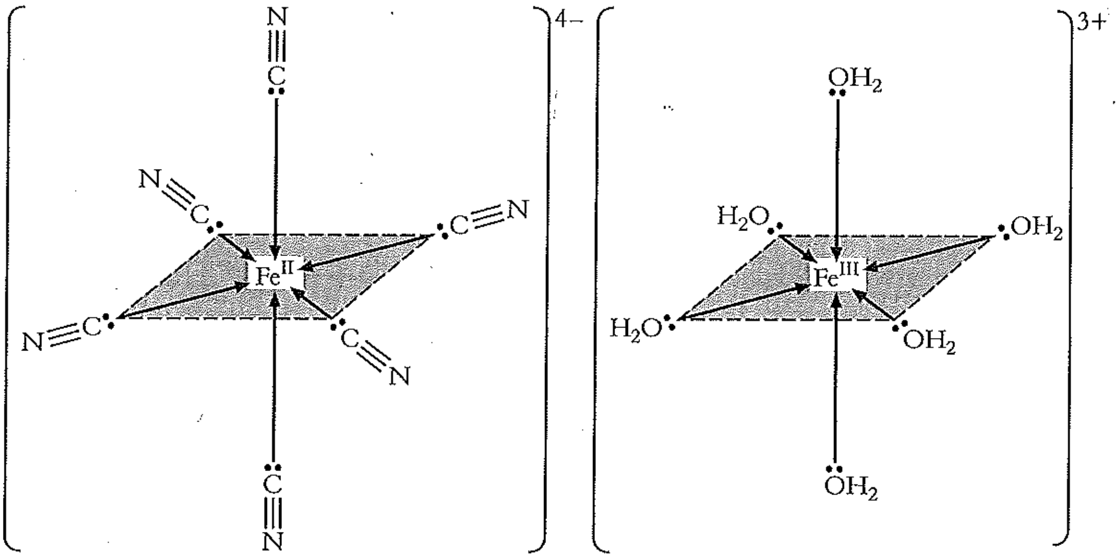


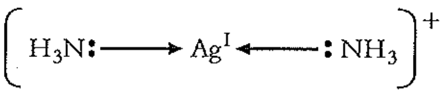
Figure 18.12
Relative energy levels for the five 3*d* orbitals of the gaseous and hydrated Ti^{3+} ion.

Figure
(a) Hexacyanoferrate(II) ion
(b) Hexaaquairon(III) ion

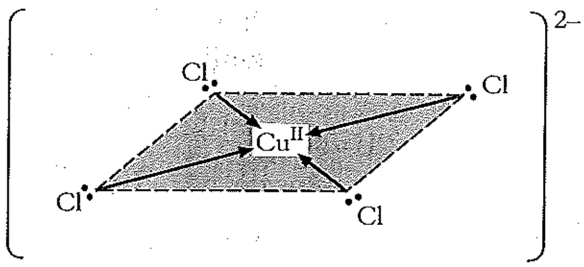
Complex ions



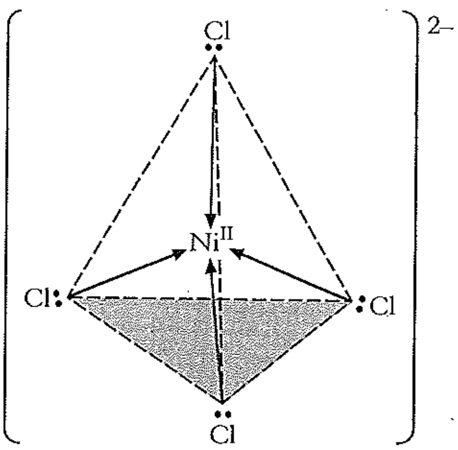
(a) (b)



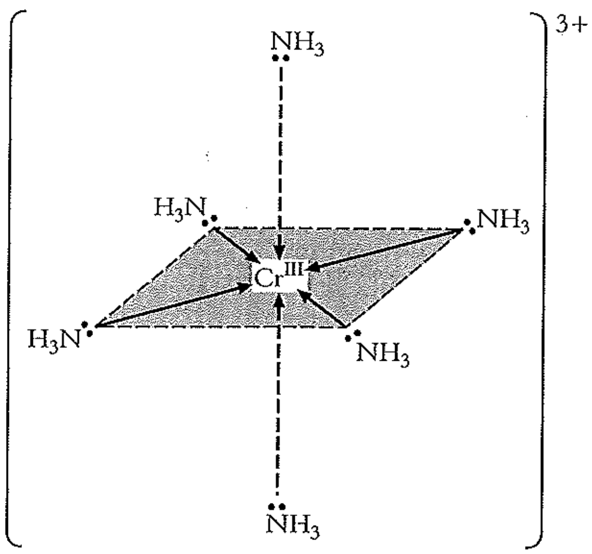
Diamminesilver(I) ion, coordination number 2, linear



Tetrachlorocuprate(II) ion, $CuCl_4^{2-}$, coordination number 4, square planar

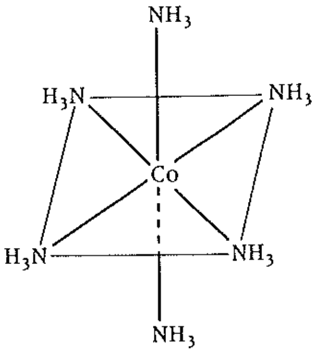


Tetrachloronickelate(II) ion, coordination number 4, tetrahedral

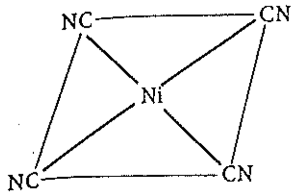


Hexaamminechromium(III) ion, coordination number 6, octahedral

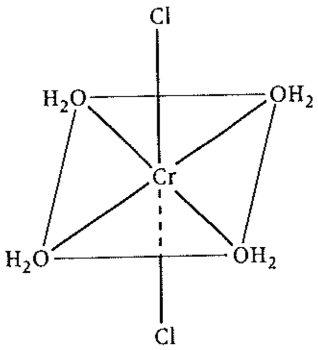
Complex ions: more examples



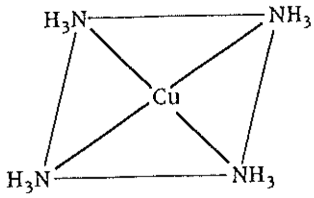
$[Co(NH_3)_6]^{3+}$



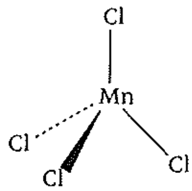
$[Ni(CN)_4]^{2-}$



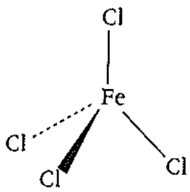
$[Cr(H_2O)_4Cl_2]^{+}$



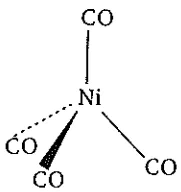
$[Cu(NH_3)_4]^{2+}$



$[MnCl_4]^{2-}$



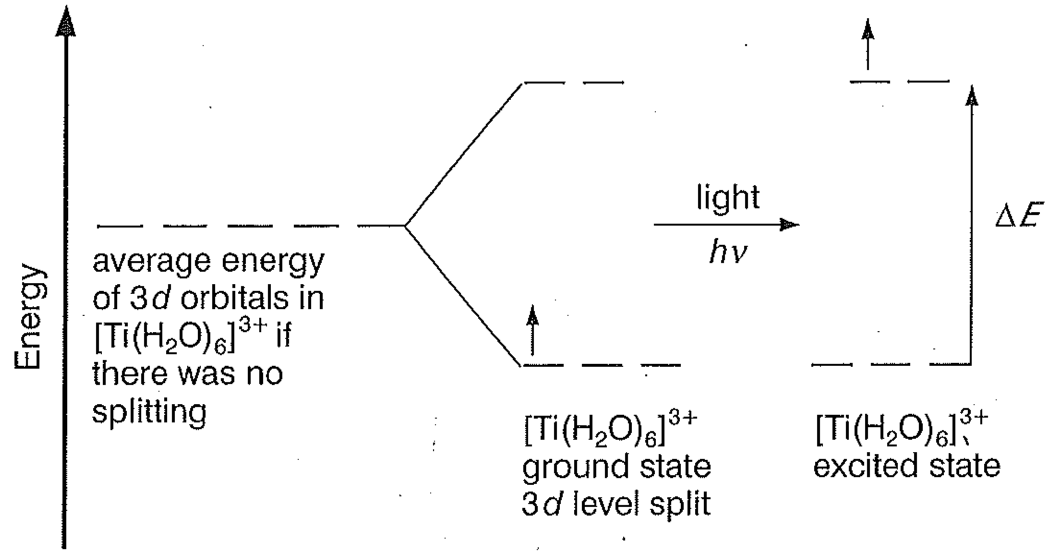
$[FeCl_4]^{-}$



$Ni(CO)_4$

Why do most complex ions have a colour?

Ligands cause field-splitting in the *3d* orbitals.

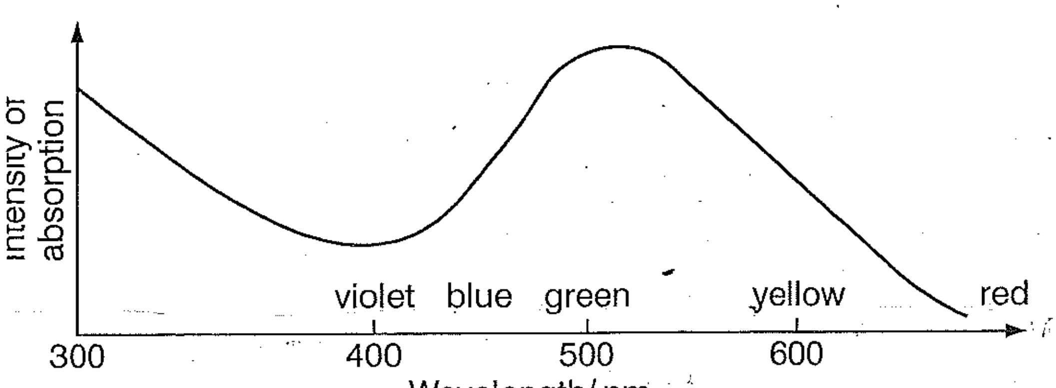


The relative energies for the five *3d* orbitals of the hydrated ion Ti^{3+}.

The frequency of the light absorbed by the electron corresponds to the energy needed for the transition of an electron from a lower energy *d* orbital to a higher energy *d* orbital.

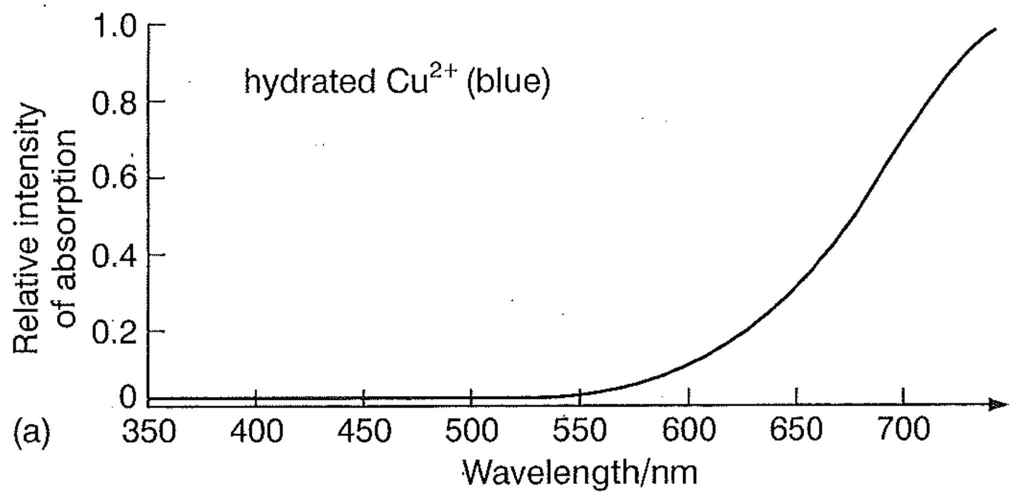
The frequency of the light absorbed depends on the energy difference between the two energy levels, ΔE (=hv). For most transition block metals the size of ΔE is such that the light absorbed fall in the visible light spectrum.

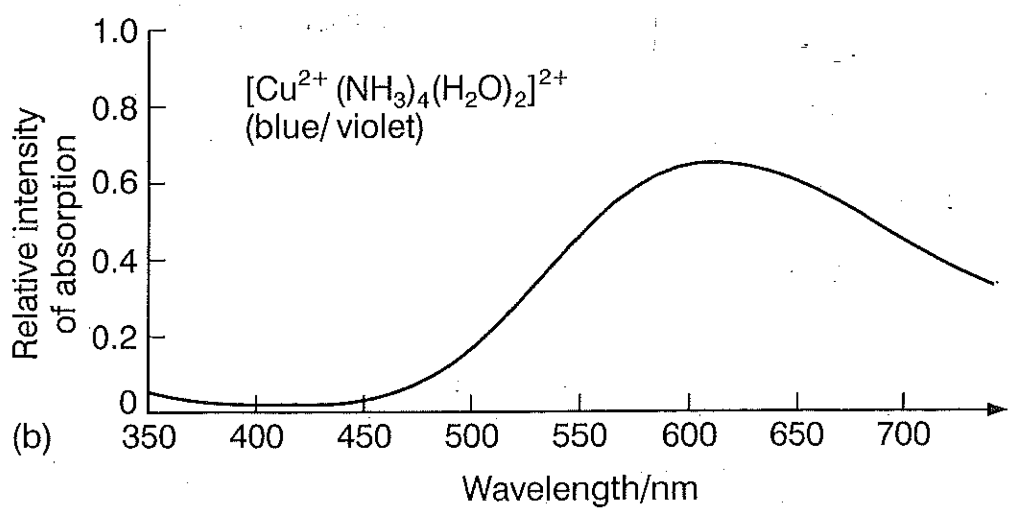
The absorption spectrum of the hydrated Ti^{3+} ion.



The nature of the ligand effects the colour of a complex.

For example in the Cu^{2+} complex, the NH_3 ligand causes a larger difference than the H_2O ligand which is why more light of a lower wavelength (higher energy) is absorbed.





CATALYSIS

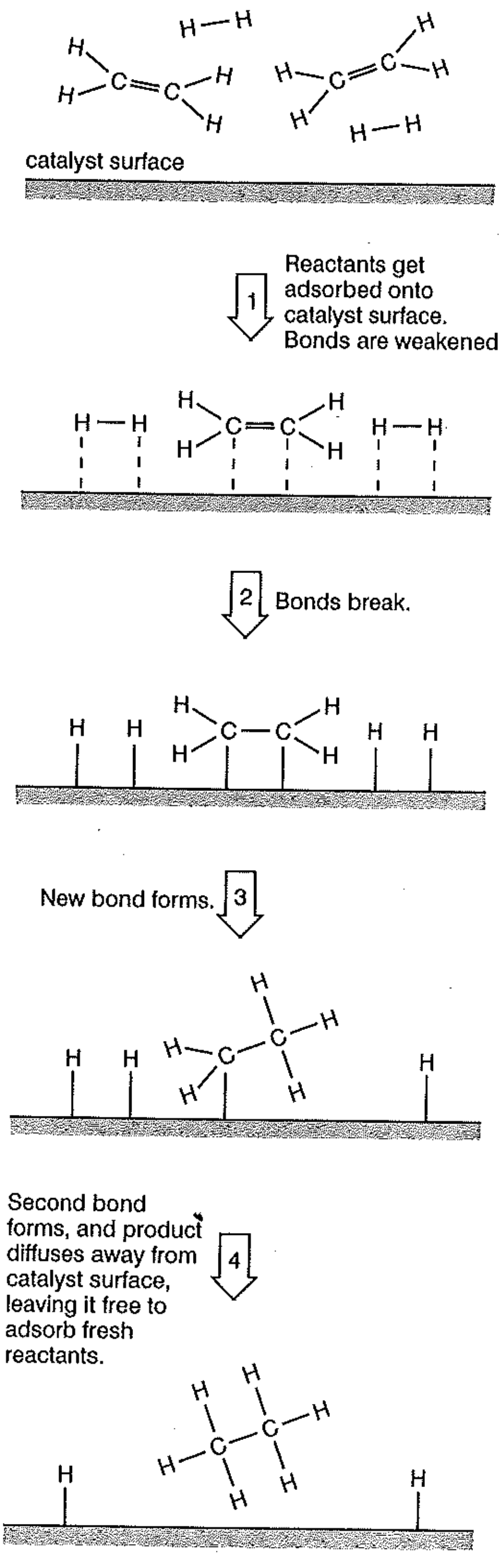
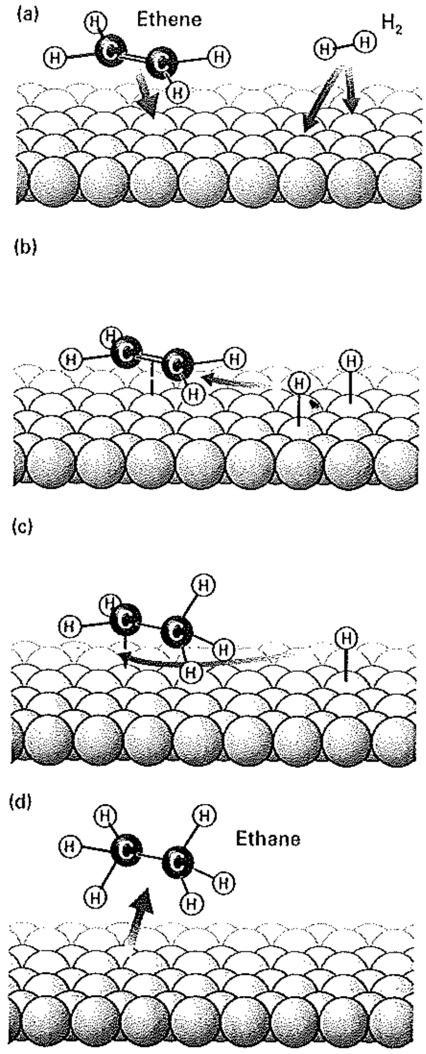
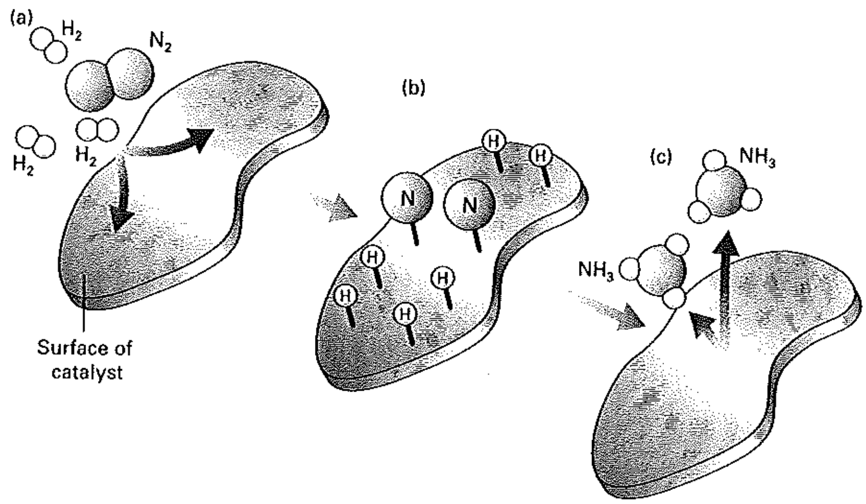


Figure 18 An example of heterogeneous catalysis. The diagrams show a possible mechanism for nickel catalysing the reaction between ethene and hydrogen to form ethane.



The four main steps in the catalytic hydrogenation of ethene: (a) Hydrogen atoms adsorb onto the surface; as does an ethene molecule. (b) Ethene reacts with a hydrogen atom; the radical $^{\bullet}CH_2$—CH_3 forms and attaches to the surface by means of the unpaired electron. (c) The radical reacts with another hydrogen atom to form CH_3—CH_3, which desorbs from the surface (d).



The reaction mechanism for the catalytic reduction of nitrogen by hydrogen on an iron surface. This diagram shows the three stages: (a) inward diffusion of reactants and (b) attachment to the catalyst surface; followed by reaction to form products; and (c) outward diffusion of products.