Kirkcaldy High School

Chemistry

Advanced Higher

Unit 1 – Inorganic Chemistry

TUTORIAL ANSWERS

(a) Electromagnetic radiation and atomic spectra

1.

   (a) Hydrogen
   (b) Helium

2. 169 kJ mol^{-1}

3.

   (a) 554 nm
   (b) 216 kJmol^{-1}

4. 302 kJ mol^{-1}

5.

   (a) 650 nm
   (b) 184 kJ mol^{-1}

6.

   (a) 588 nm
   (b) 204 in kJ mol^{-1}

7. 620 nm.
8. 389 nm
9. 405 nm
10. 487 nm
11. 326 nm
12. 617 nm

13.

(a) An electron is promoted to a higher energy level by electricity or heat and then falls back down emitting a photon of light with energy corresponding to the energy gap between the levels.

(b) The energy levels get closer together as energy increases

(c)

(i) 503 kJmol^{-1}

(ii) The smallest energy gap possible. *i.e.* a transition from n=3 to n=2

14.

(a) The largest energy transition possible (because wavelength is inversely proportional to energy) *i.e.* from level 8 to level 2.

(b) 183 kJmol^{-1}

15.
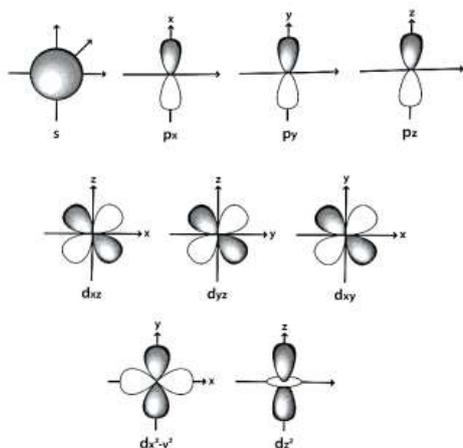
(a) Ultra-Violet

(b) 421 nm.

(c) An electron is promoted to a higher energy level by electricity and then falls back down emitting a photon of light with energy corresponding to the energy gap between the levels.

(d) To modify the properties of the steel.

16.

(a) 486 nm

(b) $n_1 = 1$. The frequency is higher so the energy gap must also be higher.

1.

2.

(a) 3

(b) 3

(c) 5

(d) 1

3. 2d

4. n=4, l=4, m_l=-4 or -3 or -2 or -1 or 0 or 1 or 2 or 3 or 4

5.

(a) 3s

(b) 2p

(c) 4d

(d) 3d

(e) 3p

6.

(a) Single electrons of opposite spins

(b) The orbital pointing along different axes.

(c)

(i) s = spherical, p= dumbell.

(ii) Orthogonal (pointing in different directions).

(d) The $2p_x$ or $2p_y$ orbitals already have electrons in them, the $2p_z$ orbital is empty. Degenerate orbitals are filled singly before electrons pair (Hund's Rule)

(e) The 3p, 4s and 3d orbitals fill before 4p. The electrons fill degenerate orbitals singly before pairing.

7.

(a)

(i) 1

(ii) 5

(b)

(i) 6

(ii) 2

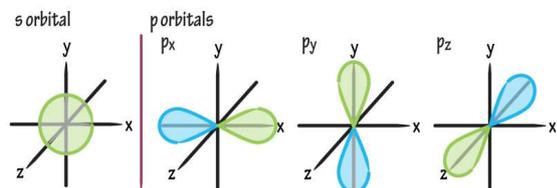(iii) 18

(c)

(i) 1

(ii) 4

8.

(a) Electrons in the same orbital must have opposite spins (Pauli Exclusion Principal)

(b) Electrons fill degenerate orbitals singly before spin pairing (Hund's Rule)

(c) Electrons fill atomic orbitals of the lowest available energy levels before occupying higher levels (Aufbau Principal)
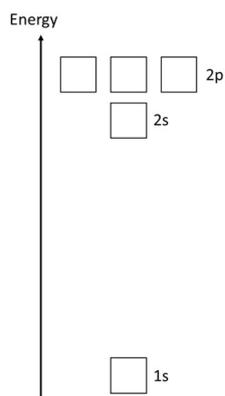
9.

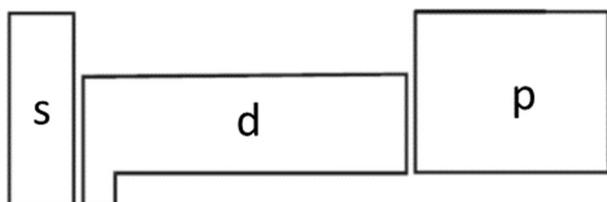(a)

(b) The energy levels that the electrons can occupy

(c) It is the principal quantum number.

(d) Same energies

(e)

10.

11.

(a) Manganese

(b) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$ OR [Ar] $4s^2 3d^5$

12.

(a) ~300kJmol^{-1}

(b) An electron is being removed from a full shell

(c)

   (i) There is only one electron to be removed to give a noble gas electron arrangement

   (ii) The number of orbitals increasing so the outer electron is more shielded from the nuclear charge by the inner electrons.

(d) The nuclear charge is increasing so there is a greater pull on the outer electron.   Shielding does not increase as the number of energy levels remains the same.

(e)

   (i) The electron in Boron is removed from a 2p orbital as opposed to the 1s orbital in Beryllium.

(f) Removal of the electron in oxygen leads to a half-filled 2p level.

13.

(a) An electron is promoted to a higher energy level by electricity and then falls back down emitting a photon of light with energy corresponding to the energy gap between the levels.

(b) The wavelengths of light emitted could be compared to literature (*e.g.* Data Book)

14.

(a) 393 nm – low wavelength = high energy.

(b) It would be the negative (*i.e.* black with coloured lines)

(c) 16 129 cm^{-1}

(d) Red

15.

(a) Heat or electricity

(b) They are promoted to a higher energy level.

(c)

   (i) The electron fall so down to a lower energy level and emits a photon of light corresponding to the gap between the levels.

   (ii) The photon of light

(d) Focus the spectrometer on one of the lines in the calcium emission spectrum (values are in literature *e.g.* Data Book)

(e) Emission Intensity

(f) A number of known concentrations of the ion are made and the intensities measured.   The plot is of intensity vs.   concentration.

(g) The intensity from the unknown concentration would be found and the plotted on the curve, the concentration is then read off the x-axis.

(h)

   (i) So that the absorption/transmission of only one frequency is measured.
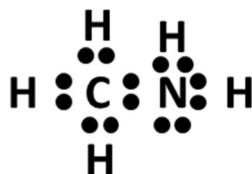
   (ii) Absorption/transmission

16.

17.
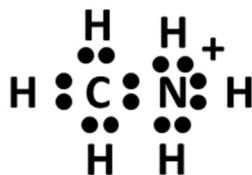
(a)

$$H_2O \rightleftharpoons H^+ + HO^-$$

$$+$$

$$H_2N\text{—}CH_3$$

$$\updownarrow$$

$$H_3\overset{+}{N}\text{—}CH_3$$
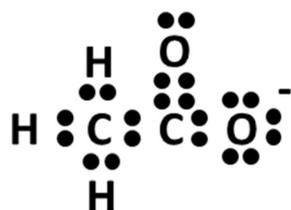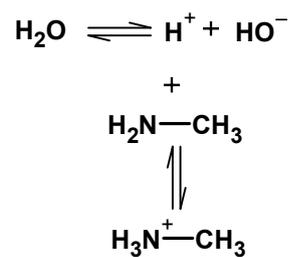
(b)

(i)

(ii)

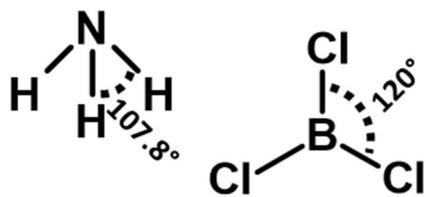

18.

(a) Trigonal planar

(b) The lone pair in NF_3 repels more than the bonding pairs so reduces the FNF angles compared to the $\angle FCF$ in $\angle CF_4$.
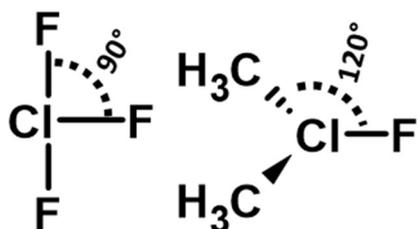
19.

(a)

(b) The nitrogen in NH_3 has a lone pair. The Boron in BCl_3 does not.

20.

(a) 5 pairs (3 bonding, two non-bonding)

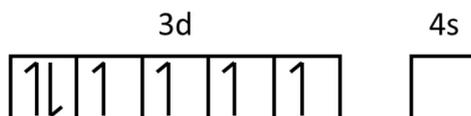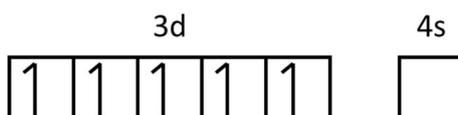(b) Trigonal bipyramidal (with equatorial lone pairs)

(c)

(c) Transition Metals

1.

(a) Fe^{2+}:

Fe^{3+}:

(b) They are both more stable that Fe^0 as the high energy 4s orbital has been removed. Fe^{3+} is particularly stable as the 3d shell is half-filled
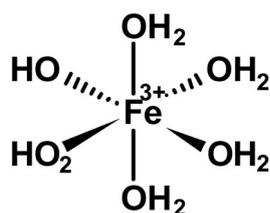
2.

(a) 1

(b) 10

(c) Electrons can be promoted from the 3d orbitals into the half-filled 4s.

3.

(a) Water and hydroxide. They form dative bonds by the donation of lone (non-bonded) pairs to the metal
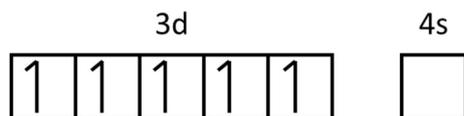
(b)

Octahedral

(c) Removing a proton (H^+) requires removing a positive charge from the complex. If the complex has a charge of 3+ then this will be easier than if it has a charge of 2+ (3+ has more to lose). Also, in $[Fe(OH_2)_5OH]^{2+}$, a proton has effectively already been removed to make the OH^-.

4.

(a) In the 3d orbitals, the electrons fill each orbital singly before spin pairing

(b)

3d   4s

| 1 | 1 | 1 | 1 | 1 | | |

(c) 4 or 1 depending on whether the complex is "high spin" or "low spin".

5. Silver chloride will remove "free" (non-bonded) Cl^-.

   (a) In the first complex there are two moles of free Cl- for every mole of complex so the formula of the complex must be $[Cu(NH_3)_4]^{2+}$.

   (b) In the second complex there is one mole of free Cl- for every mole of complex so the formula of the complex must be $[CuCl(NH_3)_3]^+$.

   (c) In the third complex there is one mole of free Cl- for every mole of complex so the formula of the complex must be $[CuCl_2(NH_3)_2]$.

   (d) They will have different gaps between the orbitals (most like split d orbitals allowing for d-d transitions).

6.

   (a) CrO_4^{2-} oxidation state of Cr = 6

       7 electrons to be removed

       4s electrons removed then 3d

       1s2 2s2 2p6 3s2 3p6

   (b) Ligand field splitting

   (c) CrO_4^{2-} oxidation state of Cr = 6

       $Cr_2O_7^{2-}$ oxidation state of Cr = 3

       Cr has been reduced. This is a redox reaction

7.

   (a) The peak is where the ratio of metal to ligand is 25:75 *i.e.*   1:3.   This suggests that the formula of the complex is $[Ni_x(NH_2CH_2CH_2NH_2)_3]^{2+}$

   (b) Each 1,2-diaminoethane molecule contains 2xN atoms, each of which has a lone pair that can form a dative bond to Ni^{2+}.

   (c) it allows the colourimeter to focus on the colour transmitted by the complex.

8. It's likely that V^{3+} in solution forms the complex $[V(OH_2)_6]^{3+}$. The 3+ oxidation state means that there will be two 3d electrons and the splitting pattern will be as follows:

11
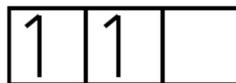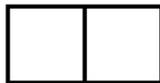
Therefore, it is possible for an electron to be transferred into the upper (e_g) level absorbing light in the visible range of the spectrum:
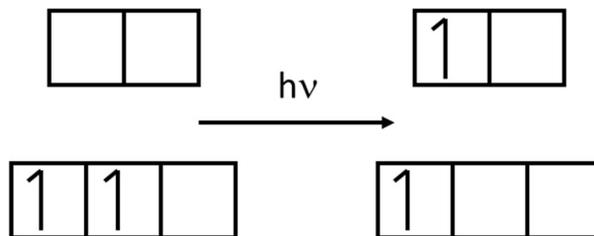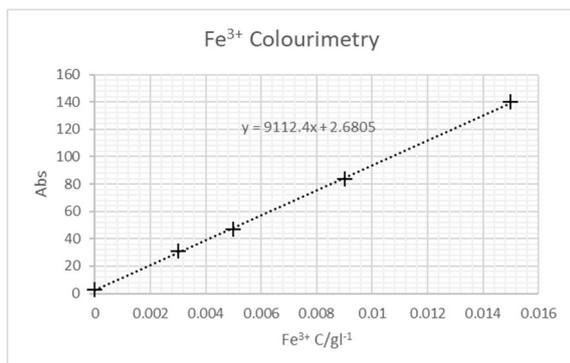

The corresponding opposite colour (from the colour wheel) be transmitted and this will be the colour seen.
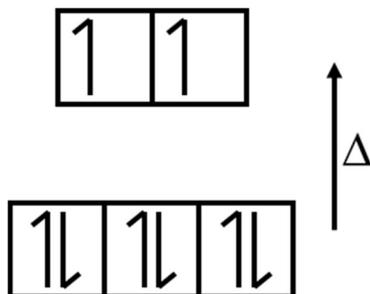
9.

(a) Red.

(b)

~0.007 gl-1

(c) Trace Fe^{3+} in the solvent..

(d) Repeat and average all results.

(e) Ligand field splitting

10.

(a) d-d transitions. Ni^{2+} has 8 3d electrons and the complex is octahedral so it has an electron arrangement of:
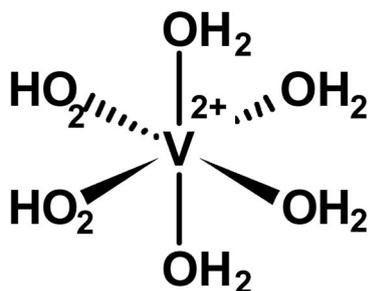

i.e. $t_{2g}^6 e_g^2$. Therefore transitions from the t_{2g} to the e_g orbitals are possible.

(b) Water ligands would reduce the value of Δ so the peak would move towards the red (lower frequency, larger wavelength)   end of the spectrum.

11.

(a) $[VO_2]^+ = V^{5+}$, $[V(OH_2)_6]^{2+} = V^{2+}$

(b)

Octahedral

(c)

(i) $1s^2 2s^2 2p^6 3s^2 3p^6$ or [Ar]

(ii) No d electrons so no opportunity for d-d transitions.

12. If the ion is colourless then the absorbance would be zero at all wavelengths within the visible spectrum.

13.

(a) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$ or $[Ar]3d^8$

(b) d-d transitions. Ni^{2+} has 8 3d electrons and the has likely formed the octahedral complex $[Ni(OH_2)_6]^{2+}$ in solution so it has an electron arrangement of:
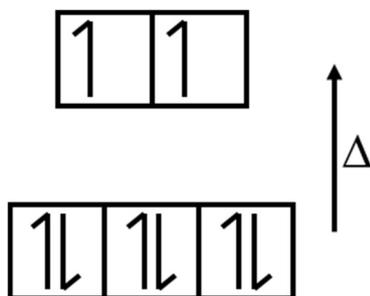
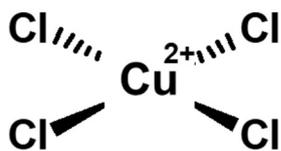*i.e.* $t_{2g}^6 e_g^2$. Therefore transitions from the t_{2g} to the e_g orbitals are possible.

(c) The aqua ligand has been exchanged for another ligand thus changing the value of Δ.

14.

(a) $[CuCl_4]^{2-}$

(b) Hexaaquachromium(II)

(c)

15.

(a) 501 nm

(b) 501 nm corresponds to green so complex would appear purple

16.

(a) Blue-green

(b) 222 kJ mol^{-1}

17.

(a) Zinc exclusively has an oxidation state of 2+ and 10 d electrons (full shell).   The fact that is has a fixed oxidation state makes it not like a conventional transition metal.

(b) Coloured and able to change valency.

(c) Iron in the Haber Process

Nickel in the hydrogenation of C=C bonds

Vanadium(V) oxide in the Contact Process

Iron ions in the reaction between persulphate ions and iodide ions

(d) The presence of unpaired d electrons or unfilled d orbitals is thought to allow activated complexes to form. This can provide reaction pathways with lower activation energies compared to the un-catalysed reaction.

18.

(a) Transition Metals

(b) The presence of unpaired d electrons or unfilled d orbitals is thought to allow activated complexes to form. This can provide reaction pathways with lower activation energies compared to the un-catalysed reaction.