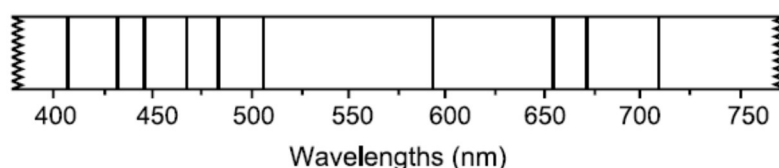# Kirkcaldy High School

Chemistry

Advanced Higher

# Unit 1 – Inorganic Chemistry

TUTORIAL QUESTIONS

(a) Electromagnetic radiation and atomic spectra

1. This spectrum was obtained from the atmosphere around the sun.

   (a) Write the name of the element which is responsible for the line at 656 nm.
   (b) Write the name of the other element present.

2. Calculate the energy, in kJ mol^{-1}, of the electron transition that causes the orange-yellow spectral line in the helium spectrum with a wavelength of 706 nm.

3. When a barium compound is placed in a flame, a green flame appears, which has a prominent line in the spectrum.

   (a) Refer to the Data Book to obtain the wavelength of the electron transition causing this line.
   (b) Calculate the energy, in kJ mol^{-1}, of the electron transition that causes this line.

4. Calculate the energy in kJ mol^{-1}, of the electron transition that causes the line in the ultra-violet area of the hydrogen spectrum with a wavelength of 397 nm.

5. When a strontium compound is placed in a flame, a red colour appears, which has a prominent line in the spectrum.

   (a) Refer to the Data Book to obtain the wavelength of this line.
   (b) Calculate the energy, in kJ mol^{-1}, of the electron transition related to this line.

6. Refer to the Data Book.

   (a) What is the wavelength of the electron transition causing an orange-yellow line in the helium spectrum?
   (b) Calculate the energy, in kJ mol^{-1}, associated with this spectral line.

7. A line in the visible spectrum is caused by an electron transition with an associated energy of 193 kJ mol^{-1}. Calculate the wavelength of this line in nanometeres.

8. A line in the ultra-violet spectrum is caused by an electron transition with an associated energy of 308 kJmol^{-1}. Calculate the wavelength of this line in nanometres.

9. A line in the visible spectrum is caused by an electron transition with an associated energy of 295 kJmol^{-1}. Calculate the wavelength of this line in nanometres.

10. A line in the visible spectrum is caused by an electron transition with an associated energy of 246 kJmol^{-1}. Calculate the wavelength of this line in nanometres.

11. When a metal compound is placed in a flame, a flame colour appears with a main spectral line with an associated energy of 368 kJmol^{-1}. Calculate the wavelength of this line in nanometres.

12. Photochemical reactions can be initiated by visible or ultra-violet light. Calculate the wavelength of radiation that would, in theory, start a reaction involving bromine (see page 11 of the Data Booklet).

13. The emission spectrum of an element is seen as a series of bright coloured lines on a dark background.
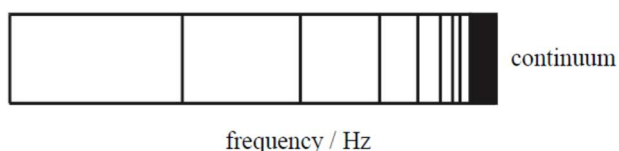

frequency / Hz

Within a series the intervals between the frequencies of each line decrease until the lines are so close together that they converge to form a continuous spectrum or continuum as shown in the diagram.

A graphical method can be used to find the start of the continuum. A plot of v against Δv can be extrapolated back to find where Δv is 0. This is the start of the continuum.
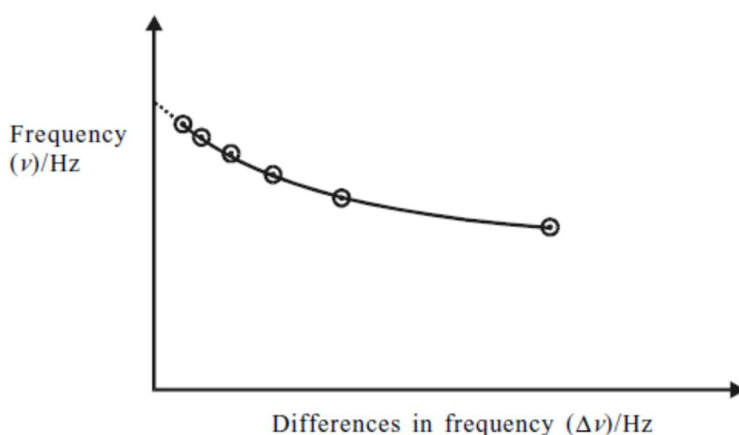

(a) What causes a line in an emission spectrum?

(b) Why do the lines converge as they reach the continuum?

(c)

   (i) Calculate the energy, in kJ mol^{-1}, of the emission line at the start of the continuum if the curve Δv intersects the y-axis (v) at 1.26×10^{15} Hz.

   (ii) What does this energy represent?

14. Below is a simplified diagram of the Balmer series in the emission spectrum of atomic hydrogen.

A

656   389
wavelength/nm
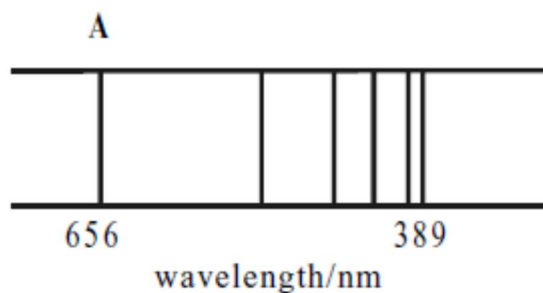
Spectral lines arise as a result of electronic transitions in atoms. The Balmer series is produced by the transitions shown in the following diagram.

Energy level

8
4
3
2

1

7
5 6
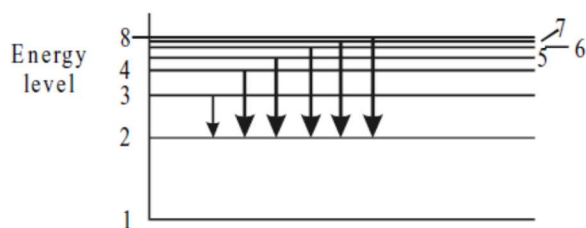
(a) What transition corresponds to a line A in the spectrum? Explain your answer.

(b) Calculate the energy difference, in kJ mol^{-1}, that gives rise to line A, with wavelength 656 nm.

15. The following technique is used to detect trace elements in steels and other alloys. The metal sample is sparked as shown in the diagram.
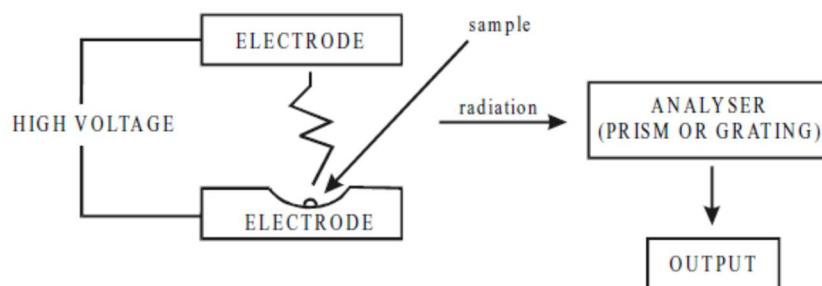
The output from one sample was as shown below.
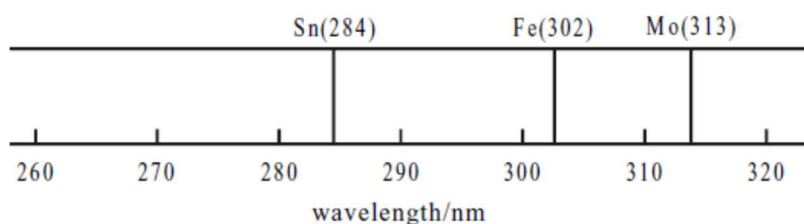
(a) In which region of the spectrum do these lines lie?

(b) Calculate the energy, in kJ mol^{-1}, of the line due to tin.

(c) Explain how this sparking procedure relates to the formation of the lines in the spectrum.

(d) Give one reason why elements are added in trace amounts to steels.

16. In the emission spectrum for hydrogen, there are several different series of 'spectral lines'. These lines result from electrons emitting energy as they fall back from higher to lower energy levels. Each spectral line may be represented by the equation:

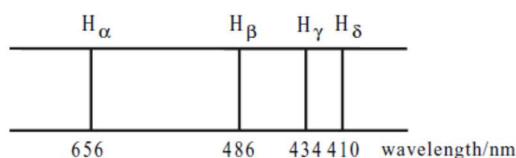$$\frac{1}{\lambda} = R_h \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Where

λ = wavelength of the spectral line

R_h = a constant, $1.097 \times 10^7 m^{-1}$

n_1 = energy level to which the electron falls

n_2 = energy level from which the electron falls.

The Balmer series occurs in the visible part of the electromagnetic spectrum, n_1 having a value of 2 for each line in the series. The first four spectral lines for this series are shown in the diagram.

(a) Use the equation to calculate the wavelength of the spectral line in the Balmer series that corresponds to the value n_2 = 4. State the colour of this spectral line.

(b) Lyman discovered a series of spectral lines for hydrogen in the ultra-violet region of the electromagnetic spectrum. What value must n_1 have for this series? Give a reason for your answer.

6

(b) Atomic orbitals, electronic configurations and the periodic table

1. What are the shapes of the s, p, and d orbitals respectively?
2. What is the maximum number of orbitals with:

    (a) n = 4, l = 1

    (b) n = 2, l = 1

    (c) n = 3, l = 2

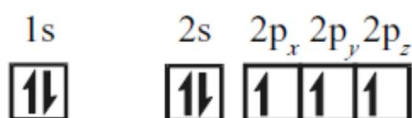   (d) n = 5, l = 1, m = -1

3. Which of the orbitals below cannot exist?

    <center>2p, 3p, 4d, 3f, 6s, 2d</center>

4. Write a set of quantum numbers for a 4f orbital.
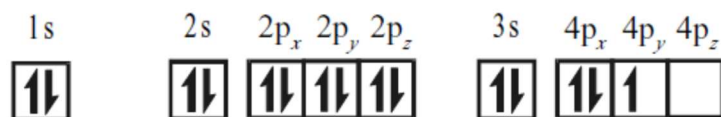5. Describe the electrons defined by the following quantum numbers:

	n	l	m
(a)	3	0	0
(b)	2	1	1
(c)	4	2	-1
(d)	3	2	2
(e)	3	1	0

6. The electron configuration for nitrogen is:

    (a) What do the symbols **1** and ⬇ represent?

    (b) What is the significance of x, y and z in the 2p sublevel?

    (c)

        (i) Describe the shape of the s and p orbitals.

        (ii) Describe the position of the p orbitals relative to each other.

    (d) Why is the $2p_z$ electron for nitrogen not placed in the $2p_x$ or $2p_y$ orbital?

(e) Phosphorus is in the same group as nitrogen but has 15 electrons. A student wrote the following configuration for phosphorus:

| 1s | 2s | 2p$_x$ 2p$_y$ 2p$_z$ | 3s | 4p$_x$ 4p$_y$ 4p$_z$ |

$$\text{1s } [\uparrow\downarrow] \quad \text{2s } [\uparrow\downarrow] \quad \text{2p}_x [\uparrow\downarrow] \text{ 2p}_y [\uparrow\downarrow] \text{ 2p}_z [\uparrow\downarrow] \quad \text{3s } [\uparrow\downarrow] \quad \text{4p}_x [\uparrow\downarrow] \text{ 4p}_y [\uparrow] [\;]$$

Explain the two mistakes in the student's answer.

7. The number of orbitals and the number of electrons in an energy level or sub-level is limited.

(a) Write the number of orbitals that make up:

(i) the s sublevel
(ii) the d sublevel.

(b) Write the number of electrons that are needed to completely fill:

(i) the p sublevel
(ii) the first energy level
(iii) the third energy level.

(c) Write the sublevels in:

(i) the first energy level
(ii) the fourth energy level.

8. There are four statements that you have come across in your study of electrons and atomic orbitals. These statements are:

The Aufbau principle
Heisenberg's uncertainty principle
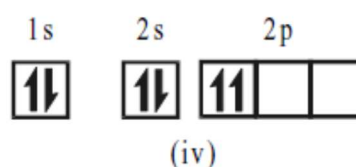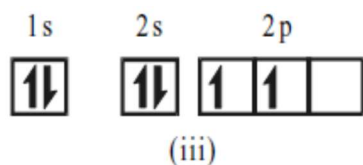**The Pauli exclusion**
Hund's rule of maximum principle multiplicity

(a) The electronic configuration for boron is given by (i) and not (ii).

$$\text{1s } [\uparrow\downarrow] \quad \text{2s } [\uparrow\downarrow] \quad \text{2p } [\uparrow][\;][\;] \qquad\qquad \text{1s } [\uparrow\downarrow] \quad \text{2s } [\uparrow\uparrow] \quad \text{2p } [\uparrow][\;][\;]$$
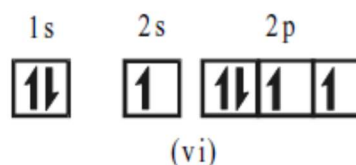$$\qquad\qquad\quad (i) \qquad\qquad\qquad\qquad\qquad\qquad\qquad (ii)$$
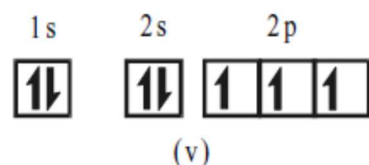
Explain why (ii) is wrong and identify which of the above statements justifies your choice.

(b) The electronic configuration for carbon is given by (iii) and not (iv).

Explain why (iv) is wrong and identify which of the above statements justifies your choice.

(c) The electronic configuration for nitrogen is given by (v) and not (vi).

Explain why (vi) is wrong and identify which of the above statements justifies your choice.

9.

(a) Draw diagrams, including axes, to represent a 2s orbital and the three 2p orbitals.

(b) What does an orbital diagram represent?

(c) What is the significance of the number 2 in the terms 2s and 2p?

(d) The three 2p orbitals are often degenerate. What does the term 'degenerate' mean in this context?

(e) Draw an energy level box diagram to represent the relative energies of the 1s, 2s and 2p orbitals in an isolated atom.

10. Copy the drawing below, which represents the Periodic Table (excluding hydrogen and helium), and mark on it 's', 'p' and 'd' to show which type of orbital is being filled in each part of the table.
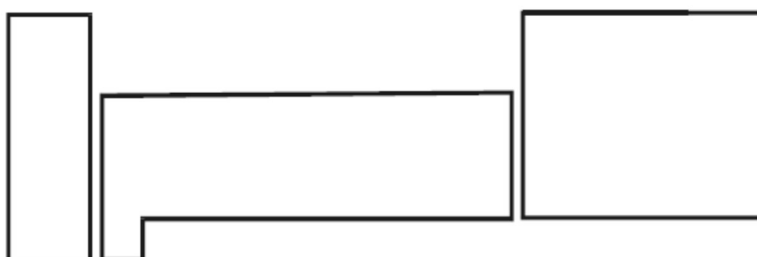
11. The electron configuration of an atom of element Y in the ground state can be represented as:
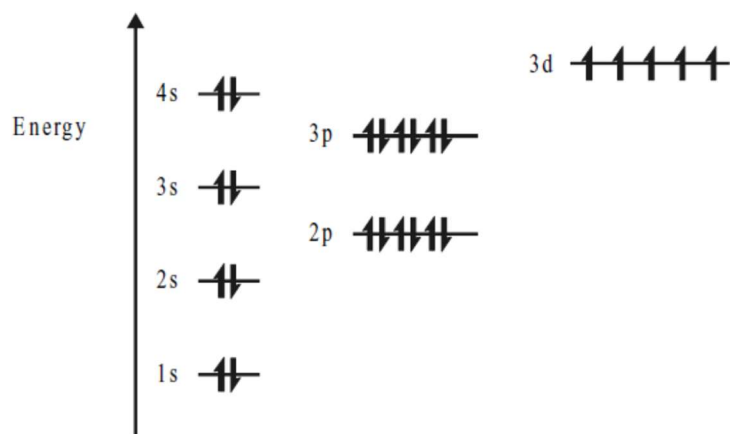
(a) Identify element Y.

(b) The electron configuration of an atom or ion may also be expressed in another form, e.g. $1s^2\ 2s^2\ 2p^1$ for boron. Give the electron configuration for Y in this form.

12. The first 20 elements show many periodic properties, *e.g.* the variation in first ionisation energy (IE).
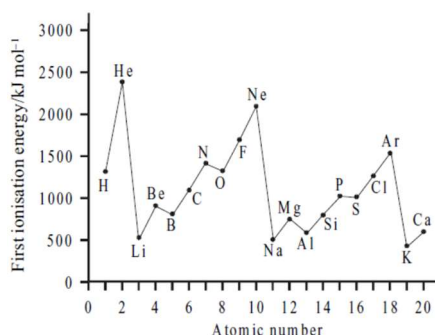
(a) Predict, from the graph, the first IE of rubidium.

(b) Explain why the noble gases have the highest values of IE in each period.

(c)

(i) Explain why the Group 1 metals have the lowest value of IE.

(ii) Explain why the values of IE decrease Li to Na to K.

(d) Explain the general increase in value of IE from Li to Ne.

(e)

(i) Explain the drop in value of IE from Be to B.

(ii) Explain the drop in value of IE from N to O.

13. When sodium vapour street lights are first switched on, they glow red before turning orange-yellow. This is because they contain some neon, which produces the red colour as the lamps warm up.

(a) Explain how the orange-yellow colour is produced by the sodium.

(b) How would the light coming from one of these street lights be analysed to prove the presence of both sodium and neon?

14. the diagram below represents part of the emission spectrum of a metal.

wavelength/nm
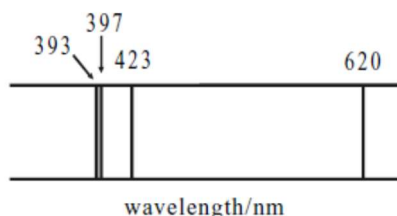
(a) Which line corresponds to the highest energy electron transition? Give a reason for your answer.

(b) In what way would an absorption spectrum of the metal differ in appearance from the above?

(c) Calculate the wavenumber, in cm^{-1}, of the 620 nm line.

(d) What colour would be observed if a salt of this metal were placed in a Bunsen flame?

15. The concentration of calcium ions in a sample of tap water can be measured by atomic emission spectroscopy (flame photometry).

    (a) How might the sample be energised?

    (b) State the effect this has on the electrons of the calcium ions.

    (c)

        (i) How then is energy emitted? (Answer in terms of the electrons.)

        (ii) What is detected by the spectrometer?

    (d) How can the chemist operating the spectrometer be certain that the emission that is measured is caused only by the calcium ions?

    (e) What property of this emission will be measured (and used to estimate the calcium ion concentration)?

    (f) Describe briefly the laboratory procedures necessary to construct a calibration curve.

    (g) State how the calibration curve would be used to find the calcium ion concentration in the water sample.

    (h) The same analysis could be performed by atomic absorption spectroscopy.

        (i) Why would it be important to use a lamp that gives light of a certain wavelength?

        (ii) What would be measured by the spectrometer using this technique?

16. The sodium salt of ethanoic acid is an ionic solid. It has the formula $CH_3COO^-Na^+$. Draw a Lewis electron dot diagram for the ethanoate ion.

17. Methylamine, CH_3NH_2, is the simplest amine. Methylamine disturbs the ionic equilibrium in water and forms an alkaline solution in exactly the same way as ammonia. The equations for the reaction between ammonia and water are:

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

$$+$$

$$NH_3$$

$$\big\updownarrow$$

$$NH_4^+$$
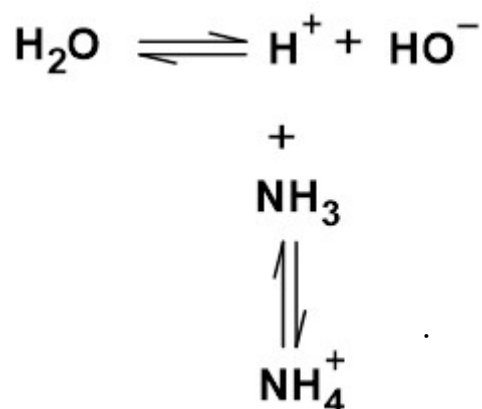
(a) Use equations to represent the reaction of methylamine with water.

(b)

   (i) Draw a Lewis electron dot diagram for methylamine.

   (ii) Draw a Lewis electron dot diagram for the methylammonium ion formed in the above reaction.

18. The table below gives information about three compounds containing fluorine.

Fluorine compound	Shape	Bond angle
$BF_3(g)$		$120°$
$CF_4(g)$	Tetrahedral	$109.5°$
$NF_3(g)$	Pyramidal	$107°$

(a) What is the shape of the BF_3 molecule?

(b) In terms of electron-pair repulsions, account for the difference in bond angle between CF_4 and NF_3.

19.

   (a) Sketch the shapes of NH_3 and BCl_3 molecules, showing clearly all the bond angles and their values.

   (b) Since both nitrogen and boron have three bonding electrons, why do NH_3 and BCl_3 not have the same molecular shape?

20. Chlorine and fluorine react to produce a compound of formula ClF_3. This molecule contains three chlorine–fluorine single bonds. Each fluorine atom contributes **one** electron to the bonding.

   (a) How many electron pairs (both bonding and non-bonding) surround the central chlorine atom in the molecule?

   (b) What would be the three-dimensional arrangement of electron pairs (both bonding and non-bonding) around the chlorine atom?

   (c) The fluorine atoms may occupy different positions in this shape, giving rise to three possible shapes for the molecule. Draw **two** of these, showing the angles between the bonds.

(c) Transition Metals

1. The 3d and 4s electronic structure for the nickel atom can be represented as follows:

    3d: $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$ $\uparrow$ 4s: $\uparrow\downarrow$

    (a) Draw the corresponding diagrams for Fe^{2+} and Fe^{3+}
    (b) How do these electron arrangements account for the relative stabilities of the two iron ions?

2. All three parts of the question below relate to the complex ion $[Cu(CN)_4]^{3-}$

    (a) What is the oxidation state of copper in the above ion?
    (b) How many electrons occupy the 3d energy levels of copper in this complex ion?
    (c) How does this ion absorb energy in the visible part of the electromagnetic spectrum?

3. Solutions of some complex ions are acidic. For example, an aqueous solution of iron(III) chloride can have a pH of 3.0. One of the processes occurring is:

    $$[Fe(OH_2)_6]^{3+} + 3Cl^-(aq) + H_2O(l) \rightleftharpoons [FeOH(OH_2)_5]^{2+} + H^+(aq) + 3Cl^-(aq)$$
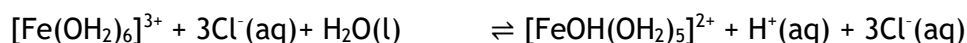
    (a) Name the two ligands in the complex structure on the right of the equation above and explain how they act as ligands.
    (b) Draw a diagram showing the shape of the complex ion on the right of the equation and name its shape.
    (c) It is more difficult to remove an proton (H^+) from $[Fe OH(OH_2)_5]^{2+}$ than from $[Fe(OH_2)_6]^{3+}$. Explain why this is so.

4. The electronic configuration of an atom of iron may be represented by:

    $[Ar]$ $\uparrow\downarrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow\downarrow$

    (a) How does this arrangement for the 3d electrons follow Hund's rule of maximum multiplicity?
    (b) Give a similar type of arrangement to represent the electronic configuration for an iron(III) ion.
    (c) In the complex ion hexacyanidoferrate(III), two of the 3d orbitals are at a higher energy level than the other three. How many unpaired 3d electrons are there in the complex ion?

5. Three compounds can result from the reaction between copper(II) chloride and ammonia. These compounds were reacted with silver(I) nitrate solution and the number of moles of silver(I) chloride formed per mole of each compound was calculated.

Compound	Empirical formula	Moles of silver(I) chloride
1	$CuCl_2.4NH_3$	2
2	$CuCl_2.3NH_3$	1
3	$CuCl_2.2NH_3$	0

(a) Using the above table, give the formula of the complex ion present in each compound. State reasons for your answers.

(b) Suggest why these three compounds have different colours from aqueous copper(II) salts.

6.

(a) The electron configuration of a neutral chromium atom is

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$$
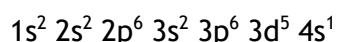
Write down the electron configuration of chromium in the yellow chromate ion, CrO_4^{2-} Show how you arrived at your answer.

(b) What is the name of the theory that explains the origin of colour in ions like chromate?

(c) Chromate ions, which are yellow, change into orange dichromate ions, $Cr_2O_7^{2-}$ on the addition of acid. Is this a redox reaction? Explain your answer.

7. Solutions of nickel(II) chloride and 1,2-diaminoethane, $NH_2CH_2CH_2NH_2$, of equal molarities were made up. From these a range of solutions of equal volume was prepared containing difference proportions of each. Each of the resulting solutions was then placed, in turn, in a colorimeter fitted with a filter that transmitted green light.
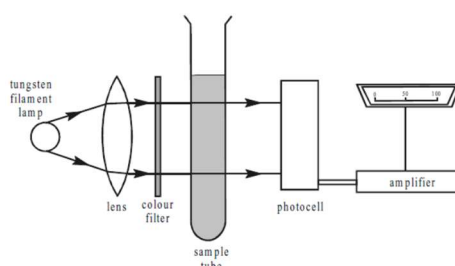
In this way the relative absorbance of each solution was determined and the following graph drawn.

Volume % of nickel(II) chloride solution

100 90   80   70   60   50   40   30   20   10   0

Volume % of 1,2-diaminoethane solution
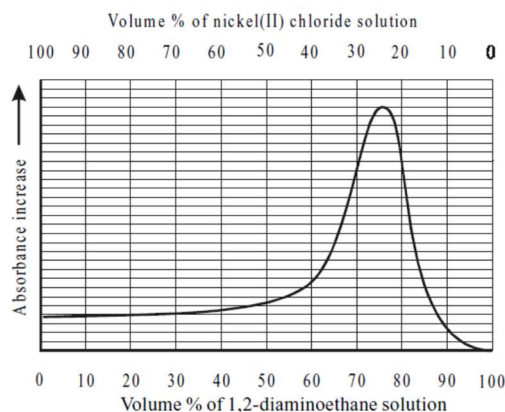
(a) The formula of the complex may be represented by: $[Ni_x(NH_2CH_2CH_2NH_2)_y]^{2+}$ Examine the graph. What are the likely values of x and y?   Explain your reasoning briefly.

(b) Suggest why 1,2-diaminoethane molecules should complex with Ni^{2+} ions.

(c) Explain the use of the green-coloured filter in the colorimeter.

8. Account for the green colour of an aqueous solution of V^{3+} ions (Make reference to ligands, electrons and the visible spectrum in your answer.).

9. In aqueous solution, Fe^{2+} forms a deep red complex with the colourless compound phenanthroline. The intensity of the colour for a particular concentration of Fe^{2+} is independent of pH in the range 2 to 9. With the aid of a single-beam colorimeter, an analysis of a series of solutions of Fe^{2+} with phenanthroline yielded the following results:

Concentration of Fe^{2+}/g l^{-1}	Reading on colorimeter
0.003	31
0.005	47
0.009	84
0.015	140
Solvent water	3
Unknown	64

(a) What colour of transmission filter should be used in the colorimeter?

(b) Evaluate the concentration of Fe^{2+} in the unknown solution.

(c) Suggest a reason why the solvent gave a reading.

(d) Suggest **one** improvement to the experimental method that would increase the accuracy of the result.

(e) Name **one** process responsible for the colour of transition metal complexes.

10. The ability of a ligand to split the d orbitals when forming a complex ion is given in the spectrochemical series. Three ligands from this series and their relative ability to split the d orbitals are:

$$NH_3 > OH_2 > Cl^-$$
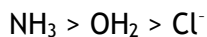
A study of part of the absorption spectrum for the complex ion, hexaaquanickel(II) shows a broad absorption band that peaks at around 410 nm.

(a) Explain the origin of the absorption band at this wavelength.

(b) State towards which end of the visible spectrum the wavelength of the absorption band would move if the water ligands were replaced by chloride ions. Give an explanation for your answer.

11. The table below gives information about complex ions containing vanadium.

Ion	Colour
$[V(OH_2)_6]^{2+}$	Violet
$[V(OH_2)_6]^{3+}$	Green
$[VO]^{2+}$	Blue
$[VO_2]^+$	

(a) Determine the oxidation number of vanadium in the ions $[VO_2]^+$ and $[V(OH_2)_6]^{2+}$

(b) Name and draw the shape of the green complex ion $[V(OH_2)_6]^{3+}$.

(c)

   (i) Give the electronic configuration for vanadium in the $[VO_2]^+$ ion.

   (ii) Suggest why you would predict this ion to be colourless.

12. Light of wavelength varying from 400 to 700 nm is passed through a solution containing $[VO]^{2+}$ ions. Copy the axes shown below and draw the absorption spectrum that you would expect to obtain.

18
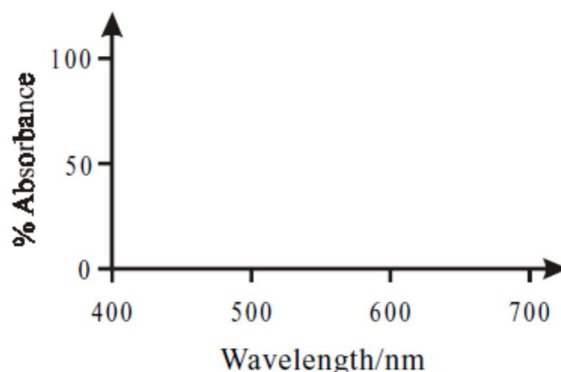
13. A green solution of nickel(II) chloride was added to a colourless solution of ammonium tetrafluoroborate, producing a pale lilac coloured complex.

(a) Write down the electronic configuration for the Ni^{2+} ion.

(b) Give a brief explanation for the green colour of the nickel(II) chloride solution.

(c) Suggest a reason for the change in colour when the two solutions react together.

14.

(a) For the complex ion tetrachloridocuprate(II), give the formula of the ion, including its charge.

(b) Dilution of a solution containing tetrachloridocuprate(II) ions with water results in all of the chlorido ligands being displaced by water ligands. An octahedral complex ion forms.
   Name the octahedral complex ion.

(c) Draw a full structural formula for tetrachloridocuprate(II).

15. In aqueous solution, the complex ion $[Ti(OH_2)_6]^{3+}$ has an available unoccupied energy level 239 kJ mol^{-1} above the highest occupied level.

(a) What wavelength of light will bring about the transition from the lower to the upper level?

(b) Using the Data Book, state the colour to which the wavelength in (a) corresponds. Hence deduce the observed colour of the solution in daylight.

16. The following are the absorption spectra of two coloured solutions containing complex cobalt(II) ions.

Spectrum of $[CuCl_4]^{2-}$:
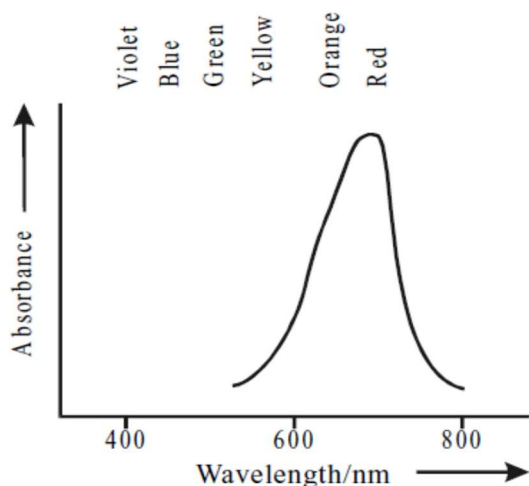
Spectrum of $[Cu(OH_2)_6]^{2+}$:
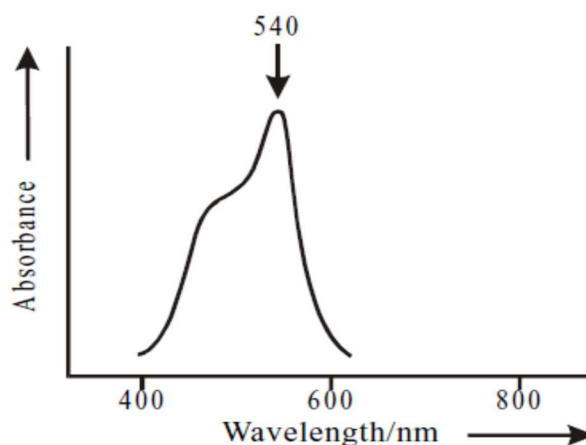
(a) Predict the colour of the solution containing $[CoCl_4]^{2-}$ ions.

(b) Calculate the energy difference, in kJ mol^{-1}, corresponding to the absorbance peak at 540 nm for the solution containing $[Co(OH_2)_6]^{2+}$ ions.

17. In some textbooks, zinc is not regarded as a transition element.

(a) Explain in terms of electronic structure why this should be so.

(b) Mention **two** characteristics of transition elements that are not shown by zinc.

(c) Name **three** different transition elements that can act as catalysts, giving the reaction or process that each catalyses.

(d) What is thought to be a reason for so many catalysts being derived from transition elements?

18. Organic chemists now use a wide variety of catalysts when producing designer molecules. These include WC, Mo_2C, VC, W_2N and $FeCl_3$.

(a) Identify an area of the Periodic Table that is common to these compounds.

(b) Explain in terms of electron orbitals how catalysts of this kind can affect the activation energy of a reaction.