University of Reading

FIRST YEAR UNDERGRADUATE CHEMISTRY

INORGANIC CHEMISTRY WORKBOOK

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'SKILLS FOR SCIENTISTS'

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Inorganic Chemistry Workbook

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The workbook contains a selection of typical questions with worked answers on the topics above. Following the example questions are questions which students can attempt themselves of a similar type. Worked answers can be found to the questions at the end of each section.

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Quantum Theory

Useful Data:
$c = 3.00 \times 10^{8}$ m s^{-1}
$h = 6.63 \times 10^{-34}$ J s
$m_{electron} = 9.11 \times 10^{-31}$ kg
$m_{neutron} = 1.67 \times 10^{-27}$ kg
$R_H = 1.10 \times 10^{7}$ m^{-1} / 3.29×10^{15} Hz
L (Avogadro's number) = 6.022×10^{23} mol^{-1}

Worked Example 1

a) Give the equation that relates the speed of light (c) to the frequency of the light (ν).

b) Give the units of each parameter in the equation.

c) Rearrange the equation to produce an equation relating the frequency of light to the wavelength.

d) Use this equation to find the frequency of light having a wavelength 456 nm.

e) Rearrange the equation to produce an expression for the wavelength.

f) What is the wavelength of light with a frequency of 2.45×10^{9} Hz?

g) In which regions of the electromagnetic spectrum would you find these wavelengths?

Answers to Worked Example 1

i) c (speed of light) = λ (wavelength) x ν (frequency)

ii) c (m s^{-1}) = λ (m) x ν (Hz) [Hz = s^{-1}]

iii) $\nu = c / \lambda$

iv) $\nu = c / \lambda$ = 3×10^{8} m s^{-1} (speed of light) / 456×10^{-9} m (wavelength provided)
= 6.58×10^{14} Hz

v) $\lambda = c / \nu$

vi) λ = 3×10^{8} m s^{-1} (speed of light) / 2.45×10^{9} s^{-1} (frequency provided)
= 0.122 m

vii) The wavelength of d) corresponds to the violet/blue visible region of the spectrum. f) corresponds to the microwave/radio wave region.

Question 1

a) Infrared radiation has wavelengths ranging from about 800 nm to 1 mm. What is the frequency of 850 nm radiation?

b) Microwaves have wavelengths greater than about 3 mm. What is the frequency of 4.10 mm radiation?

Question 2

Light with a frequency of 7.0×10^{14} Hz lies in the violet region of the visible spectrum. What is the wavelength of this frequency of light?

Question 3

When an electron bean strikes a block of copper, X-rays with a frequency of 1.5×10^{18} Hz are emitted. What is the wavelength of these X-rays?

Worked Example 2

a) The blue colour of the sky results from the scattering of sunlight by air molecules. Blue light has a frequency of about 7.5×10^{14} Hz. Calculate the energy of a single photon associated with this frequency.

b) Photochemical reactions are reactions which are initiated by light energy. Calculate the energy of a mole of photons with this energy.

c) Would the energy be sufficient to break the Cl-Cl bond in Cl_2? (Average bond enthalpy Cl-Cl = 242 kJ mol^{-1})

Answers

a) *E (Energy) = h (Planck's constant) x* ν $= 6.663 \times 10^{-34}$ J s $\times 7.5 \times 10^{14}$ s^{-1}
$= 49.7 \times 10^{-20}$ J $= 5 \times 10^{-19}$ J

b) *I mole* $= 5 \times 10^{-19}$ J $\times 6.022 \times 10^{23}$ mol^{-1} *(Avogadro's number)*
$= 30.11 \times 10^{4}$ J mol^{-1} $= 301.1 \times 10^{3}$ J mol^{-1}
$= 301$ kJ mol^{-1}

c) *This energy would be sufficient to break the Cl-Cl bond in* Cl_2 *– The Cl-Cl bond has energy of 242 kJ* mol^{-1}*, 301 kJ* mol^{-1} *is higher.*

Worked Example 3

Calculate the wavelength of an electron with a speed of 1.5×10^{8} m s^{-1}.

Answer

Consider the electron as a particle and use de Broglie's equation.

$\lambda = h / m v = 6.63 \text{ x } 10^{-34} \text{ J s} / 9.11 \text{ x } 10^{-31} \text{ kg x } 1.5 \text{ x } 10^{8} \text{ m s}^{-1}.$

$= 0.485 \text{ x } 10^{-11} \text{ m}$
$= 4.85 \text{ pm}$

Question 4

Calculate the wavelength of a baseball of mass 150 g travelling at 40 m s^{-1}.

Question 5

What is the velocity of a neutron that has a wavelength of 150 pm?

Question 6

The average speed of a helium atom at 25℃ is 1.25 x 10^3 m s^{-1}. What is the wavelength associated with the atom at 25℃?

Worked Example 4

Give the Rydberg formula for the calculation of the wavelengths emitted from transitions between energy levels in atomic hydrogen.

Answer

The Rydberg equation was developed in the 19th century and was determined by the fact that the frequencies of lines in the emission spectrum of a Hydrogen atom fell into specific lines.
In the Rydberg equation, ν *is the frequency (often 1/*λ *the wavenumber, is used), R or* R_H *is the Rydberg constant, 3.29 x* 10^{15} *Hz (or 1.10 x* 10^{7} m^{-1} *if the wavenumber is used),* n_1 *is an integer number > 0 and* n_2 *is an integer number >* n_1 + 1
n_1 *is the number of the lower energy level –* n_2 *is the upper energy level.*

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

Worked Example 5

In the spectrum of atomic hydrogen, a violet line from the Balmer series is observed at 434 nm. Determine the beginning and ending energy levels of the electron during the emission of energy that leads to this spectral line.
Answer

This requires skilful use of the Rydberg equation. A wavelength is given of 434 nm. $434 \text{ nm} = 434 \times 10^{-9} \text{ m} = 4.34 \times 10^{-7} \text{ m}$.

$1 / 4.34 \times 10^{-7}$ *gives the wavenumber in metres,* $2.304 \times 10^{6} \text{ m}^{-1}$.

$2.304 \times 10^{6} / 1.10 \times 10^{7}$ *(the Rydberg constant) = 0.209.*

We already know that this is a Balmer series, in the Balmer series $n_1 = 2$,
so $1/n_1^2 = 0.25$. *To determine* $1/n_2^2$, $0.25 – 0.209 = 0.0405$.

To determine n_2^2, $1 / 0.0405 = 25$.

To determine n_2, *square root 25 to give* $n_2 = 5$.

Energy levels are $n_1 = 2$, $n_2 = 5$.

Question 7

Complete the following sentences concerning the energy level diagram for the hydrogen atom:

a) The energy levels in the H atom get closer as n ……………………...

b) When n = infinity the energy separation of an electron from the nucleus is equal to the ………………………. energy.

c) The equation relating the energy separation between levels in the H atom to the number of the level (n) is called the ………………………. equation.

Question 8

a) Use the Rydberg formula for atomic hydrogen to calculate the wavelength for the transition from $n = 4$ to $n = 2$.

b) What is the name given to the spectroscopic series to which this transition belongs?

c) Use your Data Book to determine the region of the spectrum in which the transition takes place. If the change takes place in the visible region of the spectrum, what colour will be emitted?

Question 9

Using the Rydberg equation, calculate the ionisation energy of hydrogen.

Quantum Theory Answers

1. a) ν =c / λ = 3 x 10^8 m s^{-1} / 850 x 10^{-9} m = 3.53 x 10^{14} Hz.
   b) ν =c / λ = 3 x 10^8 m s^{-1} / 4.10 x 10^{-3} m = 7.3 x 10^{10} Hz.

2. λ = c / ν = 3 x 10^8 m s^{-1} / 7.0 x 10^{14} s^{-1} = 429 nm.

3. λ = c / ν = 3 x 10^{-8} m s^{-1} / 1.5 x 10^{18} s^{-1} = 2 x 10^{-10} m = 200 pm.

4. λ = h / m v = 6.63 x 10^{-34} J s / 0.150 kg x 40 m s^{-1} = 1.11 x 10^{-34} m

5. λ = h / m v, so v = h / m λ = 6.63 x 10^{-34} J s / 1.67 x 10^{-27} kg x 1.50 x 10^{-12} m
   = 0.0265 x 10^5 m s^{-1} = 2.65 x 10^3 m s^{-1}

6. λ = h / m v.
   1 mole He atoms (i.e. 6.022 x 10^{23} He atoms) = 4.003 g.
   Mass of 1 He atom (m) = 4.003 g / 6.022 x 10^{23} = 0.655 x 10^{-23} g.

   λ = 6.63 x 10^{-34} J s / 0.665 x 10^{-23} g x 1.25 x 10^3 m s^{-1}
   = 7.98 x 10^{-11} m
   = 79.8 pm

7. a) increases.
   b) ionisation
   c) Rydberg.

8. a)

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

$$\lambda = R\left(\frac{1}{4} - \frac{1}{16}\right)$$

   = 3.289 x 10^{15} s x 0.1875
   = 486 nm.
   b) The Balmer series
   c) The transition takes place in the visible light region of the spectrum, and blue light will be emitted.

9. When calculating the ionisation energy of hydrogen, $n_1 = 1$ and $n_2 = \infty$ (infinity).

$1/\infty^2 = 0$, so the n_2 term can be ignored.

ν = R (1 / 1^2), so ν = R.

ν = 3.29 x 10^{15} Hz.

E = h ν, therefore E = 3.29 x 10^{15} s^{-1} x 6.63 x 10^{-34} J s

= 2.19 x 1^{-18} J $atom^{-1}$, or multiply by 6.022 x 10^{23} to get an answer of 1313.6 kJ mol^{-1}

Atomic Structure

Exercise 1

The principal quantum number is given by the symbol n. It can take positive integer (whole number) values from $n = 1, 2 \ldots \infty$.

Fill in the table below which concerns the other quantum numbers found in an atom.

Quantum Number	Name	Values possible	What does it tell us about?
n	Principal quantum number	1, 2, … ∞	The energy level or shell. Its size.
l			
m_l			
m_s			

Worked Example 1

a) What values of the orbital quantum number, or angular momentum (l) and magnetic (m_l) quantum numbers are allowed for a principle quantum number (n) of 3?

b) How many orbitals are allowed for $n = 3$?

Answers to Worked Example 1

We determine allowable quantum numbers according to certain rules. The values of orbital quantum numbers (l) are positive integers from 0 to $n - 1$. The values of magnetic quantum numbers (m_l) are integers from $-l$ to 0 to $+l$. One m_l value is assigned to each orbital, so the number of m_l values gives the number of orbitals.

a) Determining l values: for $n = 3$, $l = 0, 1, 2$.
Determining m_l for each l value:
For $l = 0$, $m_l = 0$.
For $l = 1$, $m_l = -1, 0, +1$.
For $l = 2$, $m_l = -2, -1, 0, +1, +2$.

b) There are nine m_l values, so there are nine orbitals with $n = 3$.

Checking your answer: Remember that the total number of orbitals for a given n value is n^2. In this case, for $n = 3$, $n^2 = 9$ so our answer is correct.

Worked Example 2

Give the name, magnetic quantum numbers, and number of orbitals for each sublevel with the following quantum numbers:

a) $n = 3$, $l = 2$

b) $n = 2$, $l = 0$

c) $n = 5$, $l = 1$

d) $n = 4$, $l = 3$

Answers

To name the sublevel (or subshell), we combine the n value and appropriate letter designation for the l value.

Since we know l, we can find the possible m_l values, whose total number equals the number of orbitals.

	n	l	**Sublevel Name**	**Possible m_l values**	**No. of Orbitals**
a)	3	2	3d	-2, -1, 0, +1, +2	5
b)	2	0	2s	0	1
c)	5	1	5p	-1, 0, +1	3
d)	4	3	4f	-3, -2, -1, 0, +1, +2, +3	7

Checking your answer: Use the relationship
No. of orbitals = no. of m_l values = $2l + 1$

Question 1

How many subshells are there for the following principal quantum numbers?

a) $n = 2$

b) $n = 3$

Question 2

What is the name given to the subshells of the following shells?

a) $n = 2$ shell

b) $n = 3$ shell

Question 3

Write the subshell notation (e.g. 3d) and the number of orbitals relating to the following quantum numbers:

a) $n = 5$, $l = 2$

b) $n = 1$, $l = 0$

c) $n = 6$, $l = 3$

d) $n = 2$, $l = 1$

Question 4

What is the maximum number of electrons in an atom that can be defined by the following quantum numbers?

a) $n = 2$, $l = 1$

b) $n = 4$, $l = 2$, $m_l = -2$

c) $n = 2$

d) $n = 3$, $l = 2$, $m_l = +1$

Question 5

How many orbitals are there in the shell when $n = 4$, and what are they?

Question 6

State, with reasons, which of the following is/are possible set of quantum numbers for a 4d electron?

a) $n = 4$, $l = 1$, $m_l = -1$, $m_s = -\frac{1}{2}$

b) $n = 4$, $l = 2$, $m_l = -2$, $m_s = -\frac{1}{2}$

c) $n = 4$, $l = 3$, $m_l = 2$, $m_s = +\frac{1}{2}$

d) $n = 4$, $l = 1$, $m_l = 0$, $m_s = +\frac{1}{2}$

e) $n = 4$, $l = 4$, $m_l = -2$, $m_s = +\frac{1}{2}$

Question 7

What do the terms *singly degenerate* and *triply degenerate* mean? Give examples of atomic orbitals which can be described in these ways.

Question 8

Write the subshell notation (e.g. 3d) and the number of orbitals (i.e. the orbital degeneracy) for the following quantum numbers in an atom.

a) $n = 3$, $l = 2$

b) $n = 1$, $l = 0$

c) $n = 6$, $l = 3$

Exercise 2

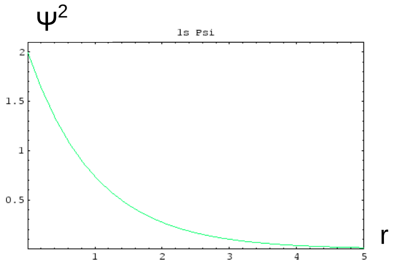
A wavefunction Ψ is a mathematical function that contains detailed information about the behaviour of an electron (the electron wavefunction). It is obtained from the solution of the Schrödinger equation.

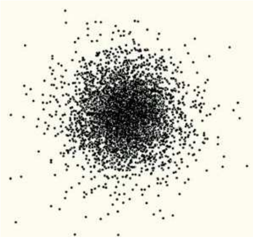
The region of space defined by the wavefunction is called an atomic orbital.

The function Ψ^2 is much more useful than Ψ.
Ψ^2 represents the probability of finding an electron at a particular point at a certain distance from the nucleus.

A plot of Ψ^2 against distance from the nucleus is given below for the 1s atomic orbital.

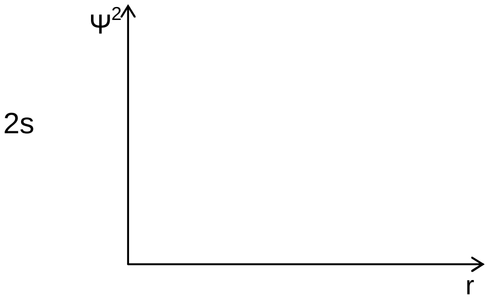
The plot shows that there is a high possibility of finding the electron near the nucleus, but this decreases with distance from the nucleus. For the radial part of the wavefunction this is called $R(r)^2$.

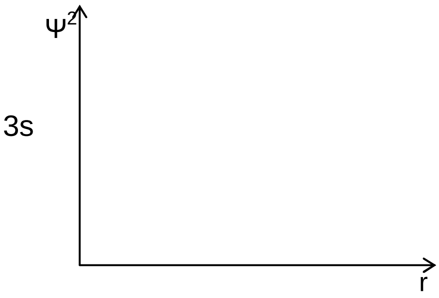




An electron density photograph of the electron in the spherical 1s orbital would show there is a concentrated region of electron density near the nucleus and less density on moving out.

a) Sketch the Ψ^2 or $R(r)^2$ functions for the 2s and 3s orbitals below.



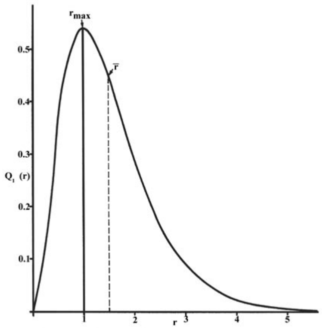


b) What would their electron density maps look like?

Exercise 3

The Radial Distribution Function $4\pi r^2R(r)^2$ represents the probability of finding an electron in a spherical shell of radius r and thickness dr (difference in r) around the atom in an atomic orbital. It represents the sum of the probabilities of finding all the electrons in that spherical shell.

For the 1s orbital, the Radial Distribution Function is shown below.



Note that there is zero probability of finding an electron at the nucleus (because the shell volume is zero).
As the radius increases, the volume increases and the probability increases.

Plot the radial distribution functions for the 2s and 3s orbitals.

Worked Example 3

A radial node is represented by a point at which the wavefunction passes through zero.

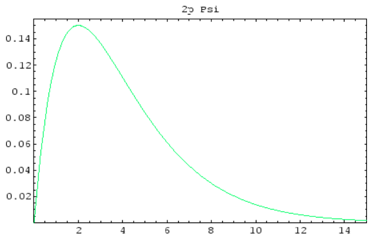
a) How many radial nodes do the following orbitals possess?

i) 1s

ii) 2s

iii) 3s

Below is the wavefunction for a 2p orbital.



Note that the wavefunction for the 2p orbital doesn't pass through the origin, but is equal to zero at the origin.

b) Sketch a $2p_z$ orbital.

c) What do you notice about the shape of the orbital at the origin (at r = 0)? How does it differ from an s orbital at the origin?

d) What type of node exists in a p orbital at the radius r = 0?

Answers

Radial nodes, or surface/spherical nodes, denote a region where there is zero probability of finding an electron.

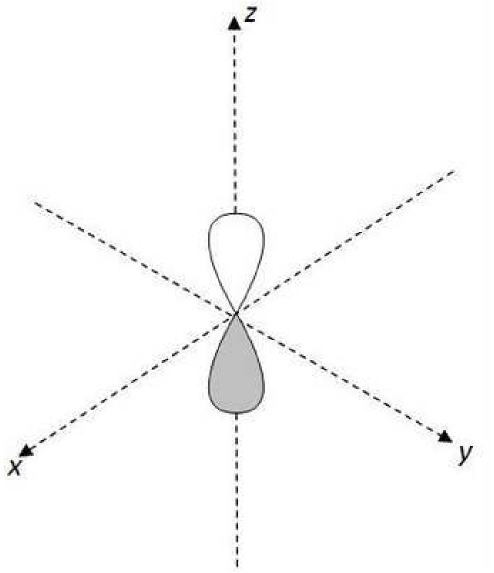
Remember that the number of radial nodes in any given atomic orbital can be determined using the quantum numbers: number of radial nodes = $n - 1 - l$

a) i) Number of radial nodes = 1 – 1 – 0 = 0

ii) Number of radial nodes = 2 – 1 – 0 = 1

iii) Number of radial nodes = 3 – 1 – 0 = 2

b) Your $2p_z$ orbital should be oriented around the z axis and should be clearly identifiable as a p-orbital shape. You may wish to shade or draw positive/negative symbols to denote a difference in phase of the wavefunction for each lobe. Remember these are NOT electrostatic charges.



c) At the origin (r = 0), the $2p_z$ orbital shape tapers to a point – the radius decreases in this region and the orbital is in effect bisected by the xy plane. In contrast, the s orbital has a constant radius all over the surface of the orbital.

d) This node is a planar node.

Question 9

a) What is meant by the following?

i) A planar node

ii) A surface node

b) What type of nodes, if any, do the following orbitals possess?

i) 1s

ii) 2s

iii) 2p

iv) $3d_{xy}$

Question 10

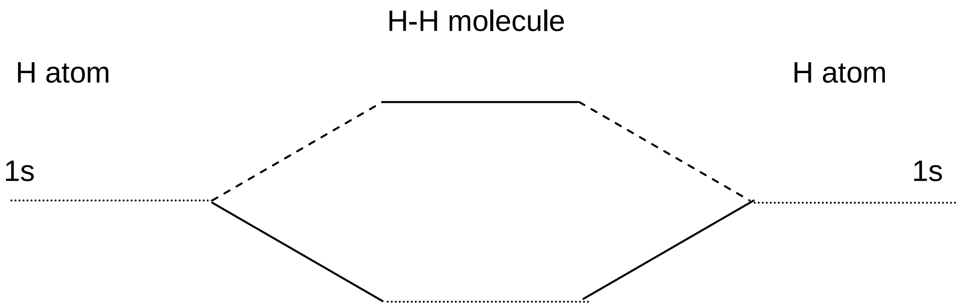
Consider the atomic orbital overlap of two hydrogen atoms.

a) Draw the two hydrogen atoms adjacent to each other.

b) Draw the molecular orbitals formed from the overlap of the two 1s atomic orbitals. (Remember, overlap of two atomic orbitals leads to two molecular orbitals.)

c) Name and label the molecular orbitals formed.

d) Complete the molecular orbital energy level diagram below for H_2. Insert the electrons from the H atoms.



e) What is the bond order in the H_2 molecule?

f) What would be the bond order in the H_2^+ molecular ion?

g) What would be the bond order in the H_2^- molecular ion?

h) Draw the equivalent molecular energy level diagram for He_2. Explain why this molecule should not exist.

Question 11

Draw the combinations of atomic orbitals you would expect to find for the three 2p orbitals of a second row X_2 molecule. Label the molecular orbitals formed assuming the z-axis is the bond axis (i.e. σ_{2p}^* etc).

Question 12

Consider the N_2 molecule. Imagine the z axis along the long, e.g. N-N z→.

a) In the diagram below, for each N atom draw the 2s atomic orbitals.

b) Under the “N-N molecule”, draw the bonding and anti-bonding molecular orbitals formed from the 2s orbitals. Label the M.O.’s σ or π as appropriate.

c) Draw under each N atom the $2p_z$ orbital and under the N-N molecule draw the bonding and anti-bonding orbitals formed from the overlap of the $2p_z$ orbitals. Label them as σ or π as appropriate.

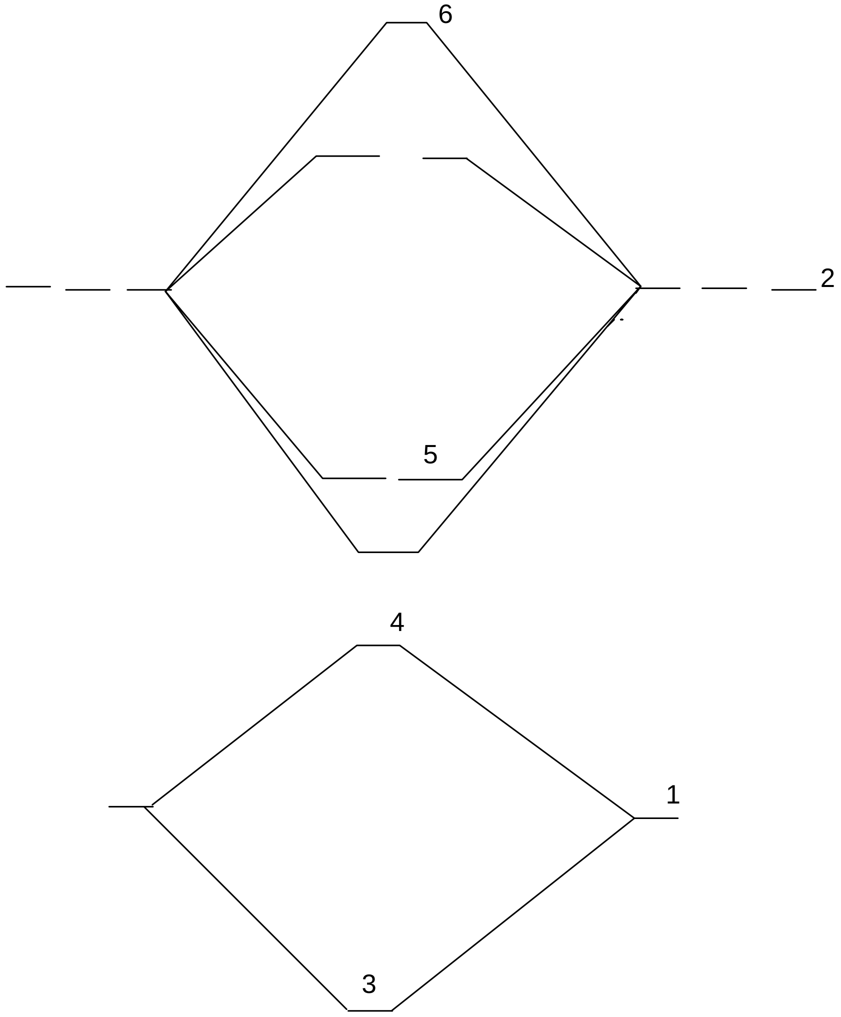
d) Draw under each N atom the $2p_y$ orbital and under the N-N molecule draw the bonding and anti-bonding orbitals formed from the overlap of the $2p_y$ orbitals. Label the M.O.'s as σ or π as appropriate.

e) Do the $2p_x$ orbitals behave as the $2p_z$ or the $2p_y$ molecules?

N atom N-N molecule N atom

Question 13

The diagram below shows a molecular energy level diagram for dioxygen, showing only valence shell electrons.



a) Label the orbitals numbered 1-6, stating whether they are atomic or molecular. Label the atomic orbitals according to their first two quantum numbers (in the form 1s etc), and label the molecular orbitals according to their bond type (e.g. σ or π, and bonding or antibonding).

b) Insert the electrons on the diagram to show their spins.

c) In what way would the molecular orbitals be different if it were for dicarbon, rather than for dioxygen? (An explanation is not required.)

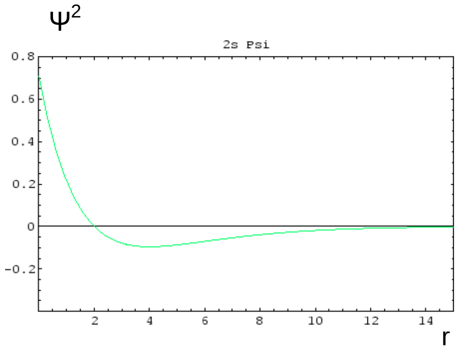
Atomic Structure Answers

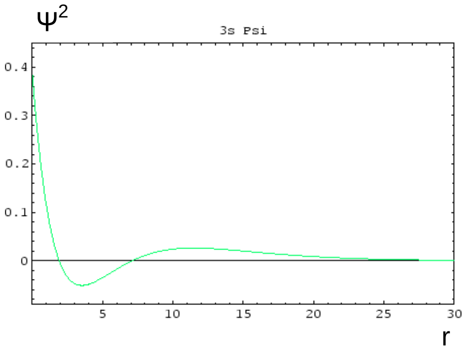
Exercises

1.

Quantum Number	Name	Values possible	What does it tell us about?
n	Principal quantum number	1, 2, … ∞	The energy level or shell. Its size.
l	Orbital/ azimuthal/ angular quantum number	0, 1, … $(n – 1)$	The shape of the orbital – angular momentum
m_l	Magnetic quantum number	$l \rightarrow 0 \rightarrow - l$	The number of orbitals and orientation of each
m_s	Spin quantum number	± ½	Directions of spin of the electrons in each orbital

2. a)



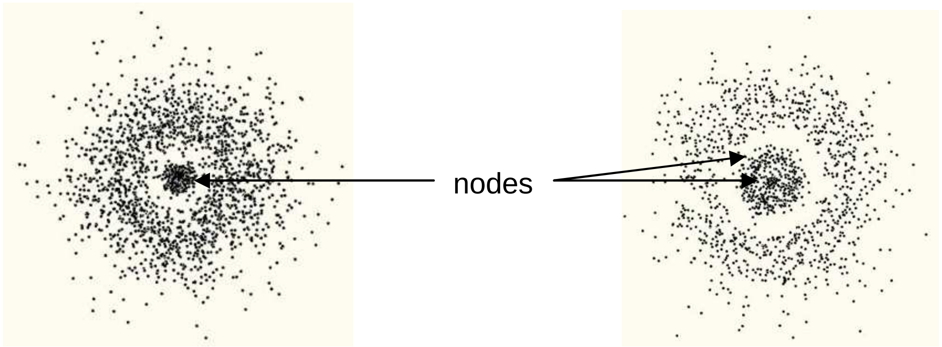


2s

3s

Note how many times the plot crosses the origin. Every time the plot line crosses the origin, this indicates the presence of a node.

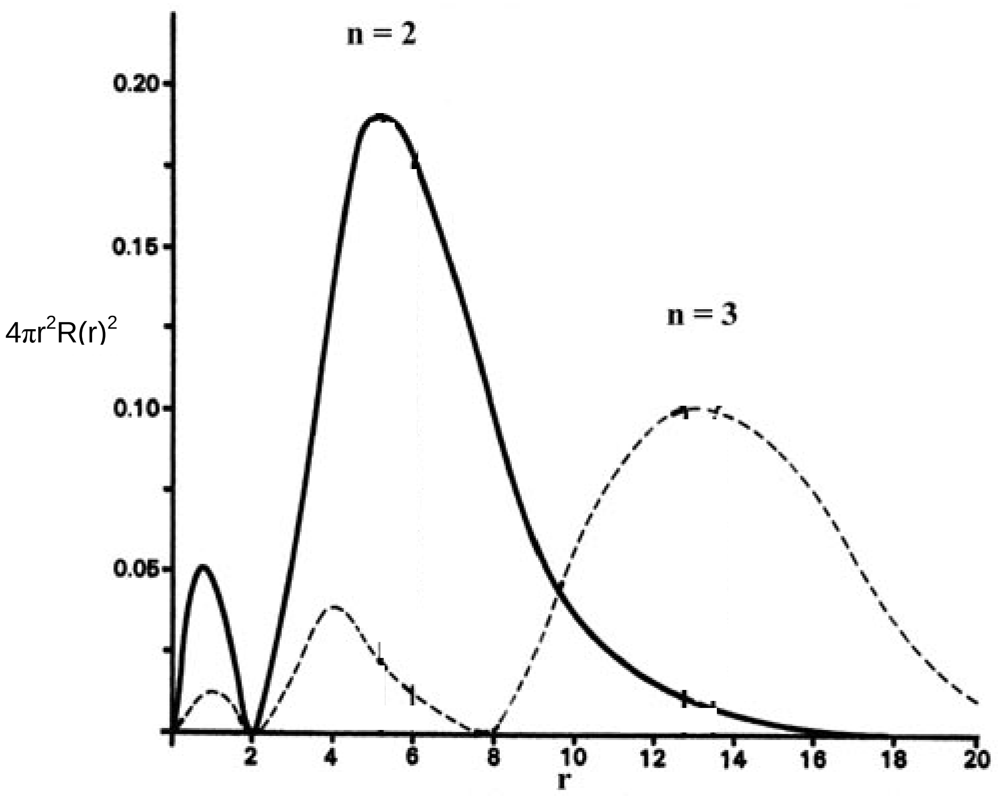
b)



2s 3s

Your electron density maps should clearly show a more sparsely populated orbital for 2s than 1s and for 3s than 2s. You should also clearly indicate (and ideally label) the nodes in these pictures. The second node in the 3s orbital picture above is difficult to identify owing to the small scale of the image.

3.



Your radial distribution plots should demonstrate that the region of maximum probability of finding the electron moves further from the nucleus for the 2s and 3s orbitals. You should demonstrate that the 2s orbital has one node and that the 3s orbital has 2. You should demonstrate the decreased magnitude of the 2s probability density curve compared to the 1s, and the decreased magnitude of the 3s compared to the 2s.

Questions

1. a) 2 subshells
   b) 3 subshells

2. a) p and s orbitals
   b) d, p and s orbitals

3. a) 5d, 5 orbitals
   b) 1s, 1 orbital
   c) 6f, 7 orbitals
   d) 2p, 3 orbitals

4. a) If *n* = 2 and *l* = 1 then this is the 2p subshell. There are 3p orbitals, each can have a maximum of 2 electrons so 3 x 2 = 6 electrons.

b) If n = 4, l = 2 and m_l = -2 then this is denotes a single orbital in the 4d subshell, the $4d_{xy}$ orbital. As it is a single orbital, it can have a maximum of 2 electrons, so 2 electrons can be defined by these quantum numbers.

c) If n = 2 then this is the second shell and this can apply to both 2s and 2p orbitals. There are three 2p orbitals and one 2s orbital, each with a maximum of 2 electrons. 4 x 2 = 8 electrons.

d) If n = 3, l = 2 and m_l = +1 then this denotes a single orbital in the 3d subshell, the $3d_{yz}$ orbital. As it is a single orbital, it can have a maximum of 2 electrons, so 2 electrons can be defined by these quantum numbers.

5. There is one s orbital, three p orbitals, five d orbitals and seven f orbitals = 16 orbitals

6. The question specifies a 4d orbital. For a d orbital, the only permissible orbital quantum number (l) would be 2 – meaning that all options except for b) are automatically impossible. b) has the correct value for n as n = 4 is compulsory for any 4d electron. It has a suitable value for l and valid numbers for m_l and m_s, so b) is the only possible set of quantum numbers.

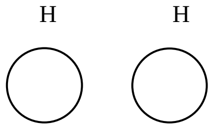
7. Singly degenerate means that there is only one orbital of that particular energy, for example the lithium 2s orbital.
Triply degenerate means that there are three orbitals of the same energy. For example, the three 2p orbitals in sodium are said to be triply degenerate as they are all of the same energy.

8. a) 3d, 5 degenerate orbitals
b) 1s, singly degenerate
c) 6f, 7 degenerate orbitals.

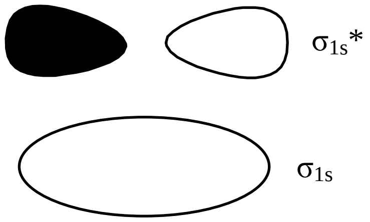
9. a) (i) A planar node is the point in a wavefunction where there is a phase change with respect to the surface boundary of an orbital, i.e. a plane where there is zero probability of finding an orbital.
(ii) A surface/radial node is a point at which the Radial Distribution function is equal to zero.
b) (i) None
(ii) One surface node
(iii) No surface nodes, one planar node.
(iv) No surface nodes, two planar nodes.

Always remember: Total number of nodes = $n - 1$
Number of planar nodes = l
Number of surface nodes = $n - 1 - l$

10. a)

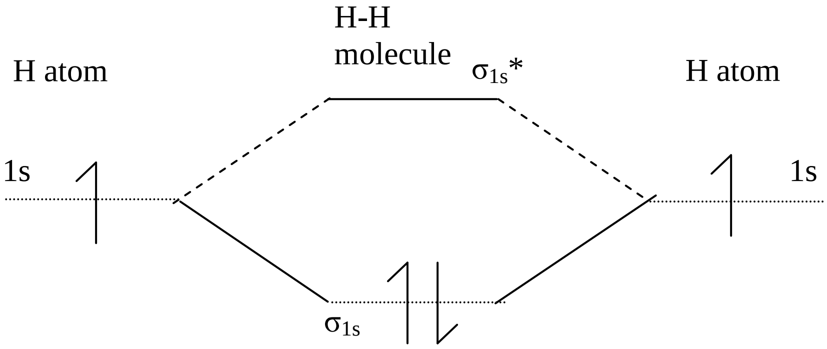


b)



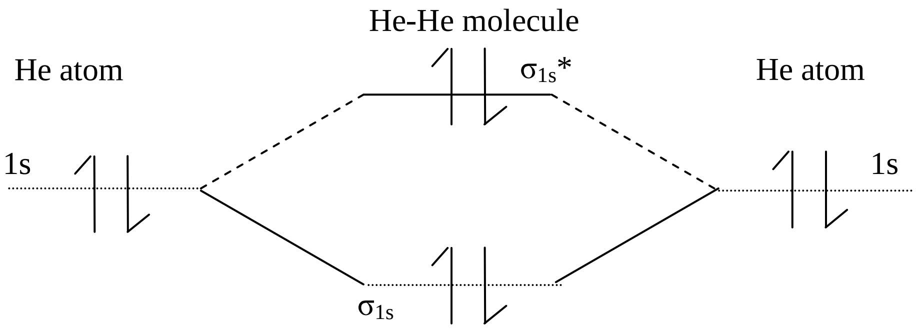
c) σ_{1s} and σ_{1s}^*

d)



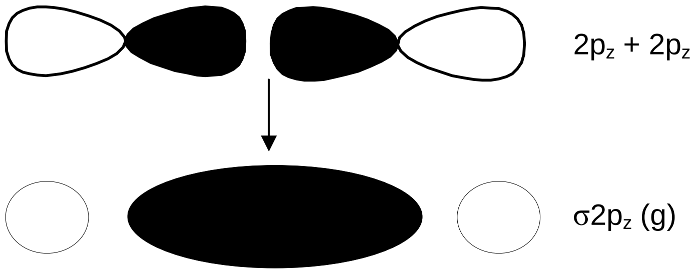
e) 1
f) ½
g) ½

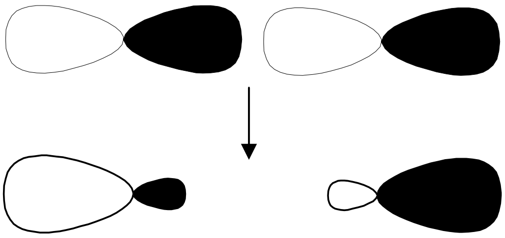
h)



Shouldn't exist because bond order = 0.

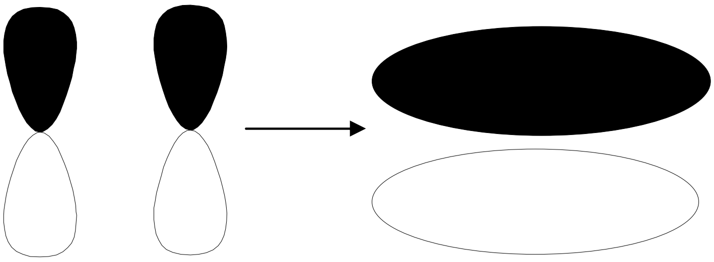
11.





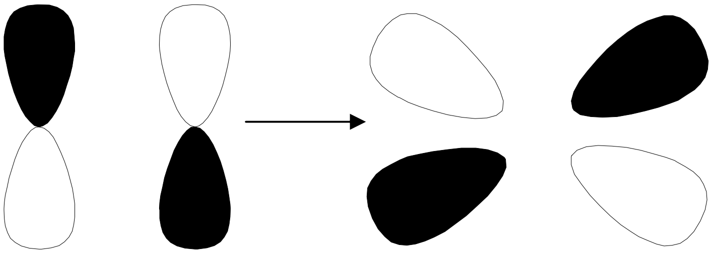
$2p_z + 2p_z$

σ^*2p_z (u)



$2p_x + 2p_x$
or $2p_y + 2p_y$

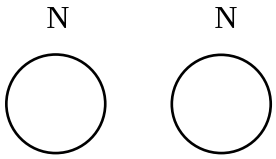
$\pi 2p_x$ (u)
or $\pi 2p_y$



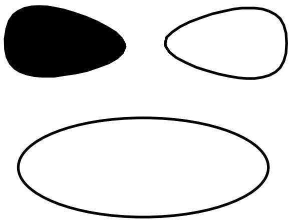
$2p_x + 2p_x$
or $2p_y + 2p_y$

π^*2p_x (g)
or π^*2p_y

12. a)



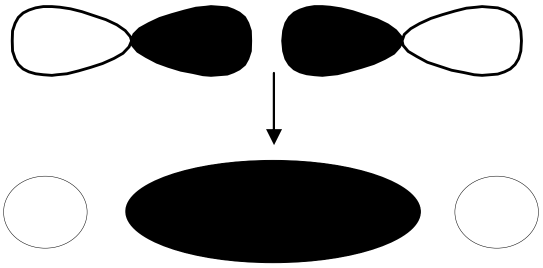
b)



σ^*2s (u)

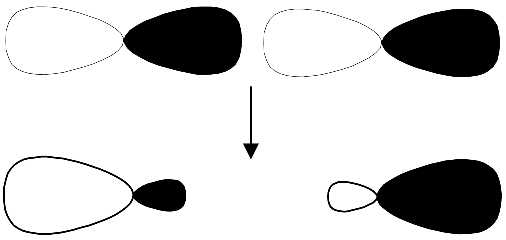
$\sigma 2s$ (g)

c)

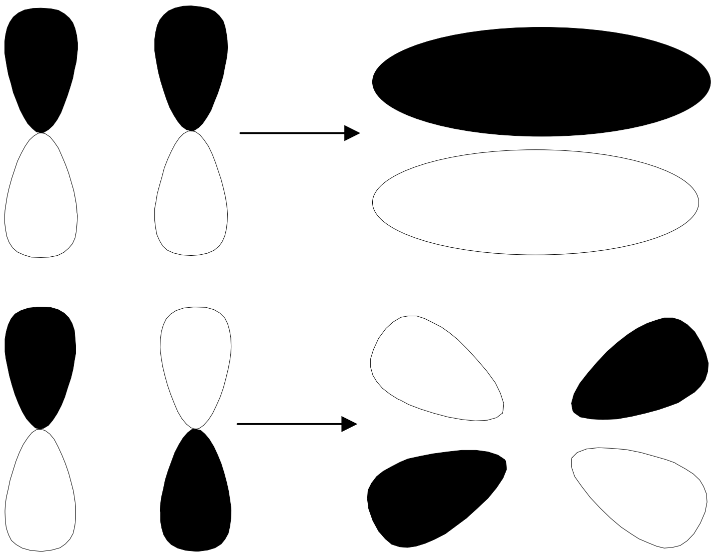


$2p_z + 2p_z$

$\sigma 2p_z$ (g)



d)

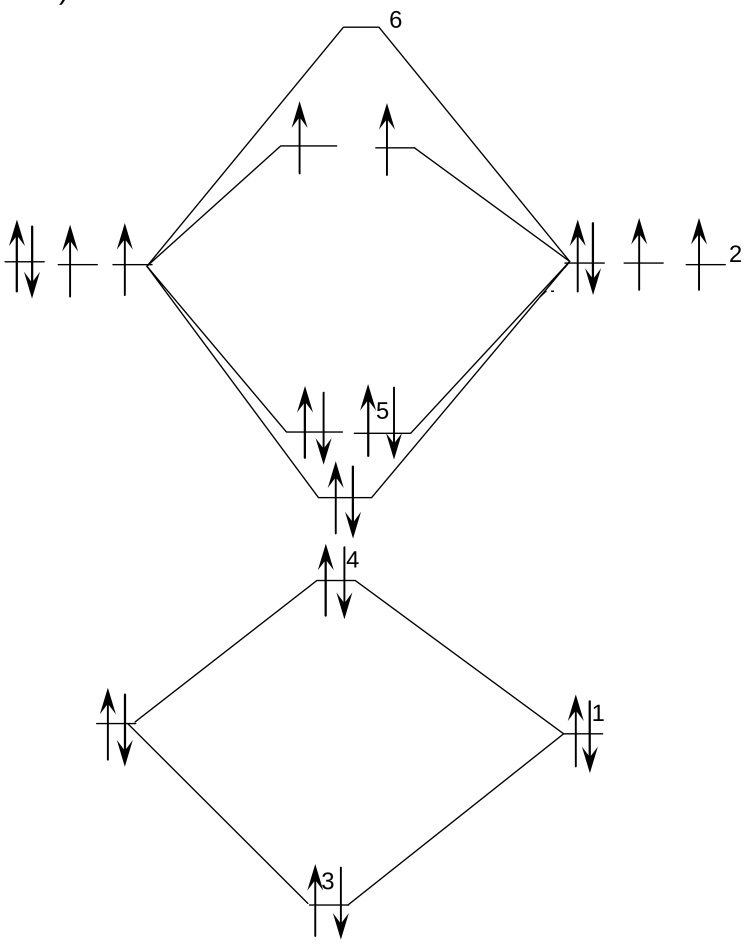


e) $2p_x$ orbitals behave like the $2p_y$ orbitals and are found perpendicular to the direction of the N-N bond.

13. a)

1 = 2s atomic orbital
2 = 2p atomic orbitals
3 = σ bonding orbital
4 = σ* antibonding orbital
5 = p π bonding orbitals
6 = p σ* antibonding orbital

b)



d) The p π and p σ bonding orbitals would be found the other way round (inverted).

Main Group Chemistry

Question 1

Suggest products for the following reactions and give balanced equations:

a) electrolysis of molten KBr

b) Heating of $SrCO_3$ to 1600 K

c) Reaction of H_2O_2 with acidified KI solution

d) Reaction of $Ca(OH)_2$ with HCl

e) Reaction of CaH_2 with H_2O

f) Reaction of Cu^{2+} with I^-

g) Reaction of Ag^+ with I^-

h) Reaction of AgCl with NH_3 (aqueous).

Question 2

The first members of periodic groups are often noted for their “anomalous” behaviour. Discuss some of the properties of a) lithium and b) beryllium that would support this statement.

Question 3

Use VSEPR to predict shapes for:

a) $[AlCl_2]^+$

b) $[SbCl_6]^-$

c) $[PCl_4]^+$

d) $[I_3]^-$

Question 4

Use VSEPR to predict structures for:

a) $FBrO_3$

b) $[ClO_2]^+$

c) $[F_2ClO_2]^-$

Main Group Chemistry Answers

1. a) $2KBr\ (l) \rightarrow 2K\ (s) + Br_2\ (l)$
   b) $SrCO_3\ (s) \rightarrow SrO\ (s) + CO_2\ (g)$
   c) $2KI\ (aq) + 2H_2SO_4\ (aq) + H_2O_2\ (l) \rightarrow 2KHSO_4\ (aq) + 2H_2O\ (l) + I_2\ (s)$
   d) $Ca(OH)_2\ (aq) + 2HCl\ (aq) \rightarrow CaCl_2\ (aq) + 2H_2O\ (l)$
   e) $CaH_2\ (s) + 2H_2O\ (l) \rightarrow Ca(OH)_2\ (s) + 2H_2\ (g)$
   f) $2Cu^{2+}\ (aq) + 4I^{-}\ (aq) \rightarrow 2CuI_2\ (s) \rightarrow 2CuI\ (s) + I_2\ (aq)$
   g) $Ag^{+}\ (aq) + I^{-}\ (aq) \rightarrow AgI\ (s)$
   h) $AgCl\ (s) + 2NH_3\ (aq) \rightarrow [Ag(NH_3)_2]^{+}\ (aq) + Cl^{-}\ (aq)$

2. Lithium is the only group 1 metal to form a nitride. This is because the lithium cation is small and highly polarising. It forms a salt with a high lattice enthalpy that drives the reaction forward. Lithium does not form a peroxide or a superoxide with O_2. This is because the highly polarising nature of the lithium cation breaks the O-O bond. The highly polarising Li^{+} means that LiCl is more readily soluble in EtOH that NaCl or KCl. Lithium can precipitate some medium size anions. This is because Li^{+} can polarise the anions, it has a high charge to size ratio and can share electrons, giving the bonds some degree of covalency. This makes the salts more stable and less soluble.

   Beryllium shows mainly covalent chemistry. This is because very large amounts of energy are required to make Be^{2+}. Be is small and highly polarising, hence can share an electron and act in a covalent manner.

3. a) $[AlCl_2]^{+}$ - Al has 3 valence electrons in its neutral form, the positive charge is assigned to the central element (this leaves 2 valence electrons). Factor in the 2 Cl groups (which both contribute 1 electron) and there are a total of 4 electrons, giving 2 electron pairs which will distribute in a linear fashion.

   b) $[SbCl_6]^{-}$ - Sb has 5 valence electrons in its neutral form, the negative charge is assigned to the central element (this gives 6 valence electrons). Factor in the 5 Cl groups (all contributing 1 electron) and there are a total of 12 electrons, giving 6 electron pairs which will distribute in an octahedral fashion.

   c) $[PCl_4]^{+}$ - P has 5 valence electrons in its neutral form, the positive charge is assigned to the central element (this leaves 4 valence electrons). Factor in the 4 Cl groups (all contributing 1 electron) and there are a total of 8 electrons, giving 4 electron pairs which will distribute in a tetrahedral fashion.

   d) $[I_3]^{-}$ - Assume that one of the I is the central element – I has 7 valence electrons in its neutral form, the negative charge is assigned to the central element (this gives 8 valence electrons). Factor in the two I groups (both contributing 2 electrons) and there are a total of 10 electrons, giving 5 electron pairs which will distribute in a trigonal bipyramidal fashion. Note that because there are only 2 bonding groups, 3 of the electron pairs will be lone pairs.

4. a) $FBrO_3$ – F is the central element. F has 7 valence electrons. The Br group contributes 1 electron – this gives 8 electrons. The O groups have no effect on the electron count and thus there are a total of 8 electrons, giving 4 electron pairs which will result in a tetrahedral structure.

b) $[ClO_2]^+$ - Cl is the central element. It is 7 valence electrons. The positive charge is assigned to the central element leaving 6 valence electrons. The O groups have no effect on the electron count and thus there are a total of 6 electrons, giving 3 electron pairs that will result in a trigonal planar structure. Note that because there are only 2 bonding groups, one of the electron pairs will be a lone pair.

c) $[F_2ClO_2]^-$ - Assume that an F is the central element (you could also assume the Cl is central and get the same answer). There are 7 valence electrons in F, the negative charge is assigned to the F giving 8 valence electrons. The F and Cl groups contribute 1 electron and the O groups have no effect, resulting in a total of 10 electrons, giving 5 electron pairs which will result in a trigonal bipyramidal structure. There are only 4 bonding groups so one of the electron pairs will be a lone pair.

Ionic Bonding and Lattices

Worked Example 1

Using the periodic table only, rank the elements in each of the following sets in order of *decreasing* IE_1:

a) Kr, He, Ar

b) Sb, Te, Sn

c) K, Ca, Rb

d) I, Xe, Cs

Answers to Worked Example 1

To solve this problem, first locate the elements in the periodic table, and then apply some general rules.
IE_1 *decreases* down a **group.**
IE_1 *increases* across a **period**.

a) He > Ar > Kr: These are all in Group 8A (otherwise referred to as Group 18 or Group 0) and IE_1 decreases down a group.

b) Te > Sb > Sn: These three are all in Period 5, and IE_1 increases across a period.

c) Ca > K > Rb: IE_1 of K is larger than IE_1 of Rb because K is higher in Group 1A (Group 1). IE_1 of Ca is larger than IE_1 of K because Ca is farther to the right in Period 4.

d) Xe > I > Cs: IE_1 of I is smaller than IE_1 of Xe because I is farther to the left. IE_1 of I is larger than IE_1 of Cs because I is farther to the right and in the previous period.

Checking your answer: Trends in IE_1 are generally the opposite of trends in size. To check your answers, rank the elements by size and ensure that you obtain the reverse order.

Question 1

Rank the elements in each of the following sets in order of decreasing IE_1:

a) Sb, Sn, I

b) Sr, Ca, Ba

Question 2

Name the Period 3 element with the following ionization energies (in kJ mol^{-1}), and write its electron configuration:

IE_1	IE_2	IE_3	IE_4	IE_5	IE_6
1012	1903	2910	4956	6278	22,230

Worked Example 2

Calculate the energy change that accompanies the process:

$\frac{1}{2} Li_2 (g) \rightarrow Li^+ (g) + e^- \quad \Delta H_x$

Given that the enthalpy of atomisation, ΔH_a, for dilithium is 55 kJ mol^{-1} and the IE_1 for lithium is 520 kJ mol^{-1}.

Answer

This energy change can be split into two steps, which can be illustrated with a Born Haber cycle:

$$\begin{tikzcd}
\frac{1}{2} Li_2 (g) \arrow[rr, "\Delta H_a (Li) = 55 \text{ kJ mol}^{-1}"] \arrow[dr, "\Delta H_x"'] & & Li (g) \arrow[dl, "\text{Ionisation energy, } IE_1"] \\
& Li^+ (g) &
\end{tikzcd}$$

$\Delta H_x = \Delta H_f (Li^+ (g)) \quad = \Delta H_a (Li) + IE_1 (Li)$

$= 55 + 520 \text{ kJ mol}^{-1}$

$= 575 \text{ kJ mol}^{-1}$

Question 3

Calculate the enthalpy change for the formation of one mole of gaseous chloride ions from the element.

Worked Example 3

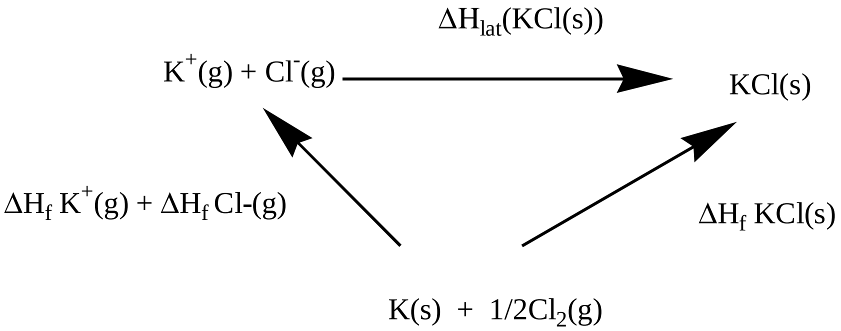
Use the Born Haber cycle to find the Lattice Enthalpy for KCl given the following values:

ΔH_f (KCl) = -437 kJ mol^{-1}
ΔH_a (K (s)) = 90 kJ mol^{-1}
ΔH_a (Cl (g)) = 121 kJ mol^{-1}
IE_1 (K (g)) = 418.8 kJ mol^{-1}
ΔH_{EA} (Cl (g)) = -349 kJ mol^{-1}

Answer

Lattice enthalpy can be defined as the energy change for the reaction:

M^+ (g) + X^- (g) → MX (s). It is denoted by ΔH_{lat}.



The energy cycle for the formation of KCl (s) is shown above. Starting from K (s) and chlorine gas, Cl_2, there are two routes to the formation of KCl. One route involves the heat of formation of KCl from the elements. The second involves creating ions of K^+ and Cl^- from the elements, then allowing the ions to combine in the lattice to form ionic KCl with a release in energy equivalent to the lattice energy.

Application of Hess's Law gives us:
ΔH_f (K^+(g)) + ΔH_f (Cl^-(g)) + ΔH_{lat} (KCl) = ΔH_f (KCl (s))

So: ΔH_{lat} (KCl) = ΔH_f (KCl(s)) - ΔH_f (K^+(g)) – ΔH_f (Cl^-(g))

Each of the quantities ΔH_f (K^+(g)) and ΔH_f (Cl^-(g)) are the enthalpies of formation of the K^+ and Cl^- ions respectively from the elements.

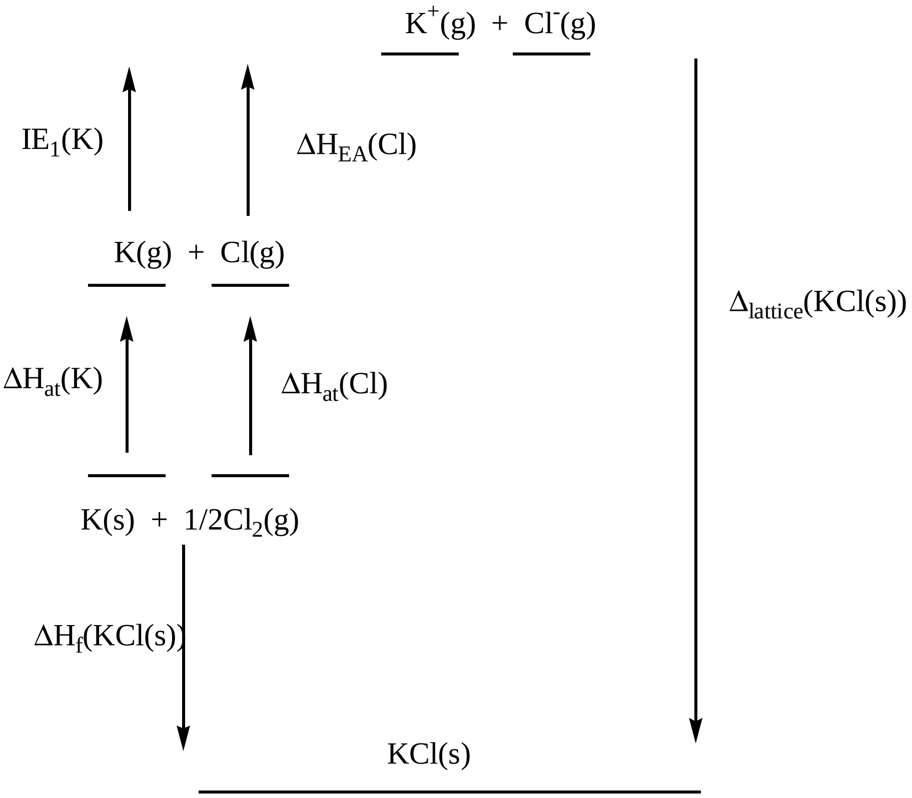
For K^+(g) this involves the enthalpy of atomisation and the ionisation energies:

ΔH_f (K^+(g)) = ΔH_{at}(K) + IE_1(K(g))

For the chloride ion this involves the enthalpy of atomisation of chlorine gas (or half the bond enthalpy) plus the electron affinity:

ΔH_f (Cl^- (g)) = ΔH_{at}(Cl) + ΔH_{EA} (Cl(g))

The overall Born Haber cycle for the formation of KCl showing the direction of the energy changes is shown below:



We have already determined that:

ΔH_{lat} (KCl) = ΔH_f (KCl(s)) - ΔH_{at}(K) + IE_1(K(g)) – ΔH_{at}(Cl) + ΔH_{EA} (Cl(g))

We can now insert the values provided into this equation.

ΔH_{lat} = -437 – 90 – 121 – 418.8 + 349 kJ mol^{-1}

= -718 kJ mol^{-1}

The negative value of ΔH_{lat} indicates that the formation of KCl from K^+ and Cl^- is an exothermic process.

You should note that in the Data Book Lattice Enthalpy relates to the endothermic process for separating the ions in a lattice to an infinite distance from each other and is therefore an endothermic process.

It is important to remember the sign when you quote or derive Lattice Enthalpies. Formation of the lattice will almost always be exothermic and negative. Separation of the lattice will be endothermic and positive.

Question 4

Write equations which describe the following terms:

a) The Enthalpy of Formation of calcium oxide

b) The Enthalpy of Atomisation of calcium

c) 1st Ionisation Energy of calcium

d) 2nd Ionisation Energy of calcium

e) The Enthalpy of Atomisation of oxygen

f) The Bond Enthalpy of oxygen

g) The 1st Electron Affinity of oxygen

h) The 2nd Electron Affinity of oxygen

i) The Lattice Enthalpy of calcium oxide

Question 5

Identify each of the energy terms described above on the diagram on the next page. Some steps may be combinations of the above terms. Some steps may have to be reversed to represent the energy changes in the direction shown on the diagram. Some terms above may not be required.

Question 6

a) Given the following data, calculate a value for ΔH_5:

ΔH_1 = +193 kJ mol^{-1}, ΔH_2 = +590 kJ mol^{-1}, ΔH_3 = +1150 kJ mol^{-1},
ΔH_4 = +248 kJ mol^{-1}, ΔH_6 = -3513 kJ mol^{-1}, ΔH_7 = -635 kJ mol^{-1}

b) Use the value of ΔH_5 you have calculated to obtain the 1st electron affinity of oxygen, given that the 2nd electron affinity of oxygen is +844 kJ mol^{-1}.

Question 7

a) Explain why the 1st electron affinity of oxygen is exothermic whilst the 2nd electron affinity of oxygen is endothermic.

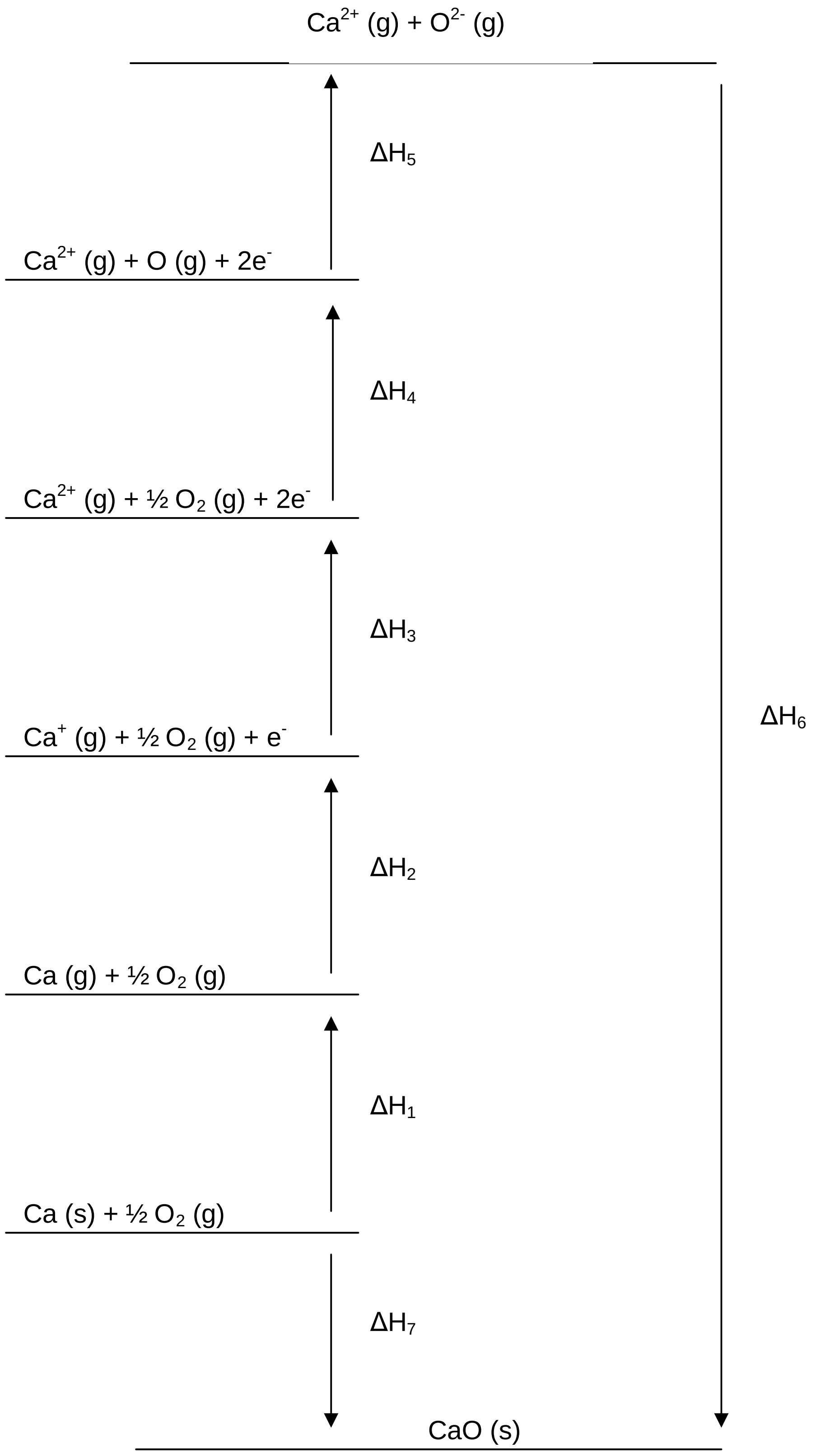
b) Explain the difference between the terms in Question 4 e) and 4 f).

c) Would the value of ΔH_2 for Mg be larger or smaller than that for Ca?

d) How would you expect the value of the lattice enthalpy to vary for the series MgO, CaO, SrO, BaO?

e) Would you expect the value of the lattice enthalpy for $CaCl_2$ to be greater or smaller than that of CaO?

Born Haber Diagram for Calcium Oxide



Question 8

Define the terms in the following equation, which gives a measure of the attractive force between two oppositely charged gaseous ions:

$$\Delta U \text{ (0 K)} = -\left(\frac{|z_+|\,|z_-|e^2}{4 \text{ x } \pi \text{ x } \varepsilon_0 \text{ x r}}\right)$$

Question 9

If the value of $\dfrac{e^2}{4\pi\varepsilon_0}$ = 2.3 x 10^{-28} J m:

Calculate the Coulombic attraction between one mole of lithium and fluoride ions where the internuclear distance is 201 pm.

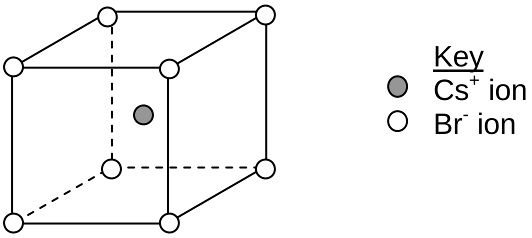
Worked Example 4

CsBr has a body-centred cubic structure (bcc).

Construct a drawing of a unit cell of CsBr by drawing a cube and placing the Br^- ions at the vertices and a Cs^+ ion at the centre of the cell.

What are the co-ordination numbers of the Cs^+ and Br^- ions in CsBr?

Answer



Co-ordination numbers -
[Cs^+] = 8
[Br^-] = 8

Question 10

a) Draw the face-centred cubic structure of NaCl by placing Cl^- ions on the corners and centres of the faces of a cube, and placing Na^+ ions on the centres of the edges and placing one Na^+ in the centre of the cell.

b) Calculate how many formula units (NaCl) are to be found in the structure by the following method:

i) Number of corner Cl^- ions?
Number of unit cells shared between?
Therefore, number of corner Cl^- ions per unit cell?

ii) Number of Cl^- ions on centres of faces?
Number of unit cells shared between?
Therefore, number of face Cl^- ions per unit cell?

iii) Thus, according to i and ii, total number of Cl^- ions per unit cell?

iv) Number of Na^+ ions on edges?
Number of unit cells shared between?
Number of Na^+ ions in centre of cell?
Therefore, total number of Na^+ ions per unit cell?

v) Therefore total number of formula units of NaCl per unit cell?

Question 11

How many tetrahedral and octahedral holes are there in a ccp array of n spheres?

Question 12

What is the coordination number of any atom in an infinite ccp array?

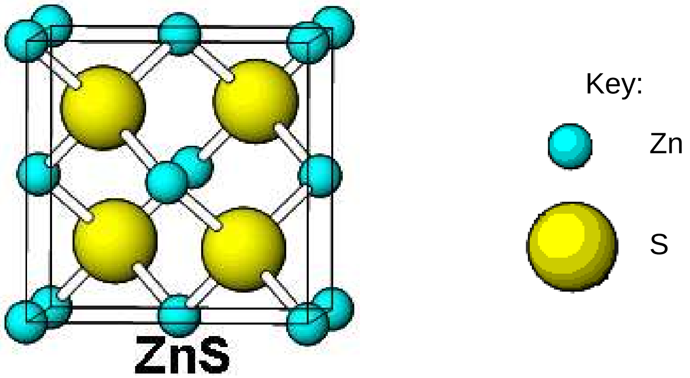
Question 13

What are the coordination numbers of Na^+ and Cl^- in the rock-salt structure?

Question 14

a) What are the coordination numbers of Zn and S in the zinc blende structure, shown below?

b) How many formula units, ZnS, are there in the zinc blende unit cell?



Question 15

A cubic unit cell contains atoms of element A at each corner and atoms of element Z on each face. What is the empirical formula of the compound?

Question 16

In a body-centred cubic unit cell, the central atom lies on an internal diagonal of the cell and touches the corner atoms.

a) Find the length of the diagonal in terms of r, the atomic radius.

b) If the edge length of the cube is a, what is the length of a *face* diagonal?

c) Derive and expression for a in terms of r.

d) How many atoms are in this unit cell?

e) What fraction of the unit cell volume is filled with spheres?

Ionic Bonding and Lattices Answers

1. a) To help understand why IE_1 increases across a period, consider the number of outermost p-electrons. Firstly, write out the outer shell electron configuration for each of these elements:
   Sn $5s^2\ 5p^2$
   Sb $5s^2\ 5p^3$
   I $5s^2\ 5p^5$
   Sn has the lowest IE_1 as it has only 2 outer p electrons.
   Sb has the next highest IE_1 – there is one more outer p electron.
   I has the highest IE_1 – there is a greater Z_{eff} moving across the period. Remember that Z_{eff} increases with more protons in the nucleus, but depends on how many electrons there are in an atom and where they reside. Electrons in p orbitals are less penetrating and therefore less stabilised and more easily removed.
   The order is Sn < Sb < I.
   b) In general, there is a decrease in IE_1 on going down a group. As the atom becomes larger, although there are more protons in the nucleus, the distance of the electrons from the nucleus decreases and so the IE_1 decreases down the group.
   Sr $5s^2$
   Ca $4s^2$
   Ba $6s^2$
   As the IE_1 increases as atomic size decreases, the order is Ba < Sr < Ca.

2. To ascertain which Period 3 element these data refer to, look for a large jump in the IE values. This occurs after all valence electrons have been removed. Then we refer to the periodic table to find the Period 3 element with this number of valence electrons and write its electron configuration.
   The exceptionally large jump occurs after IE_5, indicating that the element has five valence electrons and, thus, is in Group 5A (or Group 15).This Period 3 element is phosphorus (P). Its electron configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$.

3. This enthalpy change can be represented by:
   $\frac{1}{2}\,Cl_2\,(g) + e^- = Cl^-\,(g)$

   The energy changes involved are:

$$\begin{tikzcd}
\tfrac{1}{2}\,Cl_2\,(g) \arrow[rr, "\Delta H_a\,(Cl)"] \arrow[dr, swap, "\Delta H_f\,(Cl\,(g))"] & & Cl\,(g) \arrow[dl, "\Delta H_{EA}\,(Cl^-\,(g))"] \\
& Cl^-\,(g) &
\end{tikzcd}$$

   So the total energy change is:

$$\begin{aligned}\Delta H_f\,(Cl\,(g)) &= \Delta H_a\,(Cl\,(g)) + \Delta H_{EA}\,(Cl^-\,(g))\\ &= +121\ kJ\ mol^{-1} + (-349\ kJ\ mol^{-1})\\ &= -228\ kJ\ mol^{-1}\end{aligned}$$

4. a) $Ca (s) + ½ O_2 (g) \rightarrow CaO (s)$
   b) $Ca (s) \rightarrow Ca (g)$
   c) $Ca (g) \rightarrow Ca^+ (g) + e^-$
   d) $Ca^+ (g) \rightarrow Ca^{2+} (g) + e^-$
   e) $½ O_2 (g) \rightarrow O (g)$
   f) $O_2 (g) \rightarrow 2O (g)$
   g) $O (g) + e^- \rightarrow O^- (g)$
   h) $O^- (g) + e^- \rightarrow O^{2-} (g)$
   i) $CaO (s) \rightarrow Ca^{2+} (g) + O^{2-} (g)$

5. ΔH_1 = b), ΔH_a (Ca)
   ΔH_2 = c), IE_1 (Ca)
   ΔH_3 = d), IE_2 (Ca)
   ΔH_4 = e), ΔH_a (O_2)
   ΔH_5 = g) and h), ΔH_{EA} (O) and ΔH_{EA} (O^-)
   ΔH_6 = - i), negative of ΔH_a (CaO)
   ΔH_7 = a), ΔH_f (CaO)

6. a) $\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 = \Delta H_7$
   $\Delta H_5 = \Delta H_7 – \Delta H_1 – \Delta H_2 – \Delta H_3 – \Delta H_4 – \Delta H_5 – \Delta H_6$
   $\Delta H_5 = - 635 – 193 – 590 – 1150 – 248 - -3513$
   $\Delta H_5 = - 635 – 193 – 590 – 1150 – 248 + 3513$
   $= -2816 + 3513$
   $= +697$ kJ mol^{-1}

   b) $\Delta H_5 = +697$ kJ mol^{-1} = g + h
   h = 844 kJ mol^{-1}, therefore g = 697 – 844
   g = -147 kJ mol^{-1}

7. a) When an electron is added to an atom, there is repulsion between the incoming electron and the valence shell electrons, but there will also be an attraction between the nucleus and the extra electron. In general, the overall process of first electron affinity is exothermic.
   When an electron is added to an anion, the repulsive forces are significant and energy must be provided to overcome this repulsion. As a result, the process of second electron affinity is endothermic.

   b) The enthalpy of atomization is based on the energy required for the production of one mole of gaseous oxygen atoms from its starting state under standard conditions, requiring a starting quantity of ½ mole O_2.
   The bond dissociation enthalpy is based on the energy required to break one mole of O-O bonds, thus requiring a starting quantity of 1 mole O_2.

   c) ΔH_2 is the IE_1 for Ca. The IE_1 for Mg would be larger as IE_1 decreases down a group, and Ca is farther down Group 2 than Mg.

   d) Lattice enthalpy for salts containing the M^{2+} ion decrease down the group as M^{2+} gets larger.
   Therefore the lattice enthalpy will proceed MgO > CaO > SrO > BaO.

   e) The lattice enthalpy for CaO will be smaller than that for $CaCl_2$. The Ca^{2+} and O^{2-} ions are of a similar size and produce a stable lattice with a 1:1 anion:cation ratio. Comparatively the Ca^{2+} is considerably larger than the Cl^- ions and the chlorine anions slot into the gaps within the Ca^{2+} lattice. The lattice is less stable due to the higher ratio of anions to cations.

8. z_+ = magnitude of charge on cation
z_- = magnitude of charge on anion
e = charge on electron
ε_0 = permittivity of vacuum
r = internuclear distance between ions.

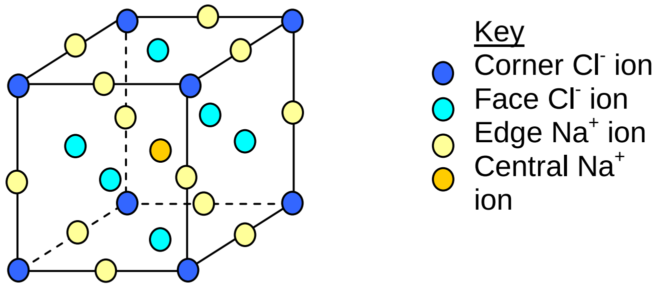
9. Remember 201 pm = 201 x 10^{-12} m, so r = 2.01 x 10^{-10} m.

$$\Delta U = -\left(\frac{|z_+||z_-|e^2}{4x\pi x\varepsilon_0 xr}\right) \text{x L}$$

So $$\Delta U = -\left(\frac{1x1}{2.01x10^{-10}\,m}\,x2.3x10^{-28}\,Jm\right) \text{ x } 6.022 \text{ x } 10^{23} \text{ mol}^{-1}$$

$$\Delta U = -\ 689 \text{ kJ mol}^{-1}$$

10. a)



b) i) 8 corner Cl^- ions, each shared between 8 unit cells, giving 1 corner Cl^- ion per unit cell.
ii)6 face Cl^- ions, each shared between 2 unit cells, giving 3 face Cl^- ions per unit cell.
iii) 3 + 1 = 4 total Cl^- ions per unit cell.
iv) 12 edge Na^+ ions, each shared between 4 unit cells gives 3 edge Na^+ ions per unit cell, plus 1 in the central position gives a total of 4 Na^+ ions per unit cell.
v) So in total there are 4 NaCl formula units per unit cell.

11. There are $2n$ tetrahedral holes and n octahedral holes; the same is true for an hcp array.

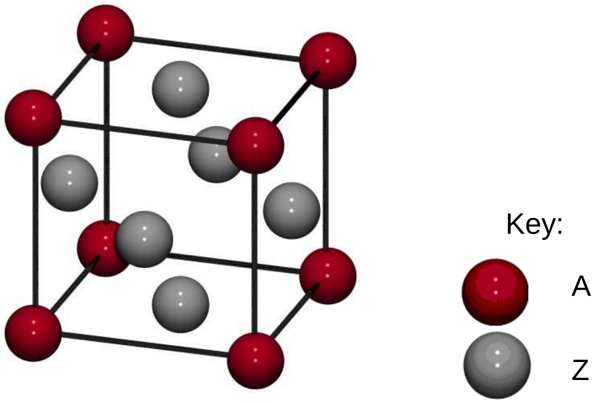
12. Twelve. Again, this is the same for an hcp array.

13. The coordination number is six for both Na^+ and Cl^- ions; each ion is octahedrally coordinated by the other.

14. a)The coordination number is four in each case. Each Zn atom is surrounded tetrahedrally by four S atoms and vice versa. Zinc blende is the cubic form of zinc sulfide but in the hexagonal form, the mineral wurtzite, both Zn and S also have a coordination number of four.

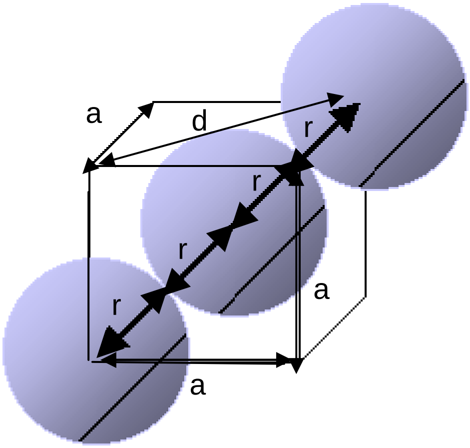
b) Four. Consider the smaller zinc atoms in the diagram. There are (6 x ½) = 3 at the centres of each face and (8 x ⅛) = 1 at the corners. These four are matched by the four sulfur atoms entirely enclosed in the cell.

15.



The question describes a face-centred cubic structure.
With A atoms at each corner of the unit cell, there are 8 atoms of A.
Each A is shared by 8 unit cells, so no. of A per unit cell = 8 / 8 = 1.
With Z atoms on each face of the unit cell, there are 6 atoms of Z.
Each Z is shared by 2 unit cells, so no. of Z per unit cell = 6 / 2 = 3.
The empirical formula of the compound is AZ_3.

16.



a) Diagonal (x) = 4 x r

b) d = face diagonal

$d^2 = a^2 + a^2$ $d^2 = 2a^2$ $d = a\sqrt{2}$

c) $a^2 + d^2 = (4r)^2$ $a^2 + 2a^2 = (4r)^2$ $3a^2 = (4r)^2$

$a^2 = \frac{(4r)^2}{3}$ $a = \frac{4r}{\sqrt{3}}$

d) No. corner atoms = 8. No. per unit cell = 8 / 8 = 1.
No. centre atoms = 1. Total no. atoms per unit cell = 2.

e) Volume of cubic cell = a^3 Volume of one atom = $\frac{4}{3}\pi r^3$

No. of atoms = 2, so total volume filled by atoms = 2 x $\frac{4}{3}\pi r^3$

$$= \frac{8}{3}\pi r^3$$

a = $\frac{4r}{\sqrt{3}}$, so a^3 = $\frac{4^3 r^3}{3\sqrt{3}}$ $\sqrt{3}\times\sqrt{3}\times\sqrt{3} = 3\sqrt{3} = \left(\sqrt{3}\right)^3$

Percentage filled = $\dfrac{\frac{8}{3}\pi \cancel{r^3}}{\frac{4^3\cancel{r^3}}{3\sqrt{3}}} = \frac{8}{\cancel{3}}\pi\times\frac{\cancel{3}\sqrt{3}}{4^3}$

$$= \frac{\overset{2}{\cancel{8}}\pi\times\sqrt{3}}{\cancel{4}\times 4\times 4} = \frac{2\pi\sqrt{3}}{16} = \frac{6.284\times 1.732}{16} = 0.68017$$

= 68 % filled with spheres.

Redox Chemistry

Worked Example 1

Determine the oxidation numbers of each element in the following:

a) $MgCl_2$

b) SO_2

c) $Cr_2O_7^{2-}$

Answers to Worked Example 1

Generally speaking we use the following rules to determine oxidation numbers:

i) For an atom in its elemental form, oxidation number (ON) = 1
ii) For a simple, one atom ion (monatomic ion), ON = charge on that ion, (e.g. Cl^-, ON = -1)
iii) The sum of the oxidation numbers for all the atoms in a compound = 0
iv) The sum of the oxidation numbers in a polyatomic ion = charge on that ion (e.g. OH^-, sum of ON's = -1)

For the oxidation numbers of specific atoms or groups of atoms, the following rules apply:

1) For group 1A atoms, ON = +1
2) For group 2A atoms, ON = +2
3) For hydrogen, ON = +1 in combination with non-metals (e.g. HCl) and ON = -1 in combination with metals (e.g. CaH_2)
4) For oxygen, ON = -2 in all compounds EXCEPT peroxides, where ON = -1.
5) For fluorine, ON = -1 in all compounds.
6) For group 7A atoms, ON = -1 in combination with all metals and non-metals (except O).

Thus for the compounds in the question:

a) $MgCl_2$
Rule 2 states ON (Mg) = +2
Rule 6 states ON (Cl) = -1

b) SO_2
Rule 4 tells us that ON (O) = -2
From the fact that the sum of the oxidation numbers for all the atoms in a compound = 0 (rule iii) we can infer that ON (S) = 2 x ON (O) (as we have two oxygen atoms for one sulfur atom), thus ON (S) = 4.

c) $Cr_2O_7^{2-}$
Rule iv tells us that the sum of the oxidation numbers on the ion = charge on the ion, so in this case the sum of the oxidation numbers = -2. Hence the two Cr atoms must have a charge which balances 6 of the 7 oxygen atoms to leave a 2- charge. To do this, Cr must have a charge of 6+, and thus rule ii tells us that ON (Cr) = +6.

Question 1

Determine the oxidation numbers of the species in the following compounds:

a) NaOH

b) PCl_3

c) H_2SO_4

d) HNO_3

e) SO_4^{2-}

f) MnO_4^-

g) $S_2O_3^{2-}$

h) $S_4O_6^{2-}$

i) VO_4^{3-}

Worked Example 2

For the following equation, determine the oxidation numbers of the species involved. Does the equation involve redox?

$Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$

Answer

Let us consider the oxygen atoms first. In the OH^- ions on the LHS the oxidation number (ON) of the oxygen is -2.
On the RHS in the ClO^- ion, ON (O) is still -2 (recall that ON (O) is always -2 except when in a peroxide). We also see that in the H_2O atom, ON (O) = -2 for the same reason.
Next we consider the hydrogen. In the OH^- ions we know the ON (O) so we can infer that ON (H) = +1 to obtain the -1 charge on the overall ion.
On the RHS, hydrogen is only present in H_2O, and as we know ON (O) = -2, and the overall charge on the compound = 0, we can infer that ON (H) = +1.
Effectively, the ON's of oxygen and hydrogen haven't changed throughout the equation.
Now we consider chlorine. In Cl_2, chlorine has an ON of 0 as species in their elemental form always have an ON of 0.
In Cl^- on the RHS it is pretty clear that ON (Cl) = -1 as it is a monoatomic ion.
However in the ClO^- ion, oxygen has an ON = -2 so chlorine must have an oxidation number of +1.
From this analysis we see that Cl has been both reduced to Cl^-, and oxidised to ClO^-, hence this is a redox reaction. Moreover, it is an example of disproportionation, where a species is simultaneously reduced *and* oxidised.

Question 2

Determine the oxidation numbers of the species in the following equations and state which equations involve redox.

a) $2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$

b) $2MnO_4^- + 6H^+ + 5SO_3^{2-} \rightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$

c) $2NaI + 3H_2SO_4 \rightarrow 2NaHSO_4 + 2H_2O + I_2 + SO_2$

Worked Example 3

Balance the following half equations then sum the equations to give the final redox equation:

$Fe^{2+} \rightarrow Fe^{3+} + \_\_$

$\_\_ + Br_2 \rightarrow \_\_Br^-$

Answer

Let us look at the first half equation:

$Fe^{2+} \rightarrow Fe^{3+} + \_\_$

First we check whether the number of atoms balance. They do, as there is one Fe atom on each side of the half equation. Now we check that the charges balance. These do not, as there is an overall 2+ on the LHS, and an overall 3+ on the RHS. We balance this by adding an electron (e^-) in the blank space on the RHS, i.e.

$Fe^{2+} \rightarrow Fe^{3+} + \underline{e^-}$ (i)

Now we look at the second half equation:

$\_\_ + Br_2 \rightarrow \_\_Br^-$

Again, we check whether the number of atoms balance. They do not, as there are two Br atoms on the LHS and only one on the RHS. We rectify this by adding a ‘2’ into the blank on the RHS to yield:

$\_\_ + Br_2 \rightarrow \underline{2}Br^-$

Now we check whether the electronic charges balance. They do not, as there is no charge on the LHS and a 2- charge on the RHS. We balance this by adding two electrons into the blank on the RHS:

$\underline{2e^-} + Br_2 \rightarrow \underline{2}Br^-$ (ii)

We obtain the overall redox reaction by balancing the number of electrons in the half equations (in this case, we must multiply equation i by 2 to give us 2 e^-s.) We then add the LHS of both i and ii to one another and add the RHS of both i and ii to one another and cancel the electrons (which should be the same number on both sides after the multiplication of i by 2).

$2Fe^{2+} + Br_2 + 2e^- \rightarrow 2Fe^{3+} + 2Br^- + 2e^-$ (cancel the 2 e^- from both sides)

$2Fe^{2+} + Br_2 \rightarrow 2Fe^{3+} + 2Br^-$

Question 3

a) __$S_2O_3^{2-} \rightarrow S_4O_6^{2-}$ + __

__ + $I_2 \rightarrow$ __I^-

b) MnO_4^- + __$H^+ \rightarrow Mn^{2+}$ + __H_2O

__$I^- \rightarrow I_2$ + __

Question 4

Addition of aqueous copper (II) ions to aqueous iodide ions gives a precipitate of copper (I) iodide and liberates iodine. The iodine can be titrated with aqueous sodium thiosulfate and thus the amount of copper present in a sample can be determined.

a) Write an equation for the reaction of copper (II) ions with iodide ions.

b) Using the equation determined in question 3 part a) above, find the volume of sodium thiosulfate solution of concentration 1.00 mol dm^{-3} needed to react with the iodine liberate from a brass screw of mass 2.00 g containing 60% copper by mass.

Question 5

In order to determine the purity of potassium manganate (VII) obtained in a lab preparation a sample was analysed as follows:

5.135 g of the dry solid was dissolved in water and the solution made up to a volume of 250 cm^3.
10.0 cm^3 portions of the solution were titrated with a solution of Fe^{3+} ions of concentration 0.250 mol dm^{-3}.
25.20 cm^3 Fe^{3+} solution were required to reach the end point.

The redox half equations are:

MnO_4^- (aq) + $8H^-$ (aq) + $5e^- \rightarrow Mn^{2+}$ (aq) + $4H_2O$ (l)

Fe^{3+} (aq) + $e^- \rightarrow Fe^{2+}$ (aq)

a) Find the overall redox equation for the reaction.

b) Calculate the percentage purity of the potassium manganate (VII).

Question 6

25.0 cm^3 of a solution of hydrogen peroxide was diluted to 250 cm^3. When 20.0 cm^3 of the diluted solution was acidified it required 19.2 cm^3 of 0.0210 mol dm^{-3} potassium manganate (VII) for oxidation.

a) Balance the redox half equations for the reaction:

$MnO_4^- + \_\_e^- \rightarrow Mn^{2+} + 4O^{2-}$

$H_2O_2 \rightarrow O_2 + 2H^+ + \_\_e^-$.

b) Sum the balanced half equations to obtain the overall redox equation for the reaction.

c) Calculate the concentration of the initial hydrogen peroxide solution (in mol dm^{-3})

Question 7

The alcohol content of a 10.0 g sample of blood from a driver required 4.23 ml of 0.07654 M $K_2Cr_2O_7$ for titration. The balanced chemical equation for the reaction is shown below. Should the police prosecute the individual for drunken driving if the legal limit of blood alcohol is 0.1% by mass?

$3CH_3CH_2OH + 2K_2Cr_2O_7 + 8H_2SO_4 \rightarrow 3CH_3COOH + 2Cr_2(SO_4)_3 + 2K_2SO_4 + 11H_2O$

Question 8

Calcium oxalate (CaC_2O_4) is insoluble in water. For this reason it can be used to determine the amount of Ca^{2+} ions in fluids such as blood. The calcium oxalate isolated from blood is dissolved in acid and titrated against a standardised $KMnO_4$ solution. In one test it is found that the calcium oxalate isolated from a 10.0 ml sample of blood required 24.2 ml of 9.56 x 10^{-4} M $KMnO_4$ for titration. Calculate the number of milligrams of calcium per millilitre of blood.

Redox Chemistry Answers

1. a) Na = +1, O = -2, H = +1
   b) Cl = -1, P = +3
   c) O = -2, H = +1, S = +6
   d) O = -2, H = +1, N = +5
   e) O = -2, S = +6
   f) O = -2, Mn = +7
   g) O = -2, S = + 2
   h) O = -2, S = + 2 ½
   i) O = -2, V = +5

2.

a)	2Cr	O_4^{2-}	$+ 2H^+ \rightarrow$	Cr_2	O_7^{2-}	$+ H_2$	O
ON's	+6	-2	+1	+6	-2	+1	-2

No species has a change in oxidation number, thus this is not redox.

b)	2Mn	O_4^-	$+ 6H^+$	+ 5S	$O_3^{2-} \rightarrow$	$2Mn^{2+}$	$+ 3H_2$	O	+ 5S	O_4^{2-}
ON's	+7	-2	+1	+4	-2	+2	+1	-2	+6	-2

It is redox: Mn is reduced (from +7 to +2) and S is oxidised (from +4 for +6)

c)	2Na	I	$+ 3H_2$	S	$O_4 \rightarrow$	2Na	H	S	O_4	$+ 2H_2$	O	$+ I_2$	+ S	O_2
ON's	+1	-1	+1	+6	-2	+1	+1	+6	-2	+1	-2	0	+4	-2

It is redox: S is reduced (from +6 to +4) and I is oxidised (from -1 to 0)

3. a) $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$
   $2e^- + I_2 \rightarrow 2I^-$
   $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

   b) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
   $2I^- \rightarrow I_2 + 2e^-$
   $2MnO_4^- + 16H^+ + 10I^- \rightarrow 2Mn^{2+} + 8H_2O + 5I_2$

4. a) $2Cu^{2+} + 2I^- \rightarrow Cu^+ + I_2$
   b) 0.0189 dm^3 (18.9 cm^3) of 1.00 mol dm^{-3} sodium thiosulfate.

5. a) MnO_4^- (aq) + $8H^+$ (aq) + $5Fe^{3+}$ (aq) → Mn^{2+}(aq) + $5Fe^{2+}$ (aq) + $4H_2O$ (l)

   b) First, calculate the quantity of MnO_4^- used in the titration.
   25.20 cm^3 of 0.250 mol dm^{-3} Fe^{3+} ions were required to reach the end-point.
   $\frac{25.20x0.250}{1000}$ = 0.0063 moles Fe^{3+} ions required to reach end-point.
   There is a 5:1 ratio of Fe^{3+} to MnO_4^- so 0.0063 / 5 = 0.00126 moles MnO_4^- ions were used in the titration.
   Now calculate the hypothetical quantity if the $KMnO_4$ were 100% pure.
   Mr of $KMnO_4$ = 158 g mol^{-1}, 5.135 g used, 5.135 / 158 = 0.0325 moles of $KMnO_4$ in 250 cm^3 flask, so 0.0325 x 4 = 0.13 M $KMnO_4$.
   10.0 cm^3 0.13 M $KMnO_4$ = 0.13 / 100 = 0.0013 moles $KMnO_4$ in titration, so 0.0013 moles MnO_4^- should be present.
   $\frac{0.00126(\text{actual no. of moles})}{0.00130(\text{hypothetical no. of moles})}$ x 100 = 97% purity.

6. a) $MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4O^{2-}$
   $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$

   b) $2MnO_4^- + 5H_2O_2 \rightarrow 2Mn^{2+} + 8O^{2-} + 5O_2 + 10H^+$

   c) 0.001 mol of H_2O_2 was oxidised by the potassium manganate (VII) thus the original hydrogen peroxide solution was of concentration 0.504 mol dm^{-3}.

7. The equation for the reaction is:

   $3CH_3CH_2OH + 2K_2Cr_2O_7 + 8H_2SO_4 \rightarrow 3CH_3COOH + 2Cr_2(SO_4)_3 + 2K_2SO_4 + 11H_2O$
   Thus no. of moles $K_2Cr_2O_7$ used = $4.23 \times 10^{-3} \times 0.0765$
   = 0.3236×10^{-3} moles

   This is equivalent to $3/2 \times 0.3236 \times 10^{-3}$ moles C_2H_5OH
   = 0.4854×10^{-3} moles C_2H_5OH.
   1 mole C_2H_5OH has Mr = 46 g mol^{-1}
   ∴ mass C_2H_5OH in sample = $0.4854 \times 10^{-3} \times 46$ g
   = 22.33×10^{-3} g
   = 0.00223 g

   % alcohol in blood = $\frac{0.0223}{10} \times 100$ = 0.223 % alcohol by mass.
   So yes – they should prosecute.

8. To solve the problem, first work out the stoichiometric equation for the reaction from the two redox half equations. Combine the equations to get the overall equation. Find the number of moles of permanganate which react, then find the number of moles of $C_2O_4^{2-}$ this is equivalent to and hence the mass of Ca^{2+} ions in 10 ml.

   $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$ (1)
   $8H^+ + MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (2)
   Multiply (1) by 5
   $5C_2O_4^{2-} \rightarrow 10CO_2 + 10e^-$
   Multiply (2) by 2
   $16H^+ + 2MnO_4^- + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$
   Sum the equations:
   $5C_2O_4^{2-} + 16H^+ + 2MnO_4^- \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$
   So 5 moles $C_2O_4^{2-} \equiv 2$ moles MnO_4^-

   No. moles MnO_4^- used = $24.2 \times 10^{-3} \times 9.56 \times 10^{-4}$
   = 231.35×10^{-7} moles MnO_4^-

   No moles $C_2O_4^{2-}$ = $5/2 \times 231.35 \times 10^{-7} = 578.4 \times 10^{-7}$ moles
   ∴ no. moles Ca^{2+} = 578.4×10^{-7} in 10.0 ml of blood.

   Mass Ca^{2+} = $578.4 \times 10^{-7} \times 40$ g (Mr of Ca = 40)
   = 23136×10^{-7} g
   = 2.134×10^{-3} g in 10 ml.
   ∴2.314×10^{-4} g in 1 ml
   = 0.231 mg per ml

Coordination Chemistry

Worked Example 1

Write down the oxidation state and valence shell electron configuration of the metal in each of the following ions: Ti^{3+}, ZrO^{2+}, RuO_4^{2-}, Ni^{3+}.

Answers to Worked Example 1

In transition metal ions, all remaining valence shell electrons are assigned to the outer shell d orbital.

Titanium is [Ar] $4s^2 3d^2$ so Ti^{3+} (oxidation state +3) is $3d^1$

Zirconium is [Kr] $5s^2 4d^2$ so ZrO^{2+} (oxidation state +4) is $4d^0$

Ruthenium is [Kr] $5s^2 4d^6$ so RuO_4^{2-} (oxidation state +6) is $4d^2$

Nickel is [Ar] $4s^2 3d^8$ so Ni^{3+} (oxidation state +3) is $3d^7$

Question 1

Write down the oxidation state and valence shell electron configuration of the metal in each of the following ions:

Cu^+, TaO_4^{3-}, OsO_4, Rh^+

Question 2

What is the coordination number of the Fe atom is $K_3\,[Fe(C_2O_4)_3]$?

Question 3

What is the coordination number of the Au atom in $K\,[Au(CN)_2(SCN)_2]$?

Question 4

Which of the following can function as a bidentate ligand?

NH_3, $C_2O_4^{2-}$, CO, OH^-

Question 5

Ethylenediaminetetraacetate ion ($EDTA^{4-}$) is commonly referred to as a

___________ ligand.

Worked Example 2

Calculate the oxidation state of the metal and the number of d electrons in the following coordination complexes:

a) $[CoCl_4]^{2-}$

b) $[Fe(bpy)_3]^{3+}$

c) $[Cu(ox)_2]^{2-}$

d) $[Cr(CO)_6]$

Answers

a) Each Cl ligand has a charge of -1, so 4 x -1 = -4
Overall charge on the complex is -2, so the oxidation state of Co = +2.
Ground state configuration for Co = [Ar] $3d^7 4s^2$
On loss of $2e^-$, Co^{2+} has configuration [Ar] $3d^7$, so 7 d electrons.

b) bpy (2,2'-Bipirydyl) is uncharged = neutral
Oxidation state of Fe = +3
Ground state configuration for Fe = [Ar] $3d^6 4s^2$
On loss of $3e^-$ Fe^{3+} has configuration [Ar] $3d^5$, so 5 d electrons.

c) ox (oxalate, $C_2O_4^{2-}$) has charge -2 per oxalate, so total = 2 x -2 = -4
Overall charge on complex = -2, so the oxidation state of Cu = +2.
Ground state configuration for Cu = [Ar] $3d^{10} 4s^1$
On loss of $2e^-$, Cu^{2+} has configuration [Ar] $3d^9$, so 9 d electrons.

d) CO is uncharged = neutral.
Oxidation state of Cr = 0.
In this case, all electrons are in 3d orbitals which are now of lower energy (because filled) than 4s orbitals.
Ground state configuration for Cr = [Ar] $3d^5 4s^1$
Configuration for Cr^0 = [Ar] $3d^6$, so 6 d electrons.

Question 6

What is the oxidation state of the metal and the d electron configuration of the following complexes?

a) $[CrBr(H_2O)(en)_2] Cl_2$

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

c) $K_2[CoBr_4]$

d) $[Ni(edta)]^{2-}$

e) $[ReCl(CO)_3(py)_2]$

Question 7

Complete the following table:

Formula of complex	Oxidation state of metal in Complex	d electron configuration
$[Cu(NH_3)_4]^{2+}$	+2	$3d^9$
K_2CoBr_4		
$TiCl_4$		
$[Ti(H_2O)_6]^{3+}$		

Worked example 3

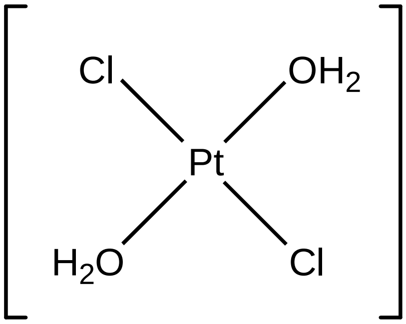
Draw the structure of the following complexes:

a) trans-diaquadichloroplatinum (II)

b) diamminetetra(isothiocyanato)chromate (III)

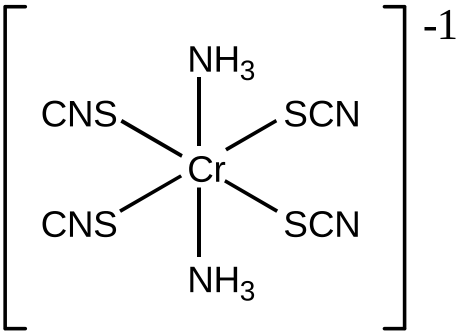
Answers

a)



H_2O (aqua) is neutral. Diaqua indicates that there are two of them.
Each Cl ligand = -1. Dichloro indicates there are two chlorine ligands.
Platinium is in the +2 oxidation state so the complex is uncharged.
Trans indicated that the Cl and H_2O ligands are located opposite each other.

b)



Ammine is NH_3, which is uncharged. There are 2 of them.
Isothiocyanato = SCN^-, which attaches through the S.
Each has a charge of -1 and there are 4.
Chromate (III) indicates that this is an anion with Cr in the 3+ oxidation state.
Charge on SCN^- = 4 x -1 = -4.
Charge on Cr = +3, so overall charge = -1.

Question 8

Draw the structures of the following complexes:

a) bromopentacarbonylmanganese (I)

b) chlorotris(triphenylphosphine)rhodium (I)

c) pentaamminenitritocobalt (III)

d) hexacyanoferrate (II)

Worked Example 4

Name the following complexes:

a) $[Pt(Cl)_2(NH_3)_4]^{2+}$

b) $[Ni(CO)_3py]$

Answers

a) Complex has 2 x Cl^- = -2.
4 x NH_3 (neutral)
The overall charge is +2, so charge on Pt = +4.
It is therefore a cationic complex of Pt (IV)

Following the alphabetical rules, ammine precedes chloro:

tetraamminedichloroplatinum (IV)

b) The complex is uncharged; Ni has an oxidation state of 0.
CO (carbonyl) is neutral.
py (pyridine) is neutral.

tricarbonylpyridinenickel (0)

Question 9

Name the following complexes:

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

b) $[Cr(SCN)(NH_3)_5]^{2+}$

Write out the formula for the following complexes:

c) tetraamminecarbonatoiron (III) chloride

d) pentaamminechlorocobalt (III) sulfate

e) dicarbonyldiiodorhodate (I)

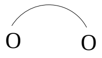
f) dichlorodiencobalt (III)

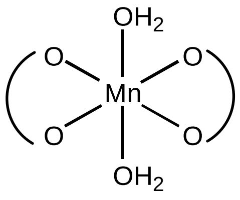
Worked Example 5

Draw the stereoisomers of octahedral $[Mn(H_2O)_2(ox)_2]^{2-}$

Answer

H_2O is monodentate.

ox is oxalate and is bidentate, represented by 



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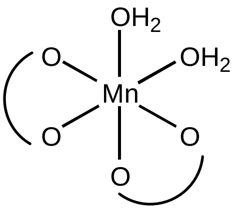

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Question 10

Draw the stereoisomers of:

a) octahedral $[Co(H_2O)(NH_3)(en)_2]^{3+}$

b) square planar $[NiCl_2(PMe_3)_2]$

Question 11

State whether either of the following complexes could be optically active:
note: (L is an anionic ligand)

a) trans-$[Co(en)_2L_2]^+$

b) $[Co(NH_3)_4L_2]^+$

Coordination Chemistry Answers

1. Cu^+ = +1, $3d^{10}$ TaO_4^{3-} = +5, $5d^0$

   OsO_4 = +8, $5d^0$ Rh^+ = +1, $4d^8$

2. The coordination number is 6. There are three bidentate ligands attached to the central metal, 3 x 2 = 6.

3. The coordination number is 4. There are four monodentate ligands attached to the central metal.

4. Only $C_2O_4^{2-}$, oxalate, is a bidentate ligand. The others are all monodentate.

5. EDTA is a hexadentate ligand.

6. a) Br = -1, H_2O = 0, en = 0. Total charge of ligands = -1.
   Charge on ion = +2.
   Charge on Cr = +3, so oxidation state of Cr = +3.
   Ground state configuration of Cr = [Ar] $3d^5 4s^1$
   Configuration of Cr^{3+} = [Ar] $3d^3$, so 3 d electrons.

   b) NH_3 is neutral, charge on ion = +2.
   Charge on Cu = +2, so oxidation state of Cu = +2.
   Ground state configuration of Cu = [Ar] $3d^{10} 4s^1$
   Configuration of Cu^{2+} = [Ar] $3d^9$, so 9 d electrons.

   c) Br = -1. 4 x -1 = -4, so total charge of ligands = -4.
   Charge on ion = -2.
   So charge on Co = +2, oxidation state of Co = +2.
   Ground state configuration of Co = [Ar] $3d^7 4s^2$
   Configuration of Co^{2+} = [Ar] $3d^7$, so 7 d electrons.

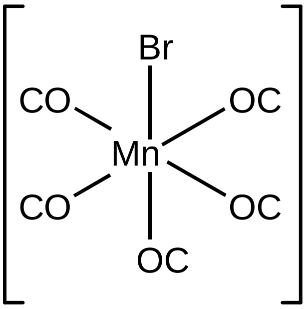
   d) edta = -4. Total charge of ligands = -4.
   Charge on ion = -2.
   Charge on Ni = +2, oxidation state of Ni = +2.
   Ground state configuration of Ni = [Ar] $3d^8 4s^2$
   Configuration of Ni^{2+} = [Ar] $3d^8$, so 8 d electrons.

   e) Cl = -1, CO = 0, py = 0. Total charge of ligands = -1.
   Complex is neutral – Charge of Re = +1, oxidation state of Re = +1.
   Ground state configuration of Re = [Xe] $5d^5 6s^2$
   Configuration of Re^+ = [Xe] $5d^6$, so 6 d electrons.

7.

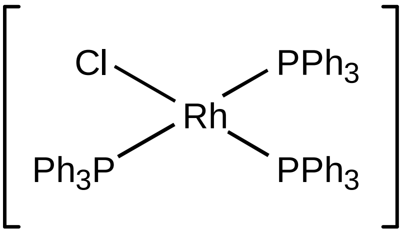
Formula of complex	Oxidation state of metal in Complex	d electron configuration
$[Cu(NH_3)_4]^{2+}$	+2	$3d^9$
K_2CoBr_4	+2	$3d^7$
$TiCl_4$	+4	$3d^0$
$[Ti(H_2O)_6]^{3+}$	+3	$3d^1$

8. a)



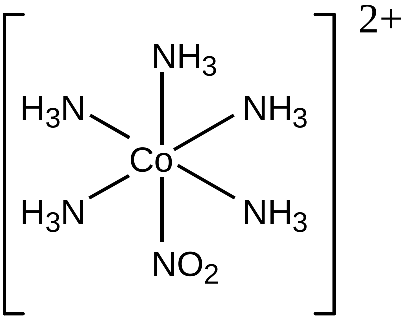
Br = -1, Mn = +1 so uncharged.

b)



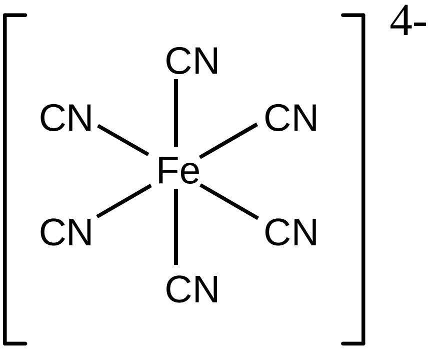
Cl = -1, Rh = +1 so uncharged.

c)



nitrito = NO_2^- = -1, ammine = NH_3 = uncharged. Charge on Co = +3, NO_2^- = -1 so overall charge = +2.

d)



CN^- = -1, hexa = 6, so 6 x CN^- = -6.
Ferrate (II) = Fe^{2+} = +2.
Charge on complex ion = (-6 + 2) = -4.

9. a) NH_3 = ammine = uncharged.
So oxidation state of Co = +3.

hexaamminecobalt (III)

b) SCN^- = thiocyanate = -1
NH_3 = ammine = uncharged.
Overall charge on ion = +2, so oxidation state of Cr = +3.

pentaaminethiocyanatechromium (III)

c) ammine = NH_3 = uncharged.
carbonato = CO_3^{2-} = -2
iron = +3
-2 +3 = Charge on ion = +1, so one chloride required to balance charge.

$[Fe(NH_3)_5(CO_3)]Cl$

d) ammine = NH_3 = uncharged.
chloro = Cl^- = -1
cobalt = +3.
-1 + 3 = Charge on ion = +2, counter balanced by one sulfate = -2.

$[Co(NH_3)_5Cl]SO_4$

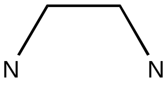
e) carbonyl = CO = uncharged
iodo = I^- = -1, it's diiodo so total = 2 x -1 = -2.
Oxidation state of Rh = 1, so charge on ion = -2 + 1 = -1.

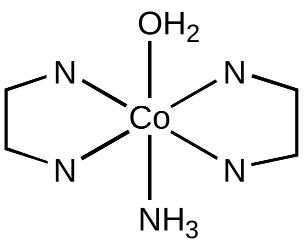
$[Rh(CO)_2I_2]^-$

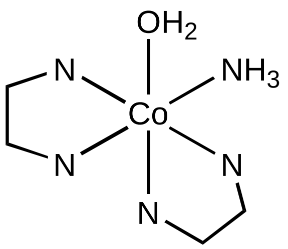
f) chloro = Cl^- = -1, it's dichloro so total = 2 x -1 = -2
en = ethylenediamine = uncharged.
cobalt = Co^{3+}, so oxidation state of +3.
Overall charge on ion = -2 + 3 = +1.

$[CoCl_2(en)_2]^+$

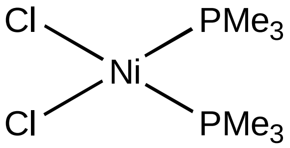
10. a) H_2O is monodentate.
NH_3 is monodentate.

en is ethylenediamine and is bidentate, represented by 





b) Both Cl and PMe_3 are monodentate ligands.
There are two ways of arranging the ligands.



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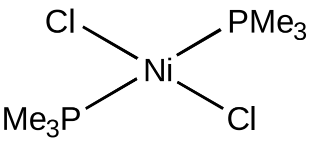

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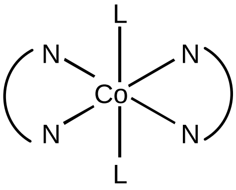
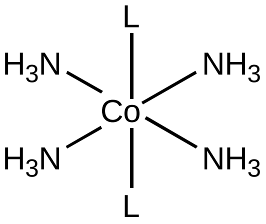
Square planar means the metal is 4 coordinate with ligands arranged in the equatorial plane to give a square shaped complex.

11. a) This is the structure of the complex described.

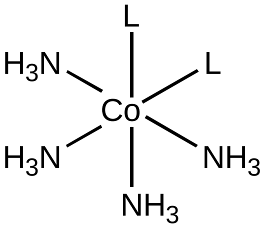


It is not optically active.

b) There are two possible structures for this complex.



Not optically active



Not optically active