γ -Radiation

Electromagnetic radiation with very short wavelength, smaller than even X-rays - arises from most nuclear disintegrations. It causes no change in atomic structure upon emission.

It is unaffected by electric and magnetic fields (as is all electromagnetic radiation *e.g.* light).

Extremely high energy and able to penetrate up to 15-20 cm of lead.

Causes extreme and rapid biological damage.



Isotopic Stability

Isotopic stability is governed by the ratio of neutrons to protons in the nucleus. The following graph shows number of neutrons vs number of protons for all the stable naturally occurring nuclei.



A smooth curve drawn through the upper and lower limits of this plot is referred to as the belt / band of stability.

For elements of low atomic number (Z < 20) there is an approximately 1:1 ratio between the number of neutrons (A-Z) and the number of protons (Z). As atomic number increases above 20, the ratio (A-Z)/(Z) shows a progressive increase to about 1.6.

It can also be shown from this plot that:

- 1. Elements of odd atomic number do not have more than two stable isotopes
- 2. Elements of even atomic number frequently have several stable isotopes

Mass Defect and Binding Energy

It is found that there is a difference between the calculated masses of nuclides and their measured masses.

e.g.
$${}^{16}\text{O} = 8 \text{ protons} + 8 \text{ neutrons} + 8 \text{ electrons}$$

= 8(1.0073) + 8(1.0087) + 8(0.0005) amu
= 16.132 amu (1 amu = 1.66043 x 10⁻²⁷ kg)

The measured mass of ¹⁶O is only 15.995 amu. There is thus a mass defect of 0.137 amu.

This missing mass creates the binding energy that holds all the protons and neutrons together in the nucleus and prevents its spontaneous disintegration. It is released as energy when a nucleus is formed.

The simple relationship between mass and energy is described in *the* most famous of equations (proposed by Albert Einstein).



Albert Einstein born 1879 in Germany.

Awarded Nobel prize for Physics in 1922 for "his services to theoretical physics". His greatest work was the special theory of relativity.



E = binding energy, m = mass defect and c = speed of light It describes the fundamental relationship between mass and energy.

Half-Life

Radioactive decay is kinetically first order in character, i.e. it is directly proportional to the number of radioactive atoms present.

 $n = n_0 e^{-\lambda t}$

 n_0 = initial number of atoms n = number of atoms after time t λ = decay constant

The half-life or $t_{1/2}$ of a decay process is the time taken for exactly half the atoms present to disintegrate.

It is INDEPENDENT of the number of atoms, is UNAFFECTED by temperature and pressure CANNOT be catalysed.

$$\lambda \times t_{1/2} = \ln 2$$

Uses of Radiation

1. Carbon-14 or Radiocarbon Dating of Artefacts

$${}^{14}_{6}C \rightarrow {}^{14}_{7}N + {}^{0}_{-1}e$$

¹⁴C decays by beta emission with a half life t_{1/2} of 5570 years

In living organisms there is a constant ratio of the isotopes of carbon. Once something dies there

is no biological means to maintain the level of ¹⁴C which thus decreases over time. Artefacts can be dated to within 5% accuracy based on the levels of ¹⁴C present.

2. Nuclear Power

Generated via the splitting or fission of high mass number nuclei such as ²³⁵U that break up to give smaller mass number nuclei with the release of extreme amounts of energy.

The destructive power of such energy release has unfortunately been used in nuclear weapons hence the terms weapons grade plutonium or uranium.

3. Nuclear Fusion

Occurs via the fusing of certain light nuclei and is the process by which our own sun radiates energy. Only occurs at very high temperature, in excess of 15 000 000 °C!

Was also unfortunately used in the hydrogen bombs towards the end of World War II.

 $^{2}_{1}D+^{3}_{1}T\rightarrow^{4}_{2}He+^{1}_{0}n + Energy$ (lots of it)

Bonding in Solids

Solids are made up of atoms, ions or molecules.

In all solids these particles are packed together. Solids may be described as crystalline or amorphous (from the Greek meaning without shape). In crystals the packing is regular and a lattice is formed. In amorphous solids the packing is random.

At temperatures greater than absolute zero the particles vibrate. As temperature is increased, so does the vibration. Eventually the energy of vibration becomes greater than the lattice energy and the solid melts.

How might we determine the structures of solids?

As the spacings between the particles in a crystal lattice are similar to the wavelength of X-rays ($\lambda \sim 10^{-10}$ m) solids diffract X-rays.

X-ray diffraction



World War II North Africa American Cemetery, Tunisia.

Planes of atoms may be considered as semitransparent mirrors. The two incident rays are in phase. The emergent rays are only in phase if the path difference is equal to a whole number of wavelengths.



The Bragg Equation $2d \sin\theta = n\lambda$ where *n* is an integer

Bonding in Metals

A metal consists of an ordered arrangement of positively charged cations surrounded by a "sea" of delocalised electrons.



Any good greengrocer knows this ordered array – it is called close-packed.





Every metallic ion is surrounded by six other ions in a hexagonal arrangement. Electrostatic attraction between the array of cations and the "sea" of electrons binds everything together. The forces are extremely strong. Metals have very high melting points often in the 1000s of °C. There are two ways to perpetuate the closepacking into the third dimension:

namely,hexagonal closepacking(hcp)andcubicclosepacking(ccp)

Hexagonal Close Packed (hcp)

The position of cations in the third layer is identical to those in the first layer. The stacking of layers continues ABABAB...



Cubic Close Packed (ccp)

The position of cations in the third layer is different to that of the both lower layers. The stacking of layers continues ABCABC...



The ccp array is sometimes known as face centred cubic (fcc).

Face-centred Cubic (fcc)



Co-ordination Number is defined as the number of particles in contact with any other particle in the structure.

For both ccp / fcc and hcp this is 12, comprising 6 particles in the plane, 3 above and 3 below. The result fills *ca.* 75% of available space – this is the best that can be achieved packing spheres giving rise to the term close packed.

Another arrangement is however possible...

Body-centred Cubic (bcc)

Here the co-ordination number is 8 resulting in a more open lattice.



68% of space is now occupied. The alkali metals, lithium, sodium, potassium, caesium and francium (Group I) have low densities. All exhibit body centred cubic structures...

Non-Metallic Crystals

1) Giant Covalent Crystals

Atoms bond together to from 2- or 3-dimensional structures with high melting points.

e.g. diamond and graphite - allotropic forms of carbon.

In diamond, all C atoms are sp³ hybridised joined by four covalent bonds to four other atoms. All C-C bonds are the same and the overall structure is the strongest known



All valence electrons are used in bonding so diamonds are colourless insulators.

Graphite is a layered structure. All atoms are sp² hybridised. C-C bonds between atoms within a layer are very strong.

Layers are only associated by weak forces (Van der Waals') and they slide over each other easily.

Graphite is therefore a good lubricant.





Each carbon atom has one mobile unhybridised p electron. Graphite is therefore a black coloured conductor.

2) Molecular Crystals

These contain discrete molecules containing strong covalent bonds. The molecules are held together in a lattice by weak Van der Waals' forces or hydrogen bonds.

A substance which exists as a molecular crystal melts at a low temperature because the intermolecular forces are weak, and NOT because the covalent bonds are weak.

Ionic-Bonding

Ionic materials are made up of 3-dimensional arrays of ions. The energy of such materials is a sum of:

- 1) Coulombic attractions
- 2) Coulombic repulsions
- 3) Minor energy terms



To be efficient an ionic compound must maximise the number of contacts between oppositely charged ions. Simultaneously it must keep ions of the same charge distant from one another. This is achieved by regular packing of the ions into a lattice (*c.f.* metallic packing).

The smallest fundamental part of a crystal lattice that is characteristic of the whole crystal is called the unit cell.

The type of crystal lattice adopted is dependent on the ionic radii and the ionic charges.

The co-ordination number of the ions is dependent on the ratio of cationic versus anionic radii - termed the radius ratio.

The co-ordination number and thus the geometry of the ions, is dependent on this radius ratio.

Co-ordinationNumber	Geometry
8	Primitive Cubic
6	Octahedral
4	Tetrahedral
3	Plane Triangular

Co-ordination Number 8

e.g. caesium chloride CsCl

The caesium cation at 0.167 nm is comparable in size to the chloride anion at 0.181 nm. 8 chloride anions pack around each caesium cation and

vice-versa. It is termed an 8:8 lattice. The lattice type is body centred cubic (bcc).

Co-ordination number 6

e.g. sodium chloride NaCl

At 0.098 nm, a sodium ion is much smaller than a caesium ion and it is only possible to pack 6 chloride ions around one. 6 sodium ions pack about each chloride ion. It is termed a 6:6 lattice. The lattice type is face centred cubic (fcc).



What holds ionic structures together?

Lattice Energy

Consider a pair of oppositely charged ions



N.B. Lattice energy is NEGATIVE

Born-Haber Cycles

These are used to calculate the formation energies or enthalpies of ionic crystals based on Hess' Law which states that "The enthalpy change of a chemical reaction is the same whether the reaction takes place in one or several steps."



From Hess' Law

 $\Delta H_{f} = \Delta H_{A_{M}} + \Delta H_{IE} + \Delta H_{A_{X}} + \Delta H_{EA} + U$

 $\Delta H_{A_{M}}$ enthalpy of atomisation of the metal $\Delta H_{A_{X}}$ enthalpy of atomisation of non-metal

- ΔH_{IE} first ionisation enthalpy
- ΔH_{EA} first electron affinity
- ΔH_{f} enthalpy of formation of crystalline salt
- U lattice enthalpy





Pure covalent and ionic bonds are extreme forms of a continuous scale. When a pair of electrons is shared equally then a pure covalent bond forms e.g. H₂. When a pair of electrons lies totally on one side a pure ionic bond forms e.g. CsF. Most bonds lie between the two extremes and have intermediate character.

Other kinds of Bonding

Hydrogen Bonding

A special example of dipole-dipole interactions

Dipole-Dipole Interactions



These arise when bonds are polar, i.e. when electronegative atoms bond to electropositive atoms. They are electrostatic in nature.

A hydrogen bond exists when a hydrogen atom is bonded to two or more atoms. Hydrogen bonds occur when hydrogen is attached to very electronegative atoms.

e.g. Fluorine, Oxygen or Nitrogen.

The hydrogen bond can be considered as an electrostatic interaction.



The result is higher melting and boiling points than would otherwise be expected.

van der Waals Forces

Arise from temporary dipoles in molecules due to electron movement. They are short ranged (α 1/r⁶) and weak. But they are important because:

They can be used to explain physical behaviour such as boiling points and melting points in related compounds

Summary

- 1. Solids held together merely by van der Waals forces melt at low temperatures. Liquids in the same class vaporise easily.
- 2. Polar molecules *e.g.* H₂O, NH₃ have higher boiling points than expected due to hydrogen bonding.
- 3. Ionic materials generally have very high melting points a reflection of the size of the internal energy U.
- 4. Purely covalent compounds *e.g.* diamond also have very high melting points.