

Allotropy

Introduction

Allotropy is a specific case of polymorphism. Allotropy occurs when an element exists in more than one form when in the same physical state, i.e. solid, liquid or gas. The atoms of an allotrope bond in different ways leading to allotropes having different physical and chemical properties. Not all elements in the periodic table have allotropes. The elements involved are mainly limited to some of those in groups 13 to 16. This includes metalloids, such as boron and silicon, and some non-metals. A few metals exhibit allotropy due to differences in the packing of the metal atoms. Two common allotropic metals are iron and cobalt.



Key Point:

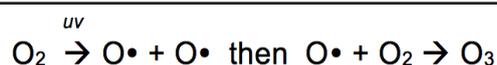
Polymorphism describes the ability of a solid material to exist in two or more forms or structures. It is found in crystalline materials, e.g. metals, minerals and polymers.

Allotropy occurs when elements adopt different physical structures, which are dependent on the physical conditions present in the environment in which they form. Elements may also have different energies in their different allotropic forms. An example is graphite. Graphite is thermodynamically more stable than diamond, but diamonds do not turn into graphite, nor are they naturally made from graphite.

Allotropes can be monotropic. This means that one of the forms is more stable under all physical conditions than the other allotropic forms. Enantiotropy occurs when different allotropes of the element are stable under different physical conditions. Allotropes may also exhibit different physical properties such as density, hardness, melting and boiling points. These forms undergo reversible changes. For instance, phosphorus has many allotropes, but these will revert to a simple tetra-phosphorus structure, P_4 , when heated.

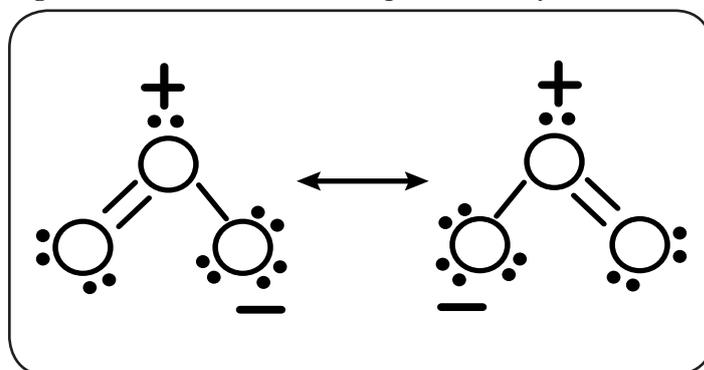
Allotropes of Oxygen

The two most common allotropes are molecular diatomic oxygen (O_2) and ozone (O_3). Diatomic oxygen is monotropic. Diatomic oxygen is a colourless gas which makes up 20.8% of the Earth's atmosphere. Its atomic number is 8 and its electron configuration is: $1s^2, 2s^2, 2p^4$. The simple view is that oxygen forms a double bond between the atoms to form an O_2 molecule. Ozone is a highly reactive allotrope of oxygen. It is a less stable allotrope than diatomic oxygen and decays rapidly to form diatomic oxygen. It is formed naturally from O_2 in the presence of UV light by the formation of oxygen free radicals. The oxygen free radical comes from the breakdown of O_2 as shown in the equation below:

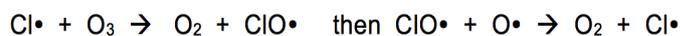


Ozone has different physical properties to diatomic oxygen, as observed by comparing their respective boiling points: $O_3 = -183^\circ\text{C}$; $O_2 = -112^\circ\text{C}$. Ozone is the stronger oxidising agent and, in concentrations greater than 100 parts-per-billion, may cause damage to the respiratory systems in animals and harm plant tissue. The structure of ozone can be represented as resonance hybrids (see **Figure 1**). This diagram shows one single bond and one double bond. However, the resulting bond lengths are observed to be equal, at 128 pm. This is due to delocalisation of the overlapping p-orbitals.

Figure 1 Ozone structure showing resonance hybrids



The ozone layer in the atmosphere lies between 10 km and 50 km above the Earth's surface. Ozone is present at a concentration of just a few parts-per-million, so most of the oxygen in this region is still diatomic oxygen. The ozone layer protects organisms from harmful ultraviolet radiation. In the 1970s, scientists discovered that ozone was being depleted due to the use of chlorofluorocarbons, CFCs, which were used in aerosols and refrigerators. CFCs breakdown in the upper atmosphere to form chlorine free-radicals, which catalyse the decomposition of ozone to diatomic oxygen:



Since the banning of CFCs, the hole in the ozone layer has begun to reduce in size.

Allotropes of Sulfur

Sulfur exists as a yellow crystalline solid at room temperature. There are many different allotropes of sulfur. The most common form is rhombic sulfur, which exists as a cyclic- S_8 structure. Monoclinic sulfur is produced by heating sulfur until it just melts, at 115°C . This temperature represents the transition temperature as the monoclinic form is only stable above this temperature (pressure = 101 kPa) (see **Figure 2**).

Figure 2 Phase diagram of sulfur

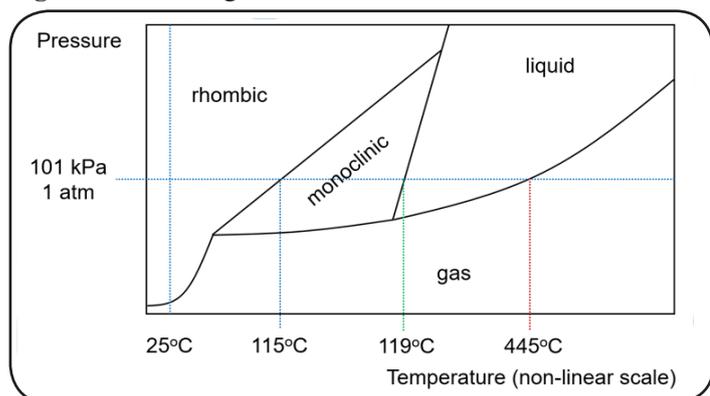


Figure 2 describes a simple phase diagram for sulfur. Phase diagrams are used to illustrate the different allotropic structures of materials at different temperatures and pressures.

Key Point:

Crystalline structures have an ordered arrangement of atoms, ions or molecules. Amorphous structures have a random arrangement.

The monoclinic structure is maintained providing the molten sulfur cools and crystallises slowly. The monoclinic form also consists of a cyclic-S₈ structure but adopts a different crystal structure to the rhombic form (see **Figure 3**).

Figure 3 Rhombic and monoclinic sulfur

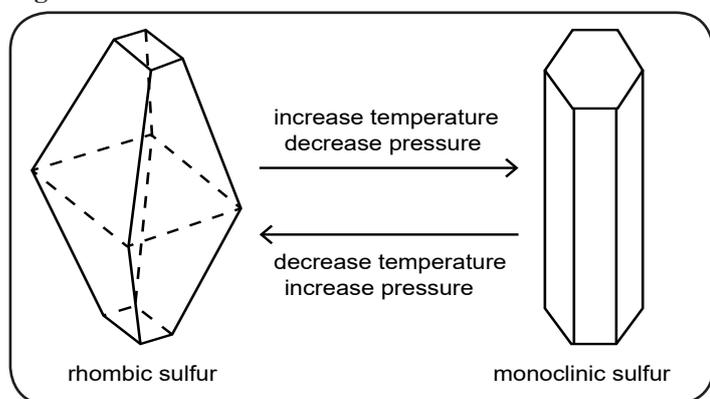
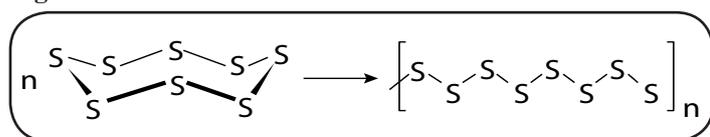


Figure 4 describes how plastic sulfur is formed by heating sulfur to its boiling point and then rapidly cooling it in cold water. It is amorphous in nature.

Figure 4 Plastic sulfur



Allotropes of Boron and Silicon

Both elements have amorphous and crystalline allotropes. Silicon can form two allotropes at room temperature, an amorphous and crystalline form. Amorphous silicon is a brown powder, whilst its crystalline allotrope has a metallic lustre and is grey in colour. Single crystals can be grown and, when doped with elements such as

boron or gallium etc., can be used in solid-state electronic devices. Amorphous boron can exist either as a brown powder or it can be glassy in appearance. The crystalline forms of boron vary in colour from red to black. The most stable form is the β-rhombohedral phase. This is a very hard substance, is less dense than aluminium, and has a melting point of 2080°C.

Allotropes of Phosphorus

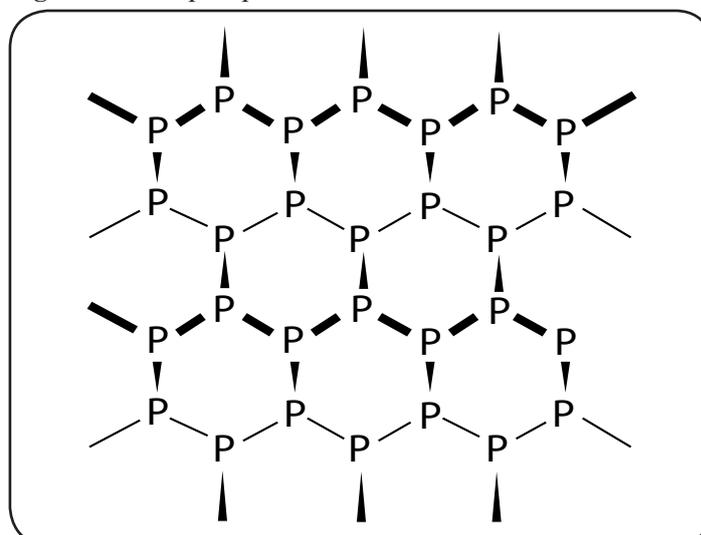
Phosphorus has several allotropic forms. The common forms are white, red and black phosphorus. White phosphorus is recognised as the standard state of phosphorus and is made up of small molecules of P₄ in a tetrahedral arrangement. The P-P bonds are highly strained. White phosphorus is so reactive it is stored under water to stop it from self-igniting. Red phosphorus is made by heating white phosphorus to 300°C in the absence of air. This produces an amorphous network that crystallises on further heating. Red phosphorus is more stable than white phosphorus and does not ignite below 240°C. Note that the heat of formation for red phosphorus is -17.6 kJ/mol, relative to white phosphorus (standard state) (see **Table 1**).

Table 1 Physical data for common phosphorus allotropes

Property	White Phosphorus	Red Phosphorus	Black Phosphorus
Density (g/cm ³)	1.82	2.34	2.70
m.p. (°C)	44	590 ^{43atm}	416
b.p. (°C)	277	200	N/A
Entropy (kJ/mol)	41.1	22.8	-
ΔH _f (kJ/mol)	0 (Standard state)	-17.6	-39.3

Black phosphorus is the more thermodynamically stable allotrope. It is formed by heating white phosphorus under high pressure. In appearance, structure and properties, black phosphorus is similar to graphite. It is black in colour, flaky and conducts electricity. Phosphorene is a single layer of black phosphorus, analogous to the 2-D structure of graphene.

Figure 5 Black phosphorus structure

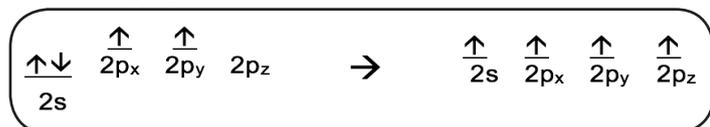


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Carbon Allotropes

Diamond is the hardest natural substance found on Earth. Diamonds occur naturally, but they can also be formed synthetically. Carbon atoms have four valence electrons in an electron configuration; $1s^2, 2s^2, 2p_x^1, 2p_y^1$. To allow the tetrahedral structure observed in diamond, the 2s orbital and three 2p orbitals hybridise to form 4 equal sp^3 orbitals (see **Figure 6**).

Figure 6 Sp^3 hybridisation

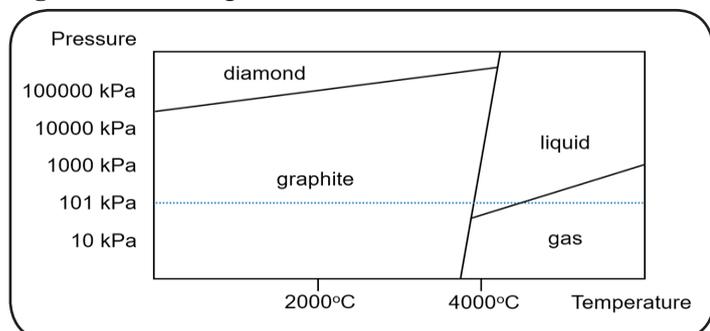


Key Point:

Hybridisation describes the mixing of atomic orbitals to form new hybrid orbitals with different energies and shapes to the original orbitals.

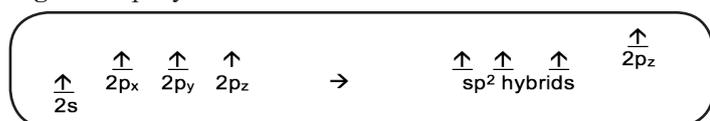
Graphite is a form of coal formed near the Earth's surface millions of years ago, whereas diamonds are formed through high-temperature, high-pressure geological processes in the mantle and in subduction zones. Synthetic diamonds are made from graphite using high temperatures and pressures. **Figure 7** shows a simple phase diagram for carbon.

Figure 7 Phase diagram for carbon



In graphite, each carbon is bonded to three other carbons. Each carbon atom has three hybridised sp^2 electron orbitals allowing for three covalent bonds in a trigonal planar arrangement forming simple plain hexagons. The single electron occupying the remaining p-orbital on each carbon atom delocalises above and below the plane of the bonded carbons. These available delocalised electrons allow graphite to conduct electricity (see **Figure 8**).

Figure 8 Sp^2 hybridisation



The different arrangements mean the C-C bond length in graphite is shorter than the C-C bond length in diamond, see **Table 2**. The table describes some of the differences observed in the physical properties of graphite and diamond.

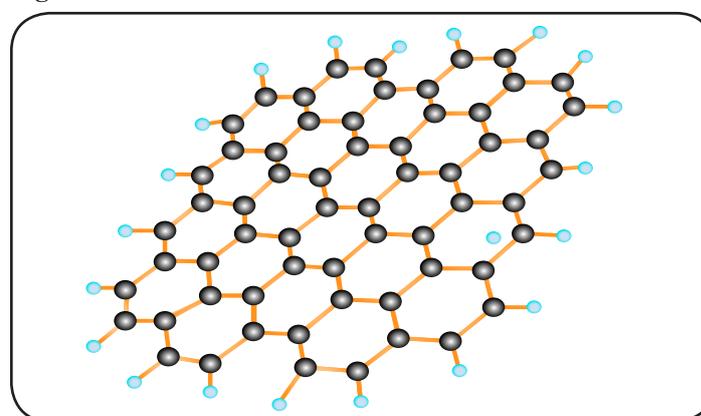
Table 2 Physical data for carbon allotropes

	graphite	diamond
appearance	dark and dull	bright and shiny
structure	hexagonal planar	tetrahedral
bond length	142 pm	154pm
	(between layers 335 pm)	
hardness (Mohs)	1-2 (very soft)	10 (hard)
density	2.267 g cm ⁻³	3.515g cm ⁻³
conductivity	conducts electricity	non-conductor

Fullerene is the general term applied to hollow spheres of carbon atoms such as Buckminster fullerene. This has the chemical formula C₆₀ since it contains 60 carbon atoms in a spherical arrangement. The uses of fullerenes are still being explored but they are currently used in several biomedical applications, including drug delivery systems and as lubricants. Chemically, fullerenes are stable, but not unreactive.

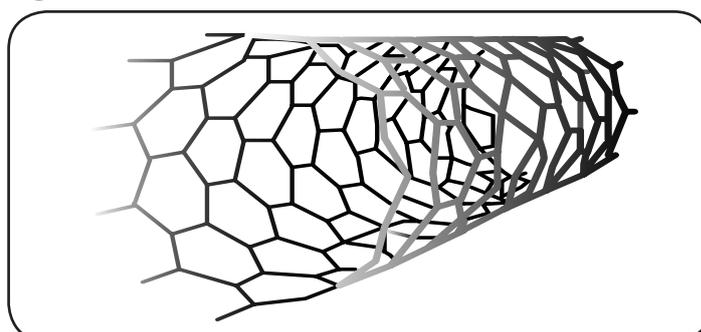
Graphene is a single layer of graphite comprising the same arrangement of atoms as graphite but is only one atom layer thick (see **Figure 9**). This makes a two-dimensional compound. As in graphite, the delocalised electrons are free to move above and below the sheet, but since there are no other layers, the electrons are able to move very quickly. This makes graphene the best-known conductor of electricity. The bonds are strengthened by this delocalised system so graphene has a high tensile strength. A single layer of graphene is transparent and has a very low density.

Figure 9



A single layer of a graphene rolled up forms a carbon nanotube (see **Figure 10**). They have high electrical conductivity and high tensile strength. In fact, they have one of the highest tensile strengths known. Currently, nanotubes can only be produced as very short tubes.

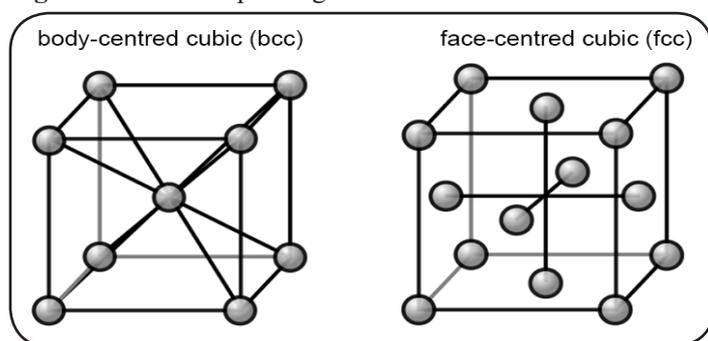
Figure 10



Allotropy in Metals

There are some metals that also exhibit allotropism. The most noted example is iron. Allotropes of iron occur due to different arrangement of the iron atoms at different temperatures. As molten iron first crystallises, at 1538°C, it forms a body-centred cubic structure (bcc) (see **Figure 11**). This is described as delta-iron. As the metal cools further, to 1394°C, it adopts a face-centred cubic (fcc), structure, described as gamma-iron. Gamma-iron can dissolve the highest amount of carbon allowing the production of high-carbon steels and cast iron. Below 912°C it reverts to body-centred cubic and is described as alpha-iron. Note that iron becomes magnetic at temperatures below 770°C. Under the extreme temperatures and pressures found in the Earth's inner core, iron adopts a hexagonal close pack (hcp) arrangement. This allotrope of iron is called epsilon-iron.

Figure 11 Different packing of atoms



Source: <https://commons.wikimedia.org/wiki/File:IronAlfa%26IronGamma.svg> (modified)

Questions

- 1) What is meant by allotropy?
- 2) What is the difference between crystalline and amorphous forms of an allotrope?
- 3) Show, using equations, how chlorine radicals act as catalyst in the breaking down of O₃.
- 4) Using the phase diagram in Figure 2, describe what happens when sulfur at 25°C is slowly heated to 200°C at atmospheric pressure.

Answers

- 1) Allotropy occurs when an element exists in one or more different forms in the same physical state, i.e. solid/liquid/gas.
- 2) Crystalline: ordered arrangement, amorphous: random arrangement
- 3) $\text{Cl}\cdot + \text{O}_3 \rightarrow \text{O}_2 + \text{ClO}\cdot$ then $\text{ClO}\cdot + \text{O}\cdot \rightarrow \text{O}_2 + \text{Cl}\cdot$
Chlorine radical regenerated and is therefore a catalyst
- 4) It changes from the rhombic form, at 115°C, into the monoclinic form and then it melts at 445°C.