Structure and Types of Solids

Properties, type and strength of bonding:
Properties could be physical or chemical

Physical Properties
M.p., b.p., latent heat, solubility in water and other solvents, conductivity when solid / liquid / gas /or when in solution, density, malleability, softness or hardness.

Physical properties normally relate directly to bonding between particles.

1. IONIC SUBSTANCES

Properties Imparted by the Ionic Bond
– are generally crystalline solids at room temperature, why ?

- relatively high M.P. and B.P. (>500°C, >100°C), why ?

(Melting point and boiling point are due both to strength of bond and to being continuous throughout crystals. Must break strong bonds before melting etc.)

– are generally soluble in polar solvents, why ?

- do not conduct an electric current in the solid state, why ?

- in the liquid phase, i.e. when molten, they are relatively good conductor of an electric current, why ?

- when soluble in water form good electrolytes, why?

- are brittle, easily broken under stress, why?

- do not readily vaporize at room temperatures. These solids have relatively low volatility, low vapour pressure, this also indicates that a....

Explanation of ionic bonds and properties
Ionic solids are generally stable and the bonds are relatively strong.

Ionic bonds are a result of electrostatic attraction between oppositely charged ions forming a 3-D crystalline lattice structure. Each ion in a solid ionic crystalline substance is surrounded by other ions of opposite charge. For example in a sodium chloride crystal, each Na^{+1} is surrounded by six Cl^{-1} ions and each Cl^{-1} ion is surrounded by six Na^{+1} ions. The electrostatic force of attraction holding the ions together is strong. Any changes that require disrupting the arrangement of ions in a crystalline ionic compound, therefore, require a large amount of energy.

Recall: Crystal lattice energy is the energy liberated when one mole of an ionic crystal is formed from the gaseous ions, thus **high stability** is attained by the compound as a result of energy being lost.

Lattice energy is dependent on two factors: (1)

(2)

As a result, ionic compounds are expected to be solids at room temperature, and have high density.
Close packed particles give high density, ionic compounds are closely packed.

Melting point and boiling point, heats of vaporization and fusion are expected to be: ______________.

For the same reasons, ionic crystalline substances are hard —a strong force is needed to break up the crystal lattice.
However, ionic substances are brittle, because when struck with a sufficient force, they will shatter along the planes between rows of ions.

Solubility: The energy given out when the substance is solvated, termed as solvation energy, (in the case of the solvent being water, it is referred to as hydration energy) must be sufficient to supply the energy required to break bonds between ions, i.e. the *lattice energy*.

In the case of ionic compounds e.g. NaCl, strong bonds exist throughout crystal, but energy is needed to break these. The energy can be obtained from the energy that is given out when ions are hydrated by water (water is also a good insulator… insulates ions from each other), referred to as *hydration energy*.

Organic solvents mainly do not solvate ions therefore cannot overcome lattice energy.

Conductivity
For a substance to conduct there must be charged particles free to move, since charged particles must relate to presence/absence of electrons or ions; thus conductivity relates to type though, not strength of bonding.

Ionic compounds – charged particles, i.e. ions are held firmly fixed in their positions in the solid therefore non-conducting.

However, when molten or in solution, their ions are free to move and carry current, therefore electrolytes.

2. MOLECULAR CRYSTALS

Covalent bonding, the sharing of electrons is known as an **intramolecular** force. Covalent bonds hold atoms together as discrete molecules (or in polyatomic ions).

Molecules usually remain intact when a molecular compound melts, evaporates or dissolves.

As a result, it is not the bonding forces but the weaker forces that act between molecules — the intermolecular forces of attraction — that determine the properties of the molecular compounds.

Properties Imparted by the Covalent Bond
Solids are soft and waxy, but are generally volatile liquids or gases at room temperature, why ?

Melting point and boiling points are relatively low, thus indicating ______________________.

Neither solids nor liquids conduct an electric current. This indicates _____________________.

Small individual molecules or atoms which are held intermolecularly by weak attractive forces such as van-der -Waals', dipole-dipole, hydrogen- bonds, then m.p, b.p. are low.
Their numerical value depends on the strength of the intermolecular forces of attraction involved, (van-der-Waal < dipole – dipole < Hydrogen- bond).

Melting involves only breaking weak intermolecular forces of attraction, not upon the strong of the covalent bonds inside molecule, e.g., I_2, melting point involves the energy required to separate individual I_2 molecules.

Molecular compounds such as I_2 – weak intermolecular forces <u>may</u> be overcome by interaction with solvent, or may not. E.g. I_2 is slightly soluble in water, more soluble in organic solvents.

Atomic Solids

Group VIII A solids which are composed of the Noble gases. They are held together by weak London dispersion forces, hence their properties include: ____.

3. NETWORK (MACROMOLECULAR) COVALENT SOLIDS

This is a type of solid we have not really talked about before, but one in which you are all familiar.

It is possible to have a 1,2 or 3 dimensional network of atoms all joined with single **covalent bonds**. The element contained in the bond could be the same or different.

Carbon exhibits allotropy. This means that it can exist in more than one physical form, or allotrope. The three main allotropes of carbon are diamond, graphite and fullerene, (C_{60}).

In all three allotropes the carbon atoms are bonded covalently, however in diamond and graphite, instead of simple molecules, the covalent bonds link across the carbon atoms to form a single large (or giant, or network) molecule. Diamond is a 3 – D network, whereas graphite is a 2–D network.

In order to break the structure down, the bonds that have to be broken are strong covalent bonds, so diamond and graphite both have extremely high melting points — ~ 4000 ^{O}C.

Let us look at each type of dimensional network.

(i) <u>Three Dimensional Network Solids</u>

Properties:
highly stable, extremely hard, poor electric conductors, insoluble in most solvents, very high melting points. Example: diamond: m.p. 3550°C, b.p. 4827°C
Examples:
diamond, silicon, silicon dioxide (silica, a.k.a. quartz: a form of silica, SiO_2),
silicon carbide, SiC (a.k.a.: carborundum)

Structure:
3-D array of carbon atoms joined by very strong covalent bonds extending uniformly throughout the entire crystal.
In diamond, each carbon atom is bonded in tetrahedral arrangement to four other carbon atoms to form a giant tetrahedral structure.
All the C — C bonds are the same length, all bond angles are 109.5°, - sp^3 hybridization; and there is no plane of weakness through the structure, so diamond is an extremely hard substance.

All the outer electrons around each carbon atom are localized to form the four bonds to other carbon atoms, so diamond does not conduct electricity; because there are no delocalized electrons.

Both silicon and silicon dioxide and silicon carbide also have a diamond structure.
In silica, SiO_2 , each Si atom is bonded to four oxygen atoms and each oxygen atom is bonded to two Si atoms in a 3-D array.

(ii) Two Dimensional Network Solids

Properties:

2-D network covalent substances also have high melting points and boiling points.
They are soft, and good conductor of electricity, why?

Examples: graphite, mica

Structure of graphite:

In graphite, each carbon atom forms strong covalent bonds to three other carbon atoms in a trigonal planar structure so that the carbon atoms link up to form layers of hexagonal rings.

The C — C bonds in the rings are shorter and stronger than the C — C bonds in diamond. Each carbon atom is joined to two others by a single σ- covalent bond and a π-bond: sp^2 hybridization,120^0 bond angle
However, the forces of attraction between the layers are very weak, because they are formed by delocalized electrons that can move between the layers, i.e. weak van-der -Waals' forces

Because of the presence of delocalized electrons in the π-bond, this means that graphite is able to conduct an electric current.

The fact that the attractive forces between the layers are weak gives graphite another useful physical property: the layers can easily slide over each other, so graphite feels waxy to the touch and is a good lubricant.

Buckminsterfullerene

In the 1980's, several research teams around the world pieced together the discovery of a third allotrope — buckminesterfullerene, C_{60}, molecules of carbon in the form of spheres.

The molecules were arranged as though a layer of graphite had curled into a ball.
The researchers were puzzled as to how this could happen until they realized that some pentagon in the array of hexagons would do the trick.
One group asked the mathematics department at their university if they had heard of this geometrical shape, only to realize that it was exactly the pattern of the panels on a soccer ball!

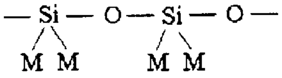
The molecule was christened buckminesterfullerene after the geodesic domes designed by the architect Richard Buckminester Fuller.

Other related molecules have been found including C_{70} in the shape of a rugby ball and also long tube-shaped molecules that can be closed or open at one end. These are called **nanotubes**, because they have an extremely small diameter in the order of one nanometer, (1 x 10^{-9} m).
Although they look odd, these molecules can undergo normal chemical reactions and chemists are beginning to make derivatives of them and look for uses of these new allotropes.

iii. One Dimensional Network Solids

Examples: - asbestos type minerals

Structure: Si and O atoms covalently bonded in long chains with metal atoms attached to the silicon a atoms.



$$—\underset{M\ \ M}{\mathrm{Si}}—O—\underset{M\ \ M}{\mathrm{Si}}—O—$$

4. Metallic Crystals

Bonding in Metals

Metals have only one or two electrons in their highest energy levels. In general, metals have low ionization energies.
Each atom in an elemental metal contributes one or more valence electrons to what has been called an "electron sea ". The free electrons no longer belong to specific atoms: the electrons become delocalized, i.e. they are free to move throughout the metallic structure.

Metallic bonding is the attraction between positive metal ions and surrounding, freely mobile electrons.

The electron cloud is held within the crystal by the electrostatic attraction of the positive metal ions, this serves as the "glue" that holds the nuclei together and is known as the — metallic bond.
The strength of the metallic bond is related to the strength of attractive forces holding the cations in the "sea of delocalized electron cloud".
This depends on the number of valence electrons delocalized from each atom, the size of the cations and the way in which the cations are packed together.

In general, the melting point decreases as the size of the cation increases, this explains why the melting point decreases down Group I (the Alkali Metals).

Properties Imparted by the Metallic Bond

The free electrons occupy energy levels so close together that they are essentially merged. Because the electrons have a wide distribution of energies, thus they can absorb and reemit visible light of many wavelengths, thus they are lustrous. These mobile electrons are able to absorb and re-emit light of all wavelengths, therefore they are good reflectors of light.

The high electric conductivity of metals is due to the mobile electrons which begin to flow when an electric potential is applied across a piece of metal.

The movement of electrons through metals also enables the transmission of kinetic energy, so metals are also good conductors of heat.

Mobility of electrons helps explain malleability and ductility. When a mechanical force is applied to a metal , cations can slip over another and in so doing, the electrons flow along with the layers...the electron cloud just distorts.
No specific bonds need to be broken, the forces between the cations and the free electrons need not be disrupted.
This explains the ease with which metals are hammered into shape, (malleability) or drawn into wires (ductility).

Alloys

These are substances having metallic properties which contain more than one element. They can act as an example of a __________________ solution.
They are mixtures and not chemical compounds because the metals are not combined in a fixed percentage by mass.
Alloys are made because they have desirable properties. In general pure metals are soft, flexible and excellent conductors of heat and electricity.
Alloys are generally harder, and less flexible because the atoms contained within it are of different sizes and so the planes of atoms do not slide over each other easily. These are known as *substitutional alloys*.
Examples: **18K gold (yellow)** Au (75%) Ag (12.5%) Cu (12.5),
18K gold (white) Au (75%) Ni (16.5) Zn (5%) Cu (3.5%)

Bond Types and Properties - Summary Table

Property	Ionic	Molecular Covalent	Giant Covalent	Metallic
Melting Point, Boiling Point, Latent Heat of Fusion	High – each +ion is attracted to many –ions and vice-versa. Attraction is hard to break and is spread throughout crystal.	Low – there is little attraction between individual molecules (v-d-W, d-d, h-b), and molecules can be easily separated.	High – each atom is attracted to others by covalent bonds right throughout the crystal – to melt solid, to break all covalent bonds.	High – each cation is held in place by many others by "sea", metallic bond right throughout crystal, .: must break bonds to melt solid.
Solubility in Water	Usually good – as water is an insulator and can reduce the attraction of the ions for each other, hydration of ions ($H_e > L_e$)	Varies – molecules easily separated from each other, so may dissolve in water or other solvents. (If polar)	Insoluble – as it would be necessary to break the covalent bonds which would require much energy.	Insoluble – too difficult to break metallic bonds and separate the atoms.
Conductivity: Solid	Poor – as the ions are fixed in position by electrostatic attraction and can not move.	Poor – as the only charged particles (the electrons) are held tight to their own atoms and can not move.	Poor – see molecular covalent.	Good – as the electrons in the sea of delocalised electron cloud can move easily from cation to cation.
Conductivity: Molten (liquid)	Good – as the ions are now free to move and (as they are charged) so they can carry the current.	Poor – the same reason as the solid.	Poor – the same reason as the solid.	Good – the electrons can still move freely.
Conductivity: In Solution in water, $_{(aq)}$	Good – the same reason as liquid.	Poor – the same reason as the solid.	Insoluble	Insoluble

Note:
All atoms, and therefore all elements and compounds, contain protons and electrons, which are both charged. The protons are always fixed in position in the nucleus and cannot move, the electrons are held firmly on the atom, ion or in the compound and cannot move except in metals.

The particles which carry the charge in ionic substance are the ions.

Acids are a special case of molecular covalent.
Their properties are the same as other molecular covalent – except that they conduct electricity when they are dissolved in water, because they react with the water forming ions – i.e. they ionize.

Assignment

1. Solid A is a molecular solid and solid B is an ionic solid, and solid C is a giant covalent network. All substances appear as white crystalline solids. Outline **three** methods that you would use to distinguish between each solid.

2. Tin (IV) Chloride, $SnCl_4$, has soft crystals with a melting point of -30.2°C. The liquid is non-conducting. What type of crystal is formed by $SnCl_4$?

3. Elemental boron is a semi-conductor, is very hard, and has a melting point of 2250°C. What type of crystal is formed by boron?

4. Titanium (IV) Bromide forms soft orange-yellow crystals that melt at 39°C to give a liquid that doesn't conduct electricity. The liquid boils at 230°C. What type of crystal does $TiBr_4$ form?

5. Columbium is another name for one of the elements. This element is shiny, soft, ductile. It melts at 2468°C and the solid conducts electricity. What kind of solid does columbium form?

6. Elemental phosphorus consists of soft, white, "waxy" crystals that are easily crushed and melt at 44°C. The solid does not conduct electricity. What type of crystal does phosphorus form?

7. The metalloid silicon, Si, forms an oxide with the formula SiO_2. The hard white crystals melt at ~ 2000 K and the resulting liquid does not conduct electricity.

a) What type of crystal does SiO_2 form?

b) Describe the attractive force holding together a SiO_2 crystal.

c) Explain the observed boiling point and the hardness of the SiO_2 crystal in terms of its bonding and structure.

8. You are given a white substance that sublimes at 3000 ^{O}C; the solid is a nonconductor of electricity and is insoluble in water. Which type of solid might this substance be?

9. Covalent bonding occurs in both molecular and covalent network solids. Why do these two kinds of solids differ so greatly in their hardness and melting point?

10. Ethan-1,2-diol, CH_2 (OH)-CH_2(OH), the major component of antifreeze, is a slightly viscous liquid that is not very volatile at room temperature and boils at 198 ^{O}C. Pentane, C_5H_{12}, which has about the same molar mass, is a non-viscous liquid that is highly volatile at room temperature and whose boiling point is 36 ^{O}C. Explain the differences in the physical properties of the two substances.

11. For each of the following pairs of substances, predict which will have the higher melting point and indicate why: (a) HF, HCl (b) SiO_2, CO_2 (c) KO_2, SiO_2 (d) Ar, Xe (e) Se, CO (f) NaF, MgF_2

12. Phosphorus molecules have covalent bonds, and can occur in two different forms (isomorphs):

I. white phosphorus, P_4 molecules:	II. red phosphorus, P_n molecules (where 'n' is a very large number

Which of these would you expect (a) to have the lower melting point, and (b) to be more soluble in a suitable solvent. Explain the reasons for your answers.