HW R&MN 4.5 P 1-5,10 Q 1,4,7 Ch. 4.6 P 1,2,4,6,7 Q 3,9

Chapter 4.6: Solids – Bonding and Properties

A solid is a collection of molecules, ions or atoms that are unable to flow (move around). Due to electromagnetic attraction.

Ex. One Na atom does <u>not</u> have a MP of 97.8'C. Melting and boiling points describe the energy required to move many particles

Liquids are collections of particles that are held together but they can flow (intermolecular forces)

Gases are collections of particles that are not held together (weak intermolecular forces)

The <u>interactions between</u> the units, in a solid, are what lead to the physical and chemical characteristics of the substance.

Solids are usually crystalline solids.

Substances are usually classified in terms of the bonding that holds the units together.

1 – Ionic Substances – ***NaCl or MgO***
structural units are oppositely charged ions and the bond is ionic.

2 – Molecular Substances – (both polar and non-polar)
non-polar – CO_2 polar – H_2O
structural units are ***molecules*** and the attractive forces between the molecules are called intermolecular forces.

3 – Network or Macromolecular solids – gigantic networks of atoms held together by covalent bonds.
Eg. *polymers, diamonds, sulfur S_8*

4 – Metallic Substances – eg. ***Na, Fe, Sn***
The structural unit is the atomic kernel (positive ion). These are held together by metallic bonds. (sea of electrons)

1 - Ionic Substances

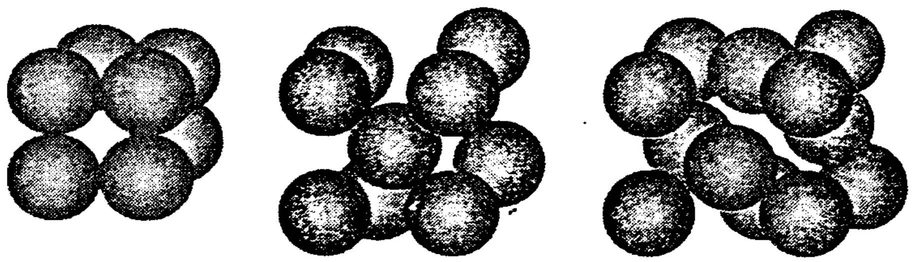
- NaCl molecule? ***NO! They are networks of oppositely charged ions.***

Properties of Ionic Substances

A -***High*** MP and BP, ***low*** volatility
B -***does not conduct*** electricity when solid
C -***does conduct*** electricity when liquid
D -***soluble*** in water to form(electrolytic)solutions
E - brittle

- the above properties can almost all be attributed to the high strength of the ionic bond.

- the solid phase of ionic substances are crystalline is called the lattice structure



Simple cubic Body-centered cubic Face-centered cubic

The crystal lattice energy is ***the energy liberated when one mole of gaseous ions forms a crystal. The crystal is more stable than the gaseous ions.***

- the high crystal lattice energy leads to high MP,BP and low volatility

Ex. $MgCl_2$ ***MP = 2800'C*** ***NaCl*** ***MP = 800'C***

This difference in MP must be because the crystal lattice energies

Physics tells us that the force of attraction between two static charges is given as:

$$F_e = \frac{kq_1q_2}{r^2}$$

a) so for larger ionic radii – ***the force of attraction is low, so crystal lattice energy is low so there is a low MP and BP***

eg] ***CsCl MP = 646'C***
NaCl MP = 800'C

b) so for larger charges – ***the force of attraction is greater so MP and BP are increased***

eg] ***MgO MP = 2800'C***
NaCl MP = 800'C

Why do solid ionic crystals not conduct? (property B)

- ***electrons are locked on the ions***
- ***ions are stuck (solid)***
- ***no charge flow***

Why do melted ionic substances act as moderate conductors? (property C)

- ***electrons are locked on the ions***
- ***ions can move slowly***
- ***can get charge flow (limited):viscosity***

Why do solvated ionic substances conduct? (property D)

- ***electrons are locked on ions***
- ***ions are free to move through polar solvent: eg. Water***
- ***can get charge flow (significant)***

Why are ionic crystals brittle? (property E) (Hint: think of the packing)

Strong bonds but once they're moved the ions repel each other. Definite boundaries along the edges of unit cells.

2 – Molecular Crystals.

In general the intramolecular forces (those within the molecule) are much greater than the intermolecular forces (those between molecules) in the molecular crystal.

The crystal structure is made of neutral molecules. (polar or non-polar)

There is a much wider variation in the properties of molecular substance than ionic substance because crystal is made up of ***complex molecules – not simple ions.***

Examples of molecular solids include: ***CO_2 (dry ice)***
H_2O (ice)
Frozen methane

In general:
A – neither the solid crystals nor the liquids conduct electricity
B – These molecular crystals have very low BP, MP and high volatility
C – the solids tend to be soft and waxy
D – there is a large amount of energy required after melting or boiling to decompose the substances chemically.

Why don't molecular substances conduct when solid or liquid? (propertyA)

- ***electrons locked on molecule***
- ***molecule carries no charge so even if molecule moves there is no charge flow***

Why do molecular solids have low BP, MP and high volatility? (property B)

-weak intermolecular forces but these force vary widely

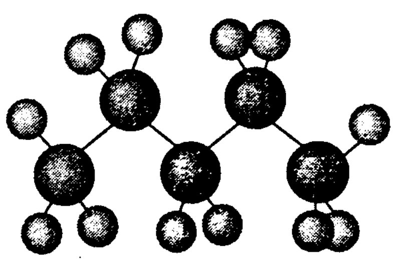
Ex. ***H_2O BP = 100'C***
CO_2 BP = -80'C

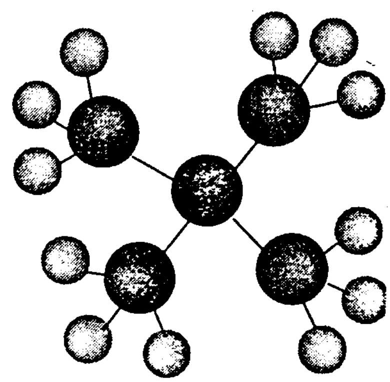
Why are molecular solids soft and waxy? (property C)

Weak intermolecular forces allow for deformation with pressure (soft) and allows sections to peel off (waxy).

Why does it take so much energy after melting or boiling to decompose the substance? (property D)

Ex. Water boils at 100'C but doesn't decompose until 2000'C. The intermolecular forces are much weaker than the intramolecular forces.





How does shape of a molecule affect the properties?

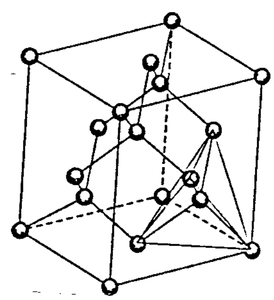
normal pentane C_5H_{12} vs. dimethyl propane C_5H_{12}

BP = 36'C ***MP = -130'C*** ***Liquid – large straight chain allows for a high degree of contact which results in strong intermolecular forces making a higher BP*** ***Solid – the long "floppy chains do not pack well resulting in a low crystal lattice energy and low MP***	***BP = 9'C*** ***MP = -20'C*** ***Liquid – compact sphere*** - ***low contact*** - ***low intermolecular forces*** - ***low BP*** ***Solid – sphere can easily occupy a lattice point so there is a higher MP***

3 - Network or Macromolecular Solids
- one, two or three dimensional networks of atoms

3D Network Solids
– ex. diamond, quartz, silicon carbide (carborundum)

- High MP (***always very high MP***) (ionics have a high MP but networks have very high MP)
- Extreme hardness
- In diamond all C-C bond angles are 109.28’ and all C-C bonds are equal strength
- A diamond is one very large molecule extended three dimensionally



- The network of atoms (each C bonded to four others) accounts for the extreme hardness and high BP.
- When the highly directional bonds are broken by an applied stress, they cannot be reformed and the crystal cleaves.

2D Network Solids

- more than one type of bond exists
- graphite (pure carbon) – the bonds between the plane can be broken easily so the planes tend to slide over each other making graphite a good lubricant
- graphite conducts in one direction – along the Pi bond plane not perpendicular to it
- soft due to weak bonds between sheets

1D Network Solids – ex. asbestos

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        O             O             O             O
        |             |             |             |
O —— Si —— O —— Si —— O —— Si —— O —— Si —— O
        |             |             |             |
        O             O             O             O
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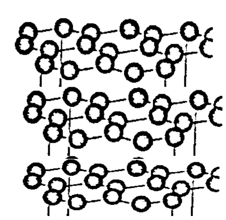

graphite

4 - Metallic Crystals or Metallic Bonds

- the properties of metals cannot be accounted for by ionic or covalent bonds

Metals in general have the following properties:

- Lustre (reflectivity)
- Good conductors (heat and electricity)
- Workability (malleability, ductility)
- electron emission by heat or light
- covalent bonds are one directional and their fixed length would resist the workability (therefore metals are not bonded covalently)

-ionic bonds are extremely resistant to deformation (therefore metals are not bonded ionically)

-Van der Waals forces are much too weak to explain the stability of metals

- We must therefore have a different type of bond called a metallic bond - positive atomic kernels in a sea of free moving electrons.

Lustre - the free electrons oscillate at the same frequency as incoming light and because they then become accelerating charges they emit light of the same incident frequency making it look reflective.

Conductivity - the tiny free electrons can move readily under applied voltage. At high temperatures the atomic kernel vibration interferes with electron flow.

Heat Conductivity- again the free electrons can carry off excess kinetic energy from one area of the metal to another.

Workability - the non-directional bond nature allows one plane of atomic kernels to slide over another plane with no change to the immediate environment of the atomic kernel. This results in no added internal stress, so the metal does not crack.

Electron Emission - when enough heat energy is added, an electron may gain enough energy to be bounced out of the lattice. When light of the proper frequency interacts with an electron, the energy is sufficient to bump the electron out.