

TOPIC 4

CHEMICAL BONDING &

STRUCTURE

4.4 Intermolecular Forces

Understandings:

- Intermolecular forces include London (dispersion) forces, dipole-dipole forces, and hydrogen bonding.

Guidance

The term 'London (dispersion) forces' refers to instantaneous dipole-induced dipole forces that exist between any atoms or groups of atoms and should be used for non-polar entities. The term 'van der Waals' is an inclusive term, which includes dipole-dipole, dipole-induced dipole, and London (dispersion) forces.

- The relative strengths of these interactions are London (dispersion) forces < dipole-dipole forces < hydrogen bonds.

Applications and skills:

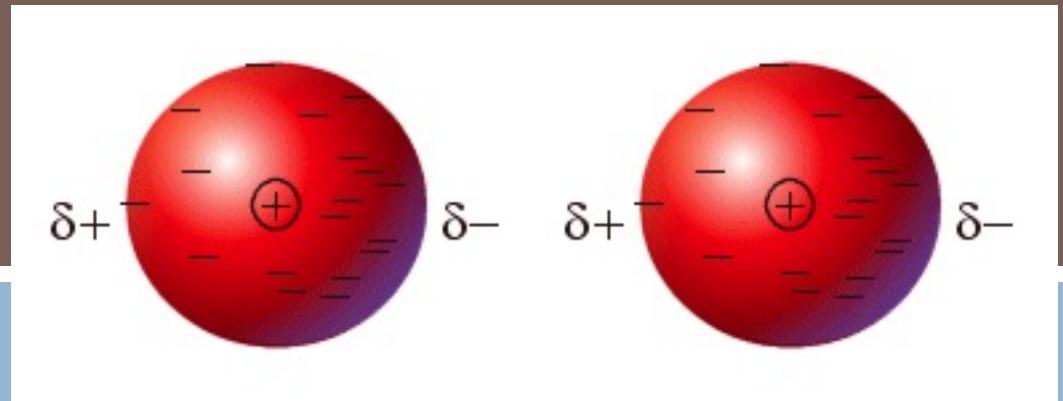
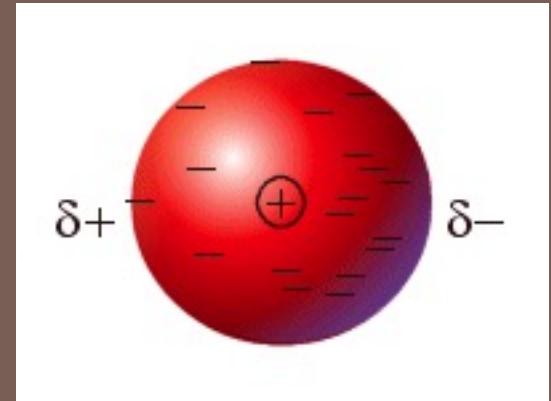
- Deduction of the types of intermolecular force present in substances, based on their structure and chemical formula.
- Explanation of the physical properties of covalent compounds (volatility, electrical conductivity, and solubility) in terms of their structure and intermolecular forces.

1 – London (dispersion) forces

The electrons in atoms are continually moving around – at any moment in time they are unlikely to be evenly spread.

This gives the atom or molecule a temporary dipole.

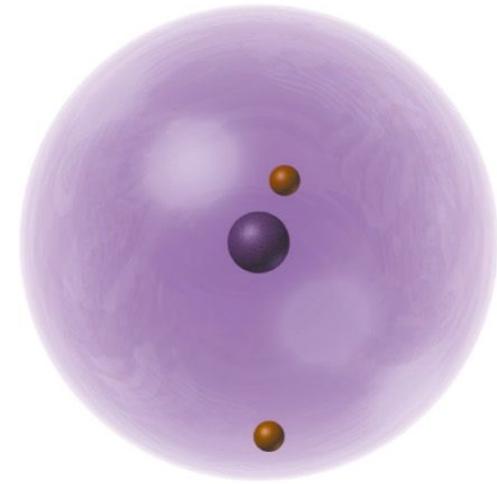
This dipole moment will induce a temporary dipole in a neighboring atom by attracting/repelling its electron charge cloud.



He

He

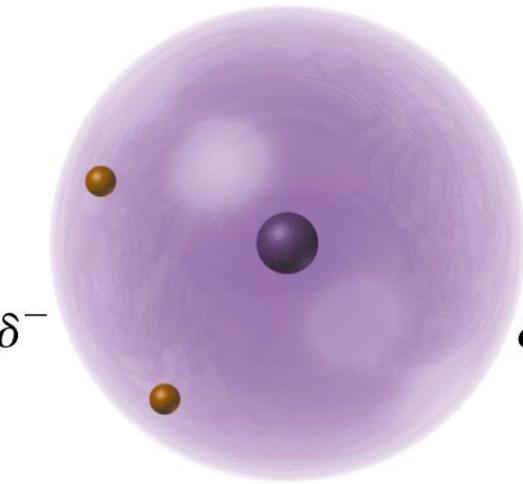
He



Frame 1

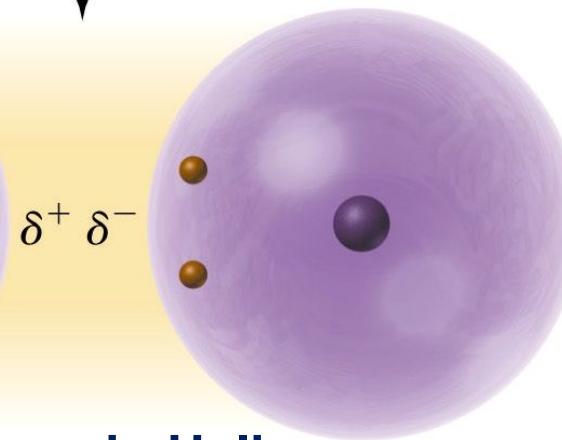
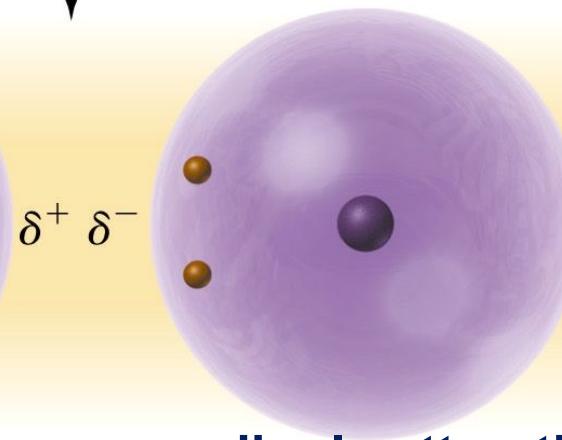
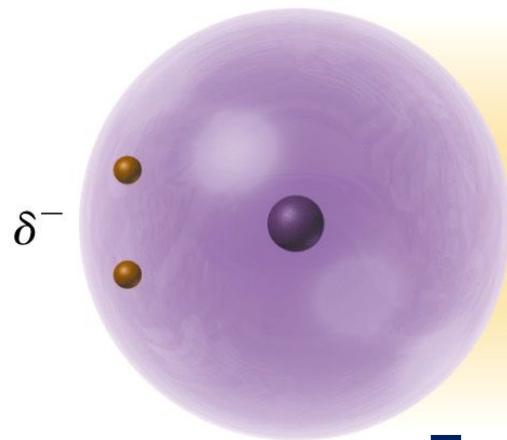


Frame 2



Frame 3

Weak attractions



Temporary dipole attractions in Helium

□ London (dispersion) force

increase w/ molar mass of molecule, owing to an increase in the # of e^- , and hence the size of the instantaneous dipoles

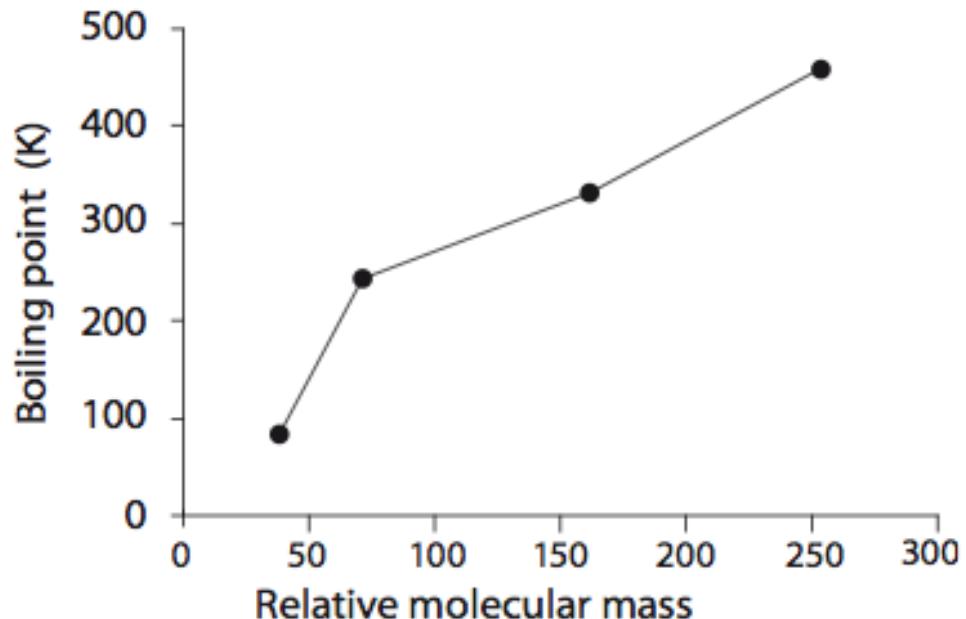
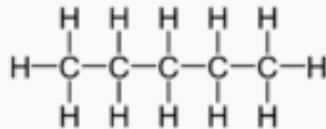
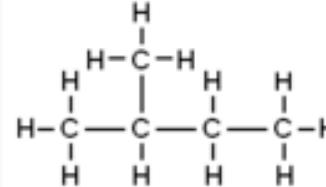
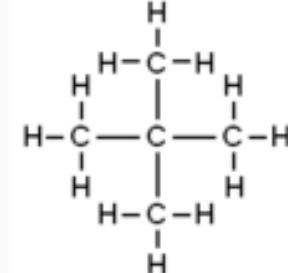
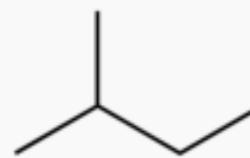


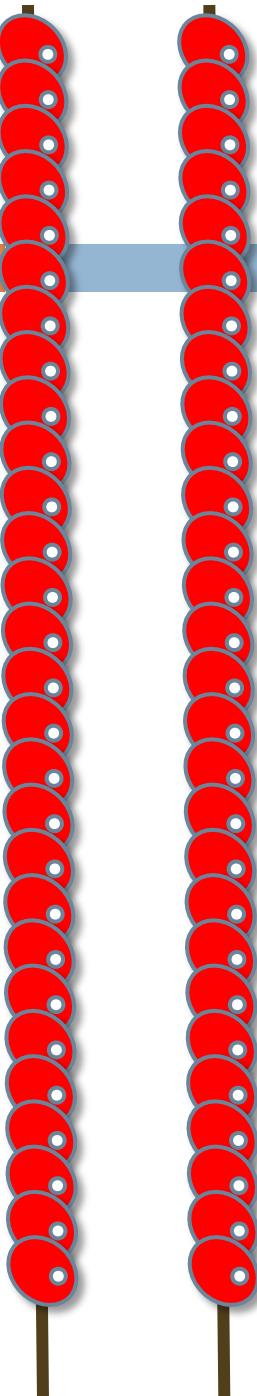
Figure 439 The variation of boiling point of the halogens with molar mass

□ London (dispersion) force

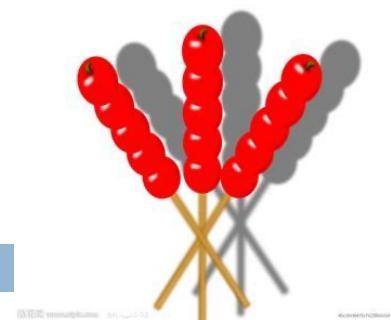
Only effective over a short range, very dependent on the **surface area** of the molecules that come into close contact w/ each other.

The **more elongated** the molecule, the stronger the London dispersion forces and the higher the boiling point.

IUPAC name	pentane	2-methylbutane	2,2-dimethylpropane
Molecular diagram			
Skeletal diagram			
Boiling Point (°C) ^[2]	36.0	27.7	9.5
Density (g/L) ^[2]	621	616	586



Surface area for contact:
Long string V.S. big branches



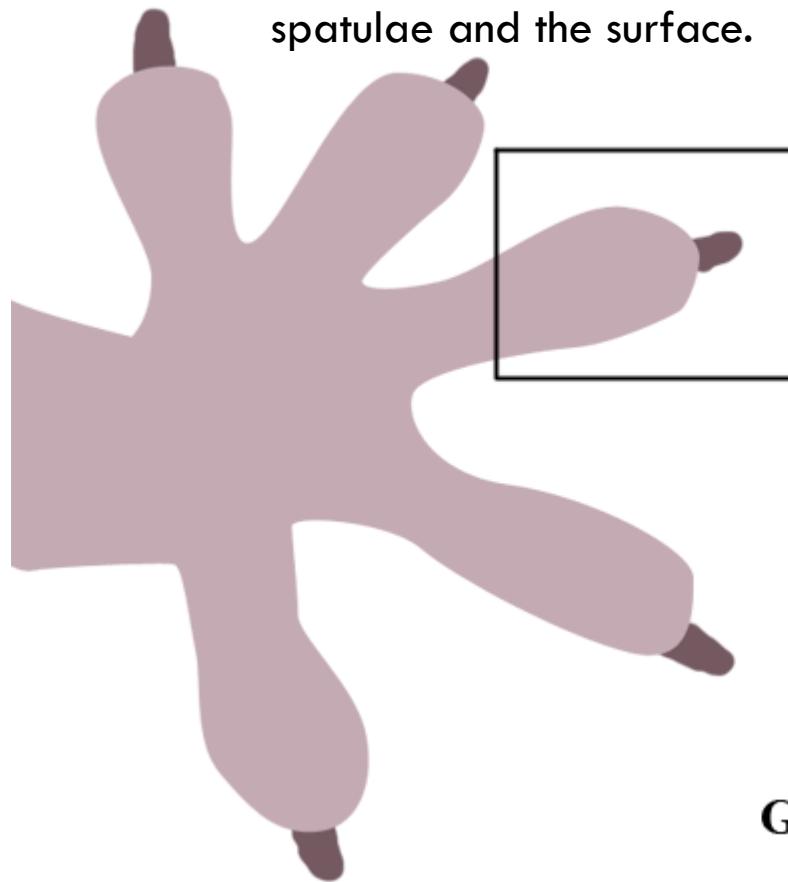
Molecular Size

- Dispersion forces are present between **all** molecules, whether they are polar or nonpolar.
- Larger and heavier atoms and molecules exhibit stronger dispersion forces than smaller and lighter ones.
- In a larger atom or molecule, the valence electrons are, on average, farther from the nuclei than in a smaller atom or molecule. They are less tightly held and can more easily form temporary dipoles.
- The ease with which the electron distribution around an atom or molecule can be distorted is called the **polarizability**.
London dispersion forces tend to be:
 - stronger between molecules that are easily polarized.
 - weaker between molecules that are not easily polarized.

Gecko tape

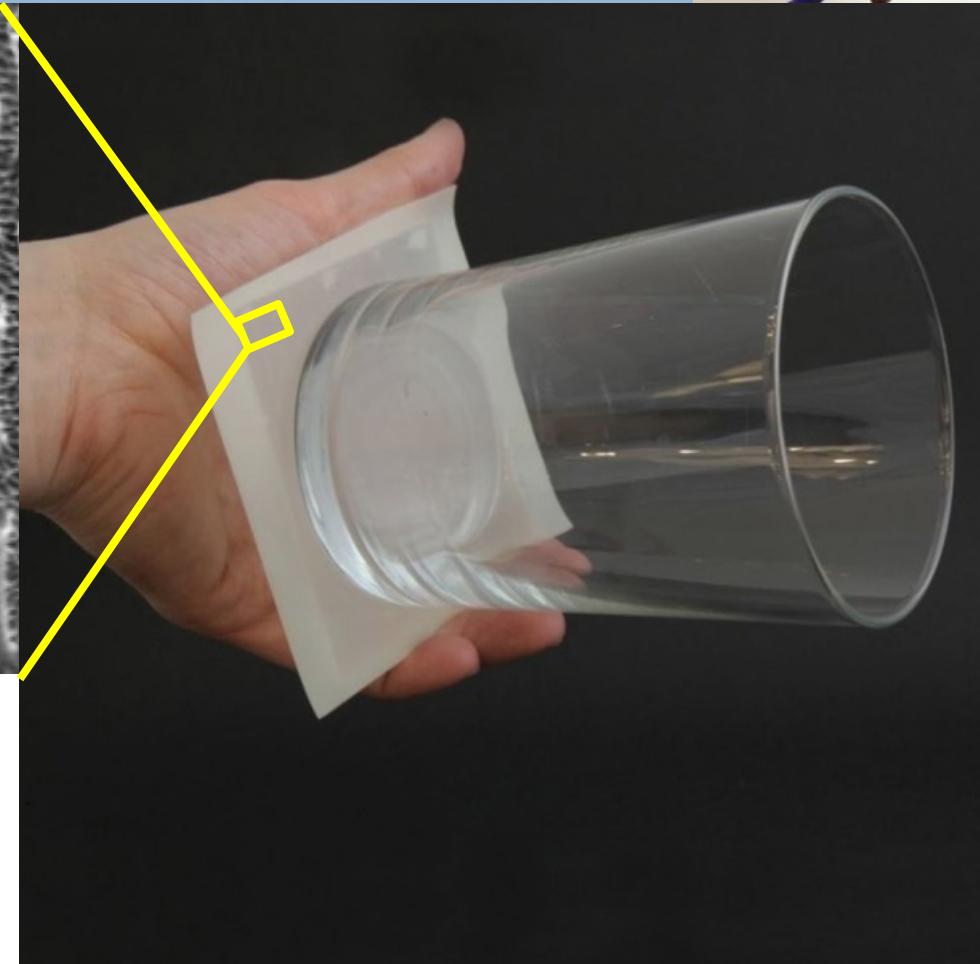
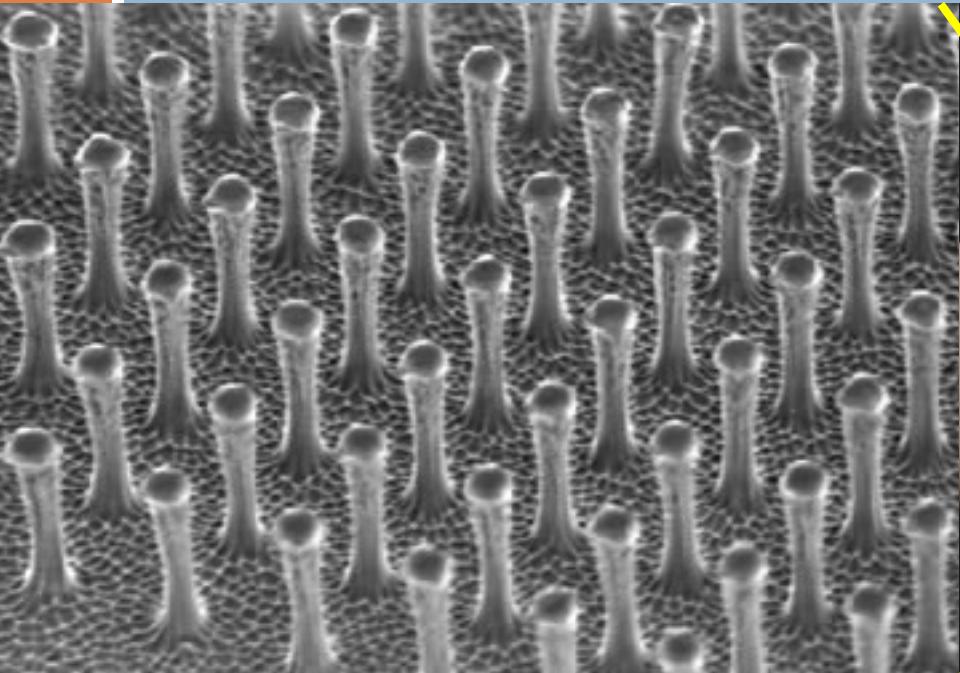


van der Waals forces created between the spatulae and the surface.



Gecko Foot

Gecko tape

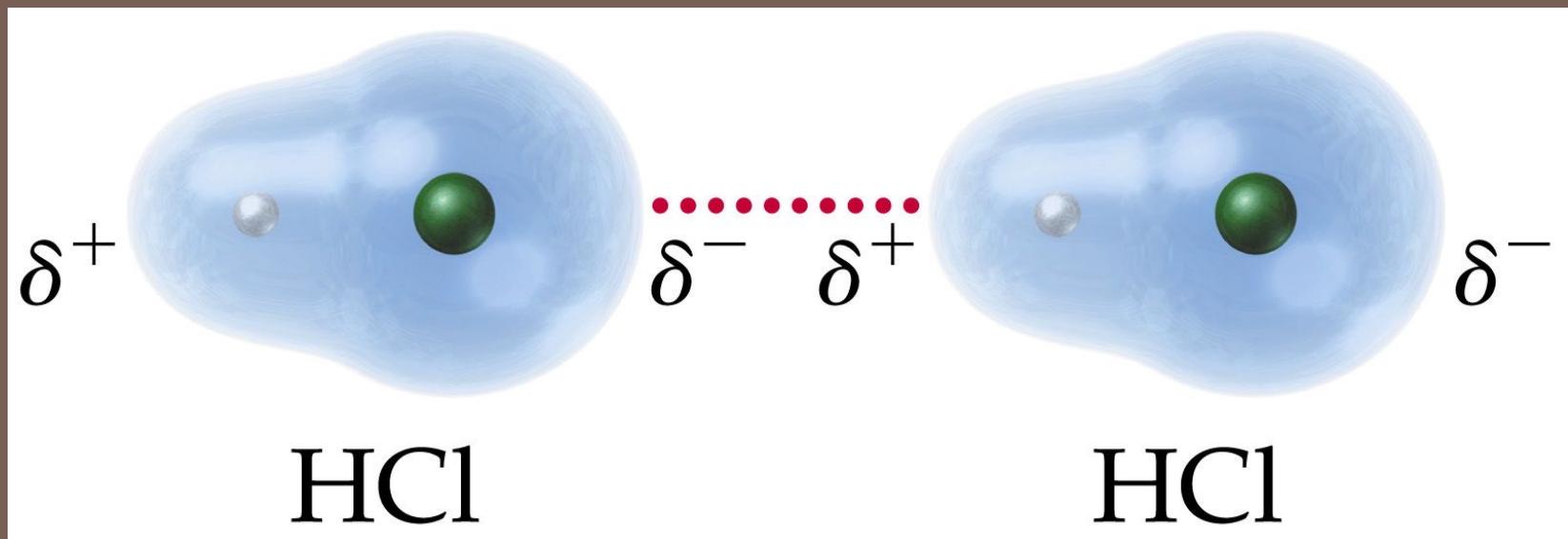


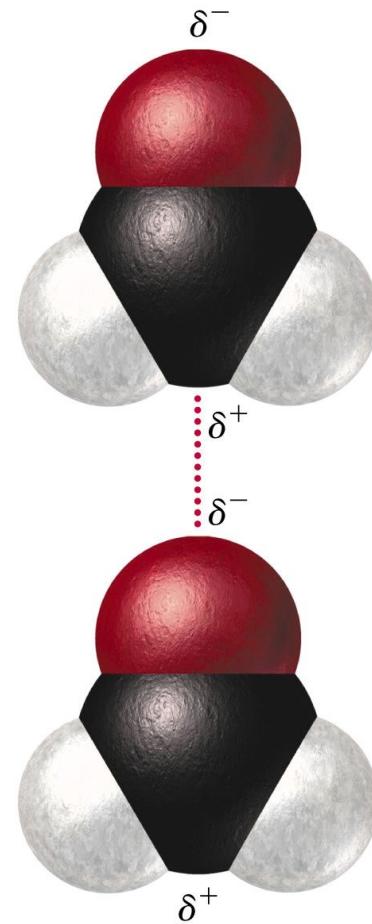
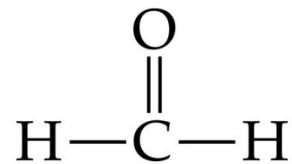
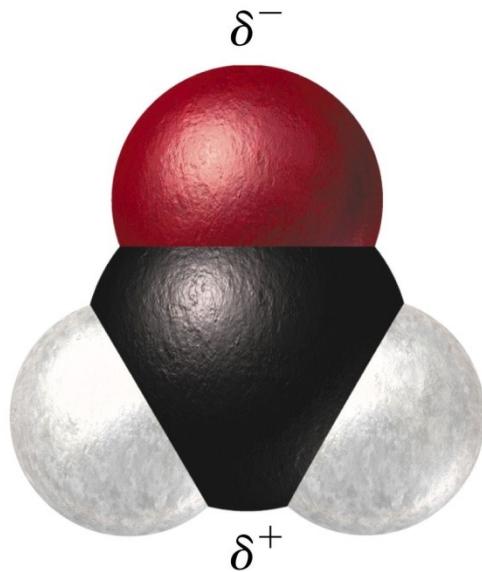
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<http://www.instituteofmaking.org.uk/materials-library/material/gecko-tape#gallery-window>

2 – Dipole-dipole forces

Polar molecules (molecules with permanent dipoles) will attract other molecules with permanent dipoles.





Dipole-dipole attractions in methanal

- Dipole-Dipole forces are stronger than London dispersion forces in molecules of a similar size

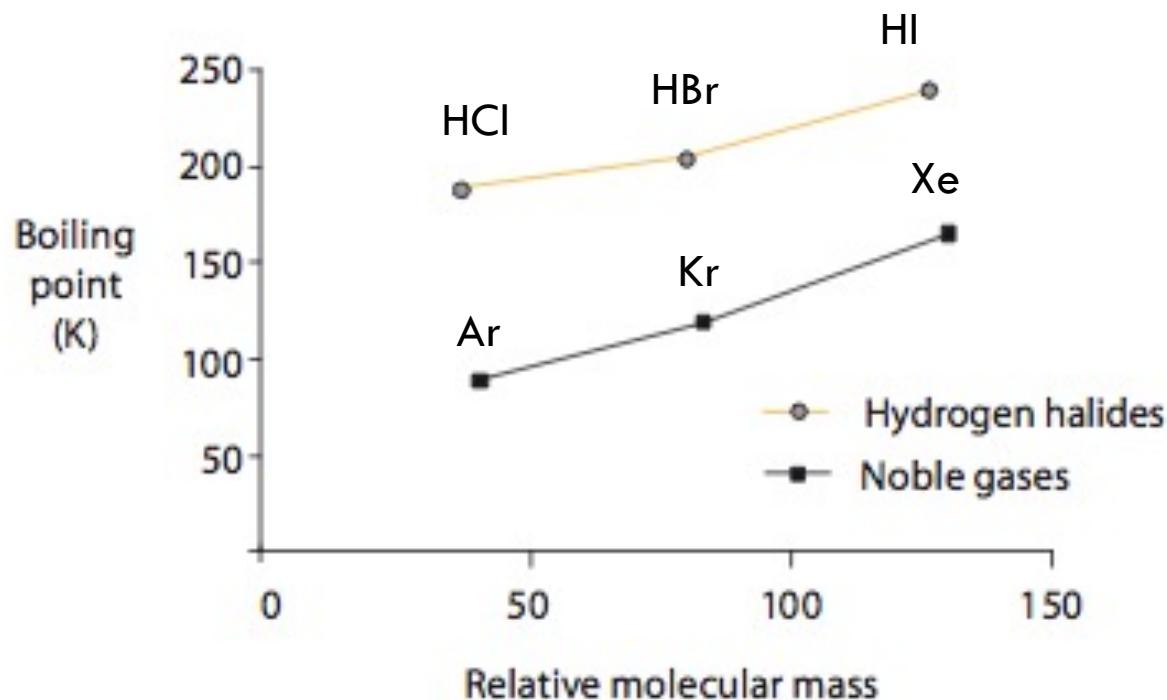


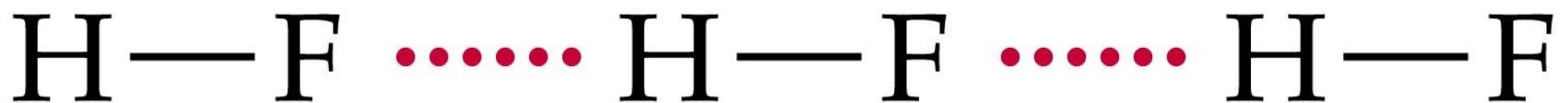
Figure 440 A comparison of the boiling points of polar and non-polar substances

3 – H-bonds

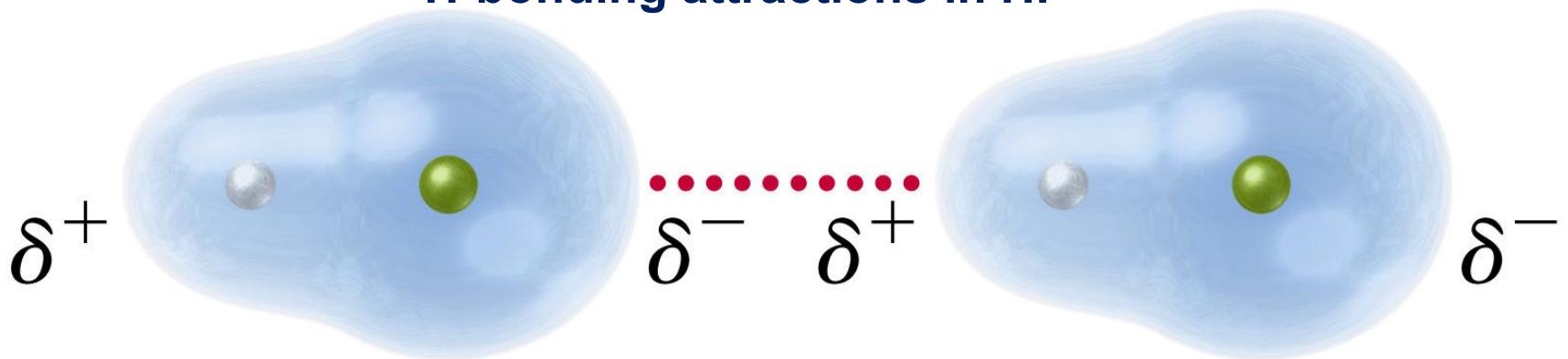
They occur when H is bonded to N, O or F (which are very electronegative).

As H only has the two electrons in the covalent bond, if they are pulled away from the H atom, the H nucleus is exposed.

The “H-bond” is the attraction between a lone pair on the N, O or F to the $\delta+$ H on a neighbouring molecule.

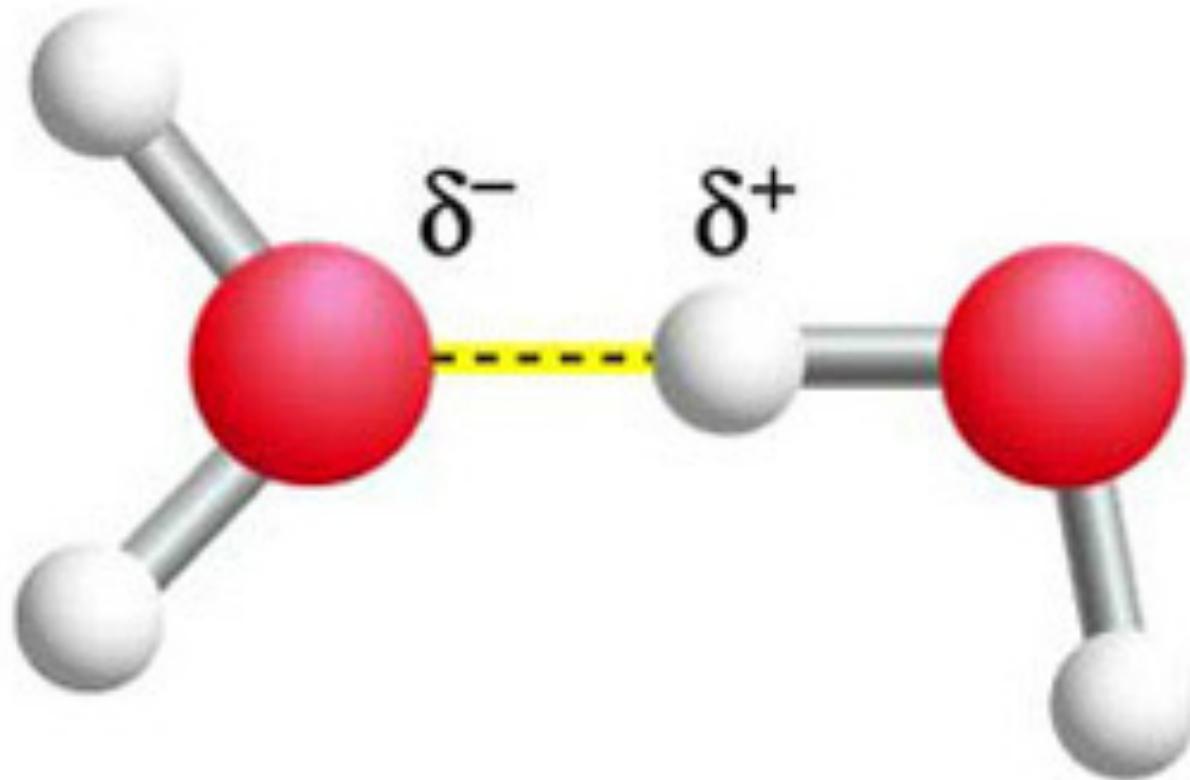


H-bonding attractions in HF



HF

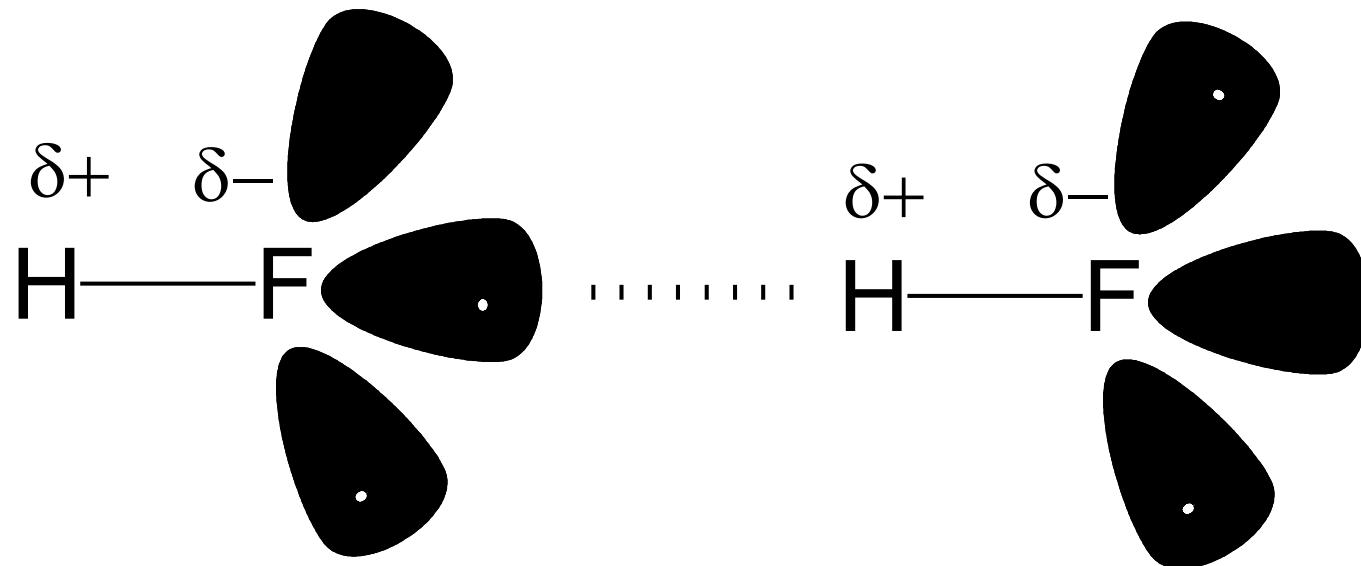
HF



H-bonding between water molecules

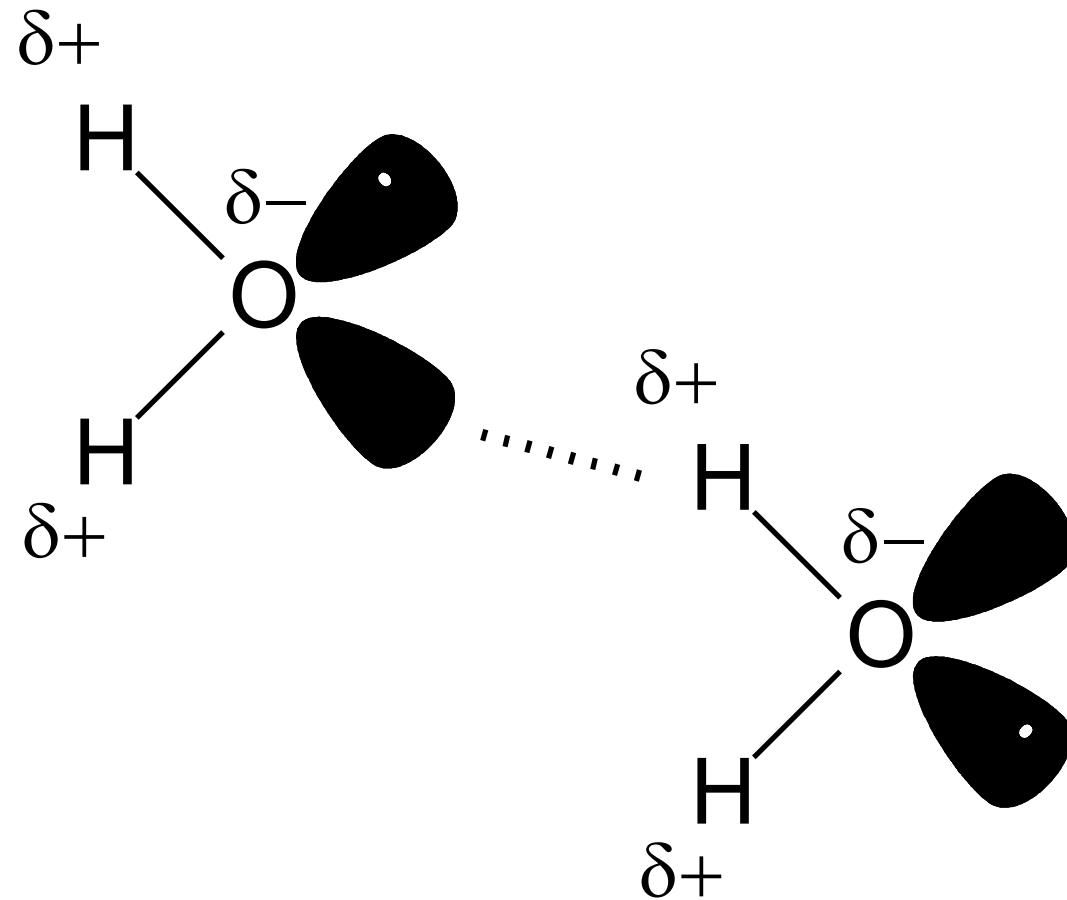
Drawing H bonds

from lone pair on N, O, F to $\delta+$ on H, e.g. HF



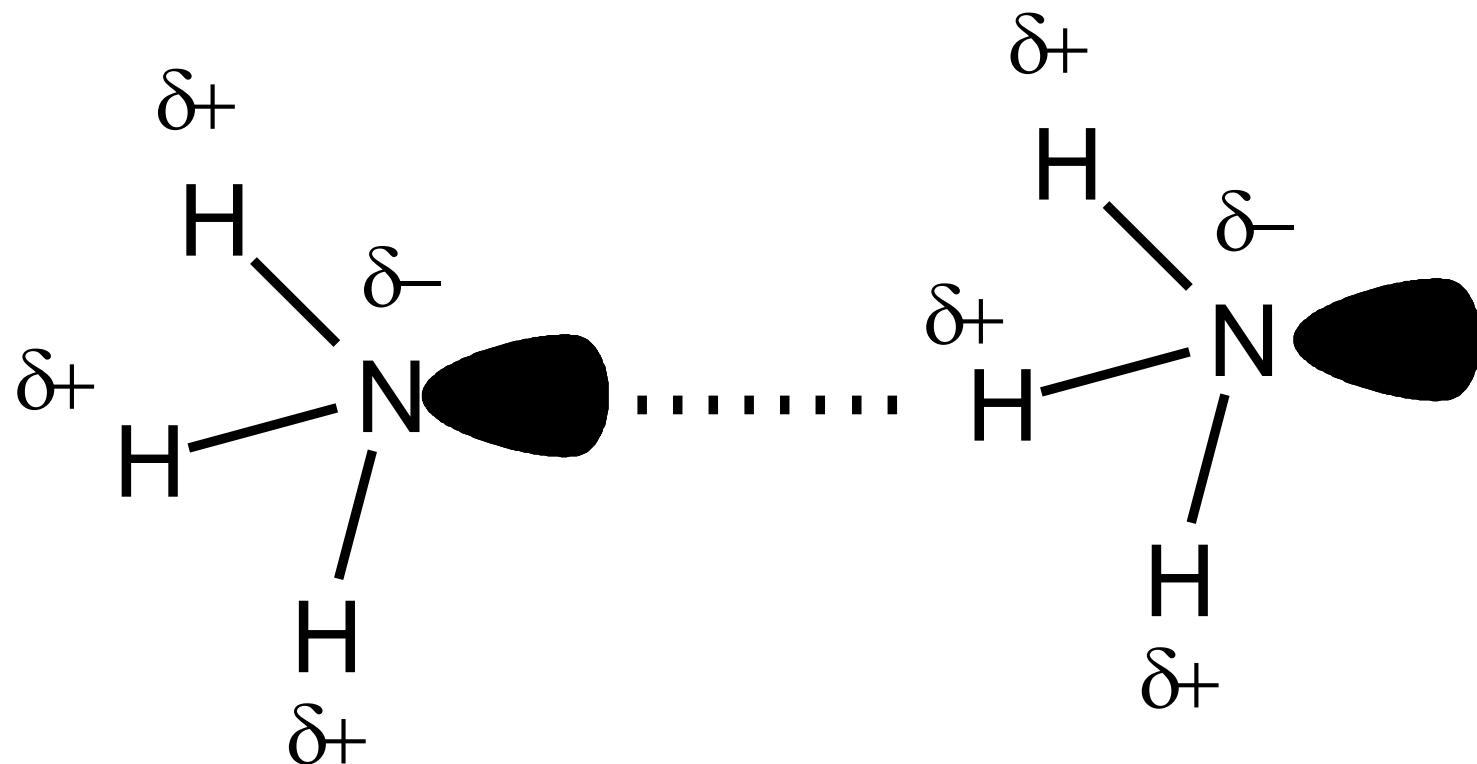
Drawing H bonds

from lone pair on N, O, F to $\delta+$ on H, e.g. H_2O



Drawing H bonds

from lone pair on N, O, F to $\delta+$ on H, e.g. NH_3

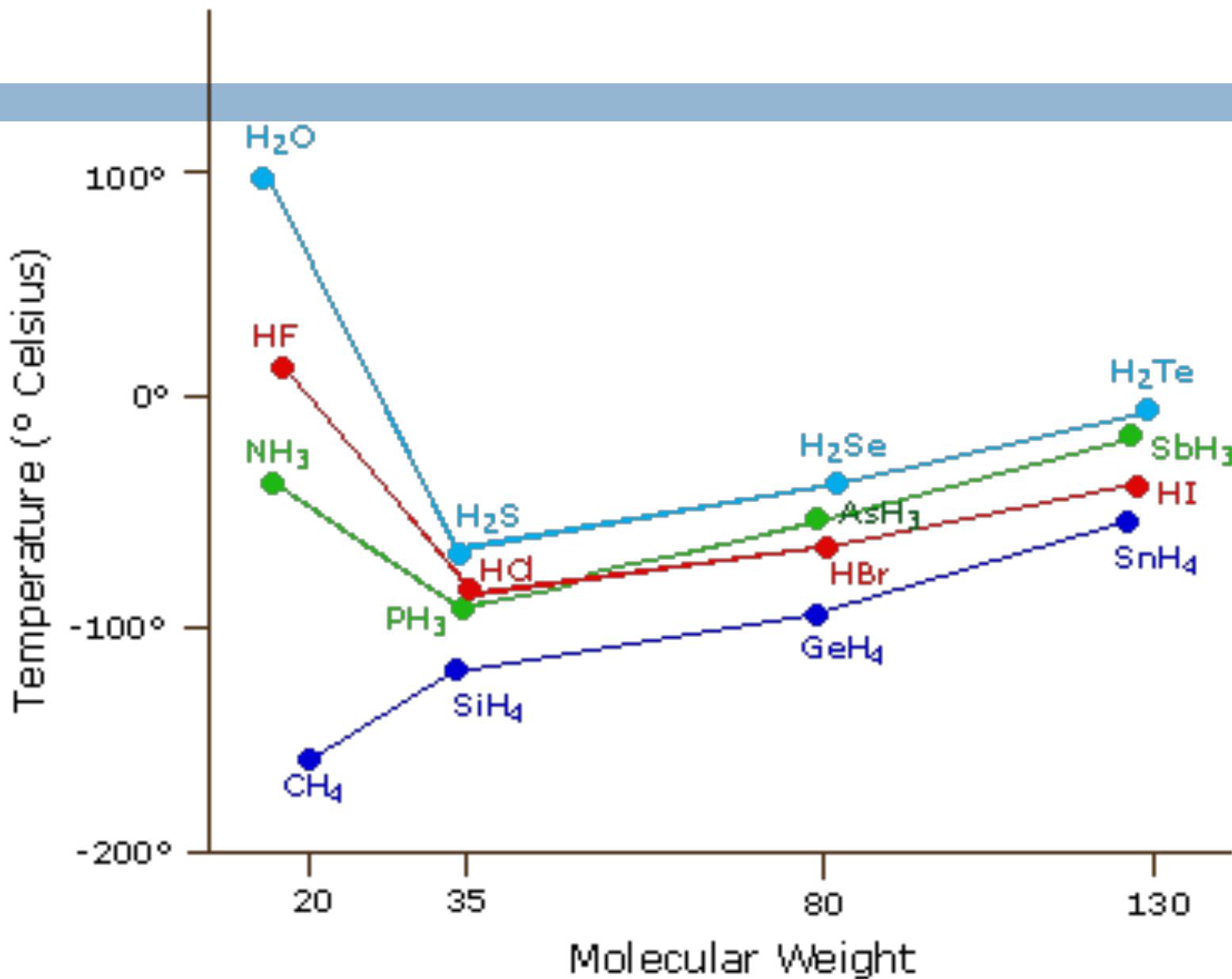


- Hydrogen bonding is stronger than London dispersion forces ,and dipole-dipole forces

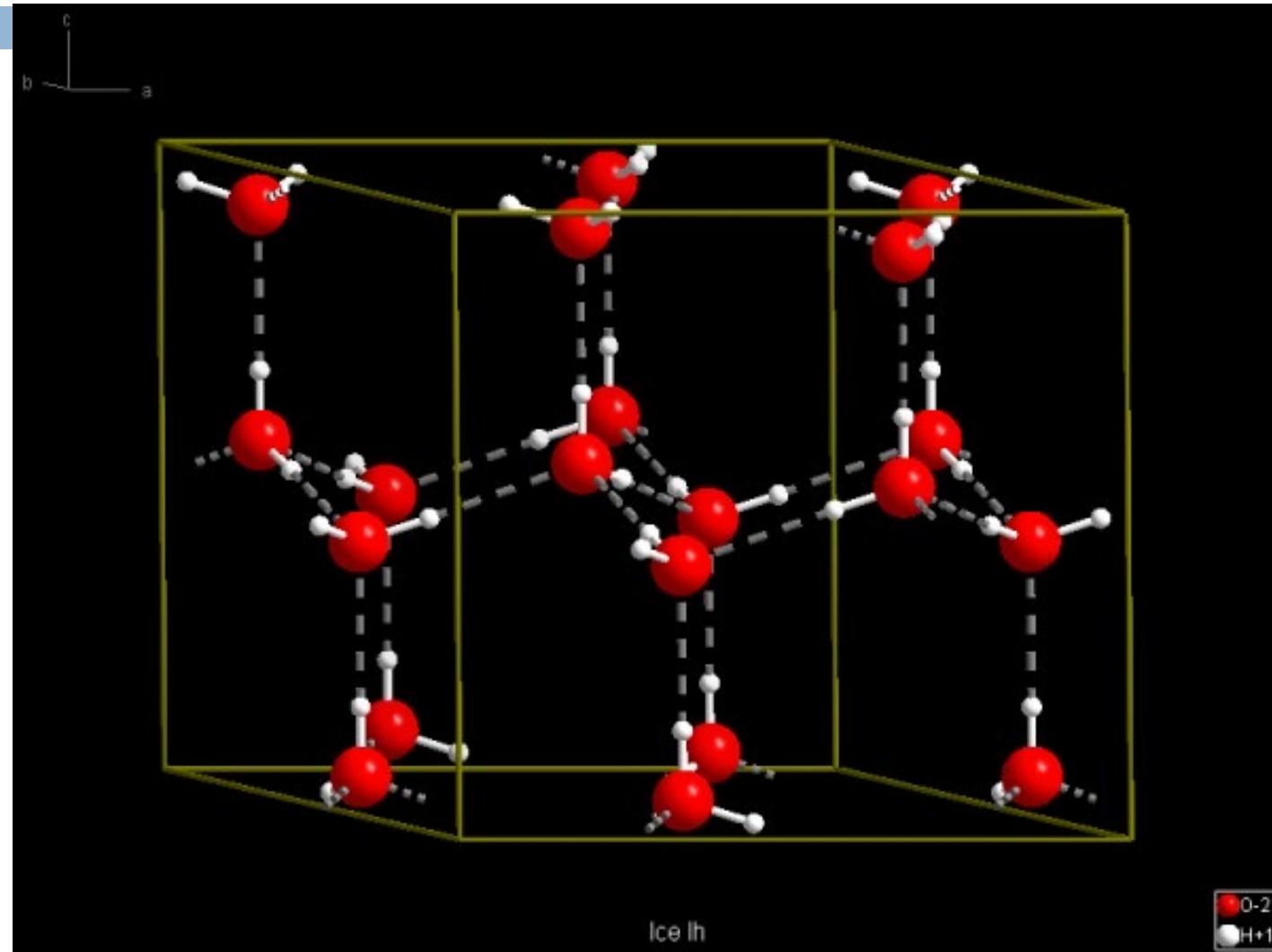
Name	Fluorine	Hydrogen Chloride	Hydrogen peroxide
Formula	F_2	HCl	H_2O_2
Molar Mass	38	36	34
Boiling point	85 K	188 K	431 K

Name	Propane	Ethanal	Ethanol
Formula	C_3H_8	CH_3-CO-H	CH_3CH_2OH
Molar Mass	44	44	46
Boiling point	231 K	294 K	352 K

Boiling points of various compounds



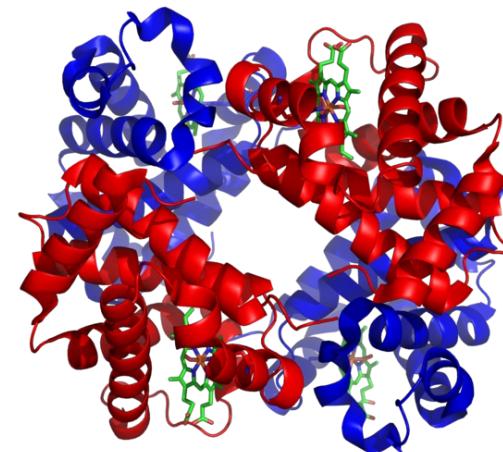
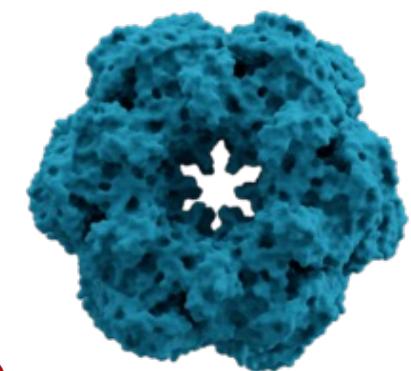
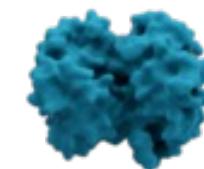
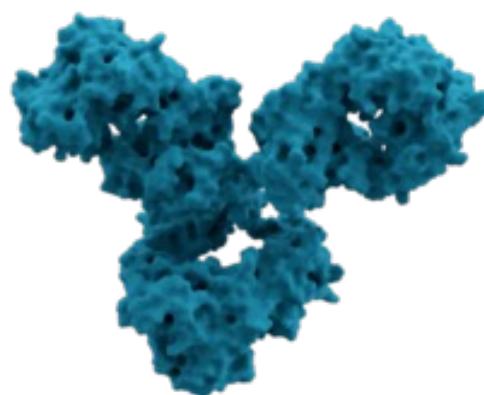
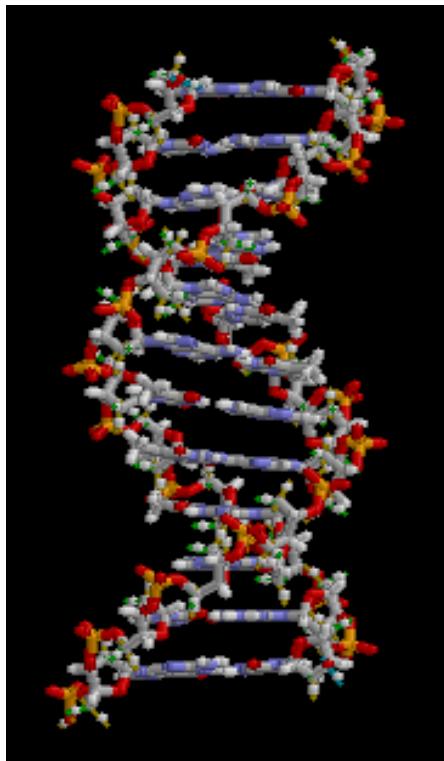
Ice has lower density than liquid water, due to H-bonds forming the open structure w/ large empty spaces enclosed in it

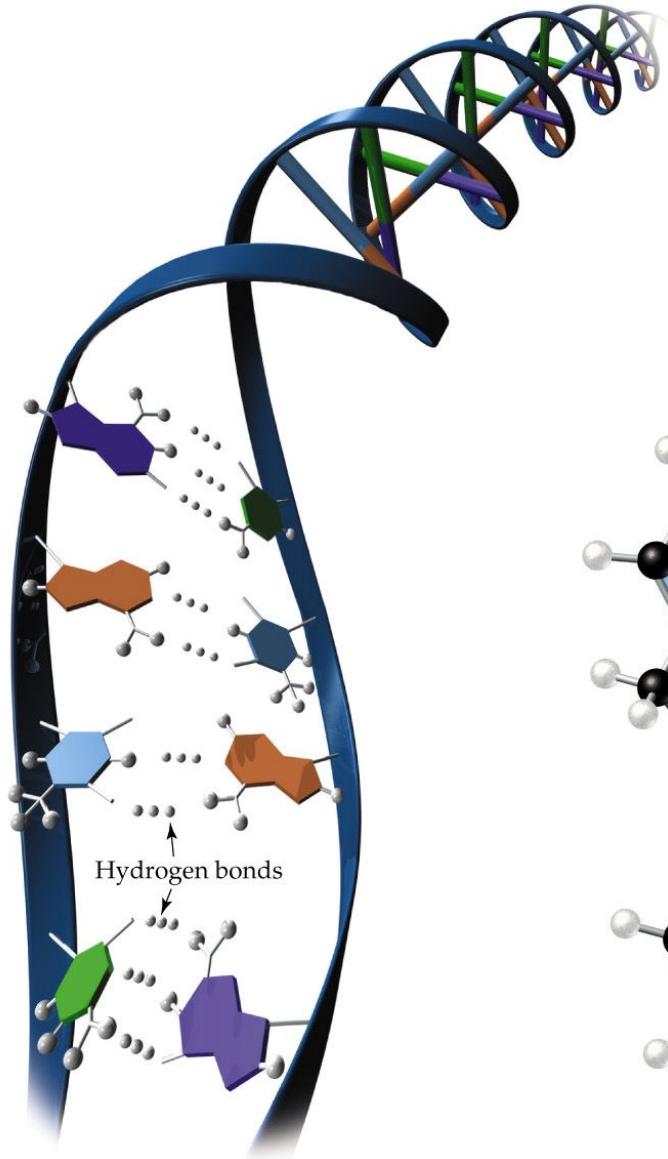


H-bonding in Ice

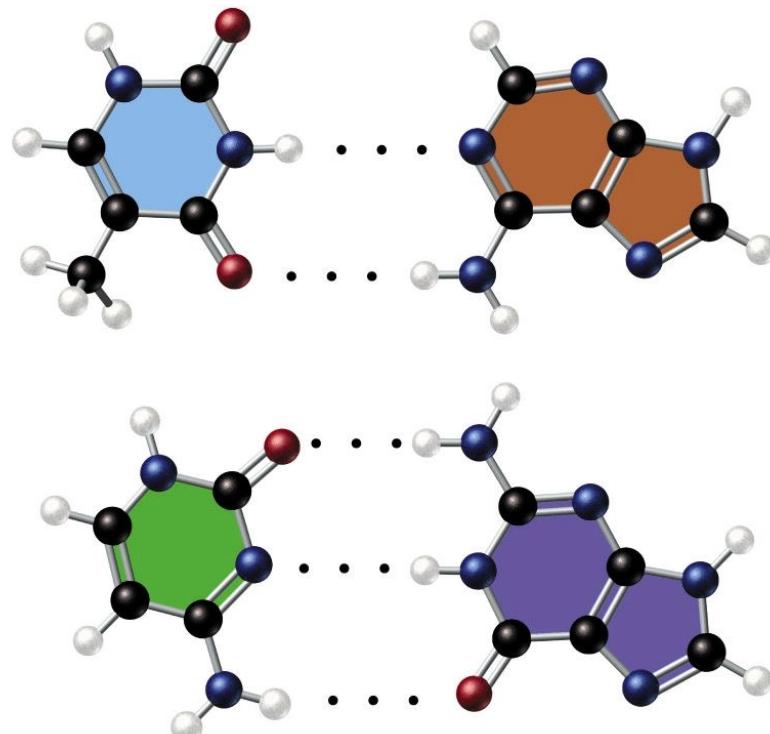
Great biological importance

H-bonding provides the basis for the pairing of bases in DNA and the α -helix and β -sheet secondary structures of protein molecules.



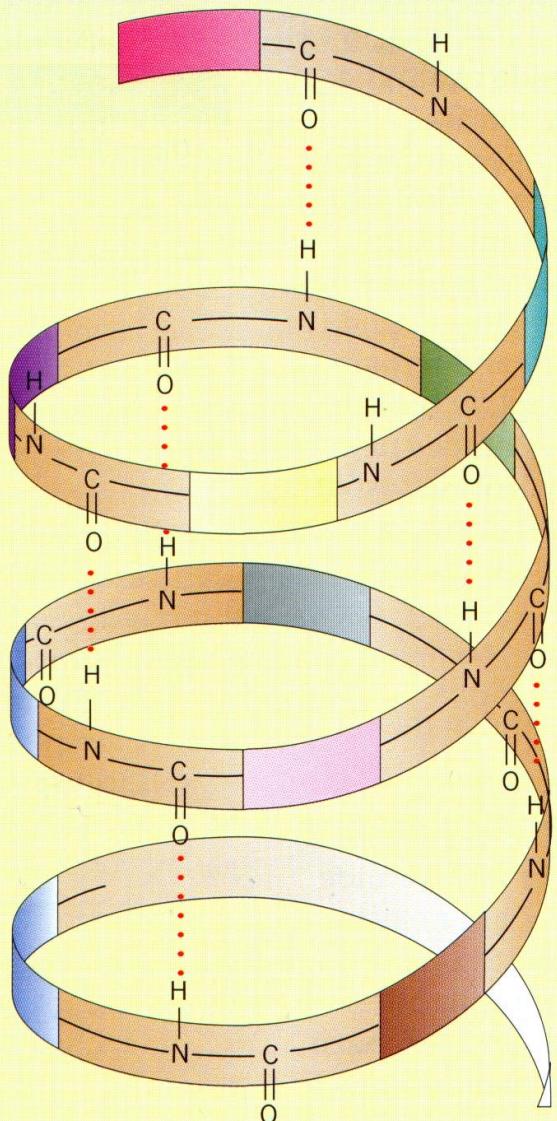


Oxygen
Nitrogen
Carbon
Hydrogen



H-bonding in DNA

Fig. 6 3D secondary structure of a protein



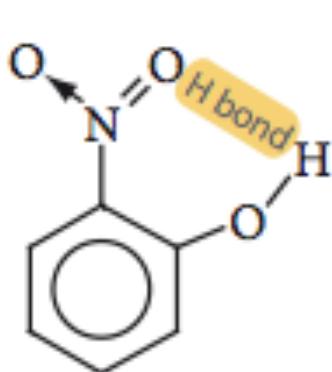
coloured patches = —C— of the different
R
|
H amino acids

Fig. 7 Tertiary structure of the muscle protein myoglobin

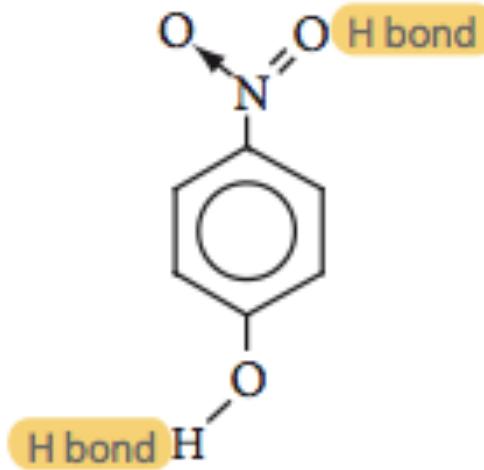


H- bonding in proteins

Intra-molecular H-bonding



2-nitrophenol



4-nitrophenol

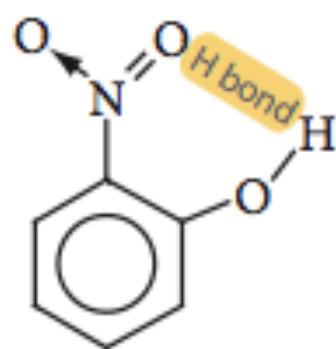
Figure 446 Hydrogen bonding in nitrophenols

Boiling point: 279°C, 216°C Who has higher b.p. ?

Intra-molecular H-bonding

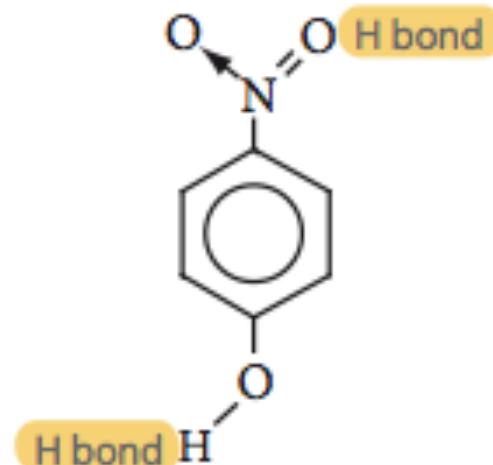
Boiling point: 216°C

H-bond mainly bonds intra-molecularly and hence weaker intermolecular forces, lower b.p.



2-nitrophenol

279°C



4-nitrophenol

Figure 446 Hydrogen bonding in nitrophenols

Different types of bonding/forces

- Ionic bonding
- Covalent bonding
- Metallic bonding
- Intermolecular force:
 - London dispersion forces
 - dipole-dipole forces
 - hydrogen-bonding

The physical properties of a substance depend on the forces between the particles of the chemical species that it is composed of.

Molecular covalent solid

The covalent bonds hold a small number of atoms together to form discrete units called **Molecules**.

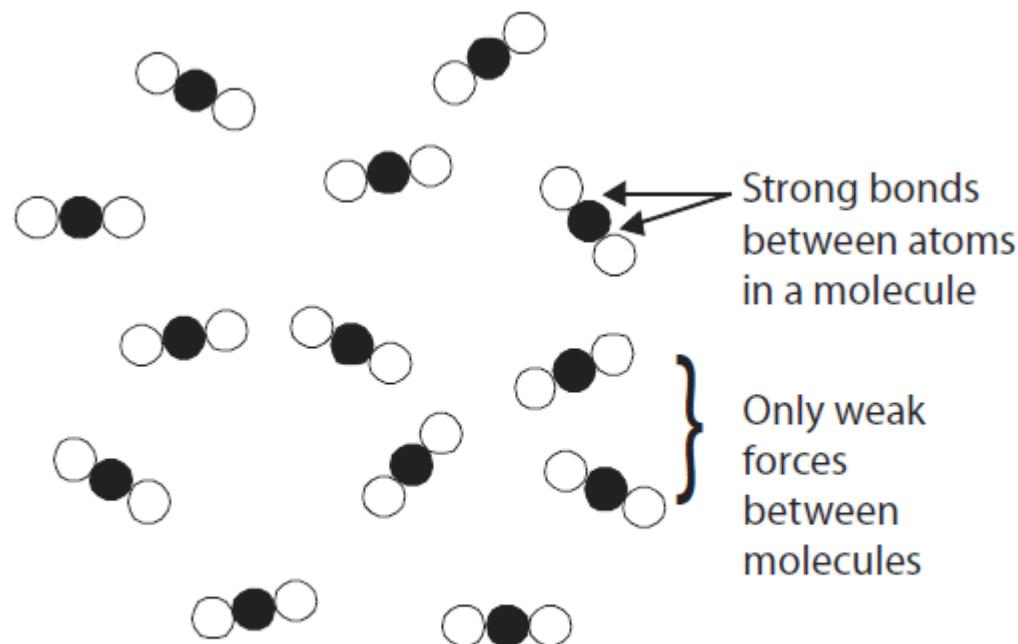


Figure 450 An illustration of molecular covalent bonding

Giant molecular / network covalent structure

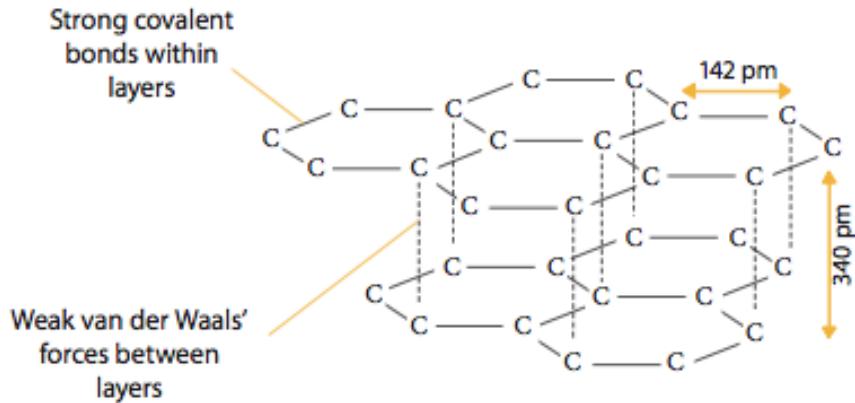


Figure 454 The structure of graphite

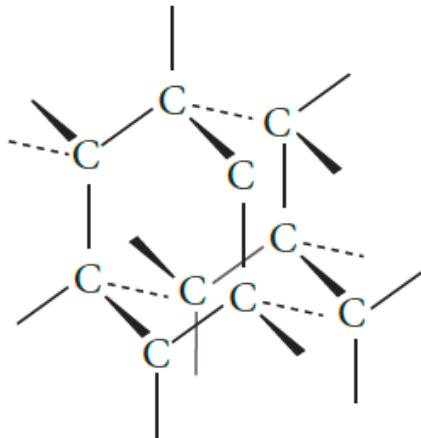


Figure 452 The covalent structure of diamond

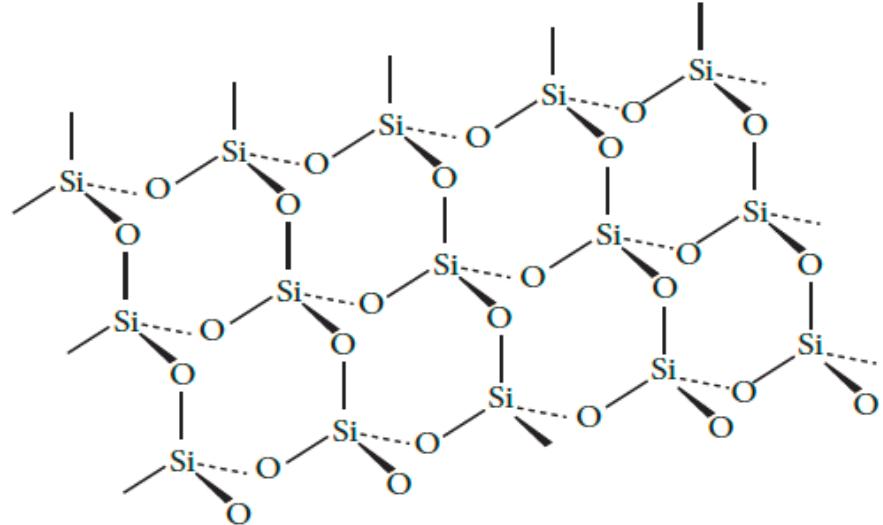


Figure 453 The bonding in silicon dioxide

Properties of molecular covalent solid V.S. Ionic compounds

- Quite soft in the solid state
- Have low m.p. and b.p. (often existing as liquids or gases at R.T.P.)
- Do not conduct electricity
- Are more soluble in non-polar solvents than in water

- Hard, brittle crystalline solids.
- Relatively high melting and boiling points.
- Do not conduct electricity when solid, but do when molten or in aqueous solution.
- Are more soluble in water than other solvents.

Ionic compounds

	Giant Metallic	Giant Ionic	Giant Covalent	Molecular Covalent
Hardness and malleability	Variable hardness, malleable rather than brittle	Hard, but brittle	Very hard, but brittle	Usually soft and malleable unless hydrogen bonded
Melting and boiling points	Very variable, dependent on number of valence electrons, but generally high	High: melting point usually over 500 °C	Very high melting point, usually over 1000 °C	Low melting point, usually under 200 °C. Liquids and gases are molecular covalent
Electrical and thermal conductivity	Good as solids and liquids	Do not conduct as solids, but do conduct when molten or in solution	Do not conduct in any state (graphite is an exception)	Do not conduct in any state
Solubility	Insoluble, except in other metals to form alloys	More soluble in water than other solvents	Insoluble in all solvents	More soluble in non-aqueous solvents, unless they can hydrogen bond to water or react with it
Examples	Iron, copper, lead, mercury, brass	Sodium chloride, calcium oxide	Carbon (diamond) silicon dioxide (quartz, sand)	Carbon dioxide, ethanol, iodine

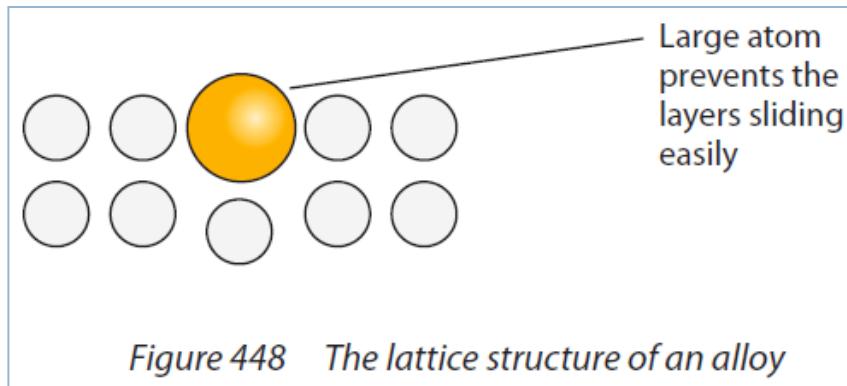
	Ionic compounds	Polar covalent compounds	Non-polar covalent compounds	Giant covalent
Volatility	low	higher	highest	low
Solubility in polar solvent, e.g. water	soluble	solubility increases as polarity increases	non-soluble	non-soluble
Solubility in non-polar solvent, e.g. hexane	non-soluble	solubility increases as polarity decreases	soluble	non-soluble
Electrical conductivity	conduct when molten (l) or dissolved in water (aq)	non-conductors	non-conductors	non-conductors except graphite, graphene and semi-conductivity of Si and fullerene

Reasons overall

- Stronger the bonding between particles, harder the substance; higher the m.p. & b.p; lower the volatility.
- Electrical conductivity depends on whether the substance contains mobile charge carriers.
- Dissolving involves the intimate mixing of the particles of two substances: the solute and solvent. The forces between solute & solvent must be as strong, or stronger, than that between solute & solute, solvent & solvent.

Solubility-Metals

- Do not dissolve in other substances unless they react with them chemically (e.g. Na + H₂O)
- Dissolve in other metals to form mixtures of variable composition called alloys. (e.g. Brass: alloy of Cu & Zn; Steel: non-metal C dissolve in Fe)



Solubility-Ionic compound

- Insoluble in most solvents
- Dissolve in highly polar solvent like water due to ion-dipole interactions

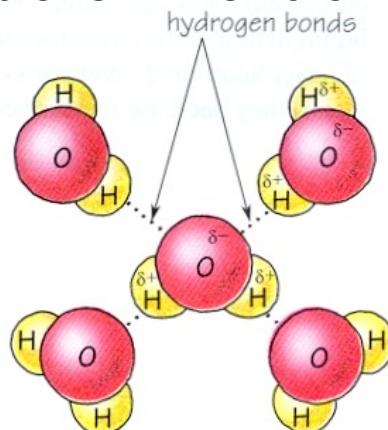
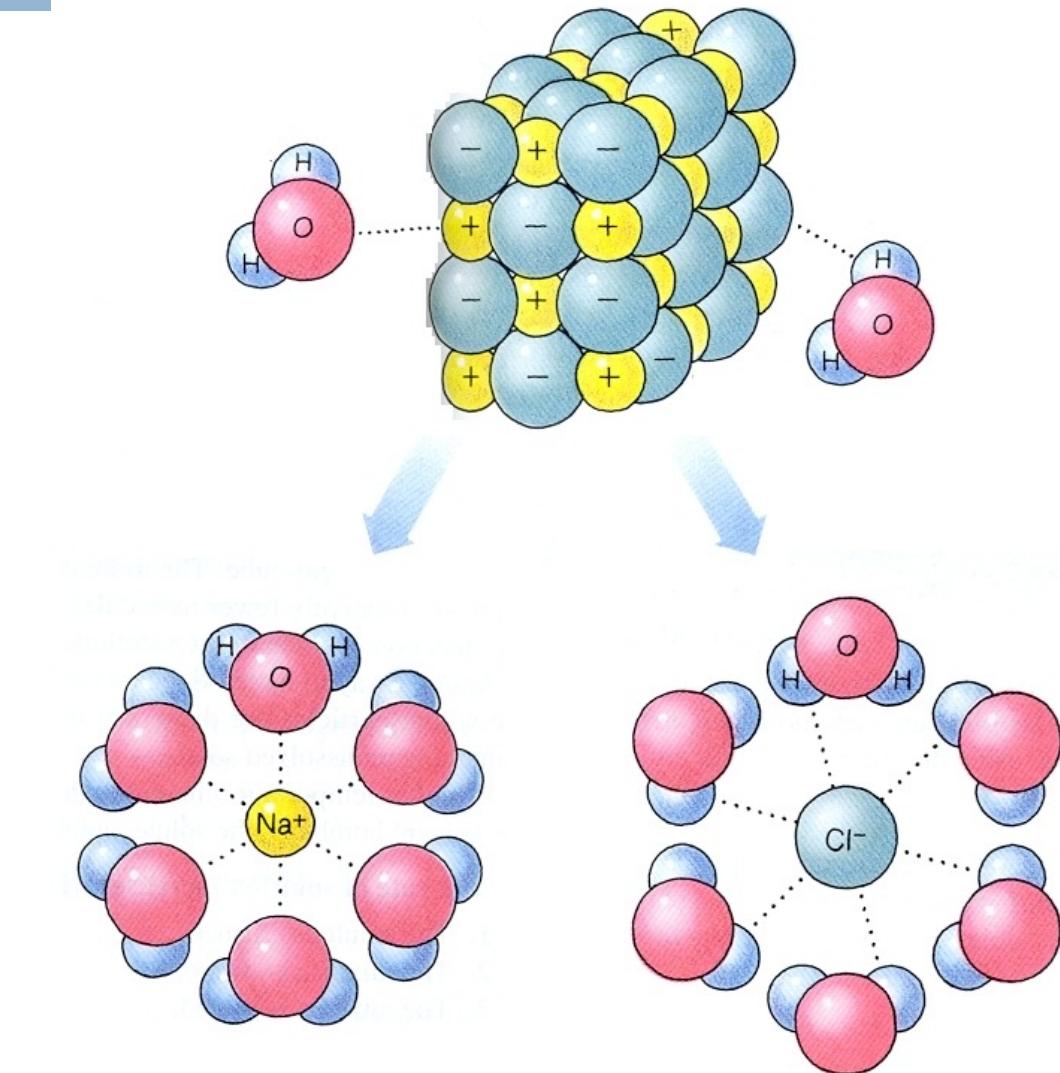


Figure 8.2 Hydrogen bonding links water molecules together.



Solubility-Ionic compound

- If the forces between ions are very strong, it will not dissolve in water

Always soluble – salts of Na^+ , K^+ , NH_4^+ and NO_3^-

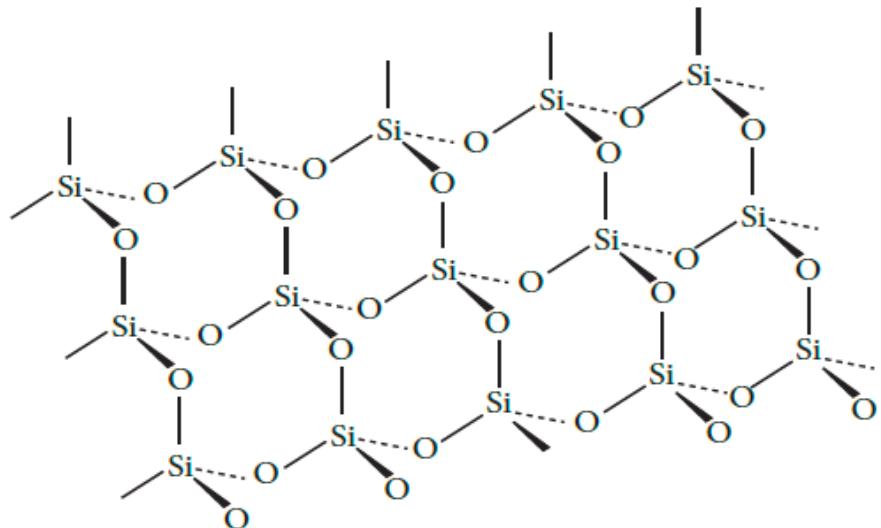
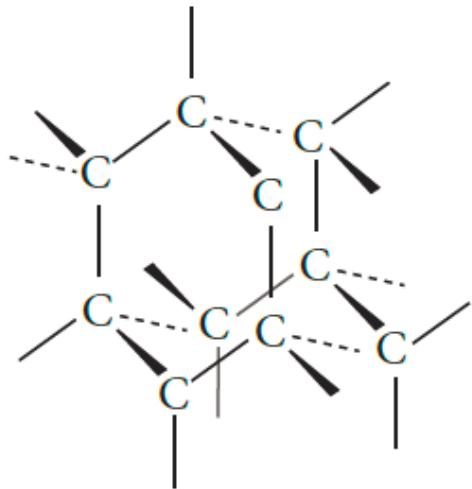
Usually soluble - salts of Cl^- and SO_4^{2-} , but AgCl , PbCl_2 , PbSO_4 and BaSO_4 are insoluble

Usually insoluble - salts of OH^- , O^{2-} , CO_3^{2-} and PO_4^{3-} , but Na^+ , K^+ , NH_4^+ salts soluble

Common slightly soluble substances – $\text{Ca}(\text{OH})_2$ and Ca SO_4

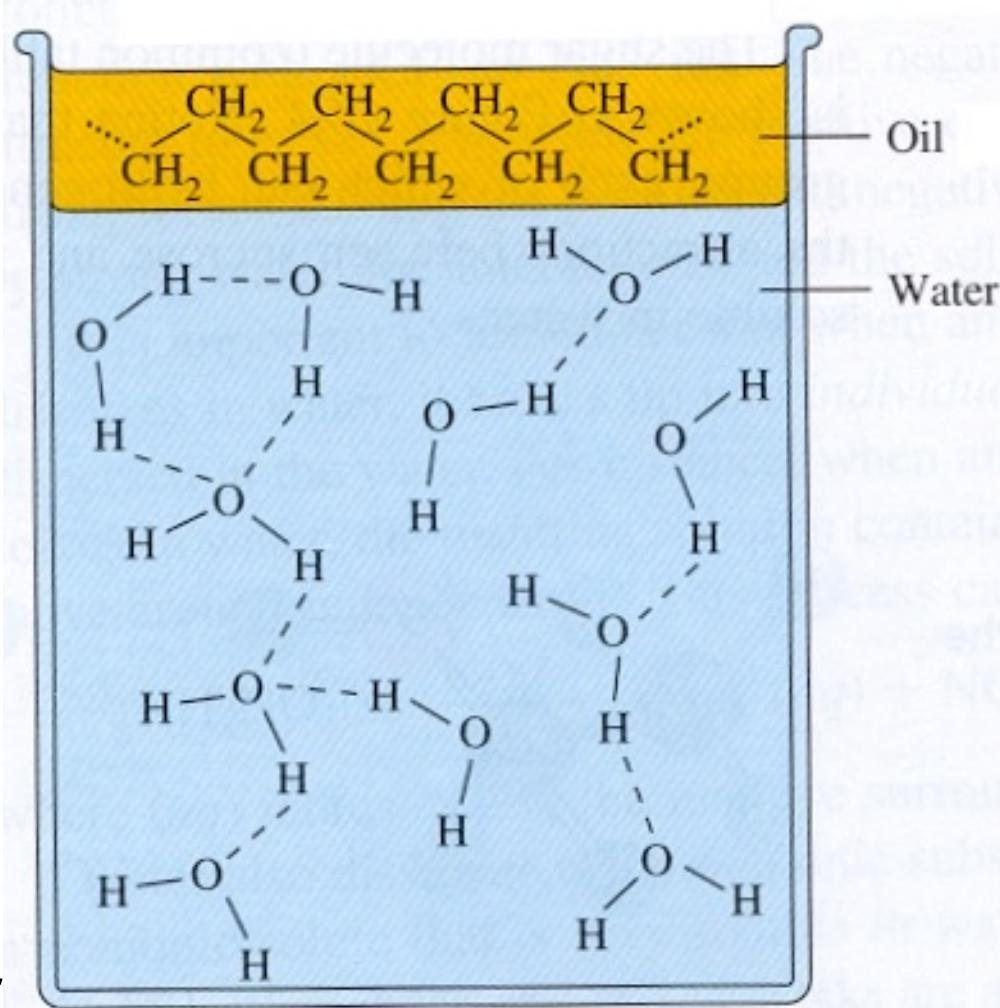
Solubility-Giant covalent structure

- Insoluble in all solvents



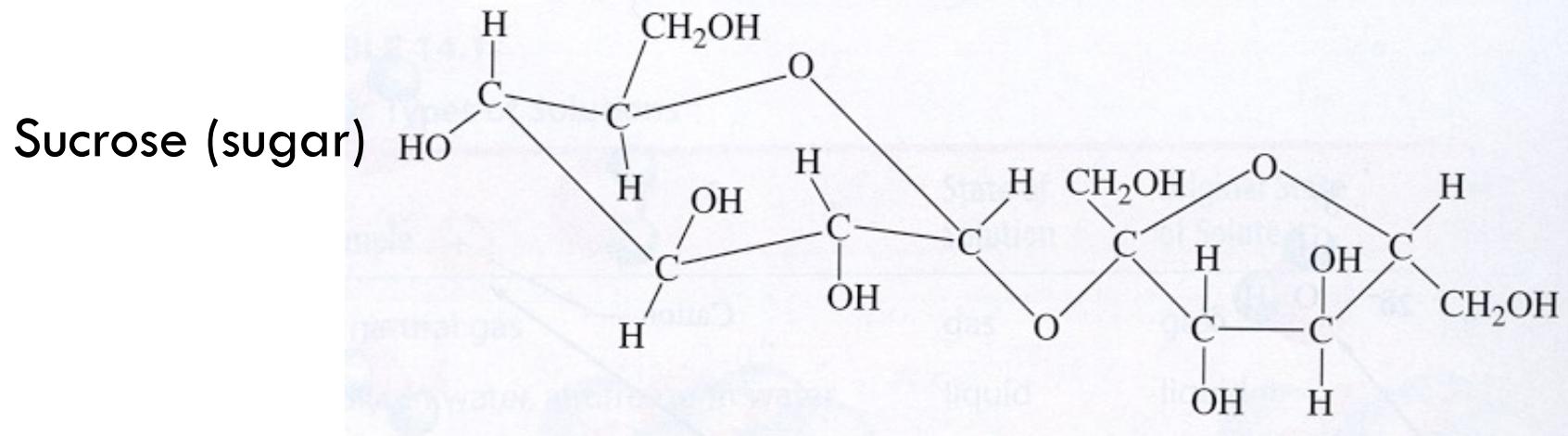
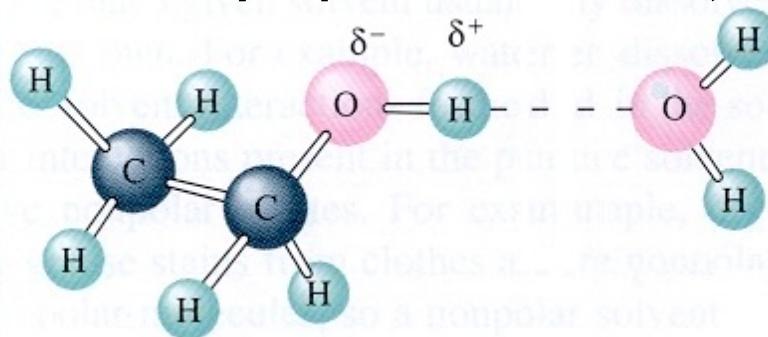
Solubility-Molecular covalent structure

- Non-polar molecular covalent substances dissolve in non-polar solvents (e.g. Hexane C_6H_{14} , cyclohexane C_6H_{12}) due to similar I.M.F. – weak London dispersion force.
- Non-polar molecular covalent substances are insoluble in very polar solvents like water, due to the strong H-bond in water



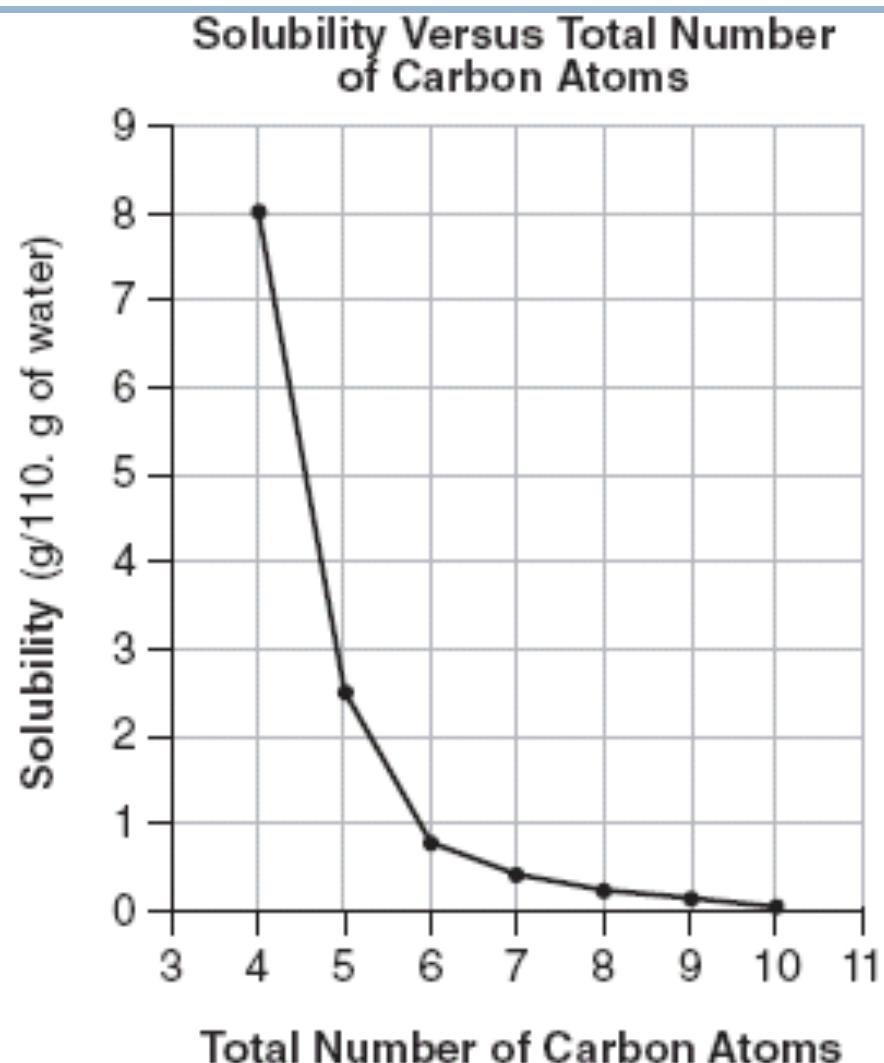
Solubility-Molecular covalent structure

- Polar molecular covalent substances if they can form H-bond with water, are usually quite soluble (R-OH , R-COOH , $\text{R-CO-R}'$)



Solubility-Molecular covalent structure

- Polar molecular covalent substances like alcohols ($R-OH$), if the hydrocarbon chain is long/big, it disrupts the H-bond with water, solubility decrease.



m.p. of the first 20 elements.

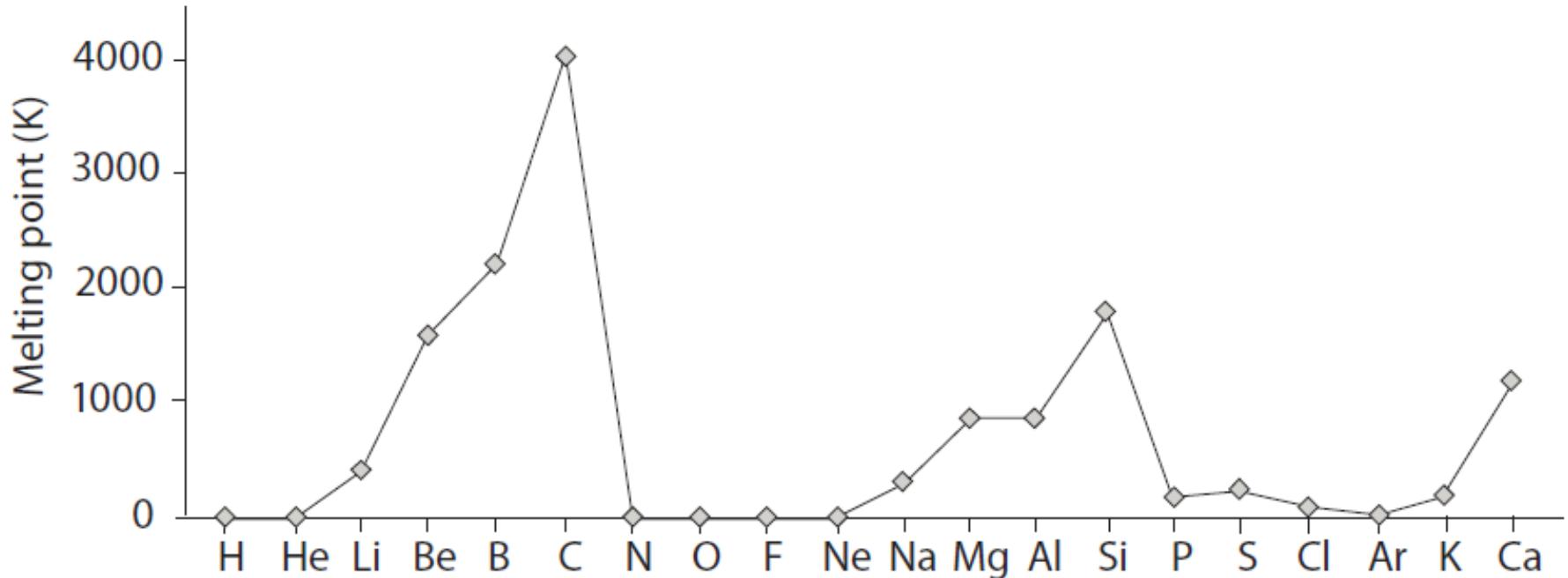


Figure 307 The melting points of the first twenty elements

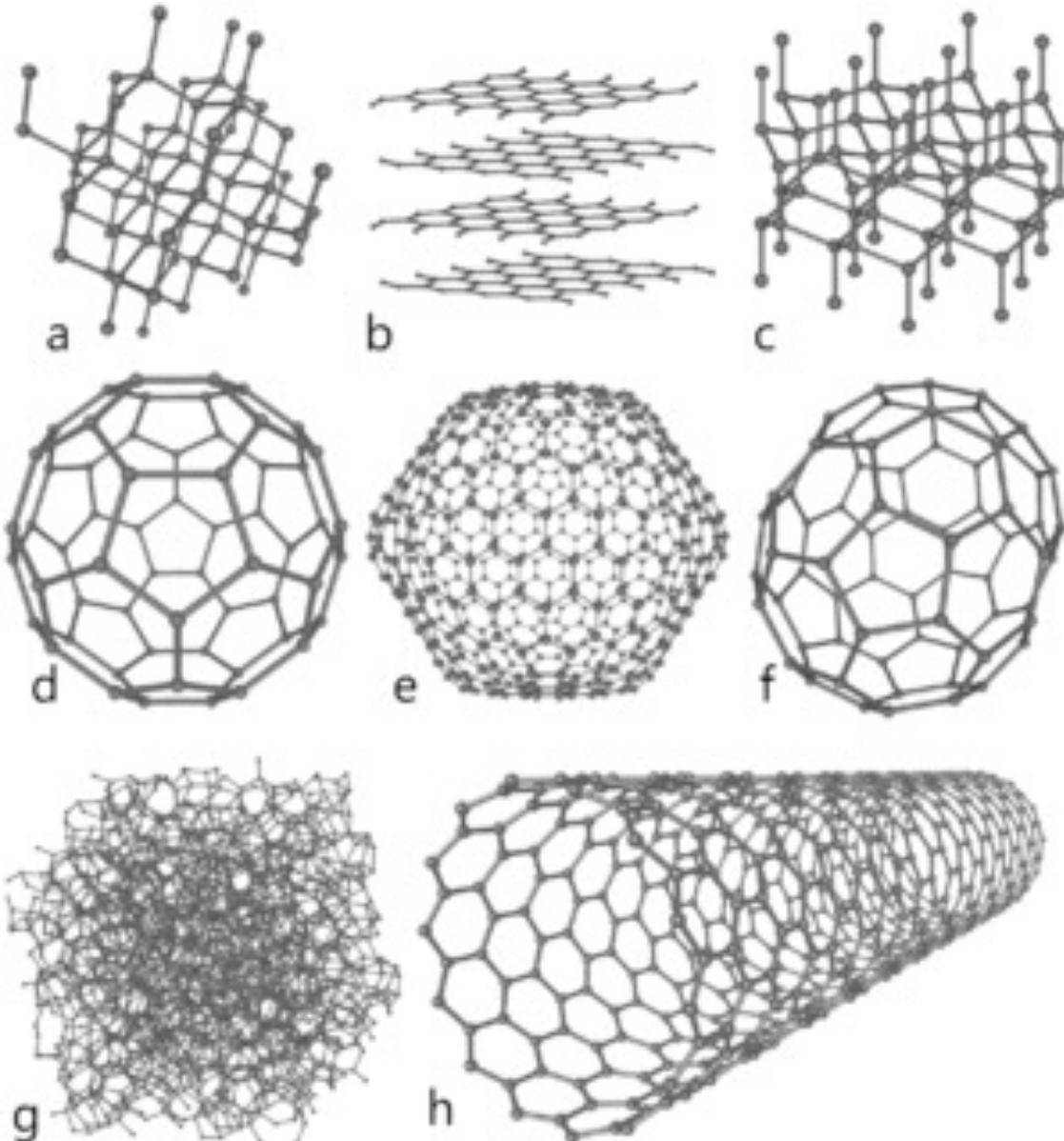
CRYSTAL TYPE	PARTICLES IN CRYSTAL	PRINCIPAL ATTRACTIVE FORCES BETWEEN PARTICLES	MELTING POINTS and BOILING POINTS	ELECTRICAL CONDUCTIVITY OF LIQUID (IN MOLTEN STATE)	CHARACTERISTICS OF THE CRYSTALS	CONDITIONS FOR FORMATION	EXAMPLES
IONIC NETWORK CRYSTALS	Positive and negative ions due to electron transfer from active metal to active non-metal, e.g., Na^+ ... Cl^- , NaCl Ca^{2+} ... O^{2-} , CaO 2K^+ ... SO_4^{2-} , K_2SO_4	Attractions between oppositely charged ions. Strong ionic bonding.	High. Non-volatile due to three dimensional arrangement of anions and cations.	High. Electrolyte in molten form or in aqueous solution. Non-electrolytes as solids.	Solid. Hard, brittle. Most dissolve in polar solvents e.g. H_2O .	Metal - non-metal combination. Formed between atoms of greatly differing electronegativity (between elements of Groups 1, 2 and 3 and 6 and 7).	NaCl , CaO , K_2SO_4 , KCl , CaF_2 , Cs_2S , MgO
COVALENT NETWORK CRYSTALS / NETWORK SOLIDS / GIANT STRUCTURES, OR MACRO-MOLECULAR	Non-metal atoms	Covalent bonds (i.e., electron sharing) throughout the whole crystal. Very strong.	Very high. Non-volatile due to 3D network arrangement.	Diamond: nil Graphite solid: moderate conductor; Fullerene: poor conductor.	Solids. Very hard. Insoluble in most ordinary liquids.	Most are formed by two elements of Group 4, e.g. C, Si	Diamond, Si, SiO_2 , graphite. Fullerene-60
METAL NETWORK CRYSTALS	Lattice of positive ions surrounded by delocalized / mobile valence electrons.	Metallic bonding. Attraction of mobile valence electrons by positive nuclei. Strong.	Most are medium to high. Non-volatile.	Very high due to presence of mobile valence electrons.	Usually solids. Most are hard yet malleable, ductile. High thermal conductivity. Insoluble in liquids. Usually soluble in molten metals.	Formed by electropositive metallic elements with low electronegativity.	Na, Cu, Ca ($\frac{3}{4}$ of the periodic table elements are metals)

Figure 463 Characteristics of Crystalline Solids - A Summary

CRYSTAL TYPE	PARTICLES IN CRYSTAL	PRINCIPAL ATTRACTIVE FORCES BETWEEN PARTICLES	MELTING POINTS and BOILING POINTS	ELECTRICAL CONDUCTIVITY OF LIQUID (IN MOLTEN STATE)	CHARACTERISTICS OF THE CRYSTALS	CONDITIONS FOR FORMATION	EXAMPLES
(SIMPLE) MOLECULAR CRYSTALS (a) POLAR	Polar molecules containing elements of high electronegativity (i.e. non-metals).	Electrostatic attraction between dipoles. Intermediate strength.	Intermediate-low molar mass compounds tend to be volatile.	Very low or non-conductors when solids, liquids and in aqueous solution. A few (e.g. HCl) react with H_2O to form electrolyte.	Many polar substances are soluble in polar solvents.	Formed from asymmetrical distribution of electron cloud containing polar covalent bonds. Such bonds are formed between atoms having a moderate difference in electronegativity.	ICl , SO_2 , HCl
(b) H-BONDING	H bonded to N, O, or F	Strengthened by hydrogen bonding if H is bonded to O, F or N.	Hydrogen-bonding increases boiling and melting points.		Most small hydrogen bonded substances are soluble in polar solvents.	Hydrogen-bonding if H is bonded to F, N, O.	Hydrogen bonding in: H_2O , H_2O_2 , HF , NH_3 , alcohols, amines, organic acids.
(c) NON-POLAR	Non-polar molecules or atoms (in the case of noble gases).	Strong covalent bonds between atoms. van der Waals' forces (weak, temporary, instantaneous dipoles) between molecules.	Low; Volatile	Non-conductors when solid and as liquid.	Soft. Usually gases or volatile liquids. Most are soluble in non-polar or slightly polar solvents. Insoluble in polar water.	Formed between atoms or from symmetrical molecules containing covalent bonds between like atoms or atoms having a small difference in electronegativity.	H_2 , Cl_2 , S_8 , C_6H_6 , CH_4 , N_2 , CO_2 , CCl_4 , I_2 . Noble gases: simple atomic substances.

Allotropes of Carbon

- Allotropes are different forms of an element that exist in the same physical state (e.g. ozone O_3 , O_2)



Examples for allotropes of carbon:

- a) Diamond, b) Graphite, c) Lonsdaleite, d) C₆₀ (buckyball), e) C₅₄₀, f) C₇₀, g) Amorphous carbon, and h) single-walled carbon nanotube

Diamond

- Giant 3-D covalent structure
- Each C is joined to four other C arranged tetrahedrally
- Exceptionally hard, very high m.p. and b.p.

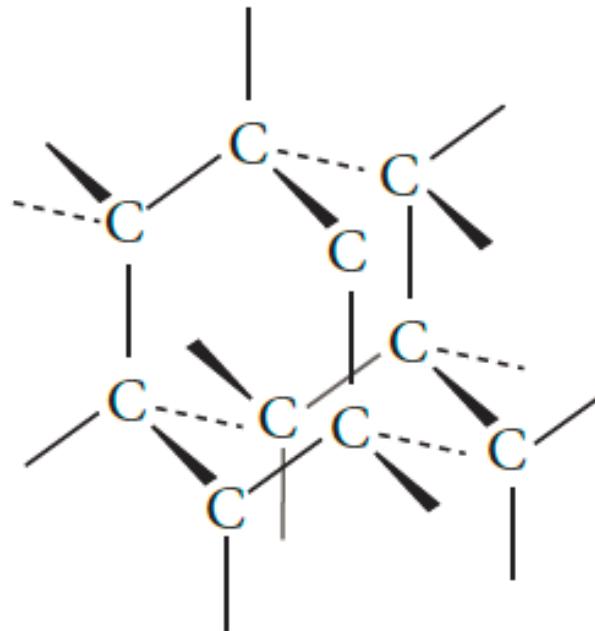
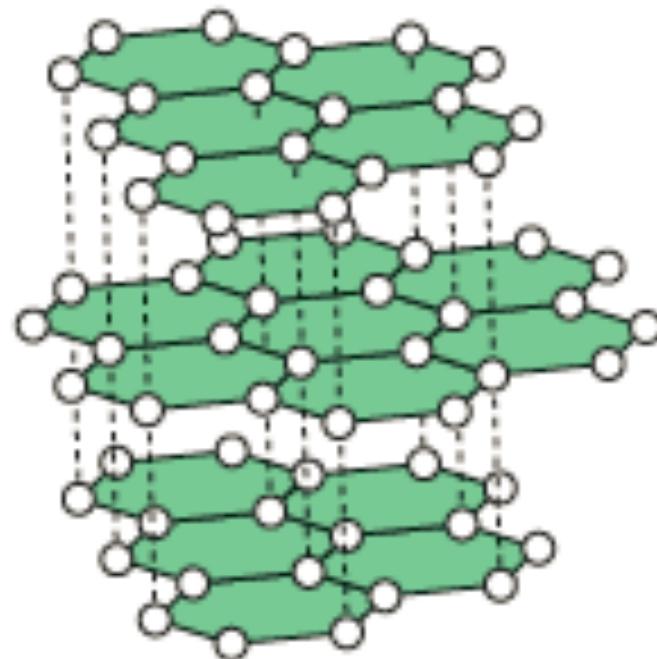


Figure 452 The covalent structure of diamond

Graphite

- Only giant covalent network in 2-D
- Only weak London dispersion forces b/w sheets of C atoms
- Low density, soft, easily slide over each other, easily be rubbed off (e.g. pencils)
- Delocalized e^- in 2-D layers, conduct electricity in 2-D



Fullerenes

Contain approximately spherical molecules made up of five- and six-membered carbon rings.

- C_{60} contains 60 C atoms, each C bond w/ 3 others
- Only a little delocalized e^- on the surface, more electrical conductive than diamond, much less than graphite.
- Non-giant, but molecular, dissolve in non-polar solvents, low m.p. compared w/ other C allotropes.

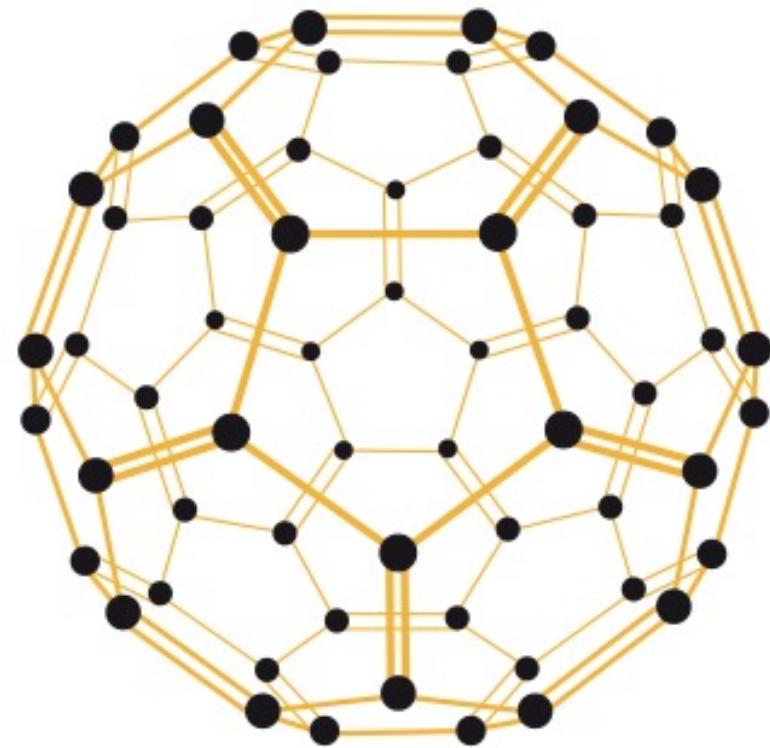
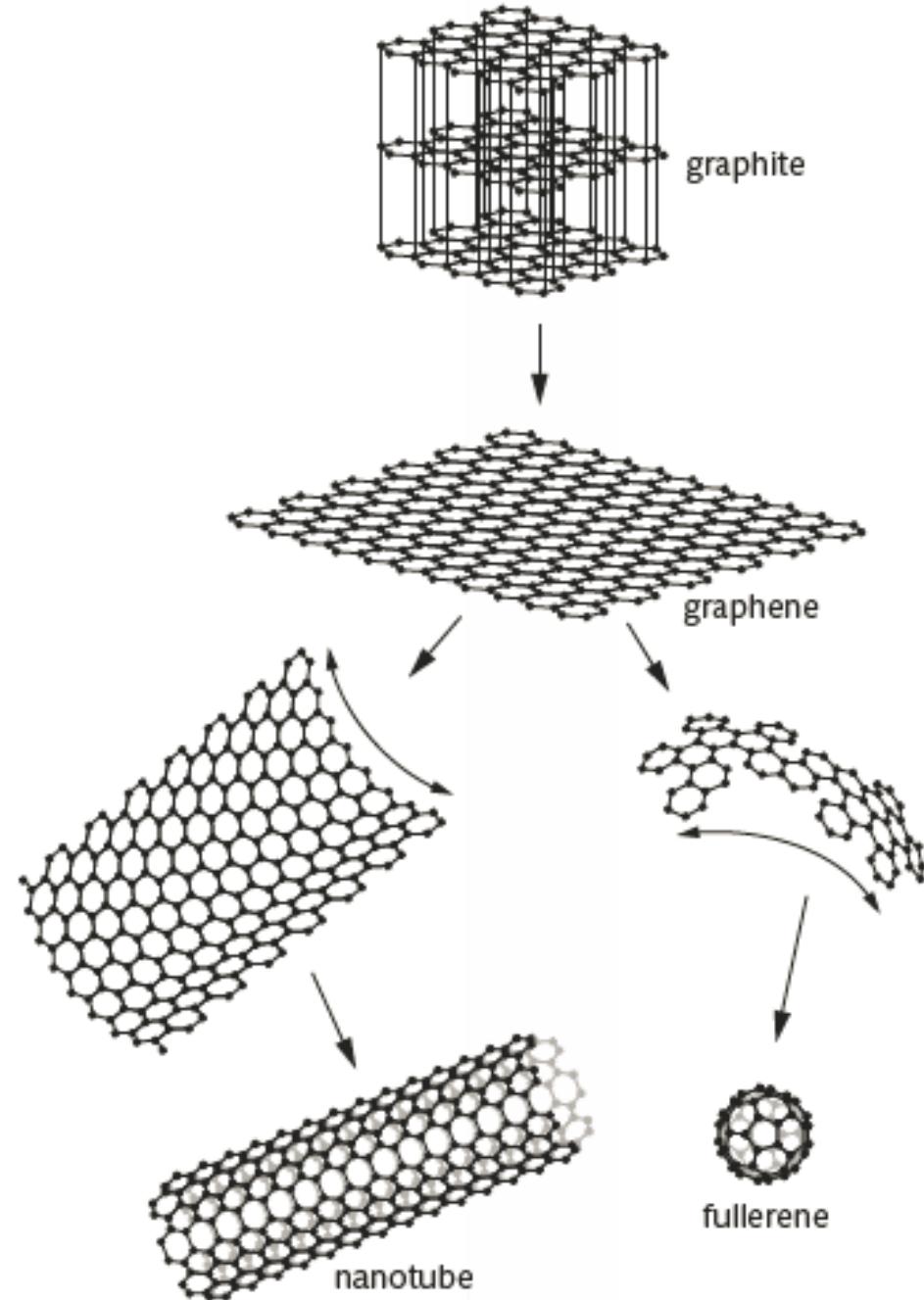


Figure 455 The structure of fullerene-60 (C_{60})

Graphene

Each C atom is covalently bonded to 3 others, as in graphite, forming hexagons with bond angles of 120° . But it is a single layer, so exists as a two-dimensional material only. It is often described as a honeycomb or chicken wire structure.

Very good electrical conductor;
one delocalized electron per atom gives electron mobility across the layers.



Silicon and Silicon dioxide (Silica)

- Giant covalent structure
- Resemble diamond, each Si bond w/ 4 others
- SiO_2 , each Si bond w/ 4 O, each O bond w/ 2 Si.

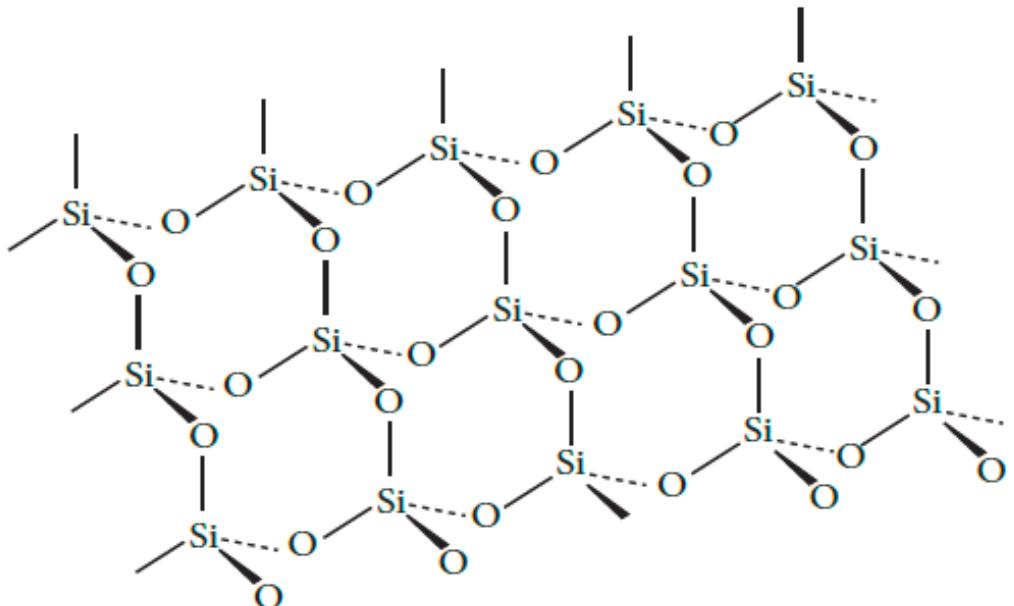
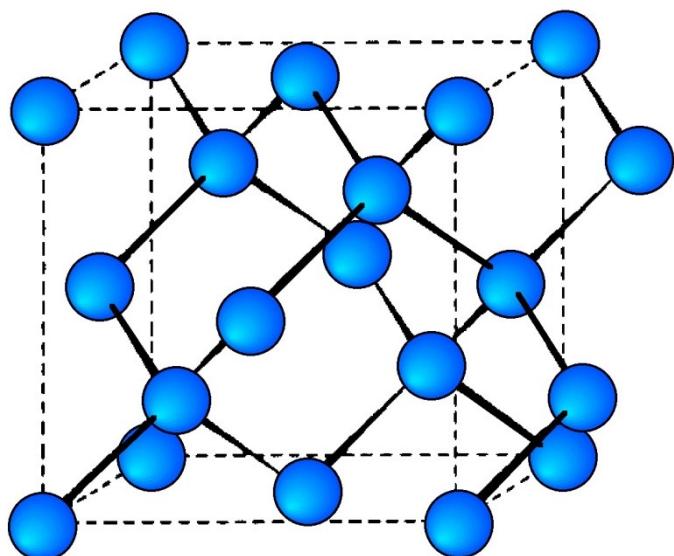


Figure 453 The bonding in silicon dioxide