Chapter 10

Liquids and Solids

Intermolecular Forces

- Occur between (rather than within) molecules
- For any pair of molecules, much weaker than chemical bonding
- We will call them “intermolecular forces” even when they are between atoms, which is the case with noble gas (Group 8A) elements.

Without intermolecular forces everything would be a gas.

There would be no liquids.

There would be no solids.

There would be no evaporation/condensation.

There would be no freezing/melting.

There would be no life.

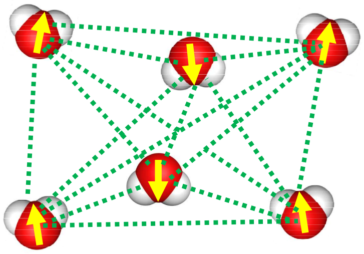
Two general categories of intermolecular forces

1. **Forces created by permanent polarization**
   - Between the molecular dipoles: **dipole-dipole**
   - Between N-H, O-H, F-H bonds and N, O, F atoms in molecules: **hydrogen bonding**
2. **Forces created by temporary polarization**
   - ➢due to fluctuations in electron density: **dispersion (London*) forces**

* Named after Fritz London

Forces created by permanent polarization
Case 1: dipole-dipole forces

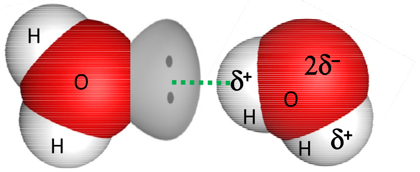
Between the molecular dipoles: dipole ……. dipole



Exists between polar molecules

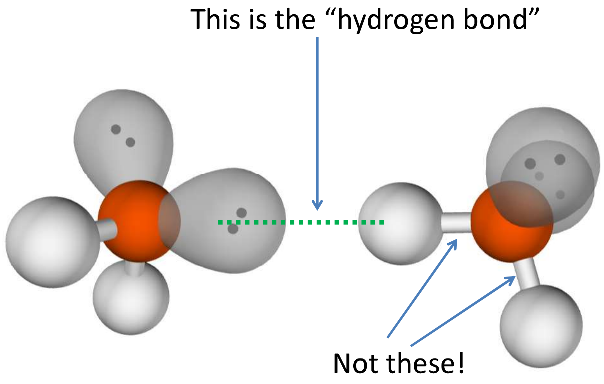
Forces created by permanent polarization
Case 2: “hydrogen bonding” forces

Attraction between the **H** in N-H, O-H, F-H bonds and the **N, O, F atoms in a neighboring molecule**



H is “electron-poor” (δ^+) when bonded to N, O, F

H is attracted to the electron-rich N, O, F on another molecule (especially their lone pair electrons)

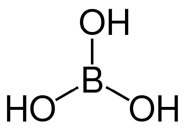


This is the “hydrogen bond”

Not these!

More on Hydrogen Bonding

- It is a strong intermolecular force
- It is an interaction between specific parts of two molecules
- It is not a generic dipole-dipole interaction
- Therefore, it can exist even if the overall molecule is nonpolar
- If we could make a molecule with symmetrically placed bond dipoles that cancel out for the total molecular dipole, it would still have hydrogen bonding interactions with other molecules.
  - And it would be a strong force



Boric acid, H_3BO_3, is a symmetric molecule with a zero dipole moment. **It is nonpolar.**

It has no dipole-dipole forces.

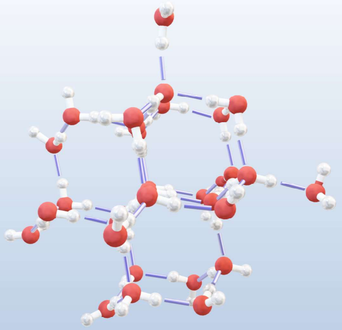
But it has strong hydrogen bonding.

It melts at 171 °C and boils at 300 °C.

- Pretty high for a small, nonpolar molecule.

High melting and boiling point indicates strong intermolecular forces.

- Harder to pull molecules away from one another

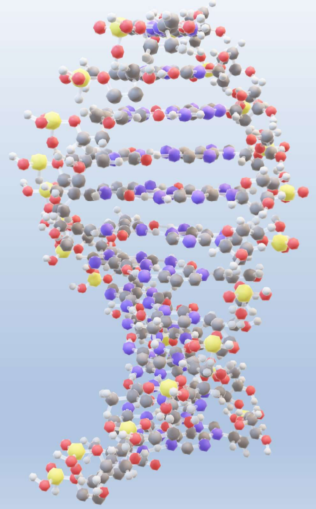


Hydrogen bonds give ice its diamond-like structure.

Its order makes it take up a bit more space than liquid form.

Ice is less dense than liquid water; it floats on water.

If it didn’t, all the lakes and oceans would have frozen solid all the way through, and life as we know it wouldn’t have a chance to evolve!



DNA strands are held in place in a very specific way by hydrogen bonds

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London (dispersion) forces

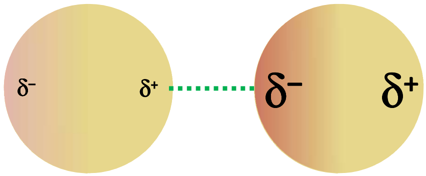
Forces created by temporary polarization due to fluctuations in electron density

All atoms randomly create temporary dipoles (a quantum mechanical effect).

A randomly created dipole on one particle induces a smaller, parallel dipole on nearby particles.

δ^- would push away electrons on other particles, creating a δ^+

Then these dipoles attract, before they pop out of existence.



More on London (dispersion) forces

- All atoms and molecules create this kind of force
  - Because electron clouds always fluctuate
- Dispersion forces exist in all materials
- Dispersion force between any pair of atoms is relatively weak; but can be very strong between molecules with many atoms
- The more electrons there are, the larger the potential fluctuations, and the stronger it gets

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Molar mass and London (dispersion) forces

- An often-used proxy for the number of electrons on an atom or a molecule is the molar mass.
  - Larger molar mass goes with more electrons
- London forces have nothing to do with how heavy a molecule is. As long as we don't let that become a misconception, using molar mass as a quick-and-dirty measure of London forces is acceptable.

Dispersion forces can easily be stronger than dipole-dipole forces, given enough electrons

HCl	**Cl_2**
Polar molecules	Nonpolar molecules
• Dipole-dipole forces	• No dipole-dipole forces
• Dispersion forces (from 1 + 17 = 18 e^-)	• Stronger dispersion forces (from 17 + 17 = 34 e^-)
Boiling point = 188 K	**Boiling point = 238 K**

Stronger intermolecular forces → higher boiling point

But hydrogen-bonding forces are harder to compete with

Example:

Predict which molecule has stronger intermolecular forces, and explain:

N_2 H_2O

- H_2O has hydrogen bonding (in addition to some London dispersion).
- N_2 exhibits London dispersion forces only, and with more electrons than H_2O, they are stronger than for H_2O, but it would take many more electrons to compete with H-bonding between H_2O molecules.

Predict which gas would behave more ideally at the same pressure and temperature, and explain.

HCN or N_2

Both molecules have the same number of electrons.

So their London forces are very similar.

HCN is a polar molecule, so it has dipole-dipole forces.

N_2 is nonpolar (lacks a dipole), so it has no dipole-dipole forces.

Since N_2 has weaker intermolecular forces, it would behave more like an ideal gas.

Vapor pressure decreases with increasing intermolecular forces

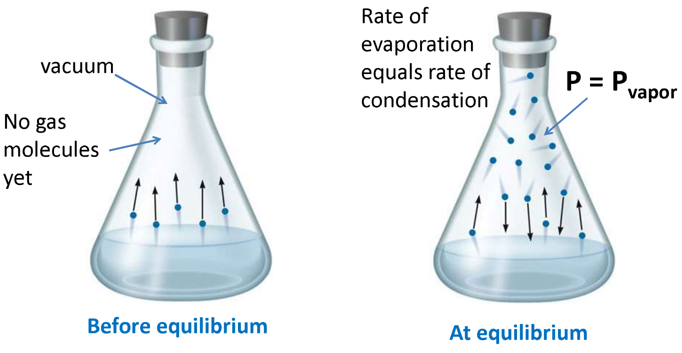
What is "Vapor Pressure"?

At a given temperature, liquid molecules that have enough energy can escape to the gas phase.

At "equilibrium", the gas pressure reaches a maximum.

That is called "vapor pressure".

Phase Transitions – Vapor Pressure


vacuum

No gas molecules yet

Rate of evaporation equals rate of condensation

$P = P_{vapor}$

Before equilibrium

At equilibrium

Phase Transitions – Vapor Pressure

At a high enough temperature vapor pressure equals the atmospheric pressure, bubbles can push against the atmosphere, and the liquid boils

At the "normal" boiling temperature (boiling point):

P_{vapor} = 1 atm

Phase Transitions – Vapor Pressure

If the ambient pressure is lower than 1 atm, P_{vapor} equals it at a lower T, and the liquid boils at lower T than the "normal boiling point".

Phase Transitions – Vapor Pressure

Conversely, in a pressure cooker the pressure is allowed to rise above 1 atm, and the boiling point is therefore higher. The constant temperature of boiling is higher than normal.

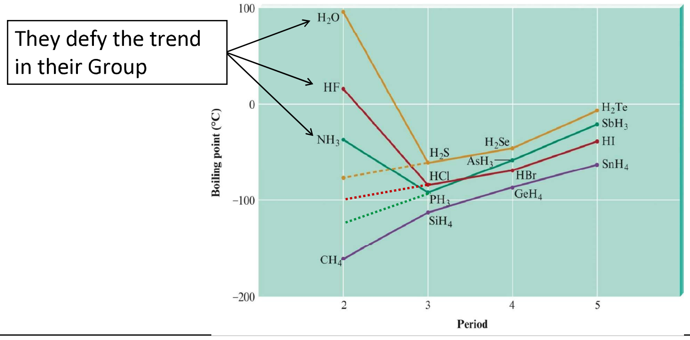
To attain a vapor pressure of 2 atm, water needs to be at 120.°C

Measures of Intermolecular forces

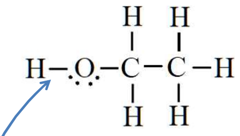
Normal boiling point is a good measure of intermolecular forces

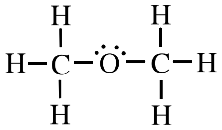
For example: Shows when hydrogen bonding happens

Hydrogen compounds of **F**, **O**, and **N** have abnormally high boiling points due to their hydrogen bonding


They defy the trend in their Group

Draw two Lewis structures for the formula C_2H_6O and compare the boiling points of the two molecules.





Has hydrogen bonding

<u>Has higher boiling point</u>

Has dipole-dipole but not hydrogen bonding

Both have the same atoms, so their London dispersion forces are very similar.

So, the one with hydrogen bonding must have a higher boiling point.

Some other properties that get larger with stronger intermolecular forces:

- Enthalpy of vaporization
  - Energy required to vaporize molecules into gas phase
- Melting point
  - Less reliable; molecules with unwieldy shapes don't fit into a crystal lattice and have lower melting points
- Surface tension
  - How hard it is to create more liquid surface
- Viscosity
  - Resistance to flow

Boiling & melting are "phase transitions"

- We have a specific melting point or a boiling point for a specific, pure substance because the "phase transition" (melting or boiling) occurs at a certain temperature.
- Temperature stays constant while we have two phases coexisting during melting or boiling.
- As we provide more and more heat during melting or boiling, the energy goes only towards melting and boiling
- The temperature does not increase
- $\Delta T = 0$ and we cannot use $q = m\,s\,\Delta T$

Energetically, we treat a phase change as a "transformation" like a chemical reaction

$H_2O(s) \rightarrow H_2O(l)$ $\Delta H = \Delta H_{fusion}(H_2O)$ fusion = melting

$H_2O(l) \rightarrow H_2O(g)$ $\Delta H = \Delta H_{vap}(H_2O)$

ΔH_{fusion} : "Heat of fusion"

ΔH_{vap} : "Heat of vaporization"

We can apply the same stoichiometric methods as we did in calculating heats of reaction in thermochemistry.

Example

How much heat is needed to melt 10.0 g of ice at 0°C?

$\Delta H_{fusion}(H_2O) = 335$ J/g

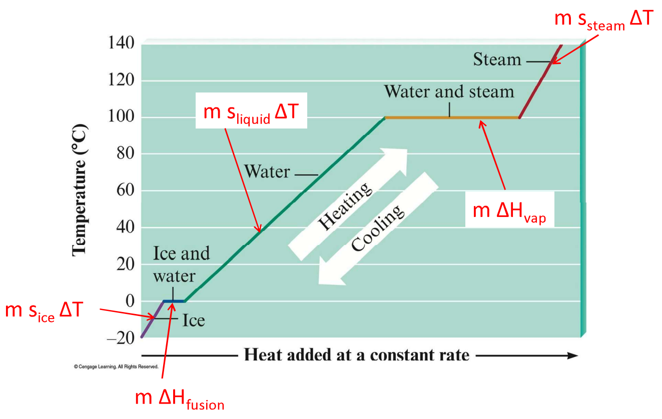
Note that the melting phase transition happens (dictated by nature) at constant temperature.

There is no T change, and $q = m\,s\,\Delta T$ is useless here.

Instead:

$q = m\,\Delta H_{fusion} = (10.0\text{ g})(335\text{ J/g}) = 33\underline{5}0\text{ J}$

Heating Curve for Water



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Example

How much heat is needed to turn 10.0 g of ice at -5.0°C into steam at 110.°C?

s_{ice}=2.04 J/(g °C) s_{water}=4.18 J/(g °C) s_{steam}=2.01 J/(g °C)

$\Delta H_{fusion}(H_2O)$ = 335 J/g $\Delta H_{vap.}(H_2O)$ = 2257 J/g

To warm the ice from -5.0°C to 0°C (melting point):

$q_1 = m\,s_{ice}\,\Delta T_1 = (10.0\text{ g})[2.04\text{ J/(g °C)}](0-(-5.00)) = 1\underline{0}2\text{ J}$

To melt the ice:

$q_2 = m\,\Delta H_{fusion} = (10.0\text{ g})(335\text{ J/g}) = 33\underline{5}0\text{ J}$

To warm the liquid water from 0°C to 100°C (melting point):

$q_3 = m\,s_{water}\,\Delta T_3 = (10.0\text{ g})[4.18\text{ J/(g °C)}](100-0)=41\underline{8}0\text{ J}$

To evaporate the water into steam:

$q_4 = m\,\Delta H_{vap.} = (10.0\text{ g})(2257\text{ J/g}) = 22\underline{5}70\text{ J}$

To warm the steam from 100°C to 110.°C (boiling point):

$q_5 = m\,s_{steam}\,\Delta T_5 = (10.0\text{ g})[4.18\text{ J/(g °C)}](110.-100) = 41\underline{8}\text{ J}$

$\mathbf{q_{total}} = q_1 + q_2 + q_3 + q_4 + q_5 = 102+3350+4180+22570+418 = 30\underline{6}20\text{ J}$

Surface tension increases with increasing intermolecular forces

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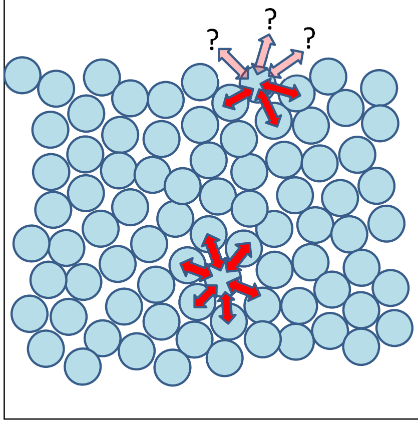
Surface Tension

Molecules at the surface have fewer neighbors to stabilize them (so they are at higher energy)



To minimize the number of molecules with missing neighbors, the "surface tension" force minimizes the surface area of the liquid.

Water droplet in the space station

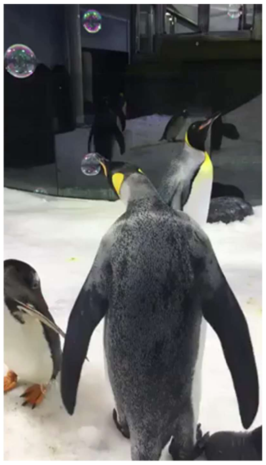
A sphere has the minimum area for a given volume

Surface tension favors a spherical shape

If there are no other forces, droplets are spherical

Bubbles also tend to be spherical unless distorted by other forces (like gravity)

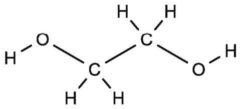
For the same reason.



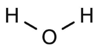
Viscosity increases with increasing intermolecular forces

Example:
Stronger intermolecular forces make glycol more viscous than water

Glycol



Water



	Glycol		Water
Boiling point:	197°C	>	100°C
Viscosity:	0.0161 Pa·s	>	0.0091 Pa·s

Why does glycol have stronger intermolecular forces?

Competition between intermolecular forces within or between different substances determine interesting and technologically important properties and behaviors

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Competition between cohesive forces and adhesive forces determine:

Wetting of Surfaces and Capillary Action

Cohesive forces:

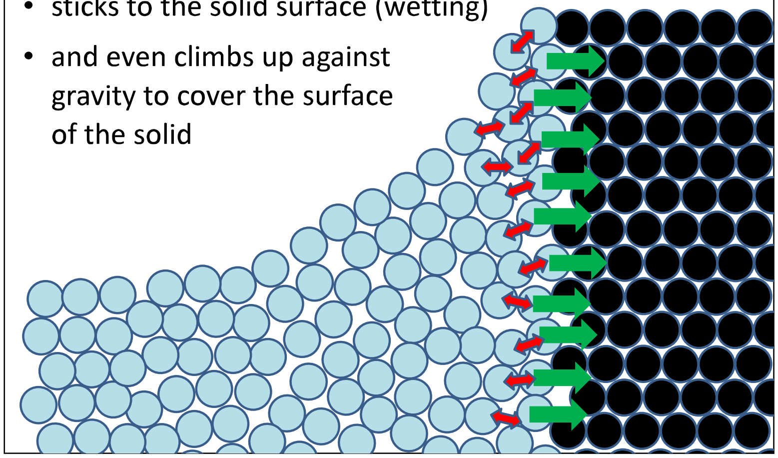
Intermolecular attraction among the molecules of the liquid.

Adhesive forces:

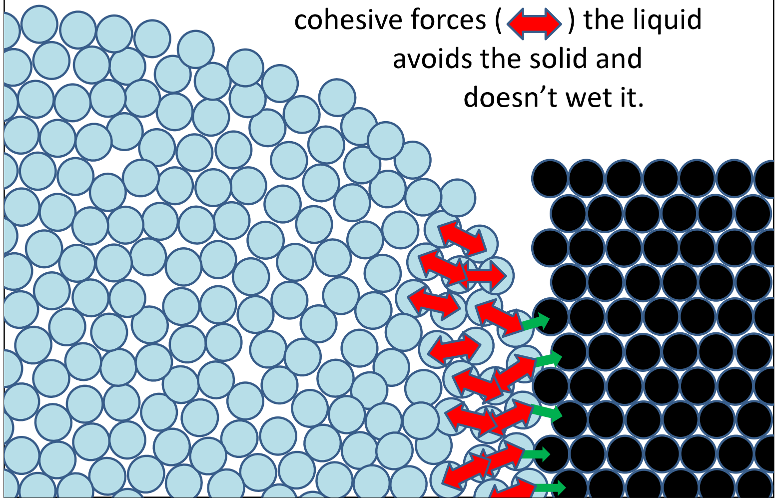
Attraction between the liquid molecules and a solid surface.

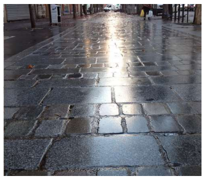
When adhesive forces (➡) are stronger than cohesive forces (↔), the liquid

- sticks to the solid surface (wetting)
- and even climbs up against gravity to cover the surface of the solid



When adhesive forces (➡) are weaker than cohesive forces (↔) the liquid avoids the solid and doesn't wet it.





Almost no wetting

Complete wetting

Water forms a **concave** “meniscus” with glass

Polar water molecules are attracted more strongly to the highly charged atoms on the glass surface than to each other

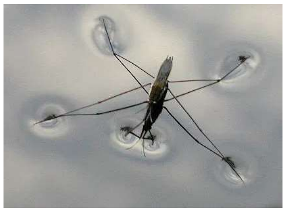
adhesive > cohesive

Mercury forms a **convex** “meniscus” with glass

Atoms in liquid mercury don’t have partial charges that attract to the charges on glass surface.

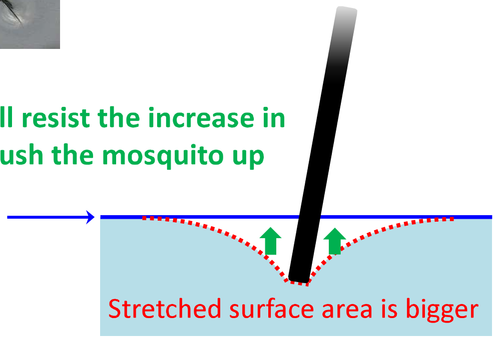
But the Hg metal atoms do have strong attraction to the bulk of the metal.

cohesive > adhesive



A mosquito can stand on water because of surface tension, <u>**and**</u> because its feet don’t get wet!

Surface tension will resist the increase in surface area and push the mosquito up



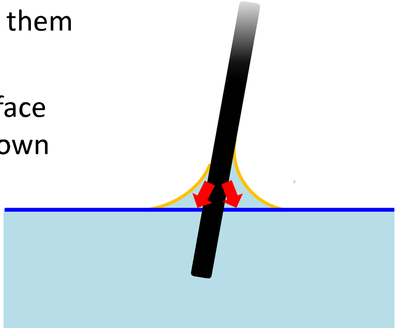
Undisturbed surface area is smallest

Stretched surface area is bigger

The feet need to repel water and stay dry

Surface tension won’t be able to support the mosquito if water climbs up its feet and pulls them towards itself!

Actually with wet feet, surface tension would pull them down to minimize surface!



Intermolecular forces also affect whether two substances will be soluble in one another

If there were no intermolecular forces, everything would freely dissolve in everything else.

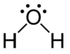
If dissolution of two substances would disrupt the intermolecular forces, their energy would go up.

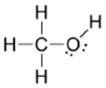
- Dissolving unfavorable; little solubility

If the two substances have intermolecular forces similar in nature, they tend to be “miscible”

- they dissolve in each other in a wide range of ratios

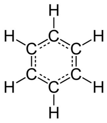
“like dissolves like”





H_2O and CH_3OH both have dipole-dipole and hydrogen bonding interactions

- Miscible (can dissolve in all proportions)



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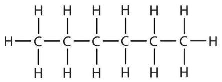
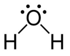
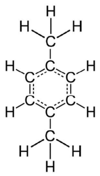


both have basically only London dispersion forces

- Miscible (can dissolve in all proportions)



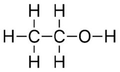
H_2O has strong hydrogen bonding and significant dipole-dipole forces, but very little dispersion



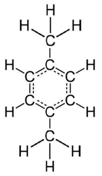
para-Xylene has strong London dispersion forces (actually a bit stronger than the forces between H_2O molecules), but no other forces

Water and para-Xylene are **insoluble in each other**

Dissolution is especially bad for water:
H-bonding and dipole-dipole interactions would be lost, and it simply doesn’t have enough electrons to have strong London-dispersion forces to replace what’s lost.



Ethanol has hydrogen bonding, dipole-dipole (it is asymmetric, therefore polar) and significant dispersion forces.



para-Xylene has strong London dispersion forces, and no other forces

Ethanol and para-Xylene are **miscible**

Since ethanol has a strong component of dispersion forces between its molecules, it is compatible enough with a substance that has only dispersion forces.

Ethanol can be seen as a more versatile solvent than water.

A survey of solids

Solids

Crystalline
- An orderly lattice of repeating structure
- Lattice positions can correspond to atoms, ions, or molecules
- Most solids, including metals

Amorphous
- Also called “glass”
- Disordered
- Atomic picture looks like a snapshot of a liquid
- Glass, ceramics

Crystalline Solids

Atomic
Lattice points are occupied by **atoms**

e.g. Metals, frozen noble gases, covalent compounds that are not molecular solids like SiO_2

Molecular
Lattice points are occupied by **molecules**

e.g. Molecular solids such as H_2O, CO_2, sugar

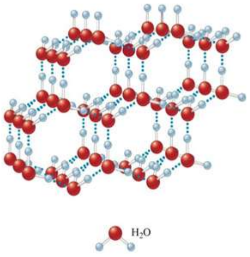
Ionic
Lattice points are occupied by **ions**

e.g. ionic solids such as NaCl, $CaCO_3$, NaOH

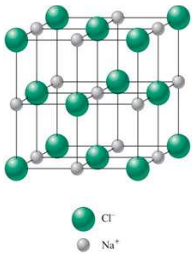
Crystalline Solids Examples

Atomic

Molecular



Ionic



Atomic Solids

Metallic

Metal atoms at lattice points

Held together by “**metallic bonding**” (a kind of non-directional, delocalized bonding)

Network

Atoms at lattice points

Held together by normal, directional **covalent bonds**

Frozen noble gas

Noble gas atoms at lattice points

Held together by **London dispersion forces**

What holds metals together?

Remember those “loose” valence electrons of metals?

Valence electrons of metals have relatively high energy.

Also remember that overlapping valence orbitals create lower-energy and higher-energy molecular orbitals (MO).

In metals, further overlap of two-atom MOs create multi-atom MOs and so on in a cascade, creating a huge number of MOs that span the entire solid, at a lower energy than atomic orbitals.

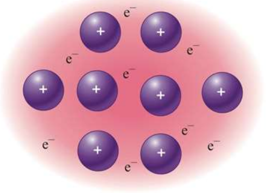
The valence electrons of metals exist in those huge MOs that cover the entire volume of the metal sample.

They are free to move in these MOs.

The result is a “**see of electrons**”:

A negatively charged glue in which the metal ions are suspended as a regular lattice

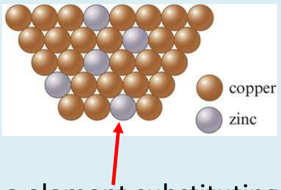
But don’t mistake it for ionic bonding.
It __is__ covalent



Metal alloys

Substitutional

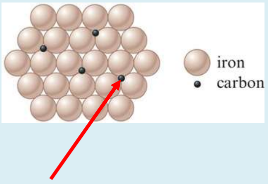
Brass



One element substituting for another one in the crystal lattice

Interstitial

Steele



Atoms of one element fitting into the spaces (interstices) between metal atoms in the crystal lattice

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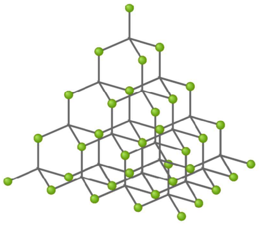
Network Solids

The “network” means a **network of covalent bonds** that make up the entire crystal.

The entire crystal is a giant molecule!

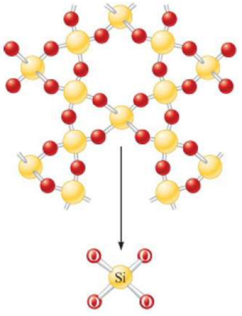


Diamond is a tetrahedral network of carbon atoms

A silicon crystal looks the same

Network atomic solids are not necessarily made up of a single element.

Lattice positions can be occupied by different atoms (i.e. it can be a compound).



For example:

SiO_2 (quartz) is composed of SiO_4 tetrahedra forming a covalent network

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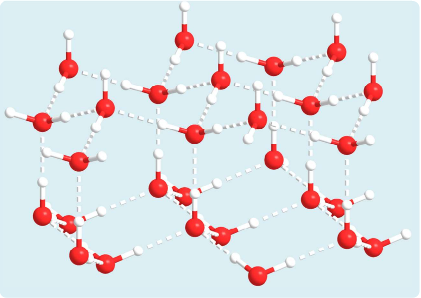
Molecular Crystals

Water ice is a molecular crystal where the lattice sites are occupied by whole molecules rather than single atoms



Also happens to be a tetrahedral arrangement.

But of molecules, not atoms

Most molecular substances can be crystallized

Sugar

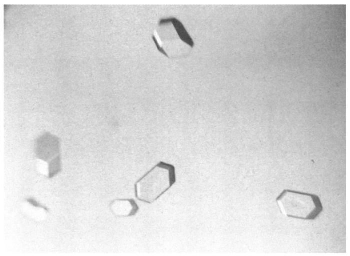
Caffeine

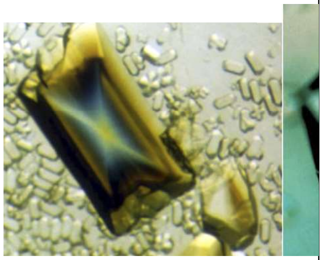
Naphthalene (mothball)

Even viruses!

They are well-defined complexes of molecules
(“supramolecular assembly”)

Crystals of Rhinovirus 14
(common cold)





Crystals of
tobacco mosaic virus

Properties of different types of solids

Metals are electrical conductors.

Metals have a wide range of hardness.

Metals have a wide range of melting points.

Nonmetallic solids in general are electrical insulators.

Network solids are hard, and have high melting points.

Ionic solids with simple, small ions have relatively high melting points, and are hard (but brittle.)

Molecular solids have relatively low melting points, and are soft.