

Chapter 12

Intermolecular Forces: 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

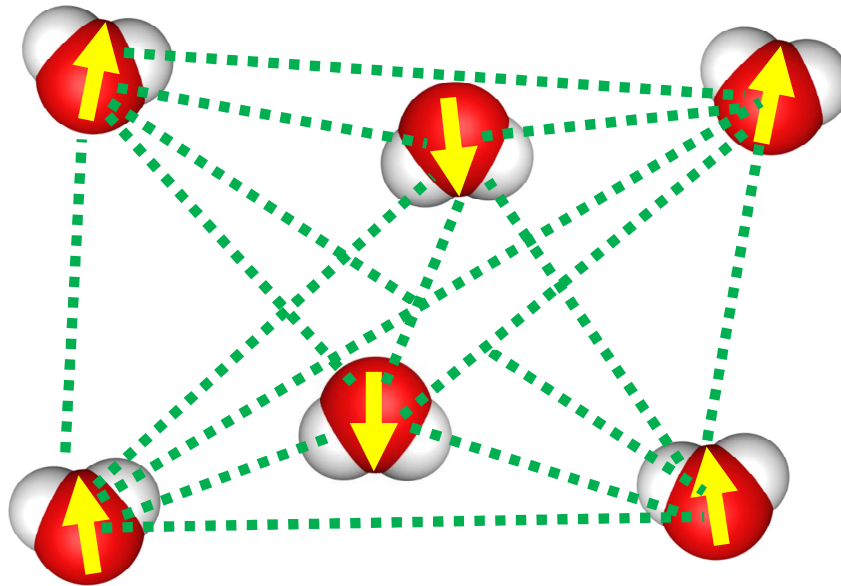
- due to fluctuations in electron density:
dispersion (London*) forces

* Named after Fritz London (and not the City 😊)

Forces created by permanent polarization

Case 1: dipole-dipole forces

Between the molecular dipoles: **dipole** **dipole**

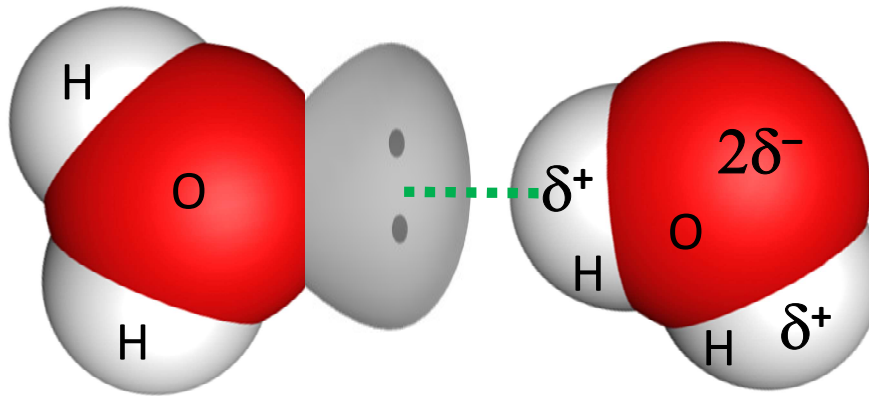


Exists between polar molecules

Forces created by permanent polarization

Case 2: “hydrogen bonding” forces

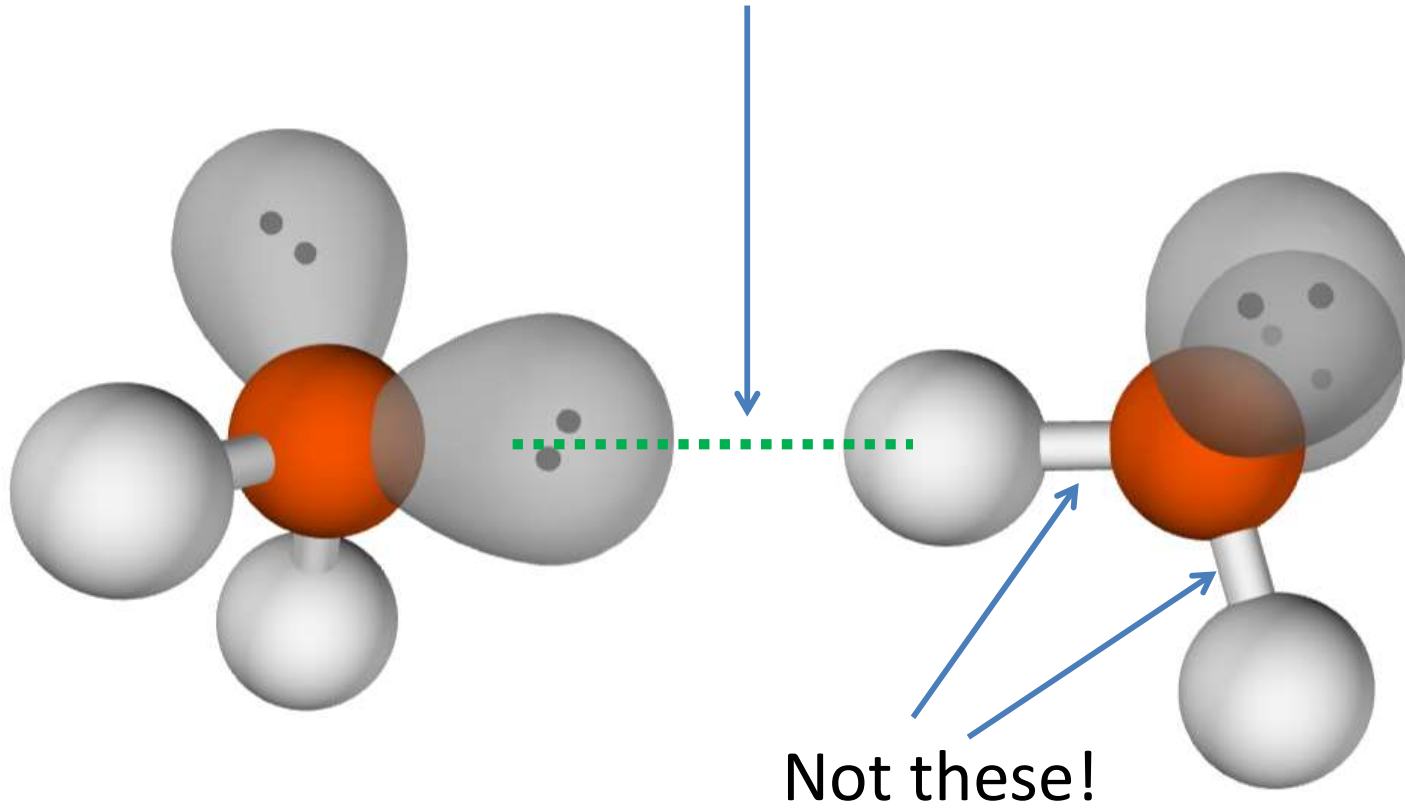
Attraction between the **H** in N-H, O-H, F-H bonds and the **N, O, F** atoms in a neighboring molecule



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

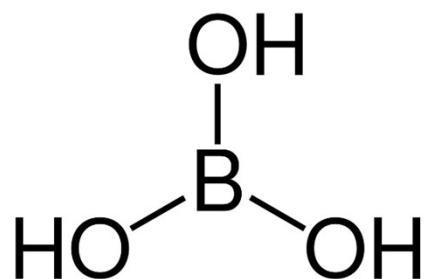
H is attracted to the electron-rich N, O, F on another molecule (especially their lone pair electrons)

This is the “hydrogen bond”



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.

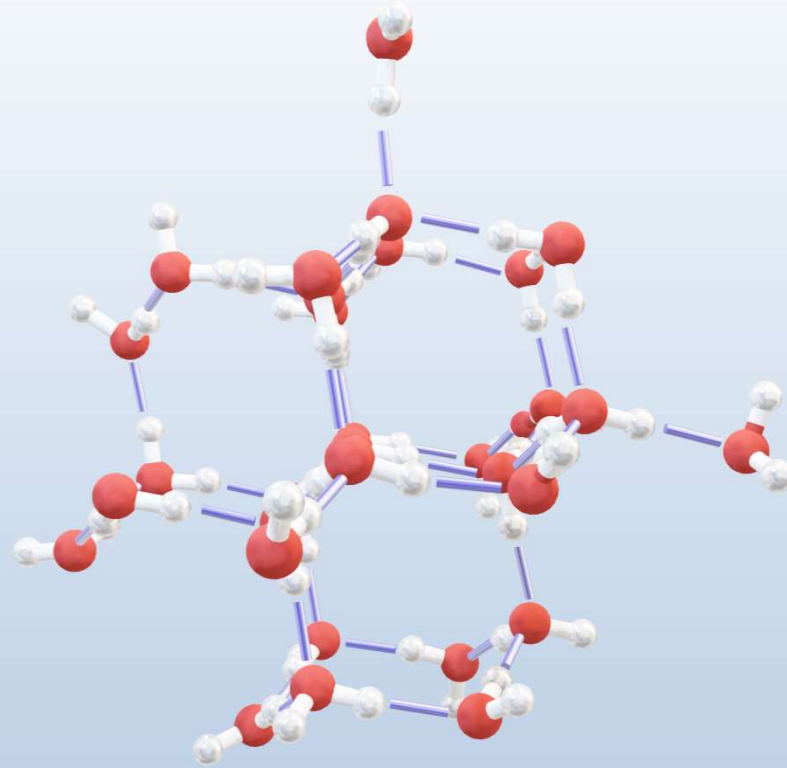
But it has strong hydrogen bonding.

It melts at $171\text{ }^\circ\text{C}$ and boils at $300\text{ }^\circ\text{C}$.

- Pretty high for a small, nonpolar molecule.

High melting and boiling point indicates strong intermolecular forces.

- Harder to pull molecules away from one another

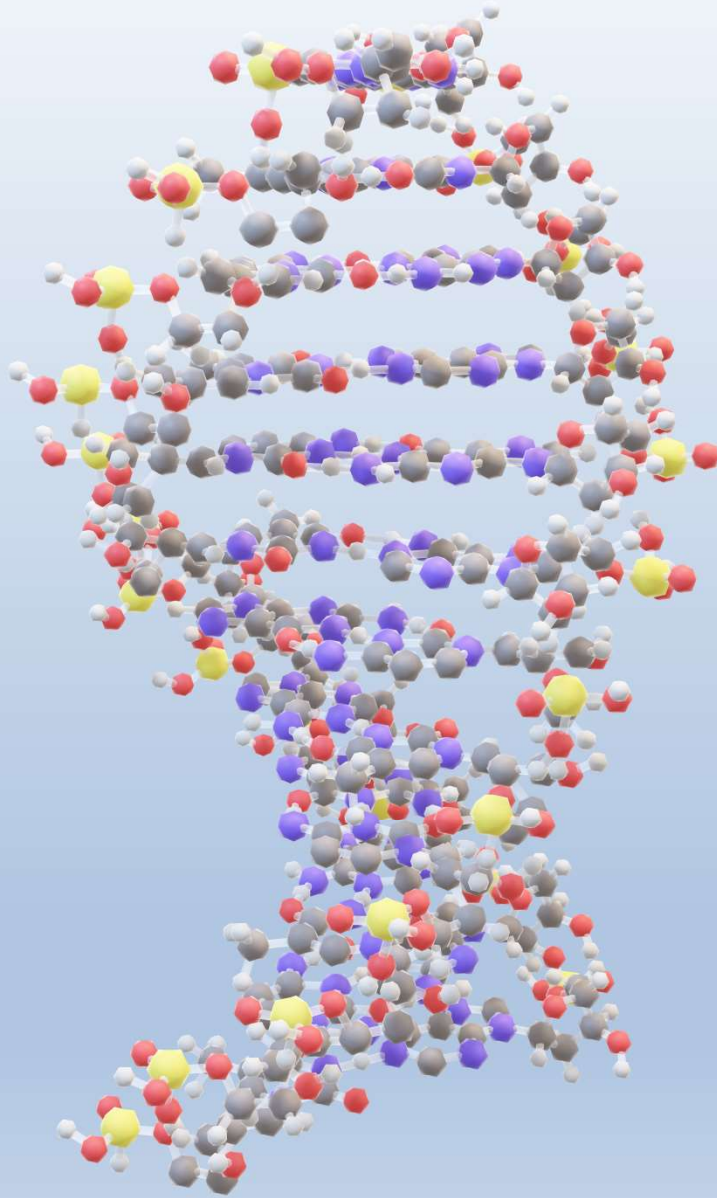


Hydrogen bonds give ice its diamond-like structure.

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 during extreme ice ages (there were a few), 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

London (dispersion) forces

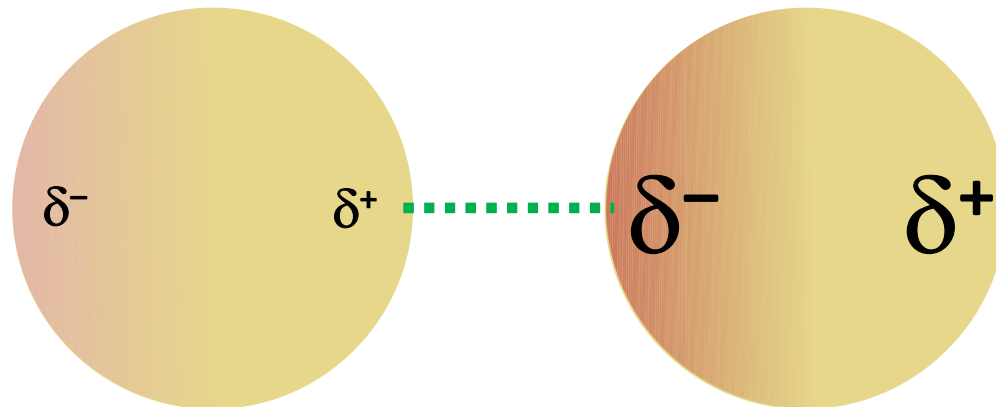
Forces created by temporary polarization due to fluctuations in electron density

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 weak
 - but can be very strong between molecules with many atoms
- The more “polarizable” the atoms, the stronger it gets
- Polarizability goes hand in hand with atomic volume
- Atomic volume is roughly proportional to no. of electrons
- No. of electrons is roughly proportional to molecular mass

Molar mass and London (dispersion) forces

- So, an often-used proxy for the strength of London dispersion forces is molar mass
- But remember:
London dispersion 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 an approximate measure of London forces is ok.
- Summing up atomic numbers is equally easy, and is a better approximation of polarizability, so we will do that here.

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

HCl

Polar molecules

- Dipole-dipole forces
- Dispersion forces
(from $1 + 17 = 18 e^-$)

Boiling point = 188 K

Cl₂

Nonpolar molecules

- No dipole-dipole forces
- Stronger dispersion forces
(from $17 + 17 = 34 e^-$)

Boiling point = 238 K

Stronger intermolecular forces → higher boiling point

But hydrogen-bonding forces are harder to compete with

Example:

Which molecule has stronger intermolecular forces; explain.



- 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.

Which gas would behave more ideally at the same pressure and temperature? Explain.

HCN or N₂

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.

N₂ is nonpolar (lacks a dipole), so it has no dipole-dipole forces.

Since N₂ has weaker intermolecular forces, it would behave more like an ideal gas.

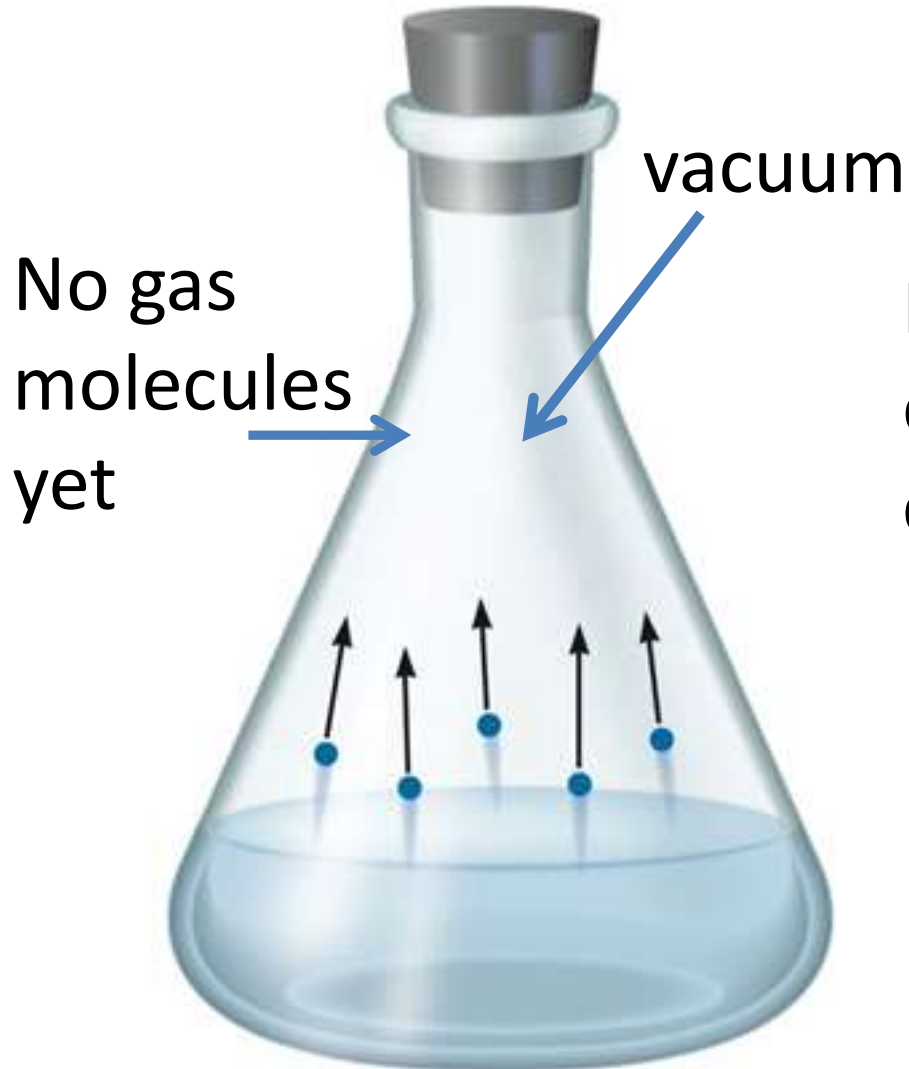
Vapor pressure decreases with increasing intermolecular forces

What is “Vapor Pressure”?

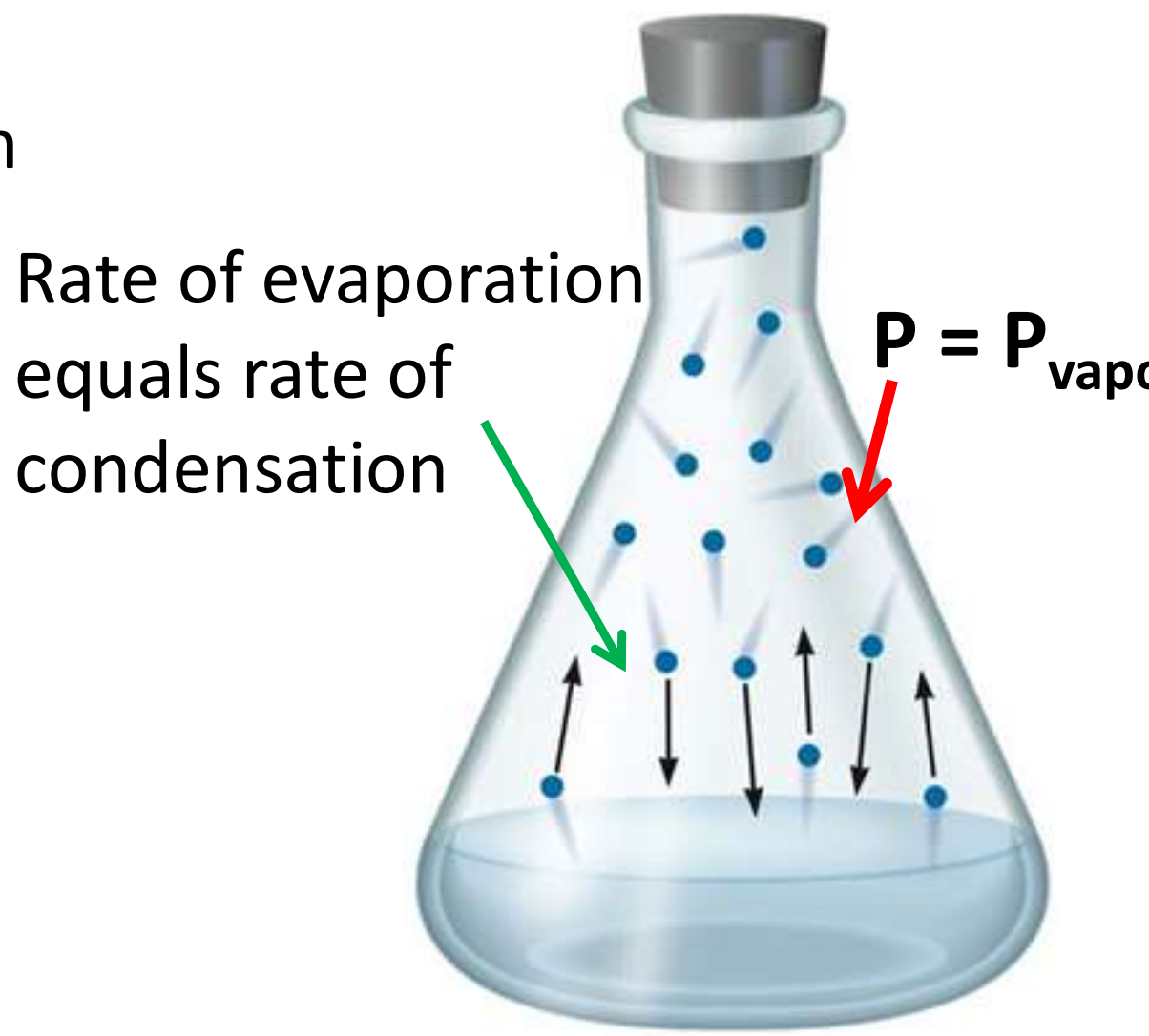
At a given temperature, liquid molecules that have enough energy can escape to the gas phase.

At “equilibrium”, the gas pressure reaches a maximum.

That is called “vapor pressure”.



Before equilibrium



At equilibrium

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):

$$P_{\text{vapor}} = 1 \text{ atm}$$

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”.



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.

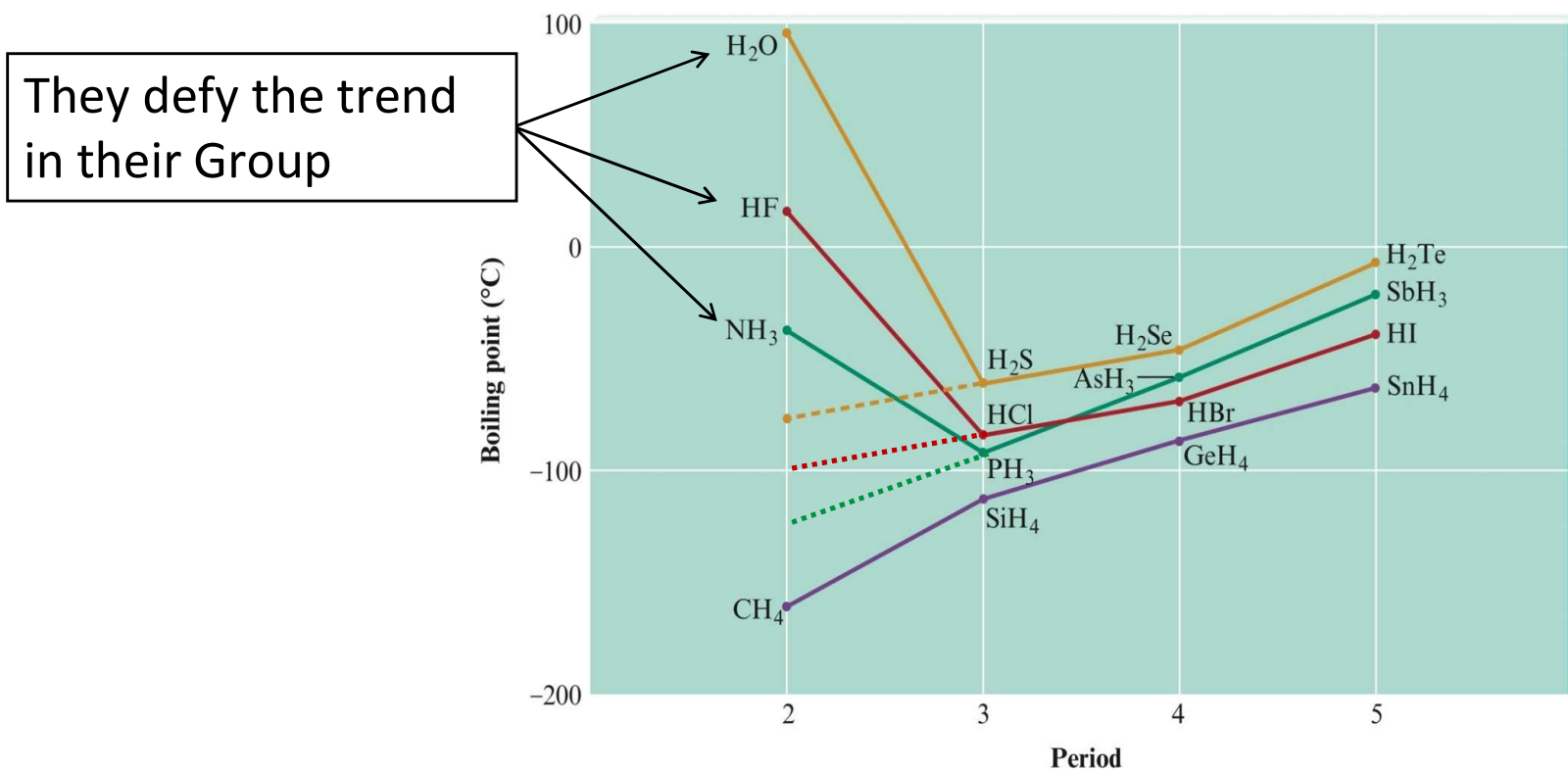
To attain a vapor pressure of 2 atm, water needs to be at 120.°C



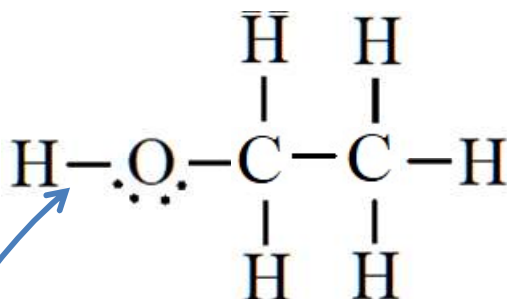
Normal boiling point is a good measure of intermolecular forces

For example: Shows when hydrogen bonding happens

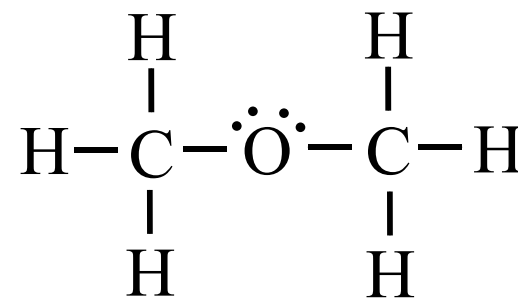
Hydrogen compounds of **F**, **O**, and **N** have abnormally high boiling points due to their hydrogen bonding



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



Has hydrogen bonding
Has higher boiling point



Has dipole-dipole but
not hydrogen bonding

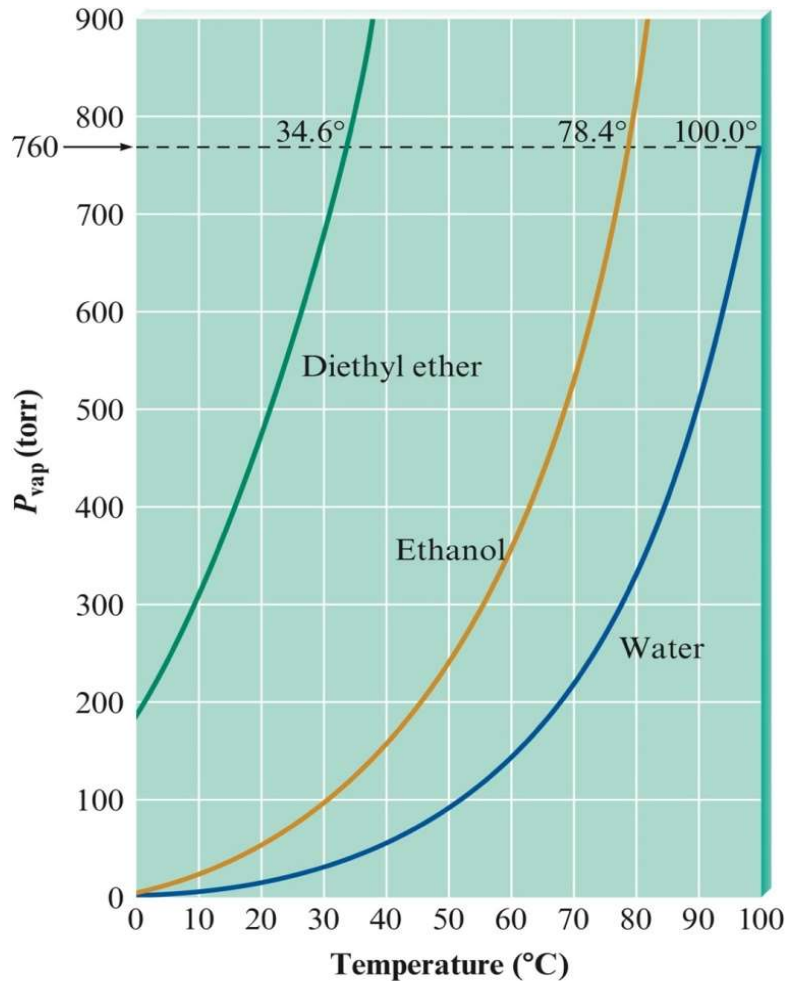
Both have the same atoms, so their London dispersion forces are very similar.

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

Vapor Pressure vs. Temperature



It has an exponential form:

$$P = Ae^{(-\Delta H_{\text{vap}}/RT)}$$

(Clausius–Clapeyron Equation)

Which can be cast in a “linear” form:

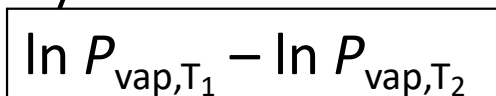
$$\boxed{\ln P} = \ln A - \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T} \right)$$

Annotations for the linear form equation:

- $\ln P$ is the **y**-axis.
- $\ln A$ is the **intercept**.
- $-\frac{\Delta H_{\text{vap}}}{R}$ is the **slope**.
- $\frac{1}{T}$ is the **x**-axis.

Clausius–Clapeyron Equation

$$\ln\left(\frac{P_{\text{vap},T_1}}{P_{\text{vap},T_2}}\right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$


$$\ln P_{\text{vap},T_1} - \ln P_{\text{vap},T_2}$$

P_{vap} = vapor pressure

ΔH_{vap} = enthalpy of vaporization

$R = 8.3145 \text{ J/K}\cdot\text{mol}$

T = temperature (in kelvin)

If you know:

- Enthalpy of vaporization ΔH_{vap}
- Vapor pressure at one temperature
- ➔ ***You can find vapor pressure at any other temperature***
- ➔ ***You can find the boiling point for a given pressure***

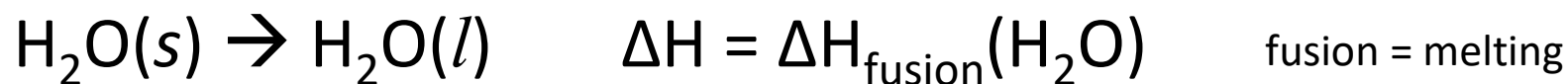
The vapor pressure of water at 25°C is 23.8 torr, and the heat of vaporization of water at 25°C is 43.9 kJ/mol. Calculate the vapor pressure of water at 65°C .

194 torr

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



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?

$$\Delta H_{\text{fusion}}(\text{H}_2\text{O}) = 335 \text{ J/g}$$

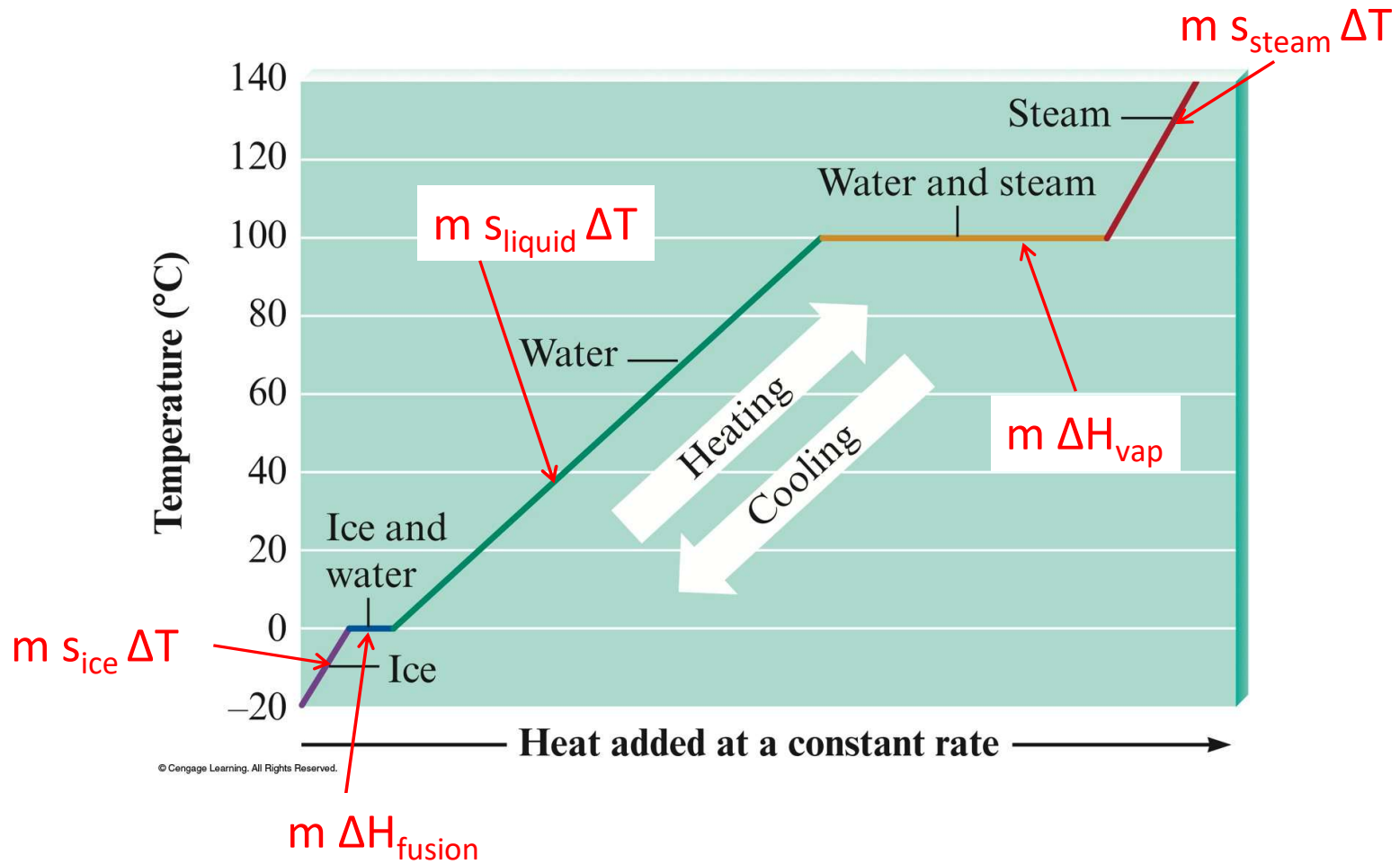
Note that the melting phase transition happens (dictated by nature) at constant temperature.

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

Instead:

$$q = m \Delta H_{\text{fusion}} = (10.0 \text{ g})(335 \text{ J/g}) = 3350 \text{ J}$$

Heating Curve for Water



Example

How much heat is needed to turn 10.0 g of ice at -5.0°C into steam at $110.^{\circ}\text{C}$?

$$s_{\text{ice}} = 2.04 \text{ J}/(\text{g } ^{\circ}\text{C}) \quad s_{\text{water}} = 4.18 \text{ J}/(\text{g } ^{\circ}\text{C}) \quad s_{\text{steam}} = 2.01 \text{ J}/(\text{g } ^{\circ}\text{C})$$

$$\Delta H_{\text{fusion}}(\text{H}_2\text{O}) = 335 \text{ J/g} \quad \Delta H_{\text{vap.}}(\text{H}_2\text{O}) = 2257 \text{ J/g}$$

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

$$q_1 = m s_{\text{ice}} \Delta T_1 = (10.0 \text{ g})[2.04 \text{ J}/(\text{g } ^{\circ}\text{C})](0 - (-5.00)) = \underline{102 \text{ J}}$$

To melt the ice:

$$q_2 = m \Delta H_{\text{fusion}} = (10.0 \text{ g})(335 \text{ J/g}) = \underline{3350 \text{ J}}$$

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

$$q_3 = m s_{\text{water}} \Delta T_3 = (10.0 \text{ g})[4.18 \text{ J}/(\text{g } ^{\circ}\text{C})](100 - 0) = \underline{4180 \text{ J}}$$

To evaporate the water into steam:

$$q_4 = m \Delta H_{\text{vap.}} = (10.0 \text{ g})(2257 \text{ J/g}) = \underline{22570 \text{ J}}$$

To warm the steam from 100°C to $110.^{\circ}\text{C}$ (boiling point):

$$q_5 = m s_{\text{steam}} \Delta T_5 = (10.0 \text{ g})[2.01 \text{ J}/(\text{g } ^{\circ}\text{C})](110. - 100) = \underline{418 \text{ J}}$$

$$q_{\text{total}} = q_1 + q_2 + q_3 + q_4 + q_5 = 102 + 3350 + 4180 + 22570 + 418 = \underline{30620 \text{ J}}$$

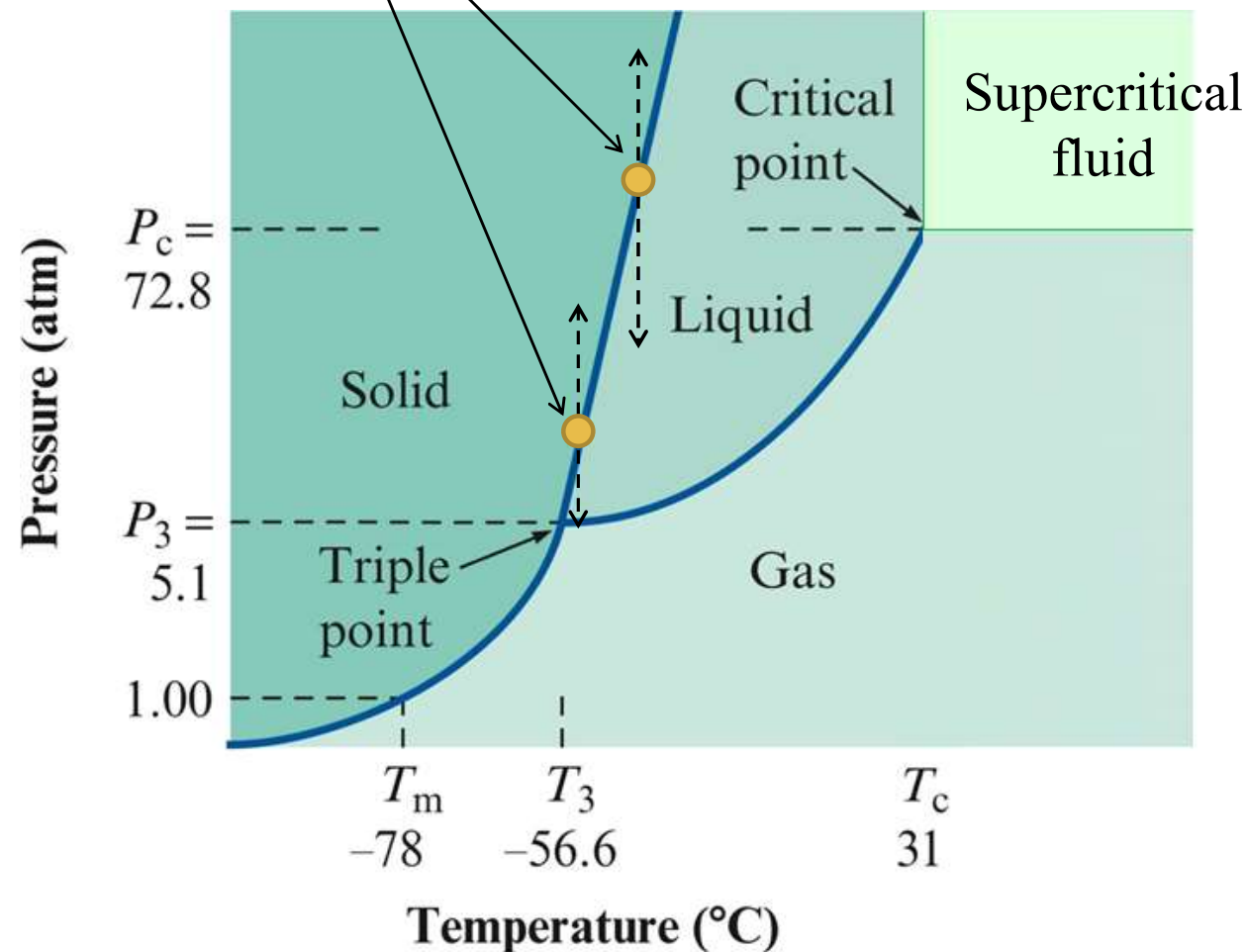
Phase Diagram

A convenient way of representing the phases of a substance as a function of temperature and pressure:

- Triple point
- Critical point
- Phase equilibrium lines

Phase Diagram for Carbon Dioxide

When $d_{\text{liquid}} < d_{\text{solid}}$
Melting T goes up with P



For $T > T_c$ & $P > P_c$

- No gas-liquid phase transition
- “Supercritical fluid” (neither gas nor liquid)

At Triple Point:

- Solid, liquid, and gas are at equilibrium
- Solid and liquid have the same vapor pressure

Water is an unusual substance in many ways.

Liquid phase being denser than solid is yet another way in which it's "strange"

State	Density (g/cm ³)
Solid (0°C, 1 atm)	0.9168
Liquid (25°C, 1 atm)	0.9971
Gas (400°C, 1 atm)	3.26×10^{-4}

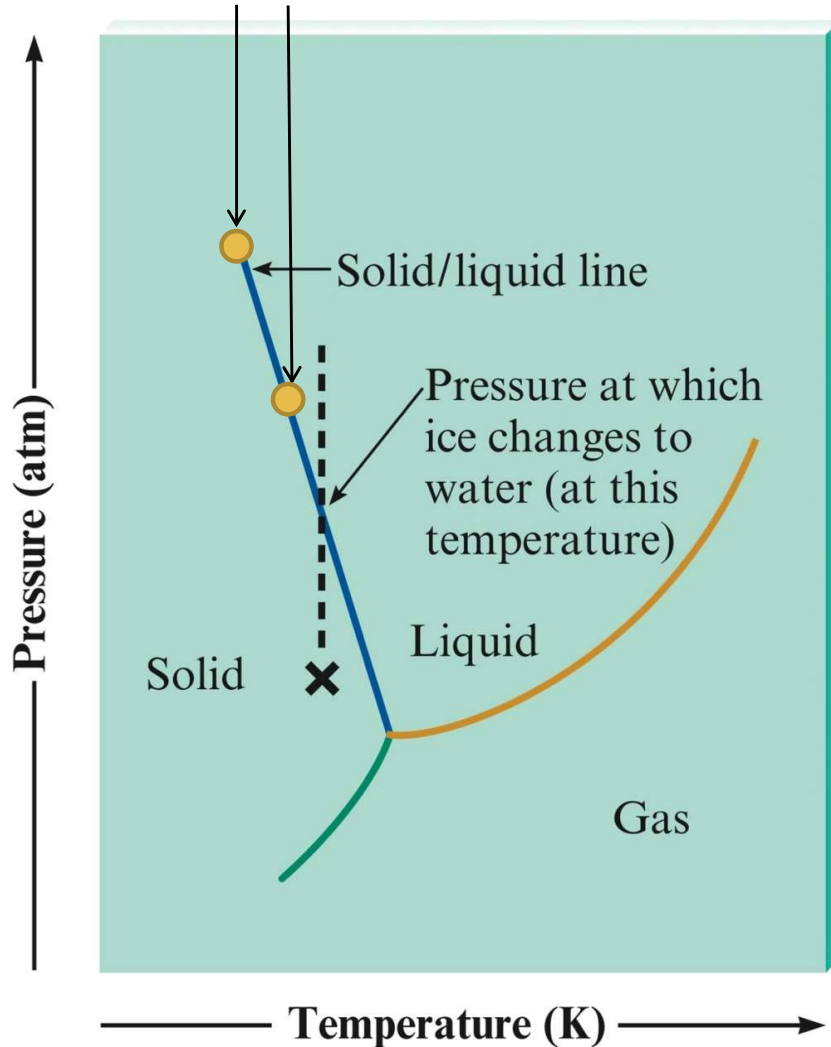
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It has consequences

Phase Diagram for Water

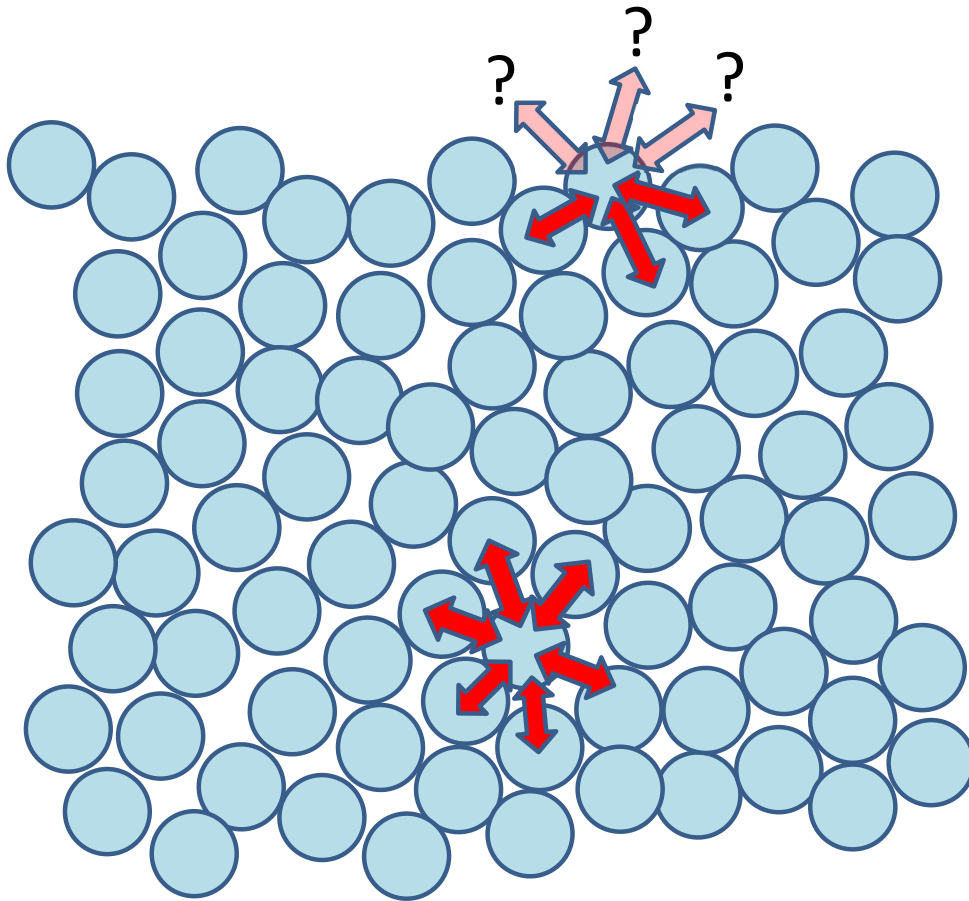
When $d_{\text{liquid}} > d_{\text{solid}}$

→ Melting T goes down with P



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

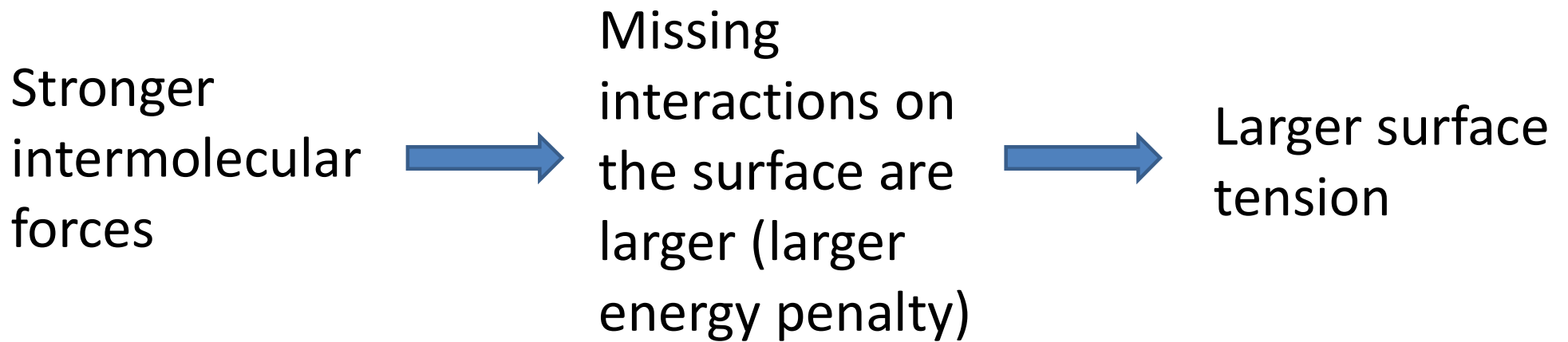
If there are no other forces, droplets are spherical

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

For the same reason.



Surface tension increases with increasing intermolecular forces



Viscosity increases with increasing intermolecular forces

Stronger
intermolecular
forces



More difficult for
molecules to slide past
one another



Higher
viscosity

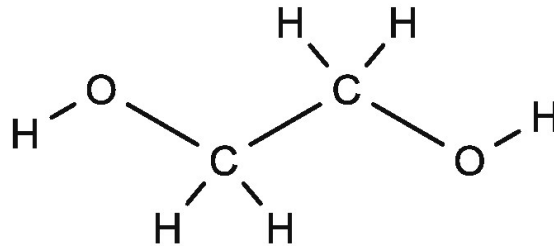
As they move, molecules have to work against the attraction of neighboring molecules until they get close to others

More important for hydrogen bonding:
You break away from one completely before forming another one

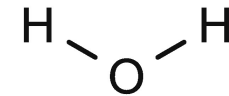
Example:

Stronger intermolecular forces make glycol more viscous than 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

Competition between cohesive forces and adhesive forces determine:



Wetting of Surfaces and Capillary Action

Cohesive forces:

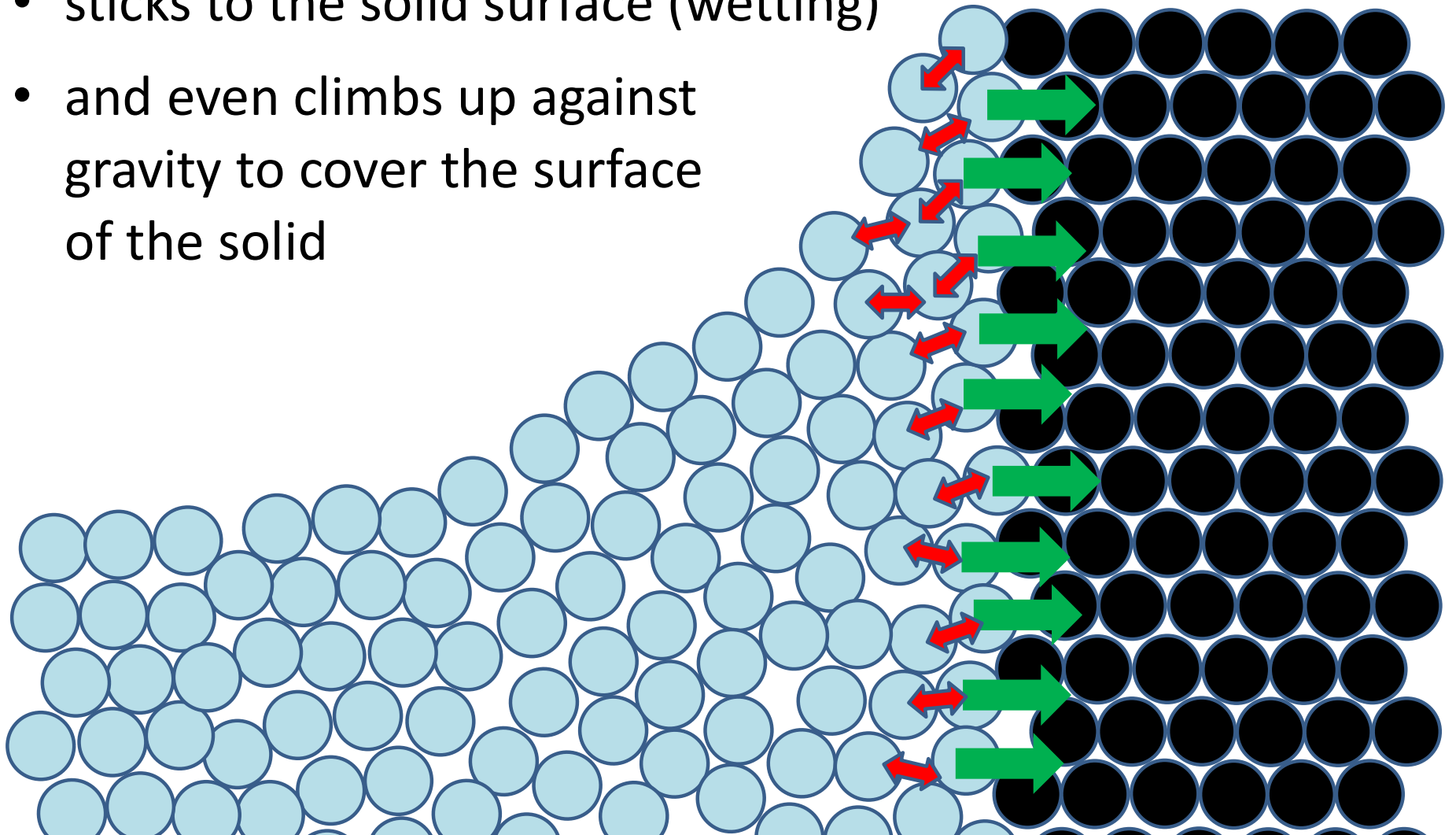
Intermolecular attraction among the molecules of the liquid.



Adhesive forces:

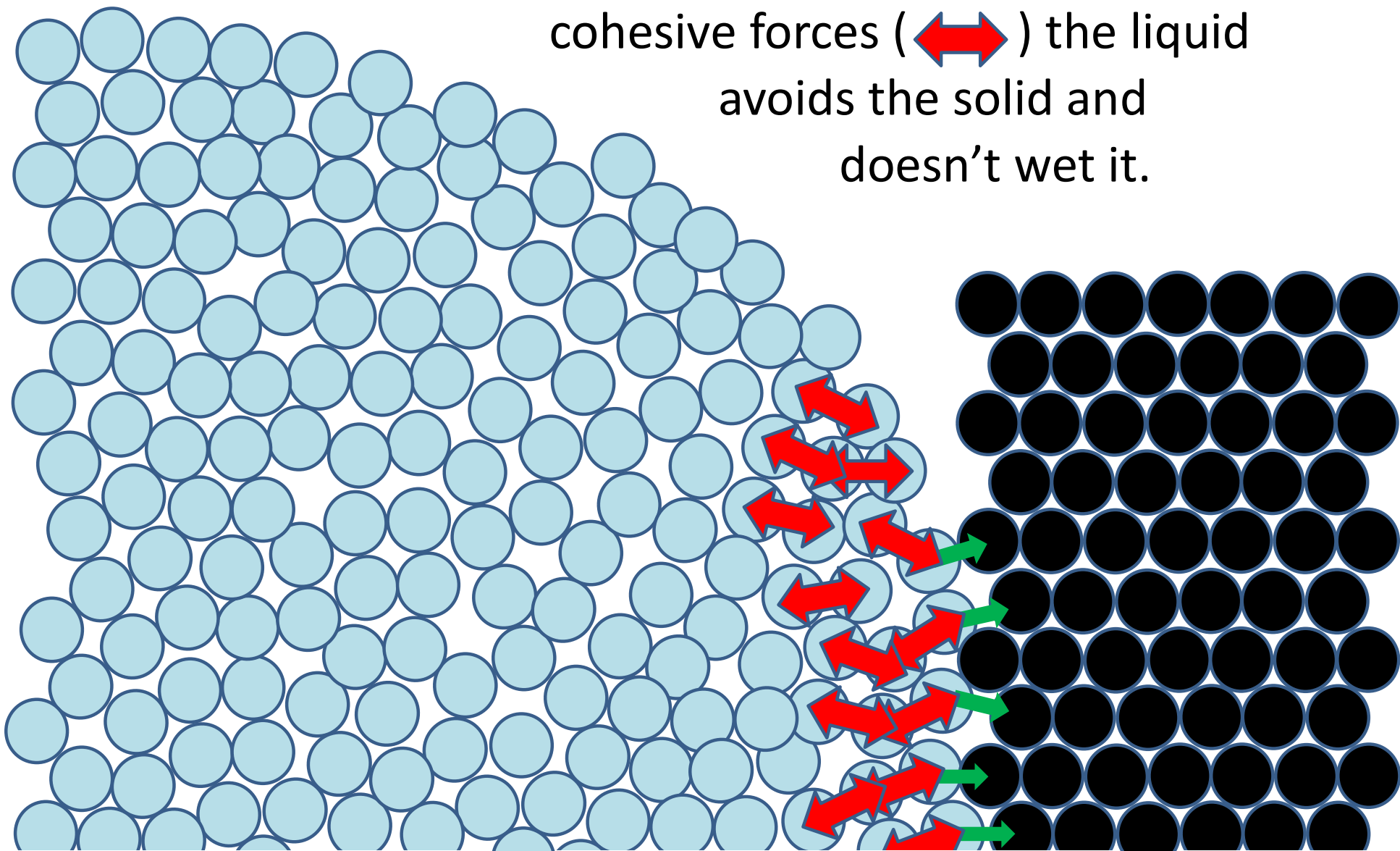
Attraction between the liquid molecules and a solid surface.

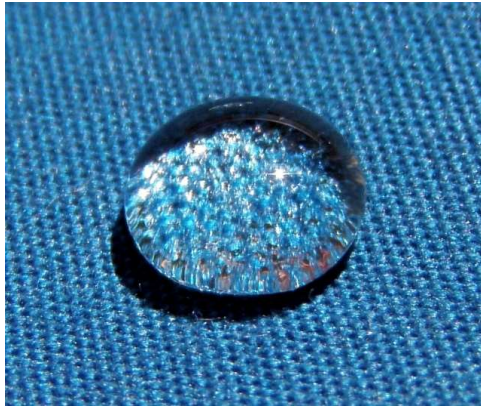
When adhesive forces () are stronger than cohesive forces (), the liquid

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



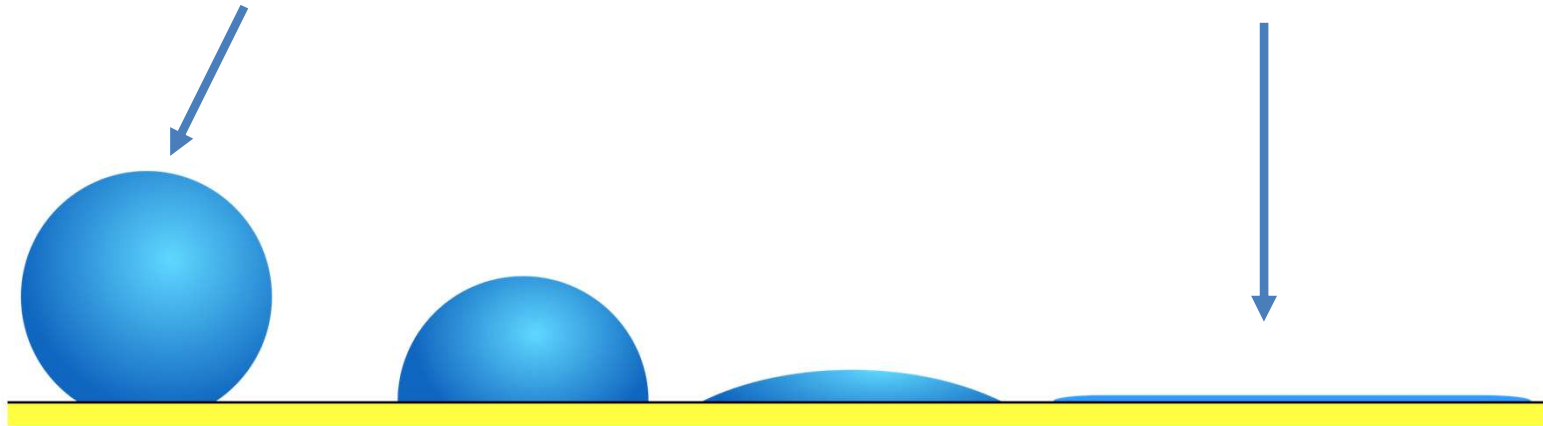
When adhesive forces () are weaker than cohesive forces () the liquid avoids the solid and doesn't wet it.



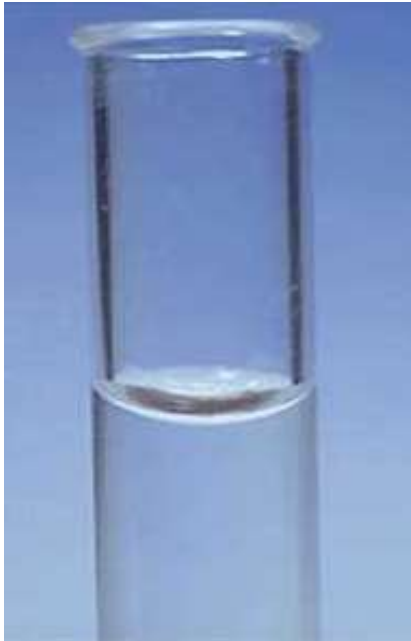


Almost no wetting

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

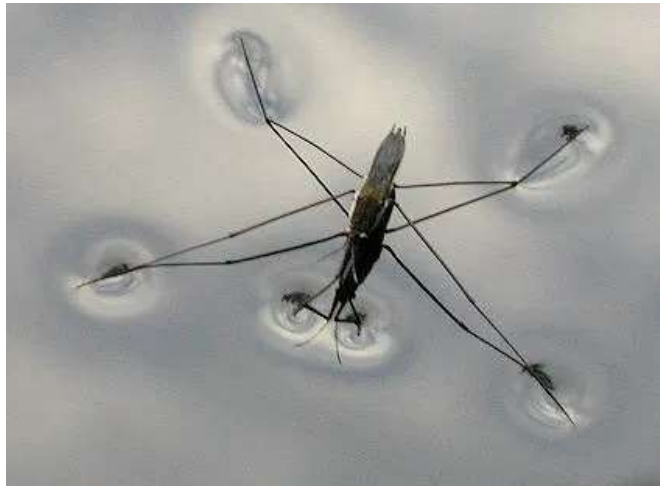
Mercury forms a **convex** “meniscus” with glass



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.

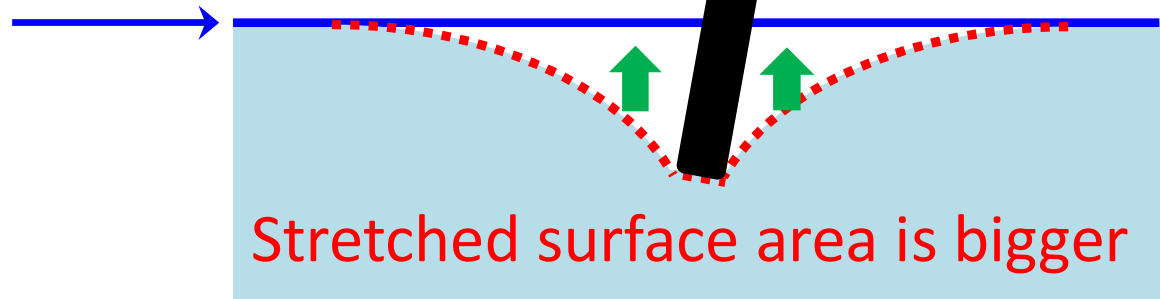
cohesive > adhesive



A mosquito can stand on water because of surface tension, **and** 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

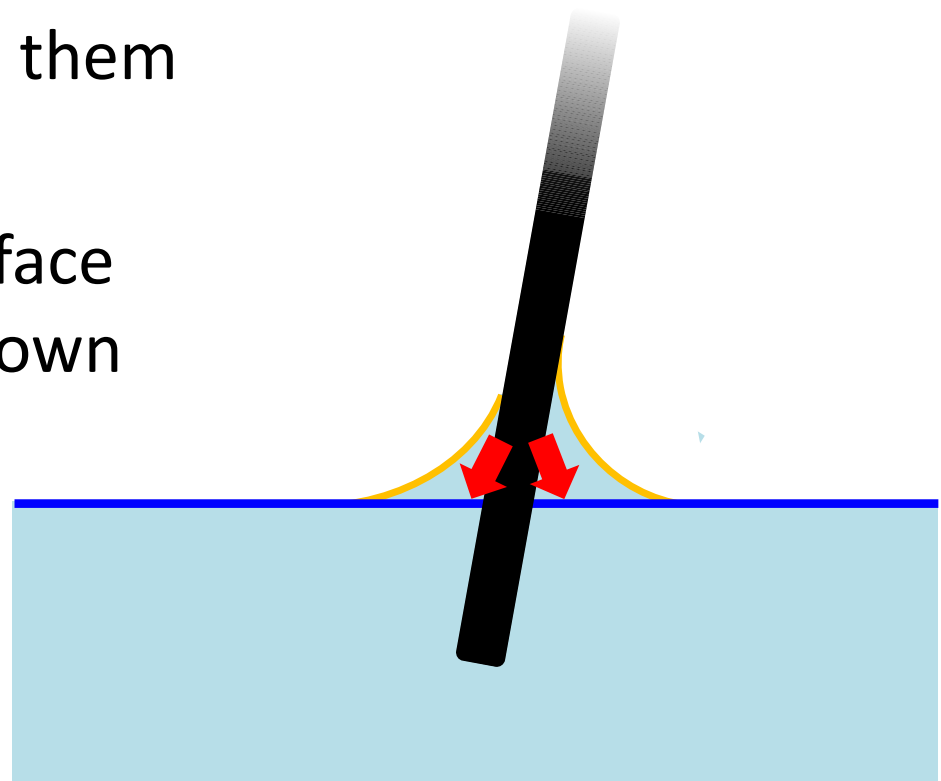


Stretched surface area is bigger

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.

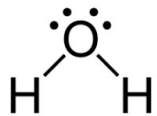
If dissolution of two substances would disrupt the intermolecular forces, their energy would go up.

- Dissolving unfavorable; little solubility

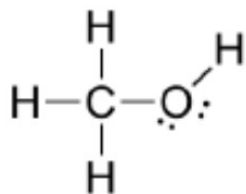
If the two substances have intermolecular forces similar in nature, they tend to be “miscible”

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

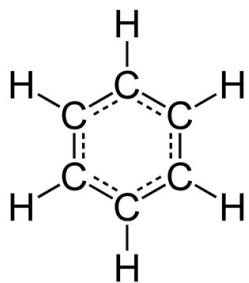
“like dissolves like”



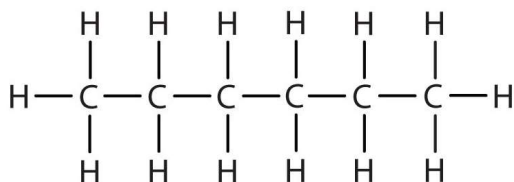
H₂O and CH₃OH both have dipole-dipole and hydrogen bonding interactions



- Miscible (can dissolve in all proportions)

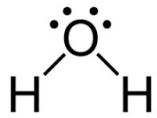


and

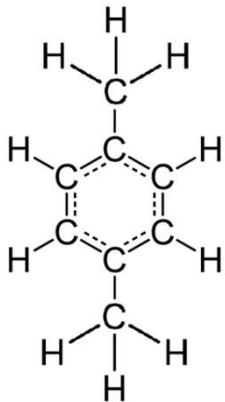


both have basically only London dispersion forces

- Miscible (can dissolve in all proportions)



H₂O has strong hydrogen bonding and significant dipole-dipole forces, but very little dispersion

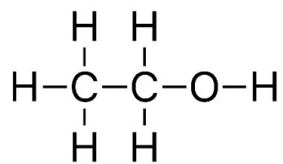


para-Xylene has strong London dispersion forces (actually a bit stronger than the forces between H₂O molecules), but no other forces

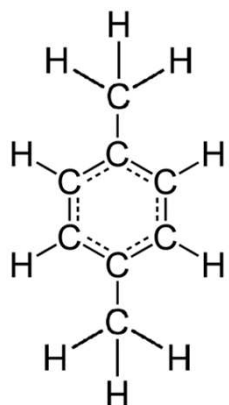
Water and para-Xylene are **insoluble in each other**

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.

CONCEPT CHECK!

Which would you predict should be **larger** for a given substance: ΔH_{vap} or ΔH_{fus} ?

Explain why.

It takes a lot more energy to break the intermolecular forces between the liquid molecules to completely break apart to form a gas.

A survey of solids

Solids

```
graph TD; Solids --> Crystalline; Solids --> Amorphous;
```

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

```
graph TD; A[Crystalline Solids] --> B[Atomic]; A --> C[Molecular]; A --> D[Ionic];
```

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**

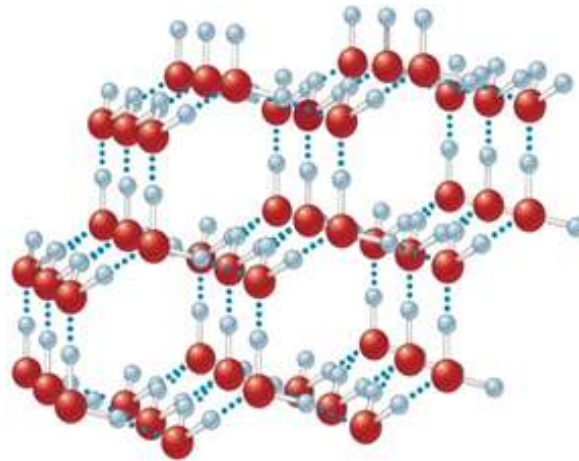
e.g. ionic solids such as NaCl , CaCO_3 , NaOH

Crystalline Solids Examples

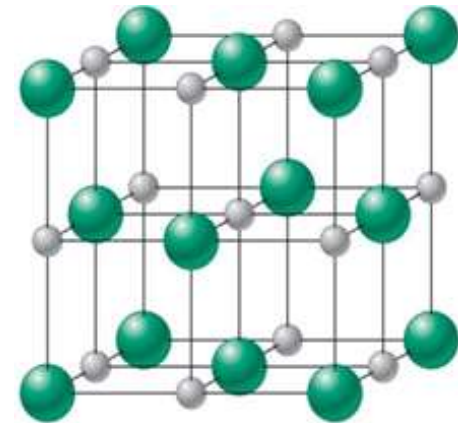
Atomic



Molecular



Ionic



Atomic Solids

```
graph TD; A[Atomic Solids] --> B[Metallic]; A --> C[Network]; A --> D[Frozen noble gas]
```

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.

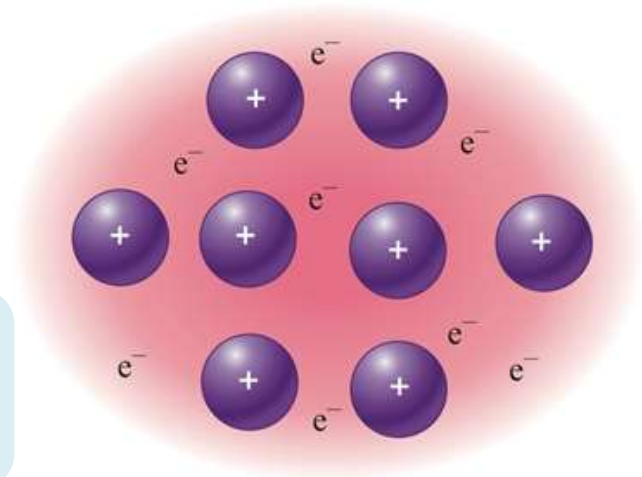
The valence electrons of metals exist in those huge MOs that cover the entire volume of the metal sample.

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

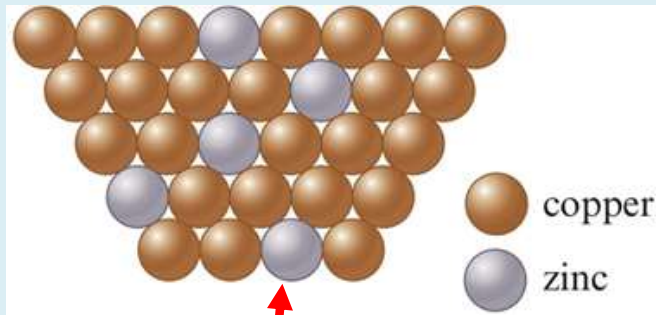
But don't mistake it for ionic bonding.
It is covalent



Metal alloys

Substitutional

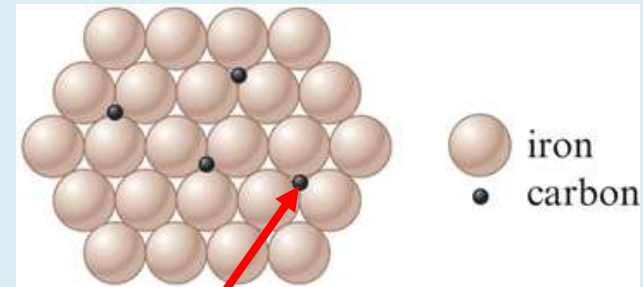
Brass



One element substituting for another one in the crystal lattice

Interstitial

Steele

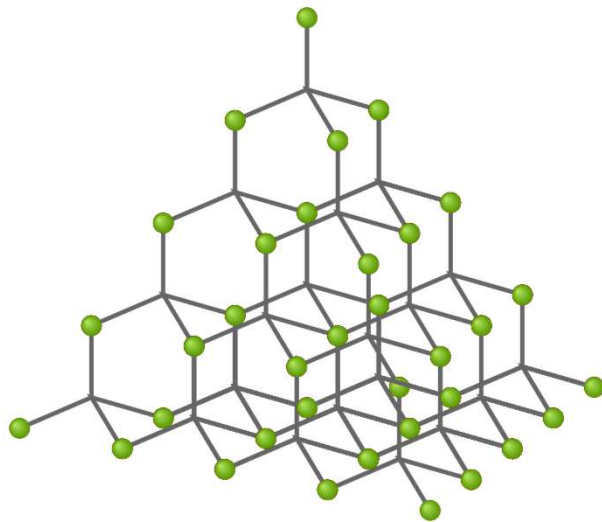


Atoms of one element fitting into the spaces (interstices) between metal atoms in the crystal lattice

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

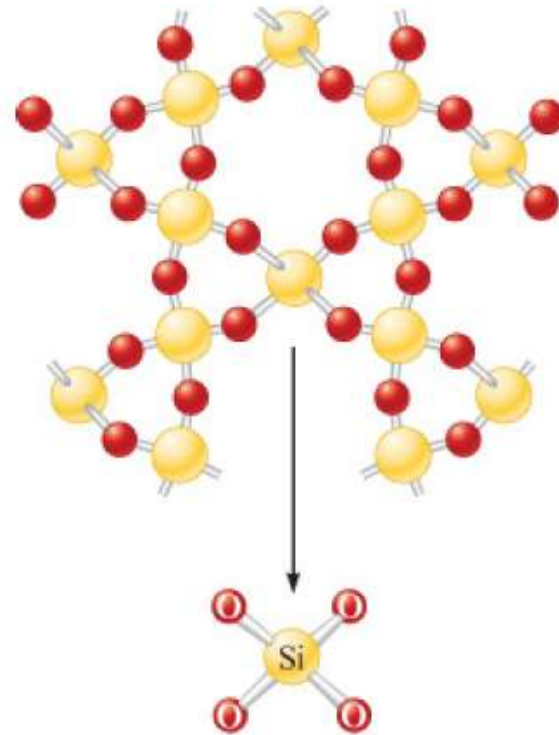
A silicon crystal looks the same

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:

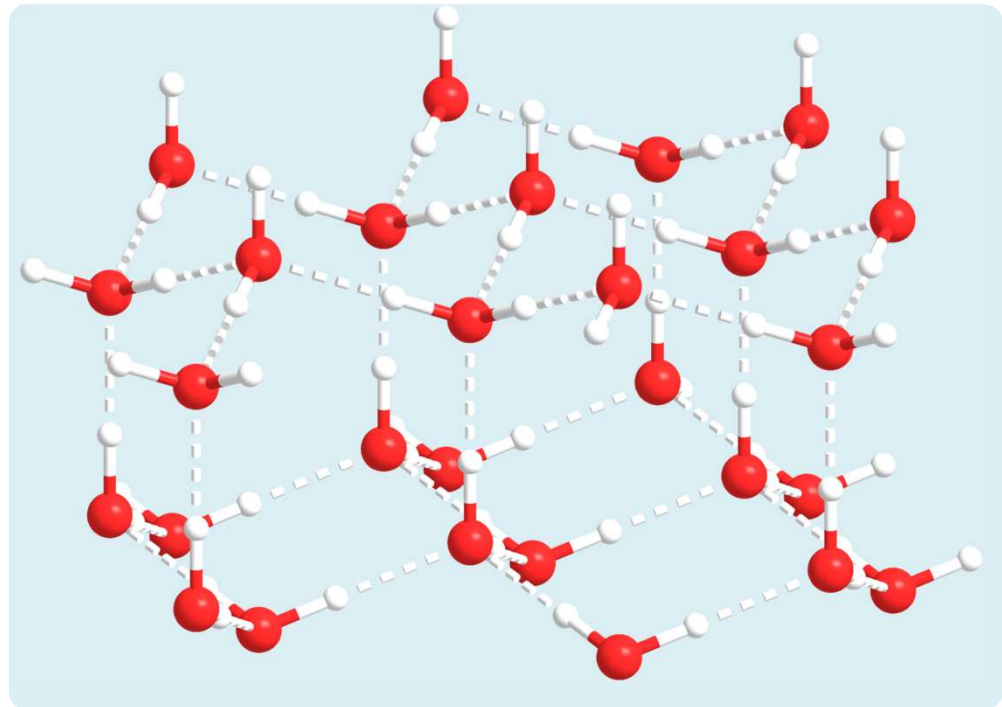
SiO_2 (quartz) is composed of SiO_4 tetrahedra forming a covalent network



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

Caffeine



Sugar

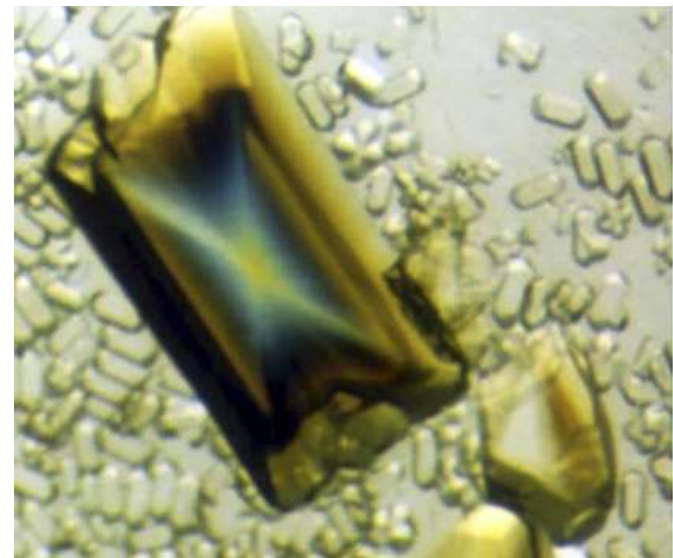
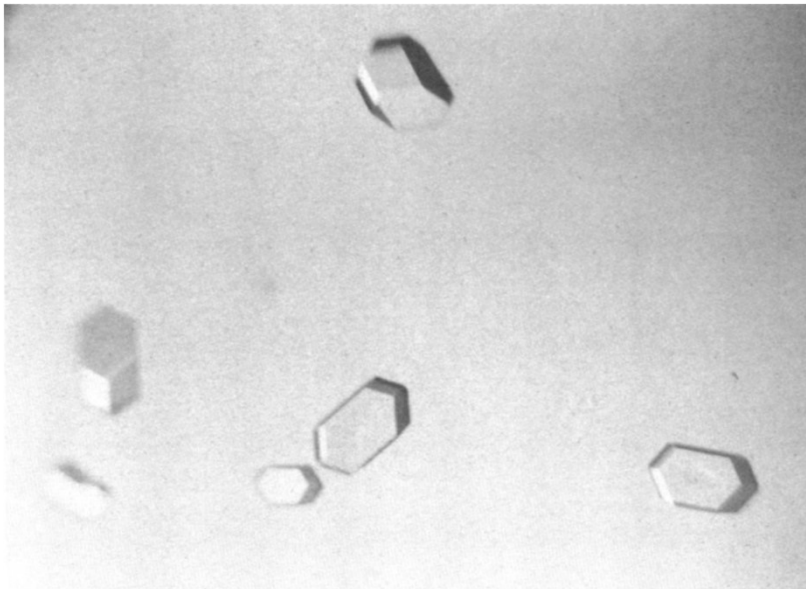


Naphthalene
(mothball)

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.

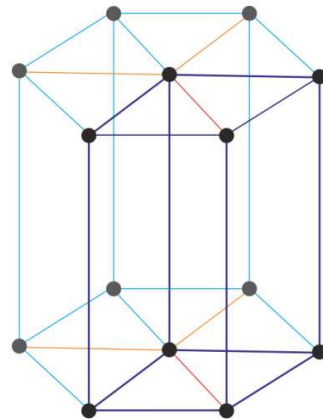
Network solids are hard, and have high melting points.

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

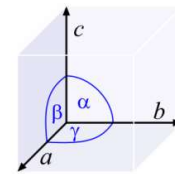
Molecular solids have relatively low melting points, and are soft.

Common packing arrangements in metals

- Cubic
- Hexagonal

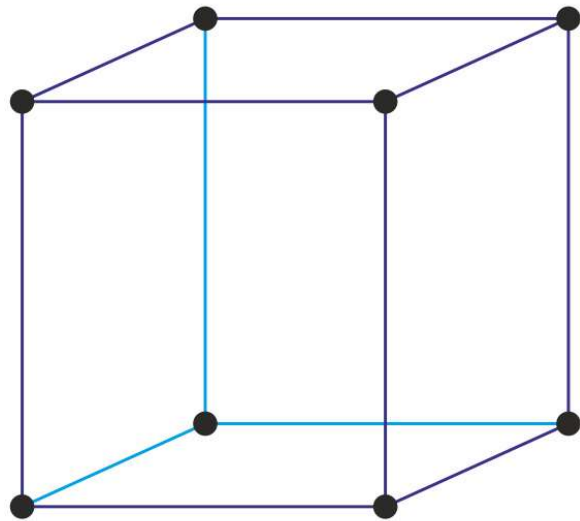


CRYSTAL LATTICE
hexagonal

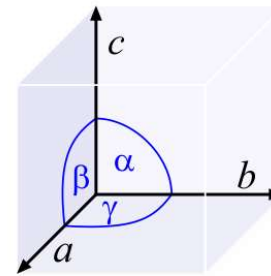


$$a = b \neq c$$

$$\alpha = \beta = 90^\circ \quad \gamma = 120^\circ$$

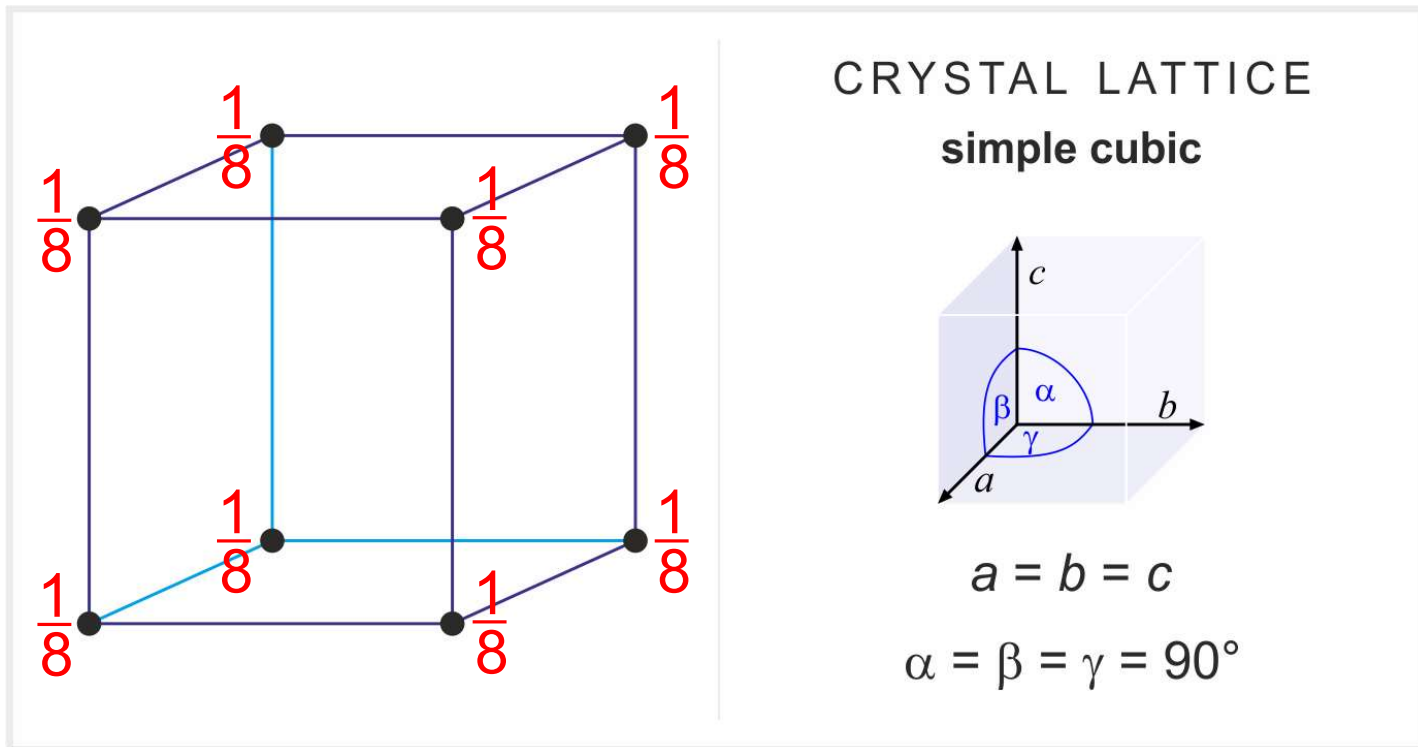


CRYSTAL LATTICE
simple cubic



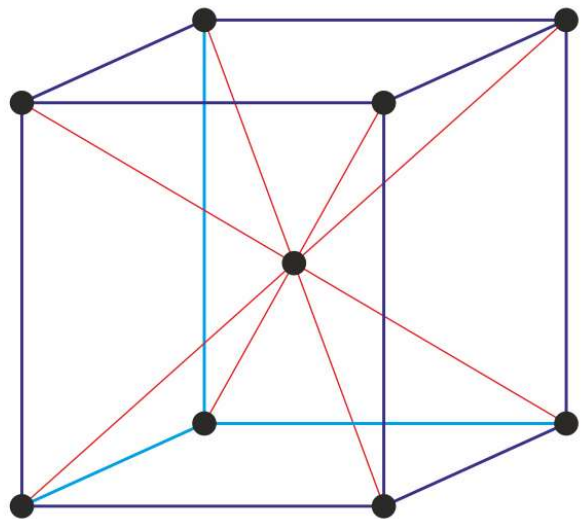
$$a = b = c$$

$$\alpha = \beta = \gamma = 90^\circ$$

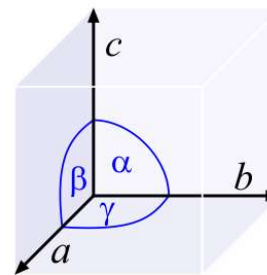


Atoms per cell = $8 \times (\frac{1}{8}) = 1$

Coordination number (no. of closest neighbors) = 6

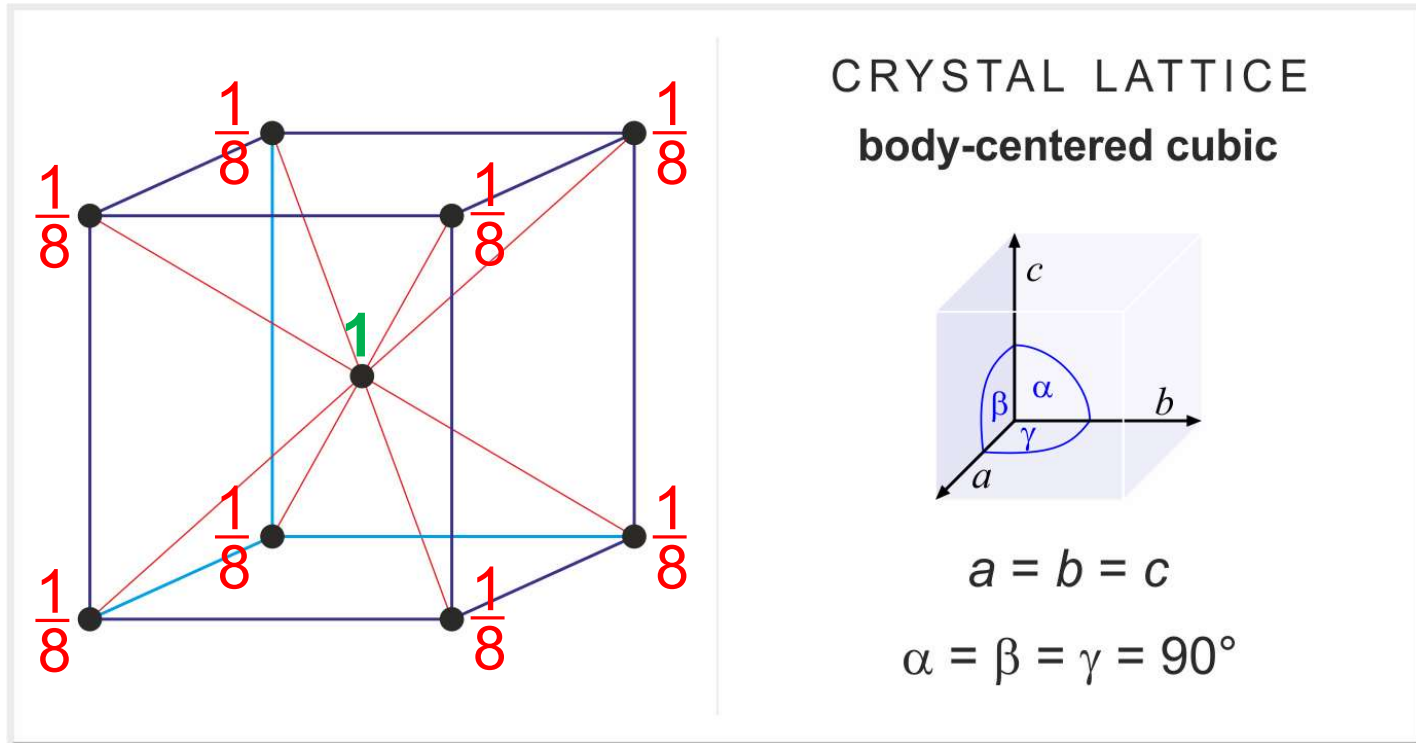


CRYSTAL LATTICE
body-centered cubic



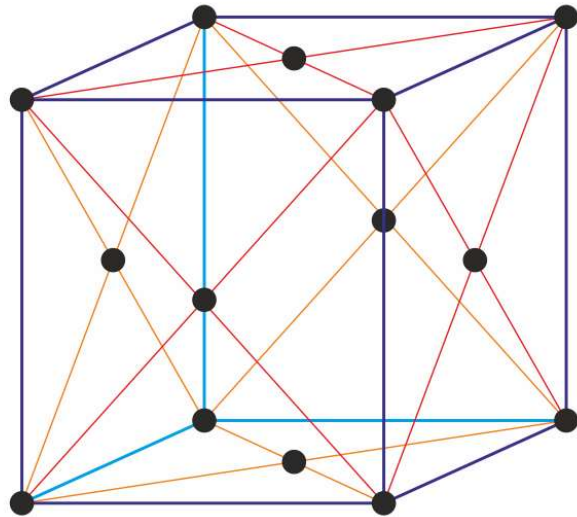
$$a = b = c$$

$$\alpha = \beta = \gamma = 90^\circ$$

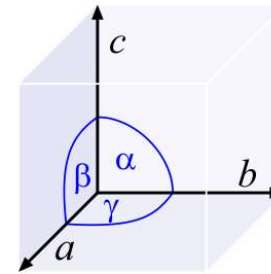


Atoms per cell = $8 \times \left(\frac{1}{8}\right) + 1 = 2$

Coordination number (no. of closest neighbors) = 8

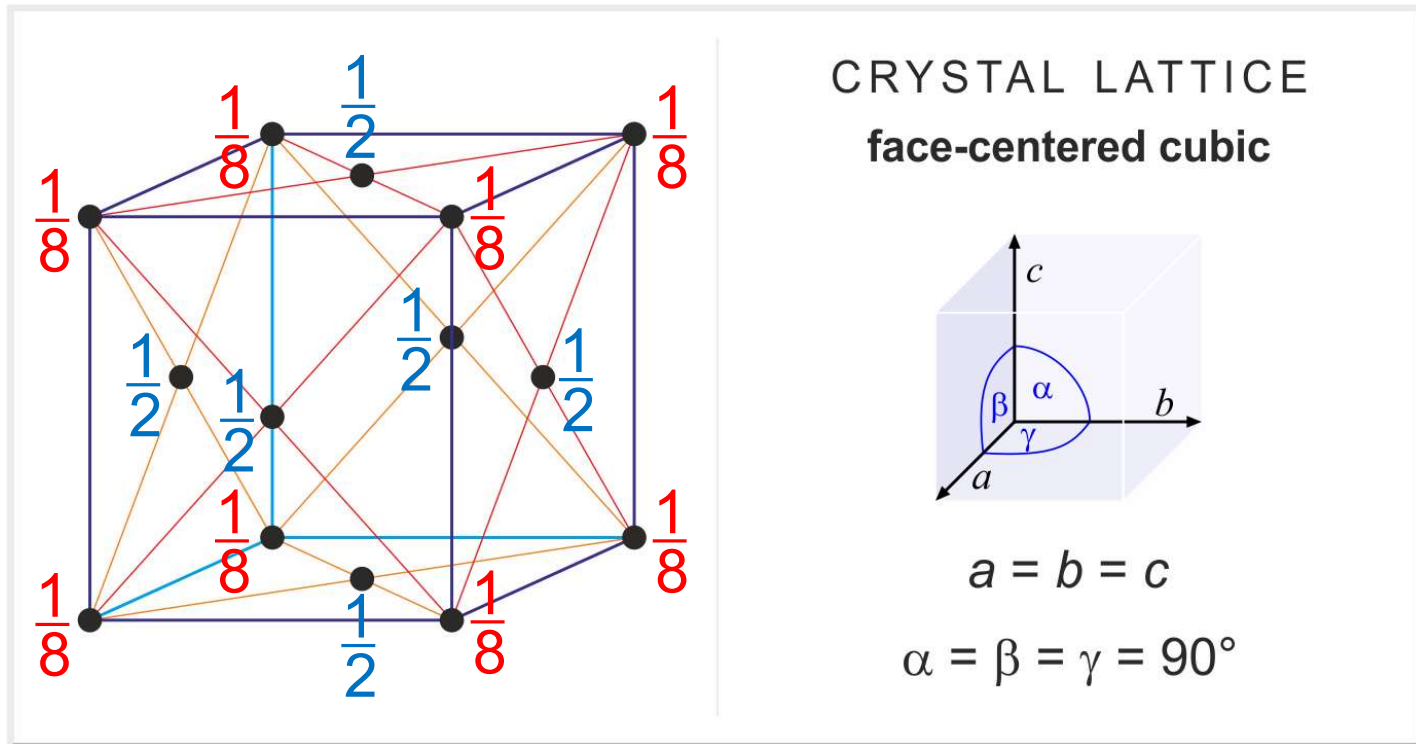


CRYSTAL LATTICE
face-centered cubic



$$a = b = c$$

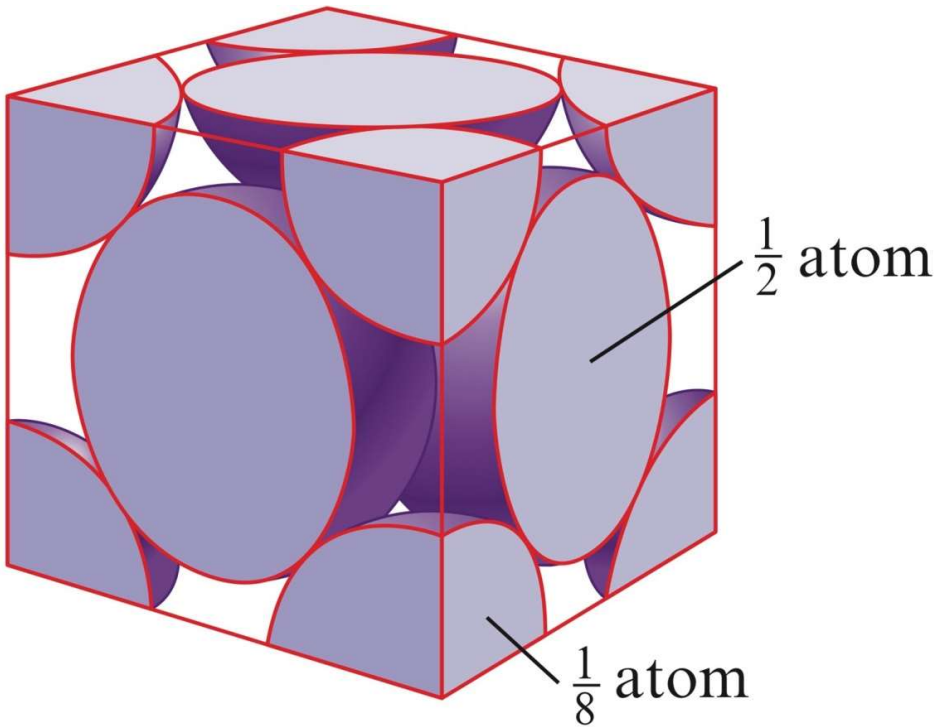
$$\alpha = \beta = \gamma = 90^\circ$$



Atoms per cell = $8 \times \left(\frac{1}{8}\right) + 6 \times \left(\frac{1}{2}\right) = 4$

Coordination number (no. of closest neighbors) = 12

The Net Number of Spheres in a Face-Centered Cubic (f.c.c.) Unit Cell



$$\text{No. of spheres} = (8 \text{ corners})(\frac{1}{8}) + (6 \text{ faces})(\frac{1}{2}) = \mathbf{4}$$

CONCEPT CHECK!

Determine the number of metal atoms in a unit cell if the packing is:

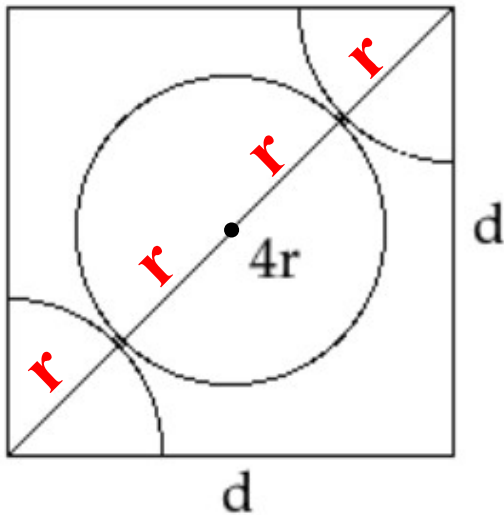
- a) Simple cubic
- b) Cubic closest packing

- a) 1 metal atom
- b) 4 metal atoms

CONCEPT CHECK!

A metal crystallizes in a face-centered cubic structure.

Determine the relationship between the **radius** of the metal atom and the **length of an edge** of the unit cell.



Using Pythagorean theorem

$$d^2 + d^2 = (4r)^2$$

$$d = \sqrt{8} r$$

CONCEPT CHECK!

Silver metal crystallizes in a **cubic closest packed structure**. The face centered cubic unit cell edge is 409 pm. Calculate the **density** of the silver metal.

Changes in energy when an ionic compound is made

- If we bring cations and anions together into a crystal lattice, the electrostatic attraction between (+) and (-) charges leads to a “favorable” (i.e. low energy) configuration.
 - The (+) and (-) charges “snap” into the most favorable configuration
- **This releases energy from the system.**
- That change in the energy of the system is called:

“lattice energy”

Strength of ionic attractions in the crystal

A measure of ionic bond strength

Lattice energy **is not the same** as the enthalpy of formation of the ionic compound from the elements!

Not this: ~~$\text{Na(s)} + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{NaCl(s)} \quad \Delta H = \Delta H_f^\circ$~~

Magnitude of the *Lattice Energy* is the energy released when the cations and anions in vacuum come together to form the crystal.

➤ It has a negative sign because it corresponds to a (very) exothermic process

Lattice Energy corresponds to an (essentially) imaginary process

But it's important because it indicates the strength of the ionic bonds in the crystal.

The conceptual process involving lattice energy

Initial state:

Ions (already formed) **infinitely separated**  i.e. in the gas phase

$E_{\text{initial}} = 0$  Zero, because ions can't sense one another

Final state:

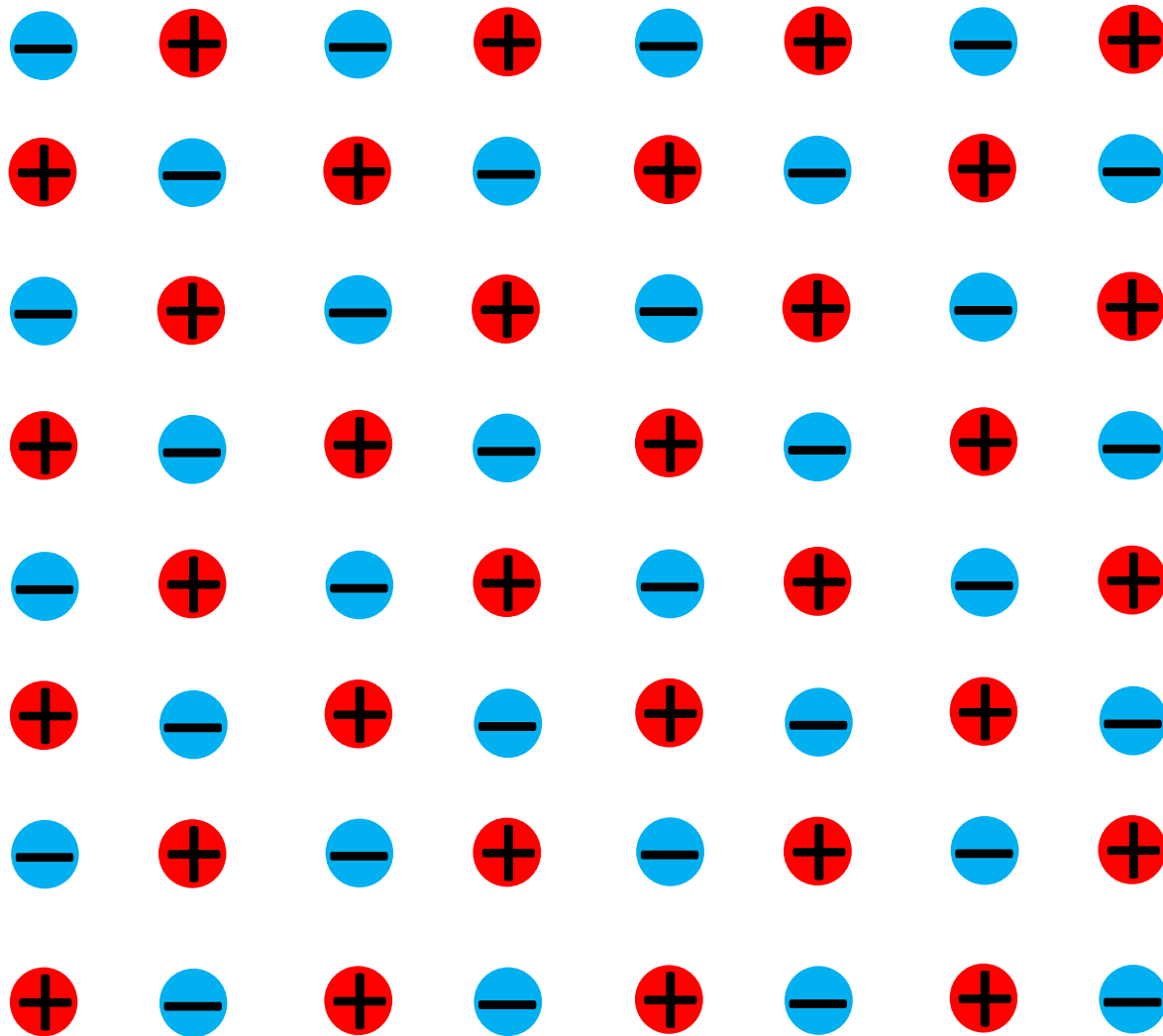
Ions in the actual crystal lattice

$E_{\text{final}} = \text{Lattice Energy}$  A large negative energy

$$\begin{aligned}\Delta E &= E_{\text{final}} - E_{\text{initial}} \\ &= (\text{Lattice Energy}) - 0 \\ &= \text{Lattice Energy}\end{aligned}$$

+/- attraction leads to low energy, going lower from zero means a large negative value

Cations and anions are brought from “infinite separation” (i.e. gas phase) to their positions in the crystal lattice



Lattice Energy

The change in energy that takes place when separated gaseous ions are packed together to form an ionic solid.

$$\text{Lattice energy} = k \left(\frac{Q_1 Q_2}{r} \right)$$

k = proportionality constant*

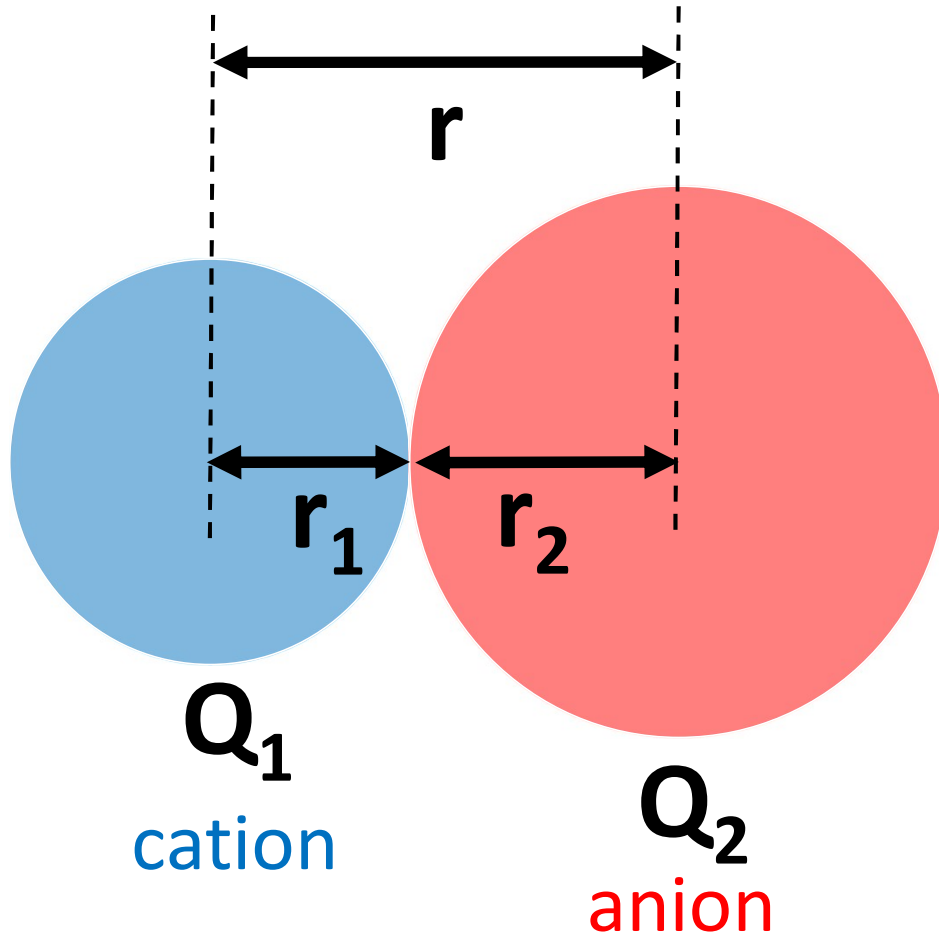
Q_1 = cation charge Q_2 = anion charge

r = shortest distance between the centers of cations and anions

We will use this formula only as a guide to compare the lattice energy (L.E.) of different ionic compounds

* k depends on the crystal type, but we can ignore its variation for the kinds of comparisons we will make

$$r \approx r_{\text{cation}} + r_{\text{anion}}$$



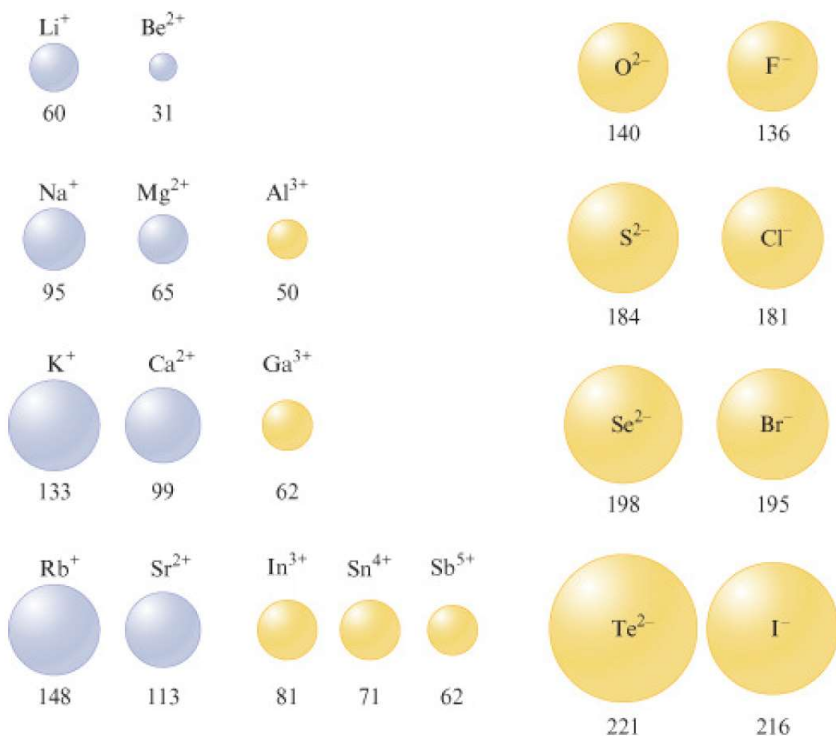
$$k \left(\frac{Q_1 Q_2}{r} \right)$$

$$r \approx r_{cation} + r_{anion}$$

We can compare r for different ionic compounds, if we know the ionic radii

For given value of $(Q_1 \cdot Q_2)$

We can guess which crystal has the higher lattice energy



We often don't need the exact ionic radii.

Just knowing the trends is enough.

For comparing lattice energies:

- Ionic charges Q_1 and Q_2 are more important than r .
- First check which compound has larger/smaller $Q_1 \cdot Q_2$
- r becomes important only for a given value of $Q_1 \cdot Q_2$

$$k \left(\frac{Q_1 Q_2}{r} \right)$$

More important than r

important only when $Q_1 \cdot Q_2$ is the same for both compounds

Practice

Which compound has larger lattice energy, CaO or CaS?

For both compounds $Q_1 \cdot Q_2 = (+2)(-2) = -4$

So we focus on the relative values of r

So we consider the ionic radii

The cation (Ca^{2+}) is the same for both compounds

So we compare the radii of O^{2-} and S^{2-}

O^{2-} is smaller than S^{2-}

$$r_{\text{CaO}} < r_{\text{CaS}}$$

Therefore:

CaO has larger lattice energy

Practice

Which compound has larger lattice energy, Na₂O or MgO?

$Q_1 \cdot Q_2$ is different for the two compounds

$$Q_1 \cdot Q_2 \text{ (for Na}_2\text{O)} = (+1)(-2) = -2$$

$$Q_1 \cdot Q_2 \text{ (for MgO)} = (+2)(-2) = -4$$

So, we don't worry about the ionic sizes because

$$|Q_1 \cdot Q_2|_{\text{MgO}} \neq |Q_1 \cdot Q_2|_{\text{Na}_2\text{O}}$$

$$|Q_1 \cdot Q_2|_{\text{MgO}} > |Q_1 \cdot Q_2|_{\text{Na}_2\text{O}}$$

Therefore:

MgO has larger lattice energy

So far, we have just compared lattice energies ...

But there is a way to calculate lattice energies without using the formula $k \left(\frac{Q_1 Q_2}{r} \right)$

We can use Hess's Law

“Born-Haber Cycle”

The formation reaction of a binary ionic compound from **solid metal** and the **nonmetal element** is deconstructed into little steps.

- The last of these steps involves lattice energy.
- We normally know the ΔE (or ΔH , the two are close enough for our purposes) for the overall formation reaction and all the steps except for **lattice energy**
- We can then solve for the lattice energy

Steps in the formation of an ionic solid from elements

Sublimation of the solid metal



Ionization of the metal atoms



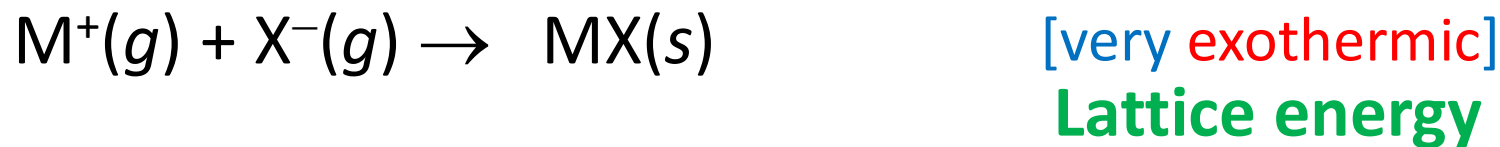
Dissociation of the nonmetal



Creation of nonmetal anions in the gas phase



Creation of the solid ionic compound from gas-phase ions



Born-Haber cycle for the formation of LiF

Process	Energy Change (kJ)
$\text{Li}(s) \rightarrow \text{Li}(g)$	161
$\text{Li}(g) \rightarrow \text{Li}^+(g) + e^-$	520
$\frac{1}{2} \text{F}_2(g) \rightarrow \text{F}(g)$	77
$\text{F}(g) + e^- \rightarrow \text{F}^-(g)$	-328
<u>$\text{Li}^+(g) + \text{F}^-(g) \rightarrow \text{LiF}(s)$</u>	<u>Lattice energy (LE)</u>
Overall: $\text{Li}(s) + \frac{1}{2} \text{F}_2(g) \rightarrow \text{LiF}(s)$	-617 kJ (per mole of LiF)

$$161 + 520 + 77 + (-328) + \text{LE} = -617$$

$$\text{LE} = -1047 \text{ kJ}$$

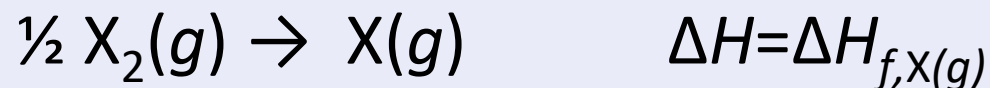
“Sublimation of the solid metal”

can instead be called “Formation reaction of M(g)”



“Dissociation of the nonmetal”

(also the formation reaction of X(g))



can instead be given in the form of:

Bond dissociation of X₂

