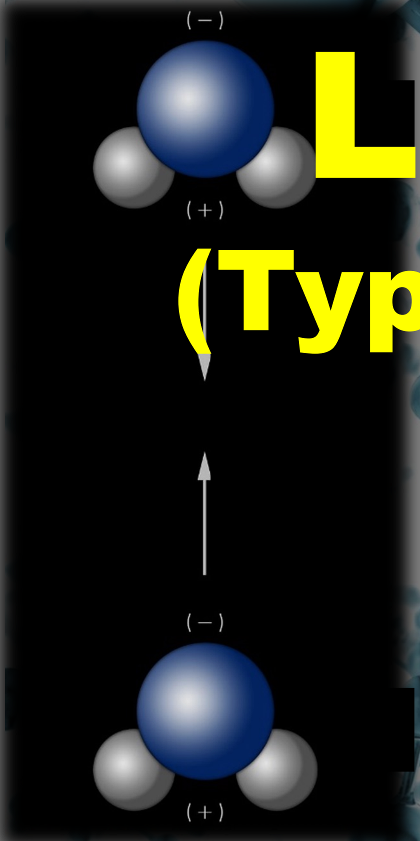
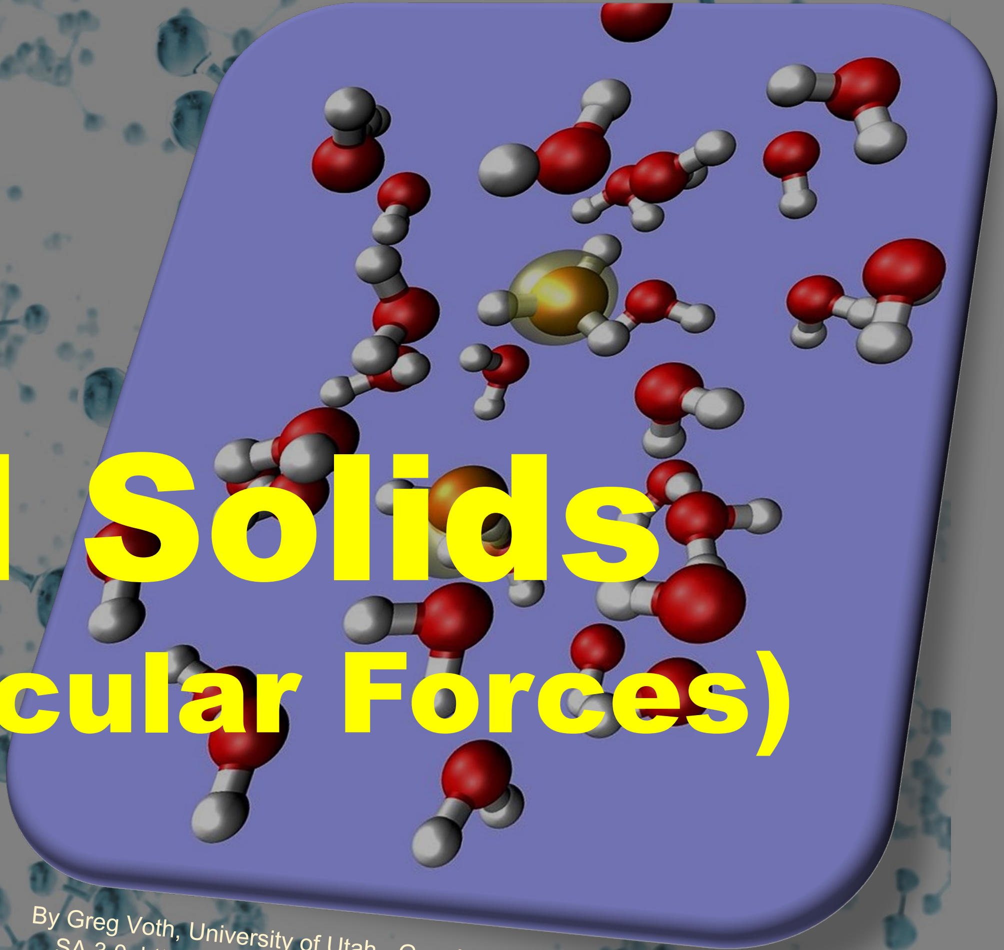
Liquids and Solids

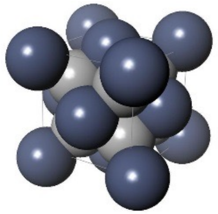
(Types of Intermolecular Forces)





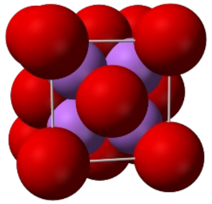
Intramolecular Forces

<u>Metallic bonding</u>: Cu, Cr, Fe, Be



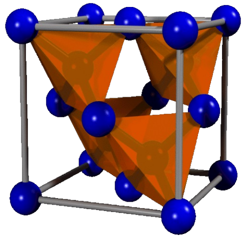
chromium

<u>Ion-Ion bonding</u>: NaCl, Li_2O



lithium oxide

<u>Covalent network bonding</u>: C (diamond), Si

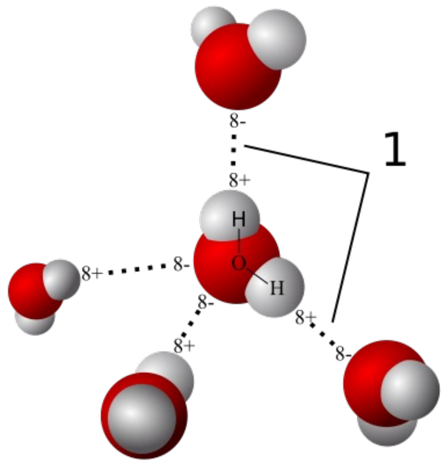


diamond

Intermolecular Forces

Increasing Strength

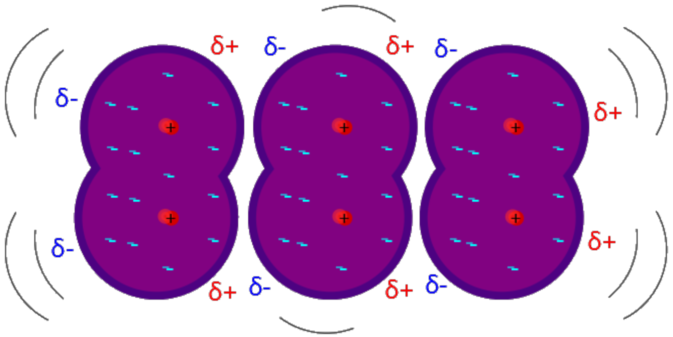
Hydrogen bonding: H-F, H-N, or H-O



Dipole-dipole – H-Cl, C-O, S-H

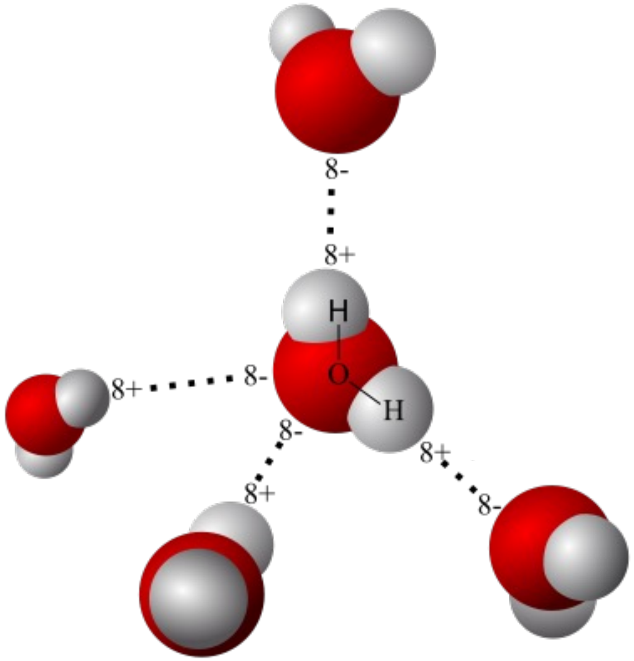
$$\overset{\delta+}{H}\text{—}\overset{\delta-}{Cl}\text{- - - - -}\overset{\delta+}{H}\text{—}\overset{\delta-}{Cl}$$

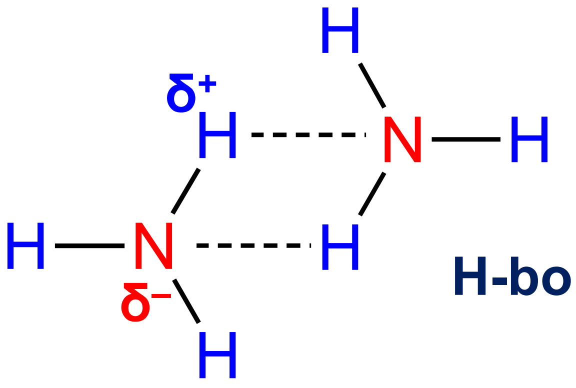
Dispersion Forces (also called London or van der Waals forces) – C_nH_x (hydrocarbons), other nonpolar molecules



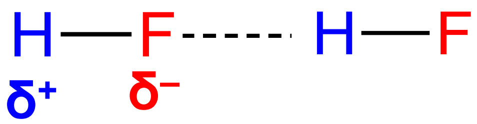
Hydrogen Bonding

When a molecule has a hydrogen atom that is bonded to a nitrogen, oxygen, or fluorine, the molecule can experience an intermolecular force called ***hydrogen bonding***. This is the strongest of the three ***intermolecular forces*** shown on the previous slide:





H-bonding in NH_3

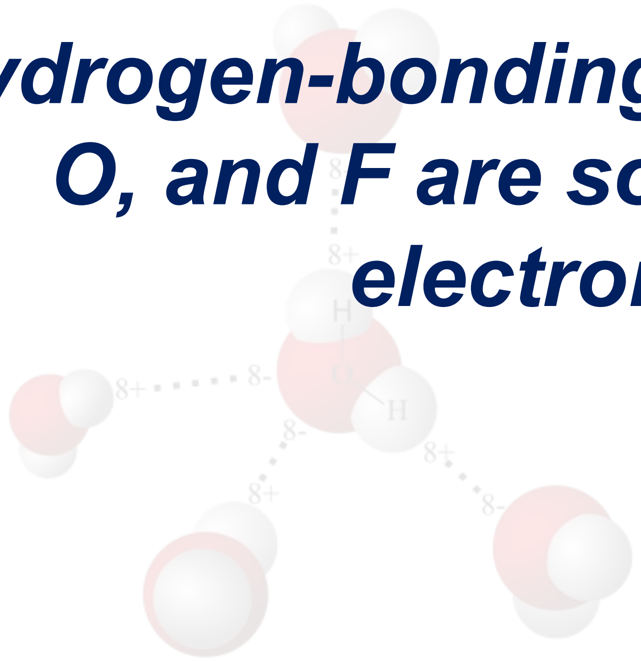


H-bonding in HF

Hydrogen Bonding

Hydrogen-bonding only applies to molecules that have H bonded to N, O, or F.

Hydrogen-bonding is very strong because N, O, and F are so much larger and more electronegative than H.



H-bonding in HF

Dipole-Dipole Forces

When a molecule has a polar bond in it (caused when two bonded atoms have a significant electronegativity difference), it causes the molecule to have a partial negative charge on one atom and a partial positive charge on another. When two or more molecules like this cluster together, they line up and stick together in a complementary fashion, like this:

$$\underset{\delta^{+}}{H} - \underset{\delta^{-}}{Cl} \cdots\cdots H - Cl$$

This ***intermolecular force*** is called a ***dipole-dipole force***.

Dipole-Dipole Forces

Dipole-dipole Forces: When a molecule has a polar bond in it (caused when two bonded atoms have a significant electronegativity difference), it causes the molecule to have a partial negative charge on one atom and a partial positive charge on another. When two or more molecules like this cluster together, they line up and stick together in a complemen

Dipole-dipole forces only apply to polar, non-ionic molecules that do NOT have H bonded to O, N, of F.

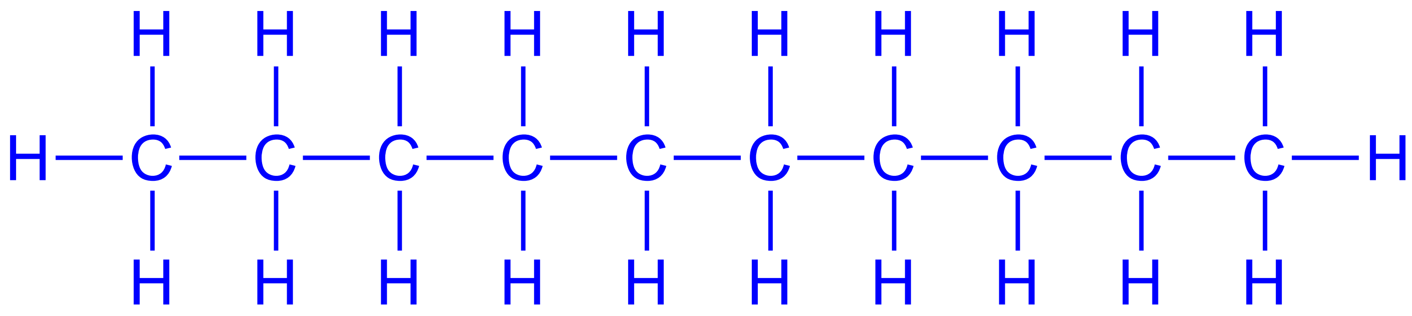
H—Cl------H—Cl

δ^+ δ^-

This ***intermolecular force*** is called a ***dipole-dipole force***.

Dispersion Forces

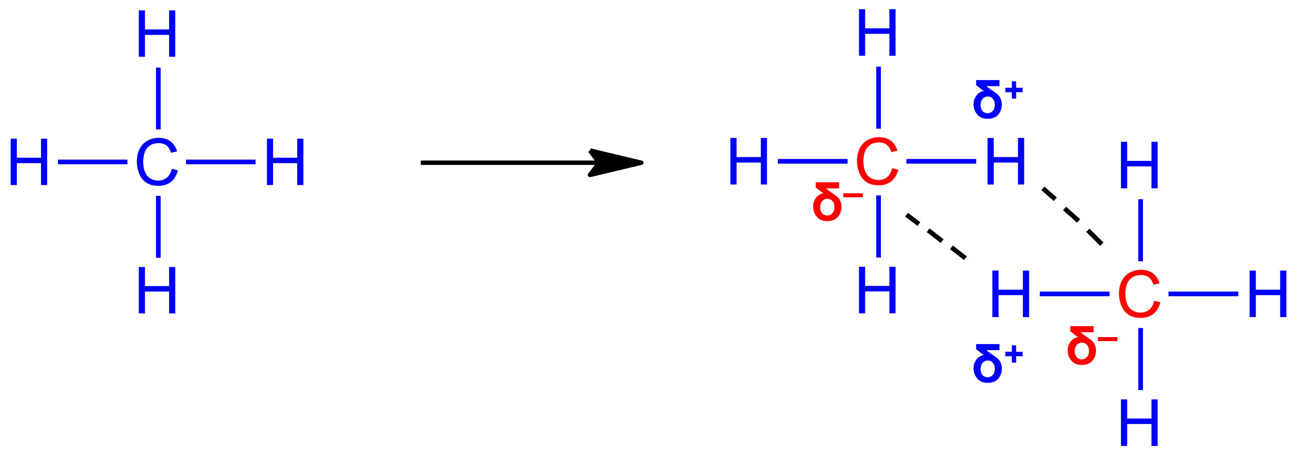
Keeping in mind that carbon and hydrogen are almost equally ***electronegative***, do you think the molecule shown here is ***polar*** or ***nonpolar***?



Nonpolar, of course.

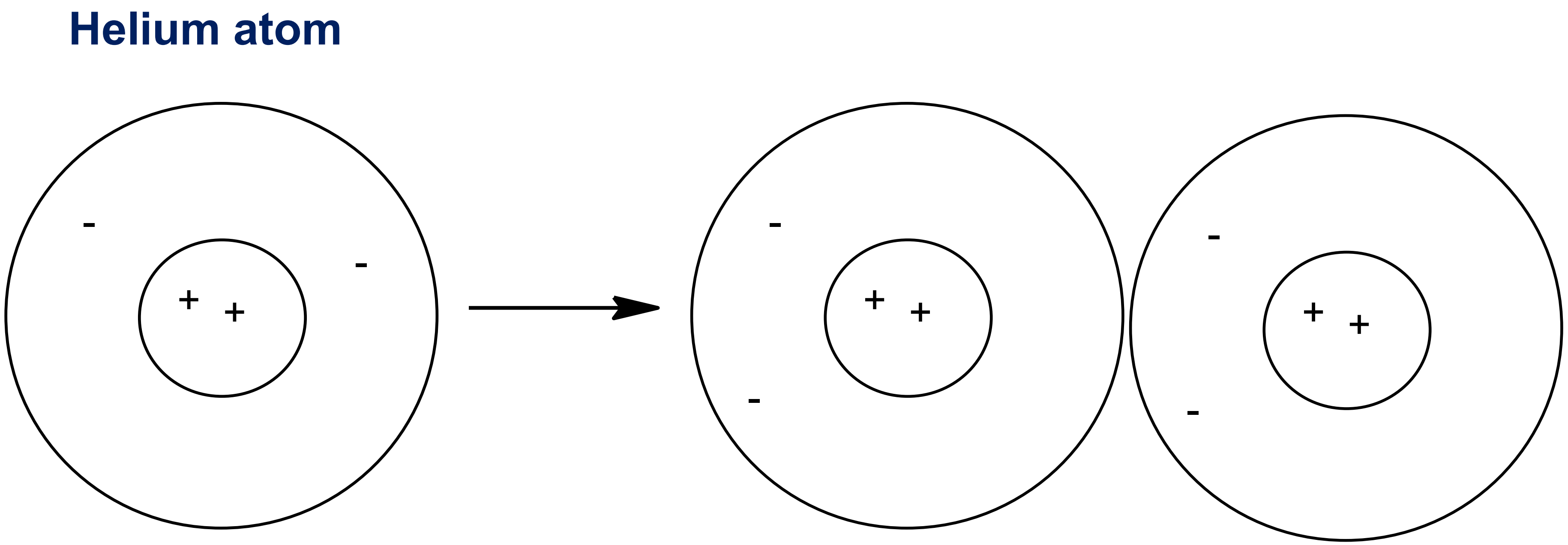
Nonpolar molecules that do not have any ***hydrogen-bonding*** or ***dipole-dipole forces*** have only ***dispersion forces***. These are sometimes called ***London*** or ***Van der Waals forces***.

How Do Dispersion Forces Work?



How Do Dispersion Forces Work?

Dispersion forces can even occur in individual atoms:



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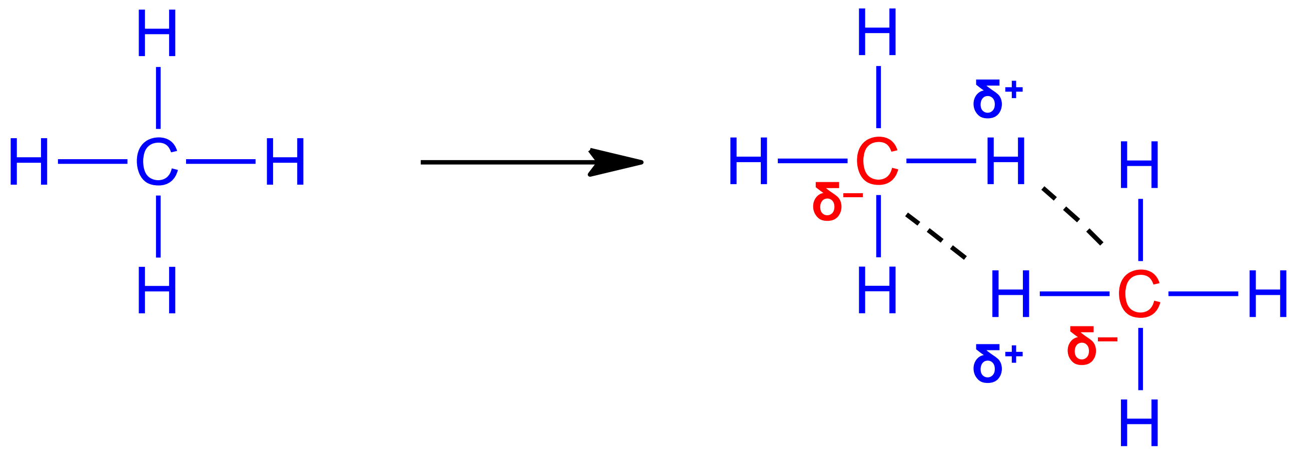
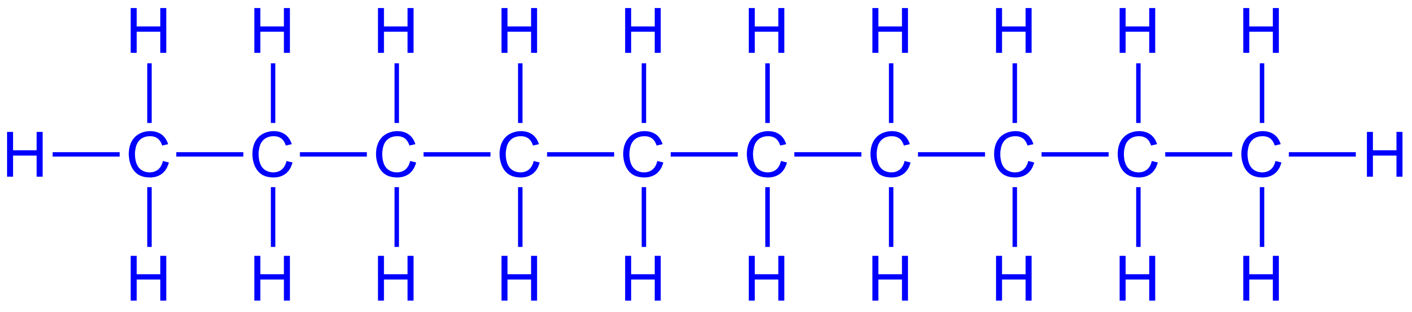


Would you expect this molecule to have more or fewer dispersion forces than CH_4? Would it have a higher or lower boiling point than CH_4?



How Do Dispersion Forces Work?

- **Dispersion forces are the weakest of the intermolecular forces.**
- **<u>ALL molecules</u>, including those with hydrogen-bonding and dipole-dipole forces, have dispersion forces.**
- **The larger the molecule, the more dispersion forces it has. So generally, if you compare two molecules that both have the same kind(s) of intermolecular force(s), the larger the molecule, the higher the boiling point.**

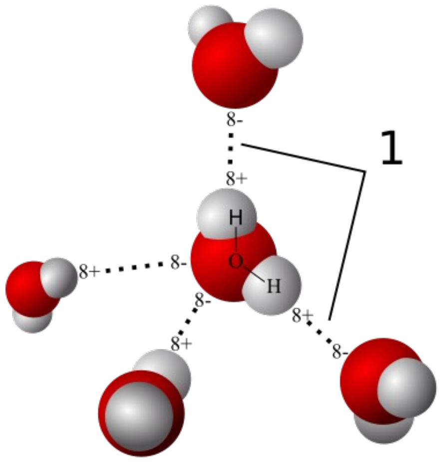
Would you expect this molecule to have more or fewer dispersion forces than CH_4? Would it have a higher or lower boiling point than CH_4?

Intermolecular Forces

Intermolecular forces are responsible for molecules' boiling points. The stronger the ***intermolecular force***, the harder it is to separate molecules. The harder the separation, the higher the boiling point.

Increasing Strength

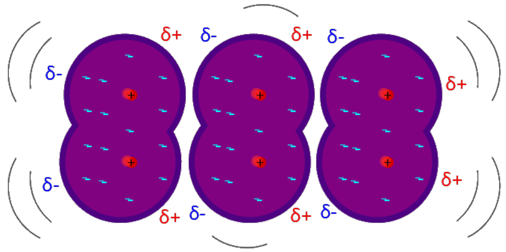
<u>Hydrogen bonding</u>: H-F, H-N, or H-O



<u>Dipole-dipole</u> – H-Cl, C-O, S-H

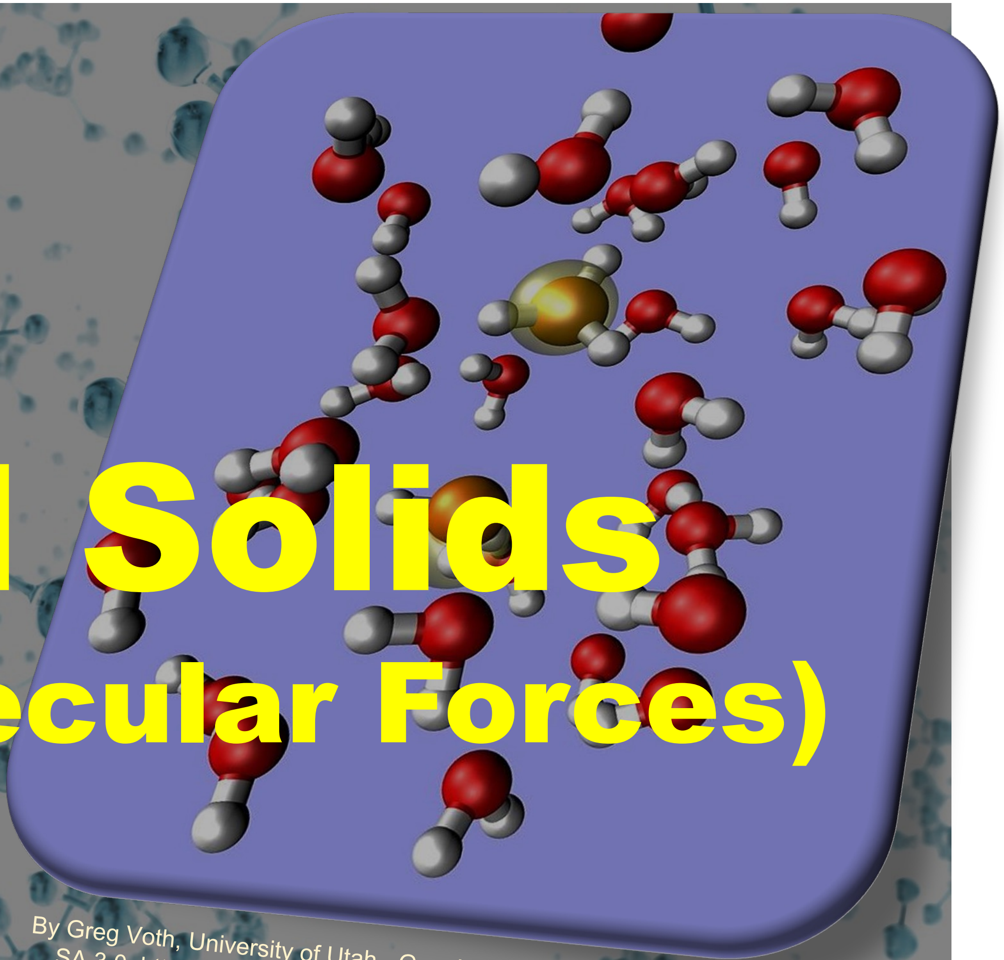
$$\overset{\delta+}{\mathrm{H}}\text{—}\overset{\delta-}{\mathrm{Cl}}\text{- - - - -}\overset{\delta+}{\mathrm{H}}\text{—}\overset{\delta-}{\mathrm{Cl}}$$

<u>Dispersion Forces</u> (also called London or van der Waals forces) – C_nH_x (hydrocarbons), other nonpolar molecules



Liquids and Solids

(Effects of Intermolecular Forces)



Intermolecular Forces

Intermolecular forces are the forces that attract molecules to each other. The stronger the IM forces, the more intensely molecules are attracted to each other and hence, “stick” together.

So, molecules with strong IM forces stick to each other more than molecules with weak IM forces. Thus, it takes more heat to get strong IM-force molecules to separate and convert from solid to liquid, or from liquid to gas.

Intermolecular Forces

Thus, strong IM forces means:

- High boiling point
- High viscosity
- High surface tension
- Low vapor pressure

"Water boiling in a pot on a stove" by Tomwsulcer - Own work. Licensed under CC0 via Wikimedia Commons

"Wasserläufer bei der Paarung crop" by Markus Gayda. Licensed under CC BY-SA 3.0 via Wikimedia Commons -

High Boiling Point

(High Heat of Vaporization)

Once again, molecules with strong ***intermolecular forces*** are more intensely attracted to each other. They therefore “stick” together more strongly.

Thus, it takes more heat to get strong IM-force molecules to separate and convert from liquid to gas –that is, to ***vaporize***. Thus:

↑IM Force ≈ ↑boiling point ≈ ↑heat of vaporization

High Viscosity

Viscosity is more-or-less how thick a substance is. The thicker the substance, the more slowly it pours. Thus, molasses is more ***viscous*** (has a higher ***viscosity***) than water.

We see, then, that:

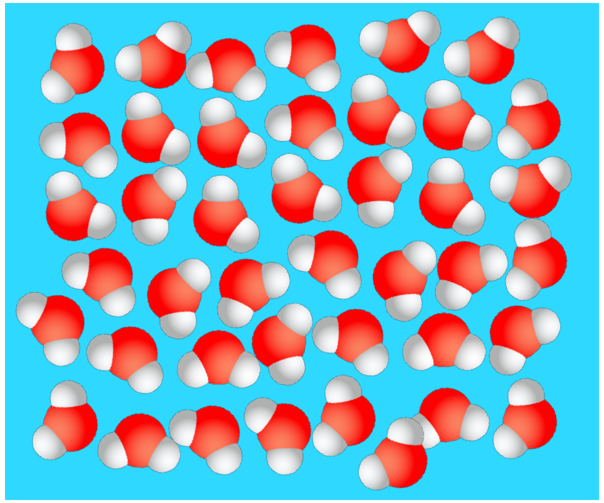
↑IM Force ≈ ↑viscosity

high-viscosity molasses

High Surface Tension

Surface tension allows a substance's surface to support weight, seen when water skeeters (also called water striders, water bugs, pond skaters, and water skippers) glide across water's surface.

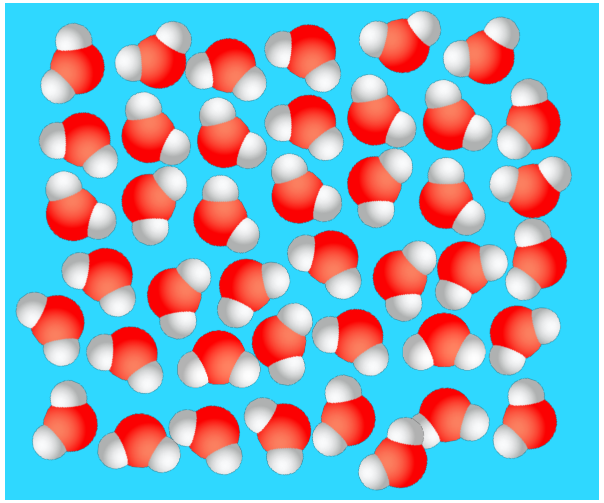
In a body of water, for instance, all the water molecules are attracted to each other by ***IM forces***.

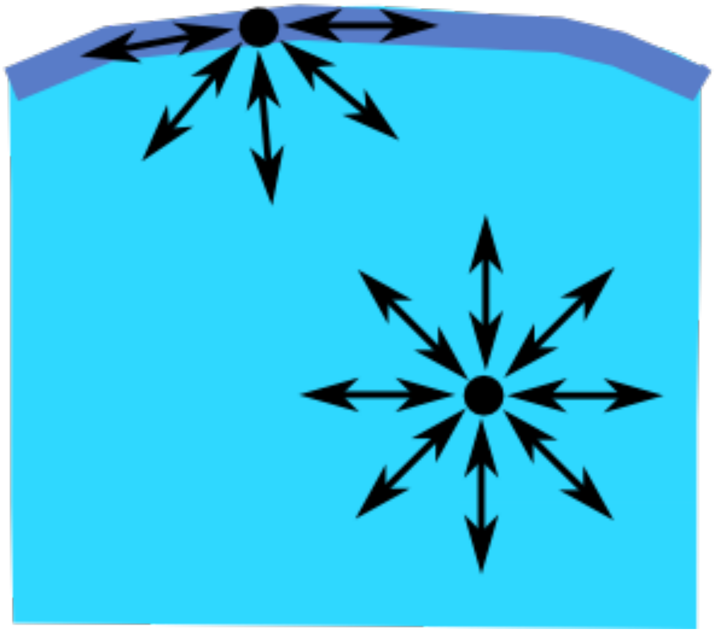


"Wasserläufer bei der Paarung crop" by Markus Gayda.

High Surface Tension

Because the H_2O molecules at the top are experiencing downward and side-to-side attraction from neighboring molecules, it creates a thin film at the water's surface, which can be traversed lightly by insects like water skeeters. This, again, is called ***surface tension***.





High Surface Tension

Because the H_2O molecules at the top are experiencing downward and side-to-side attraction from neighboring molecules, it creates a thin film at the water's surface, which can be traversed lightly by insects like water skeeters. This, again, is called ***surface tension***.

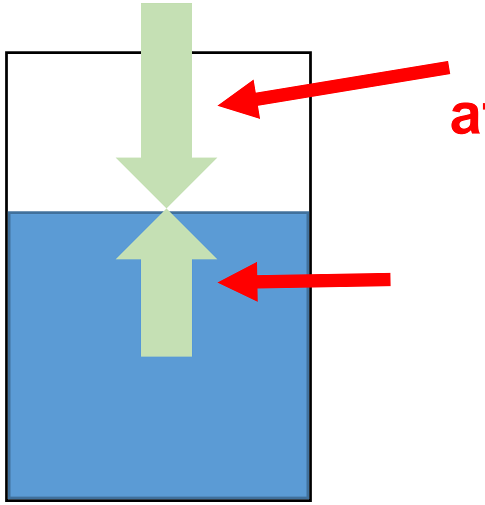
We see, then, that:

↑IM Force ≈ ↑surface tension

Vapor Pressure

When liquids evaporate in an open container, gas molecules escape pretty much permanently, never to be reclaimed by the liquid. This is called ***boiling***.

So, ***boiling*** occurs when the pressure exerted by the liquid molecules upward against (toward) the atmosphere *equals* the pressure exerted by the atmosphere down upon the liquid molecules.



Downward pressure exerted by the atmosphere ("atmospheric pressure")

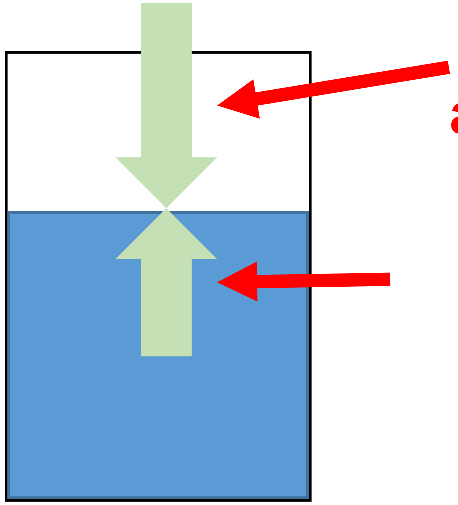
Upward pressure exerted by the substance on the atmosphere ("vapor pressure")

Vapor Pressure

When the ***vapor pressure*** equals or exceeds the ***atmospheric pressure***, the liquid boils.

We see, then, that:

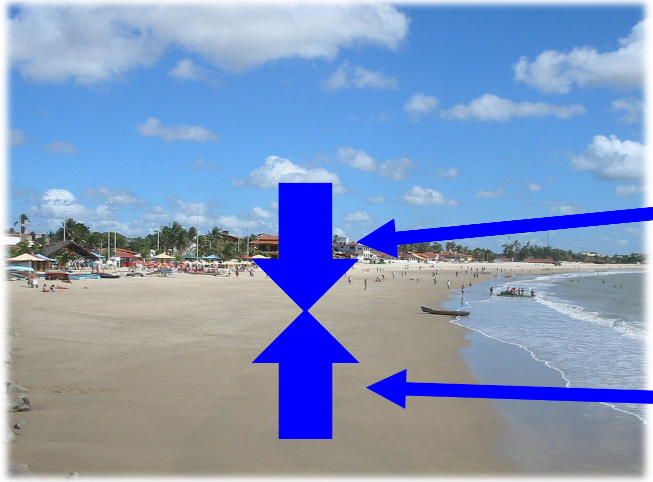
$\uparrow$IM Force ≈ $\uparrow$boiling point ≈ $\downarrow$vapor pressure



Vapor Pressure

lower atmospheric pressure

lower boiling point
(<100 °C)



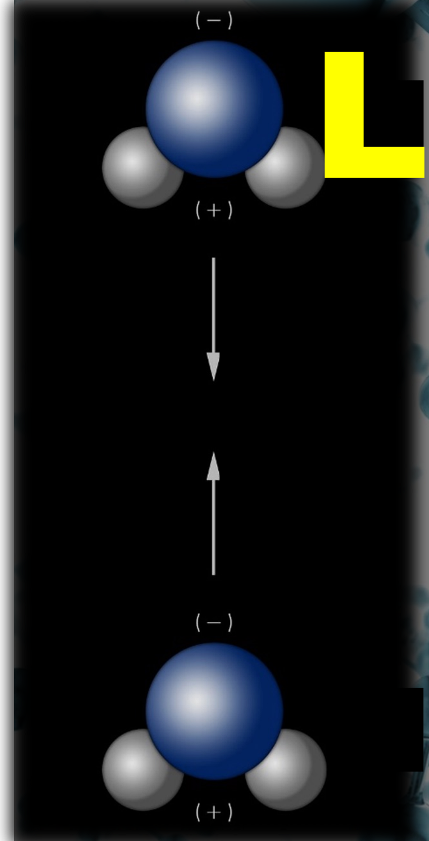
higher atmospheric pressure

higher boiling point
(100 °C)

To Summarize

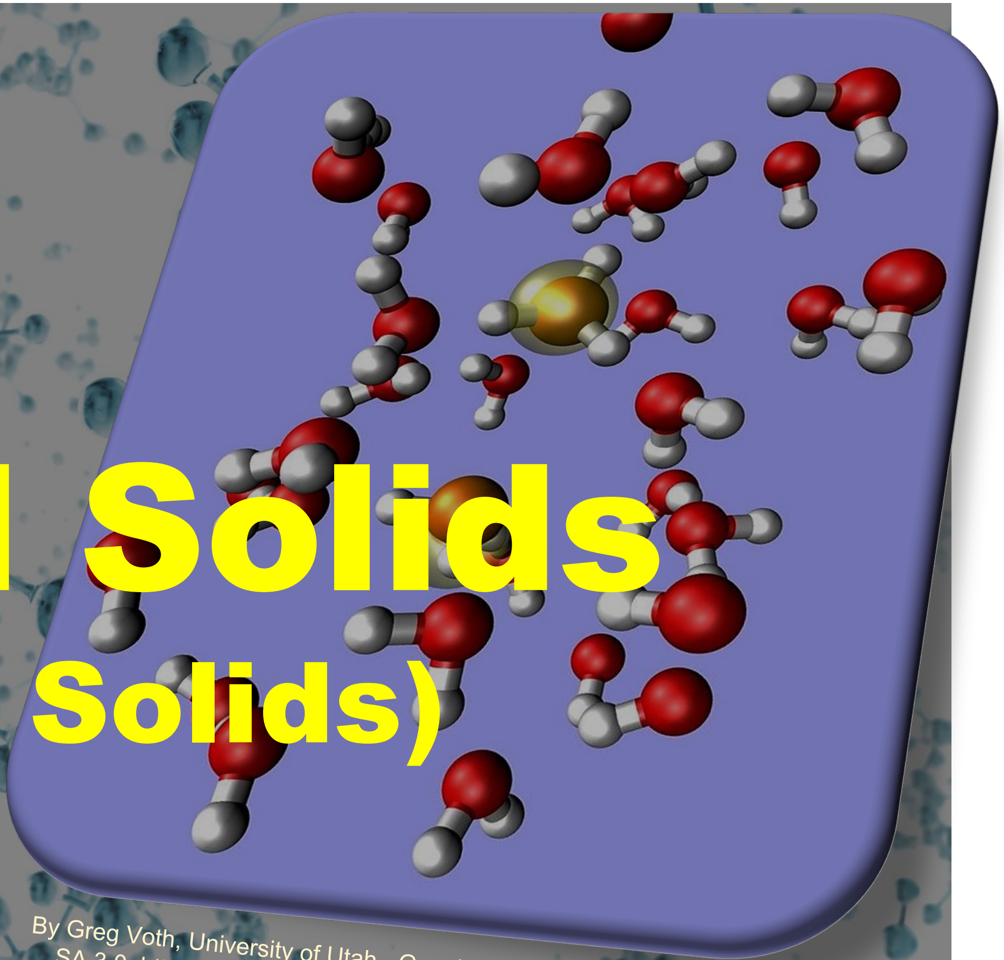
$\uparrow$ IM Force ≈ $\uparrow$ boiling point ≈ $\uparrow$ heat of vaporization ≈ $\uparrow$ viscosity ≈ $\uparrow$ surface tension ≈ $\downarrow$ vapor pressure

$\downarrow$ IM Force ≈ $\downarrow$ boiling point ≈ $\downarrow$ heat of vaporization ≈ $\downarrow$ viscosity ≈ $\downarrow$ surface tension ≈ $\uparrow$ vapor pressure



Liquids and Solids

(Structures of Solids)



Types of Solids

There are four classes of solids that you may encounter on the EXAM: ***metallic*** solids, ***ionic*** solids, ***covalent-network*** solids, and ***molecular*** solids.

Metallic solids: Held together be a delocalized “sea” of shared electrons, flowing around nuclei “islands." This allows metals to conduct electricity and be strong but not brittle. Examples: Cu, Fe.

Ionic solids: Held together by the strong attraction between cations and anions. Their electrical and mechanical properties are much different from those of metals. Generally speaking, ionic compounds do NOT conduct electricity. Examples: NaCl, MgO.

Types of Solids

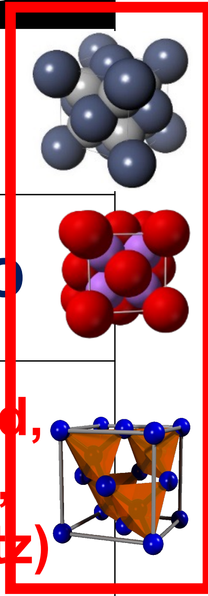
There are four classes of solids that you may encounter on the DAT: metallic solids, ionic solids, covalent-network solids, and molecular solids.

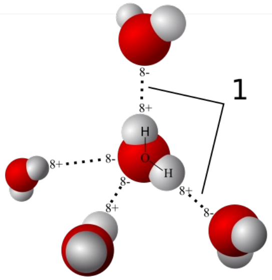
Covalent-network solids: Held together by an extended network of covalent bonds. This bonding type can make materials be very hard, like diamond (a covalent network of carbon atoms). Also gives semiconductors their properties. Examples: diamond, graphite, Si

Molecular solids: Held together by the ***intermolecular forces*** we discussed in a prior video (***hydrogen-bonding***, ***dipole-dipole***, and ***dispersion forces***). These forces are weaker than those of other solids, so these compounds are usually soft and have low melting points. Examples: HBr, H_2O

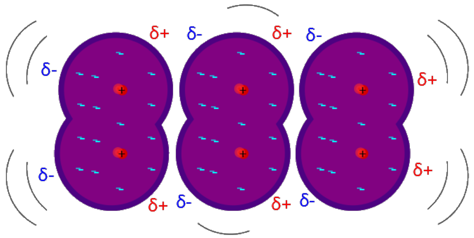
Types of Solids

Type of Solid	Interaction	Properties	Examples
Metallic	Metallic Bonding	Variable hardness and melting point, conductive	Fe, Mg
Ionic	Ionic bonding	High melting point, brittle, hard	NaCl, MgO
Covalent Network	Network of Covalent bonds	High melting point, hard, non-conductive	C (diamond, graphite), SiO_2 (quartz)
Molecular	H-bonding, dipole-dipole, London dispersion	Low melting point, non-conductive	H_2, CO_2





$$\overset{\delta+}{H}—\overset{\delta-}{Cl}\text{- - - - -}\overset{\delta+}{H}—\overset{\delta-}{Cl}$$



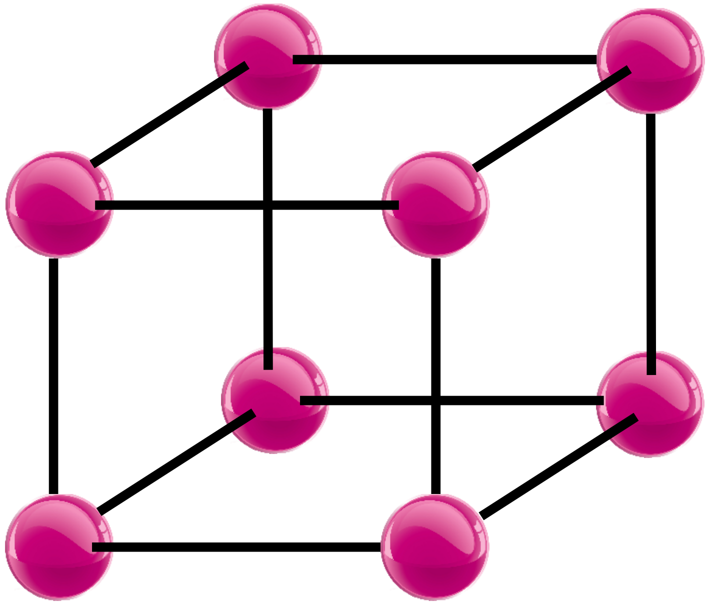
Unit Cells

If you could zoom in to examine a crystalline solid closely enough, you would see that the entire solid is comprised of a small repeating unit, called a ***unit cell***, stacked over and over, three-dimensionally, in all directions.

On this subject, you do NOT need to know very much for the EXAM. However, you <u>do</u> need to know how many atoms are in each of the unit cells that I will now describe.

Simple Cubic

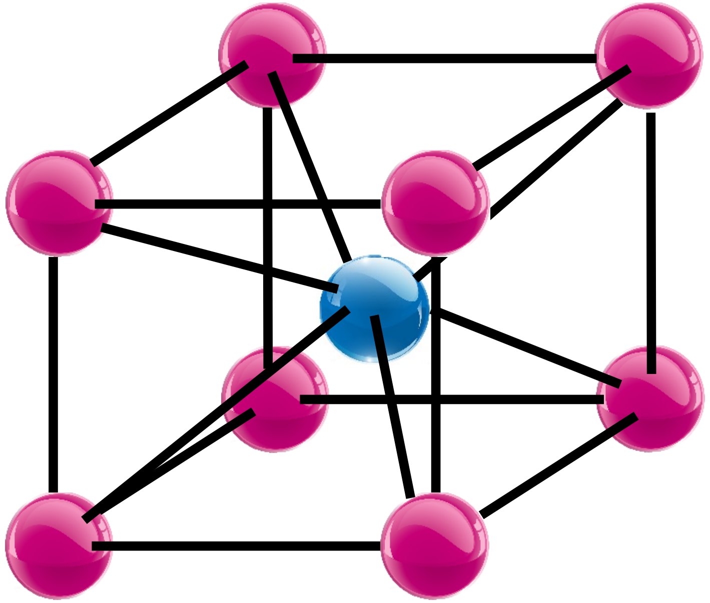
The ***simple cubic unit cell*** looks like this:



It only has one total atom inside the cell. Okay, it *actually* has eight total atoms: one straddling each corner, but each one of those counts as being 1/8 inside the box. Thus, there is only one total atom inside the cell.

Body-Centered Cubic

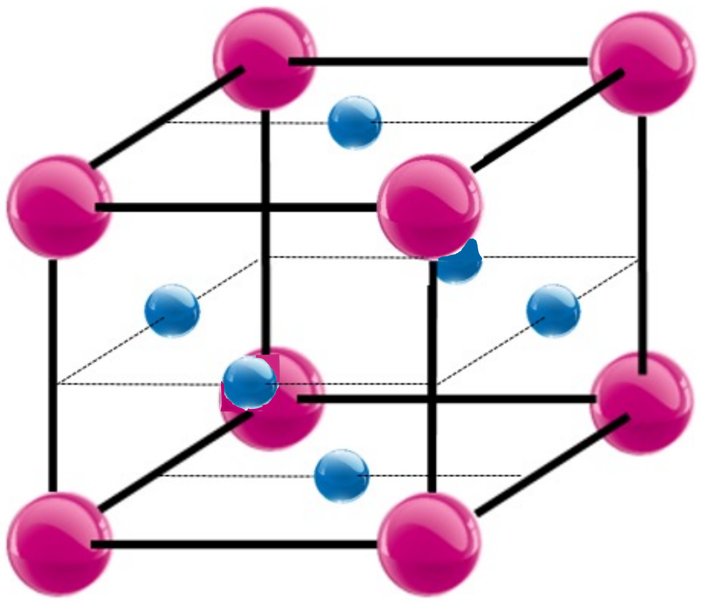
The ***body-centered cubic unit cell*** looks like this:



It has two atoms per cell: one inside the cell and eight straddling each corner ($1/8 \times 8 = 1$).

Face-Centered Cubic

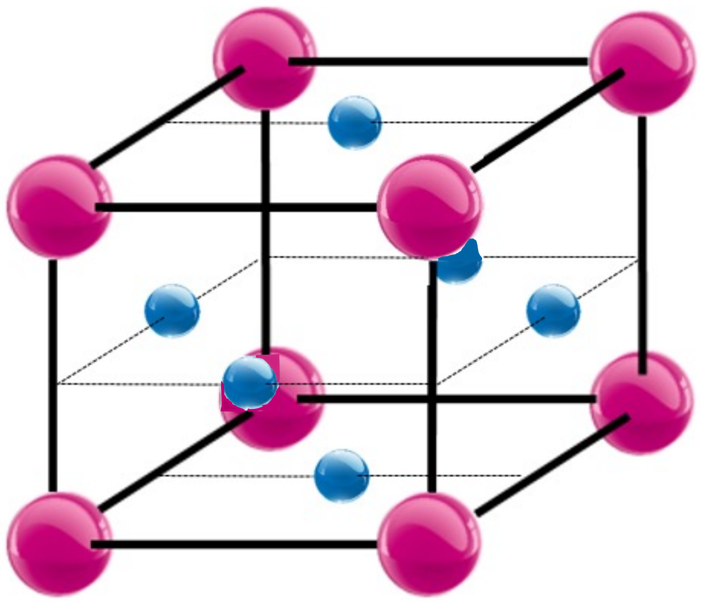
The ***face-centered cubic unit cell*** looks like this:



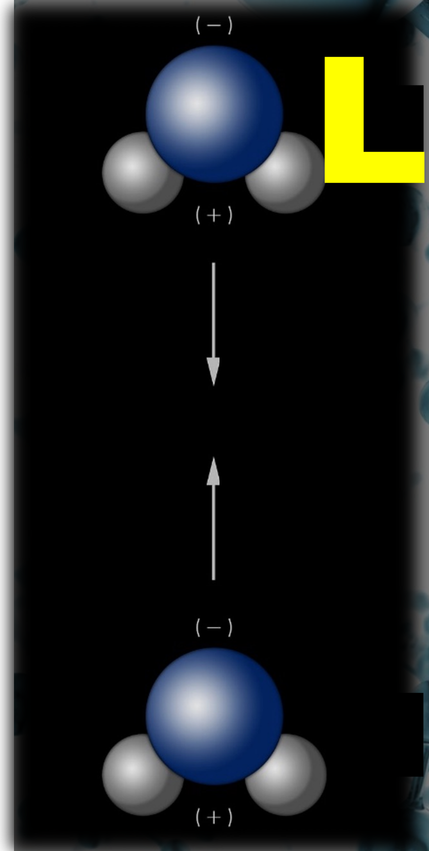
<u>It has four atoms per cell</u>: eight atoms at each corner ($8 \times 1/8 = 1$), plus one atom straddling each face ($6 \times ½ = 3$).

Face-Centered Cubic

The ***face-centered cubic unit cell*** looks like this:

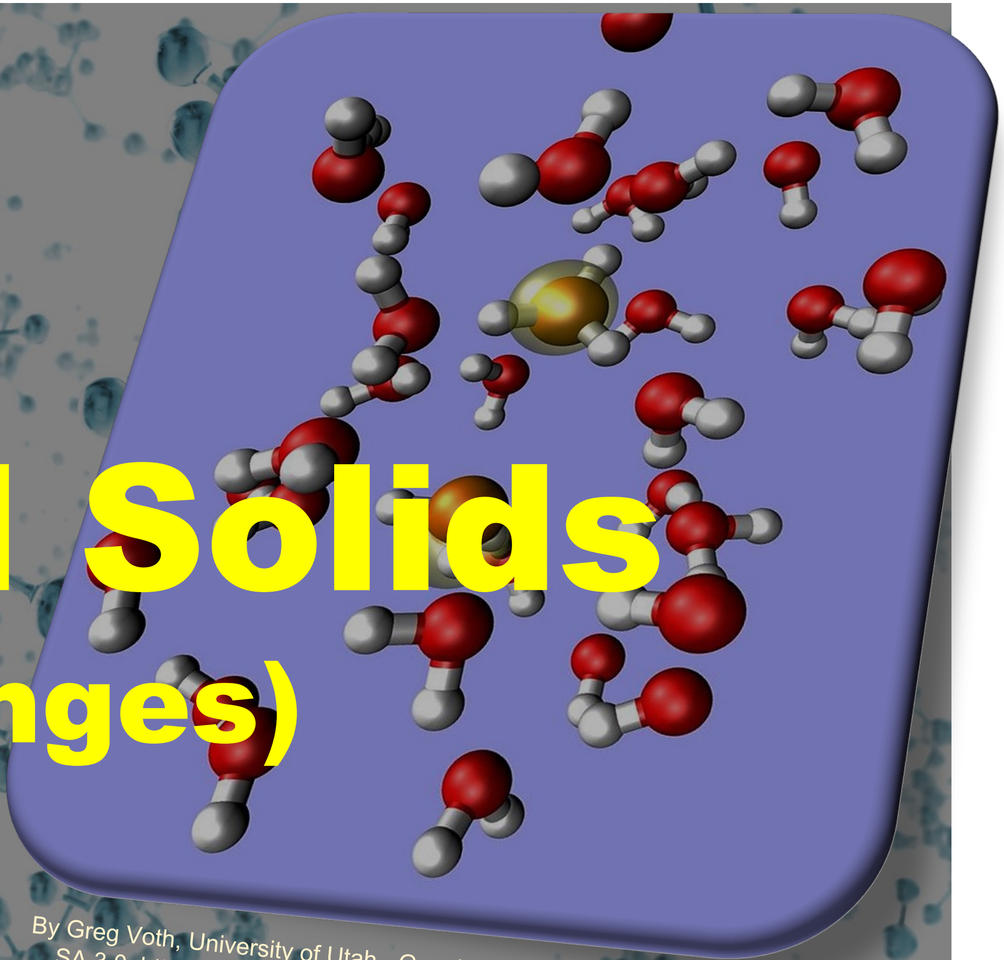


<u>It has four atoms per cell</u>: eight atoms at each corner (8 × 1/8 = $\boxed{1}$), plus one atom straddling each face (6 × ½ = $\boxed{3}$).

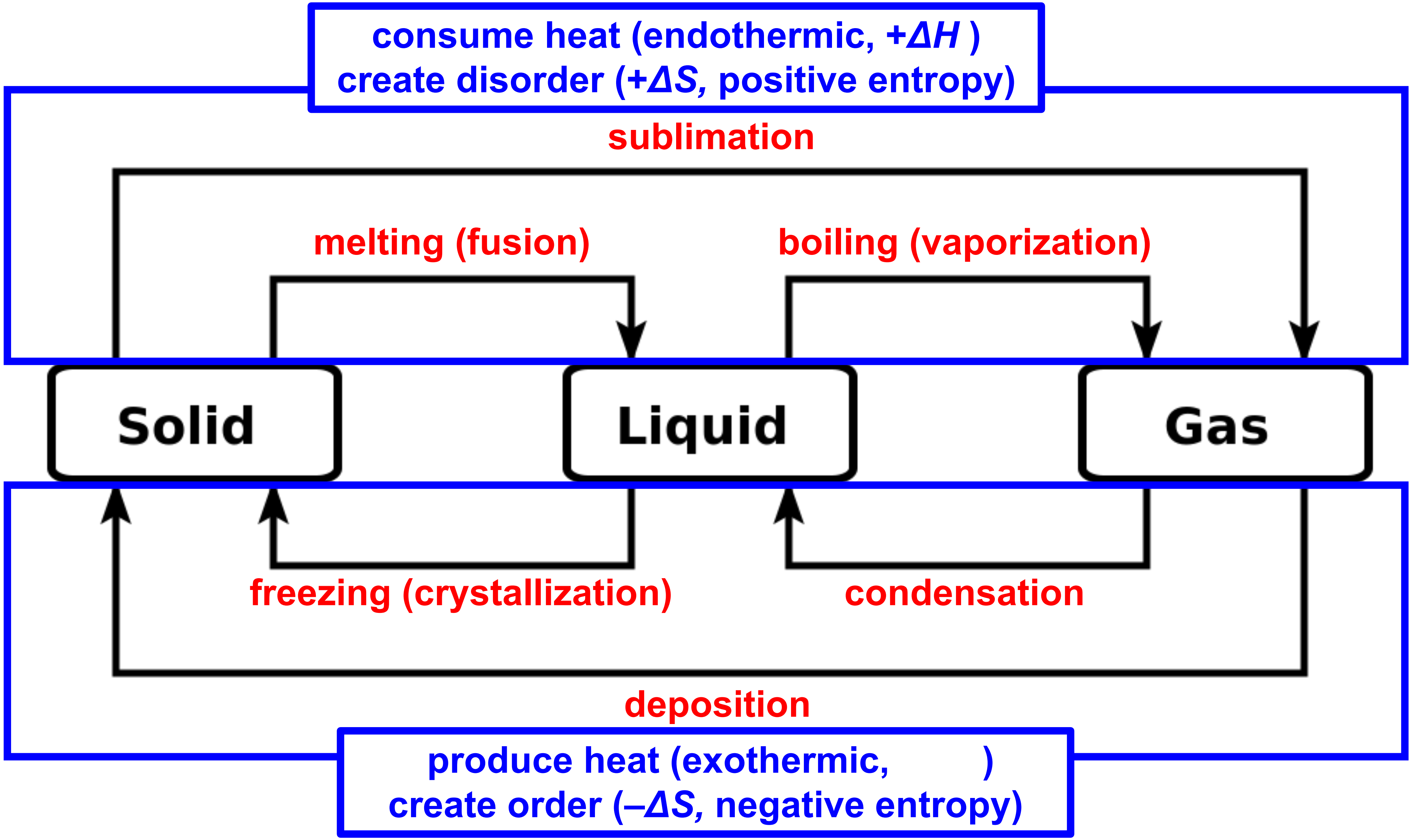


Liquids and Solids

(Phase Changes)



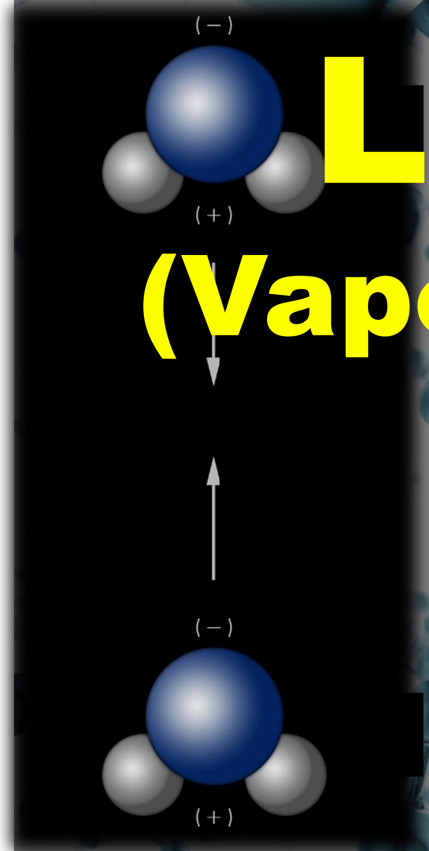
Phase Changes



Phase Changes

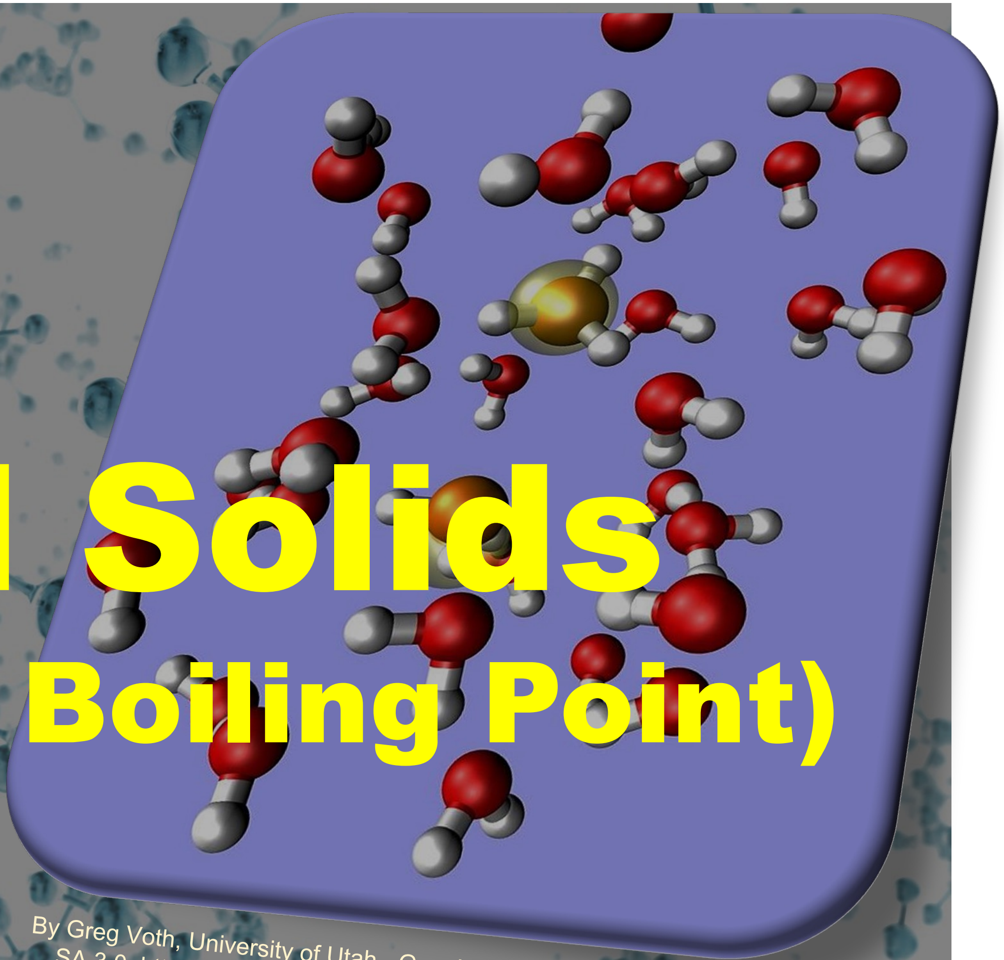
Converting from a . . .	to a . . .	is called:	*ΔH*	*ΔS*
solid	liquid	fusion		
liquid	gas	vaporization	+ (endothermic)	+
solid	gas	sublimation		
gas	solid	deposition		
gas	liquid	condensation	– (exothermic)	–
liquid	solid	crystallization		

We'll talk more about all of these in a later chapter on ***thermodynamics***.



Liquids and Solids

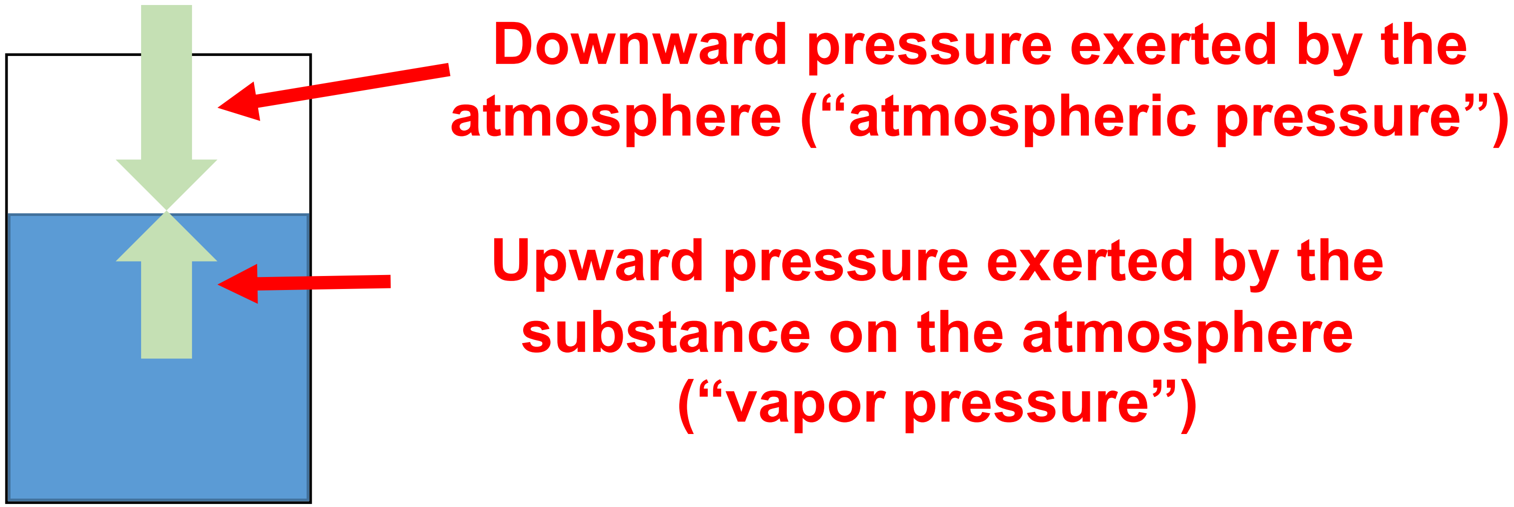
(Vapor Pressure and Boiling Point)



Vapor Pressure and Boiling Point

When liquids evaporate in an open container, gas molecules escape pretty much permanently, never to be reclaimed by the liquid. This is called ***boiling***.

So, ***boiling*** occurs when the pressure exerted by the liquid molecules upward against (toward) the atmosphere *equals* the pressure exerted by the atmosphere down upon the liquid molecules.



Vapor Pressure and Boiling Point

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So, ***boiling*** occurs when the pressure exerted by the liquid molecules upward against (toward) the atmosphere *equals* the pressure exerted by the atmosphere down upon the liquid molecules.

EXAM Tip

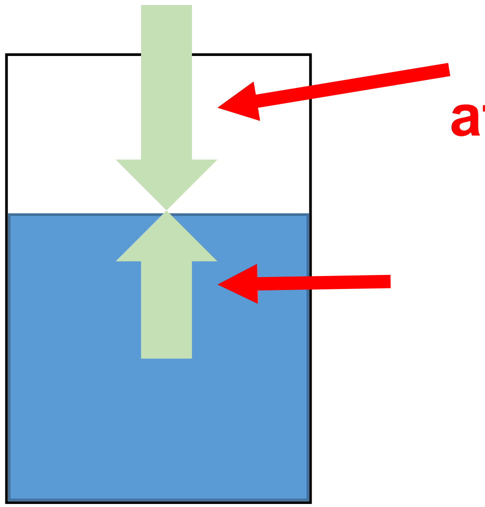
Boiling Point: when the ***vapor pressure = external pressure***

Vapor Pressure and Boiling Point

When the ***vapor pressure*** equals or exceeds the ***atmospheric pressure***, the liquid boils.

We see, then, that:

$\uparrow$ **boiling point** $\approx$ $\downarrow$ **vapor pressure**



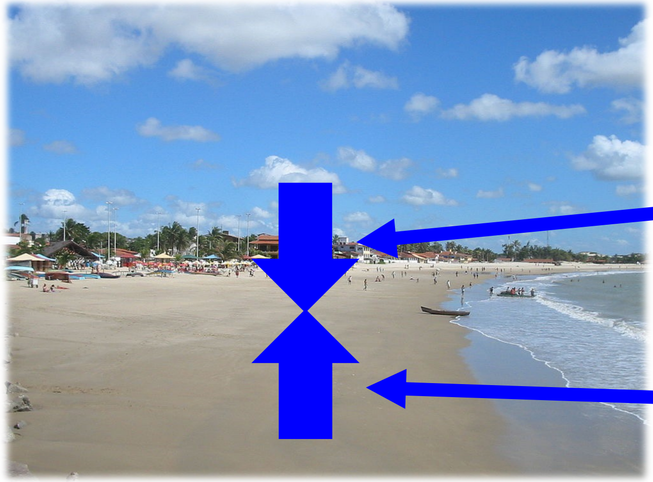
Downward pressure exerted by the atmosphere ("atmospheric pressure")

Upward pressure exerted by the substance on the atmosphere ("vapor pressure")

Vapor Pressure and Altitude

lower atmospheric pressure

lower boiling point
(<100 °C)



higher atmospheric pressure

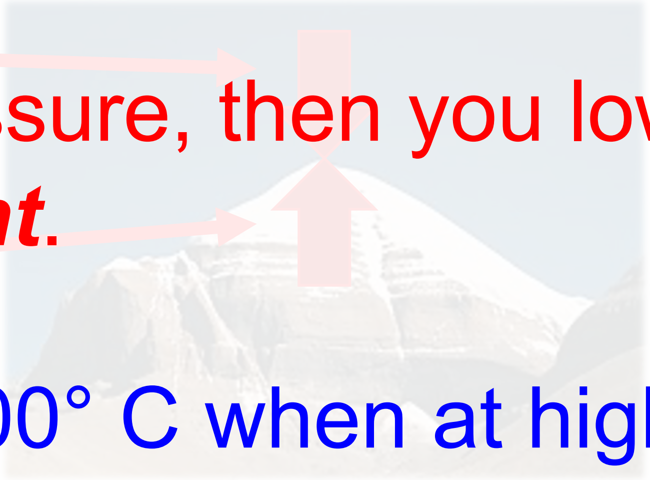
higher boiling point
(100 °C)

Vapor Pressure and Altitude

lower atmospheric pressure

Thus, if you lower the external pressure, then you lower the ***boiling point***.

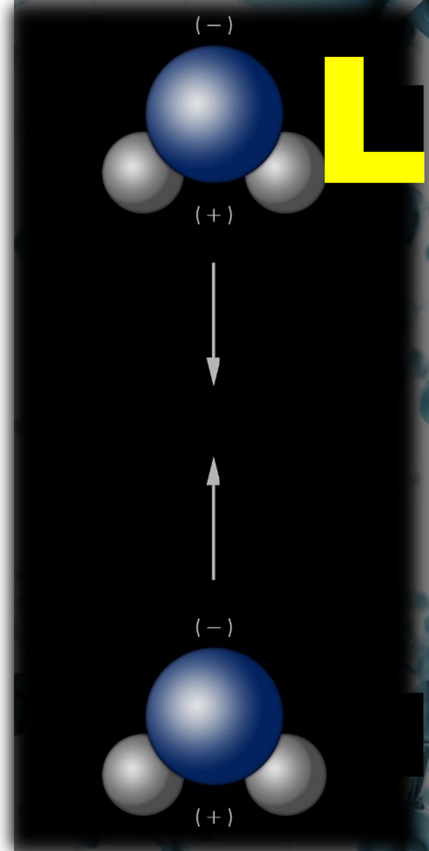
lower boiling point
(<100 °C)



This is why water boils at less than 100° C when at high altitude. If you go high up enough into the atmosphere, you can boil water at room temperature.

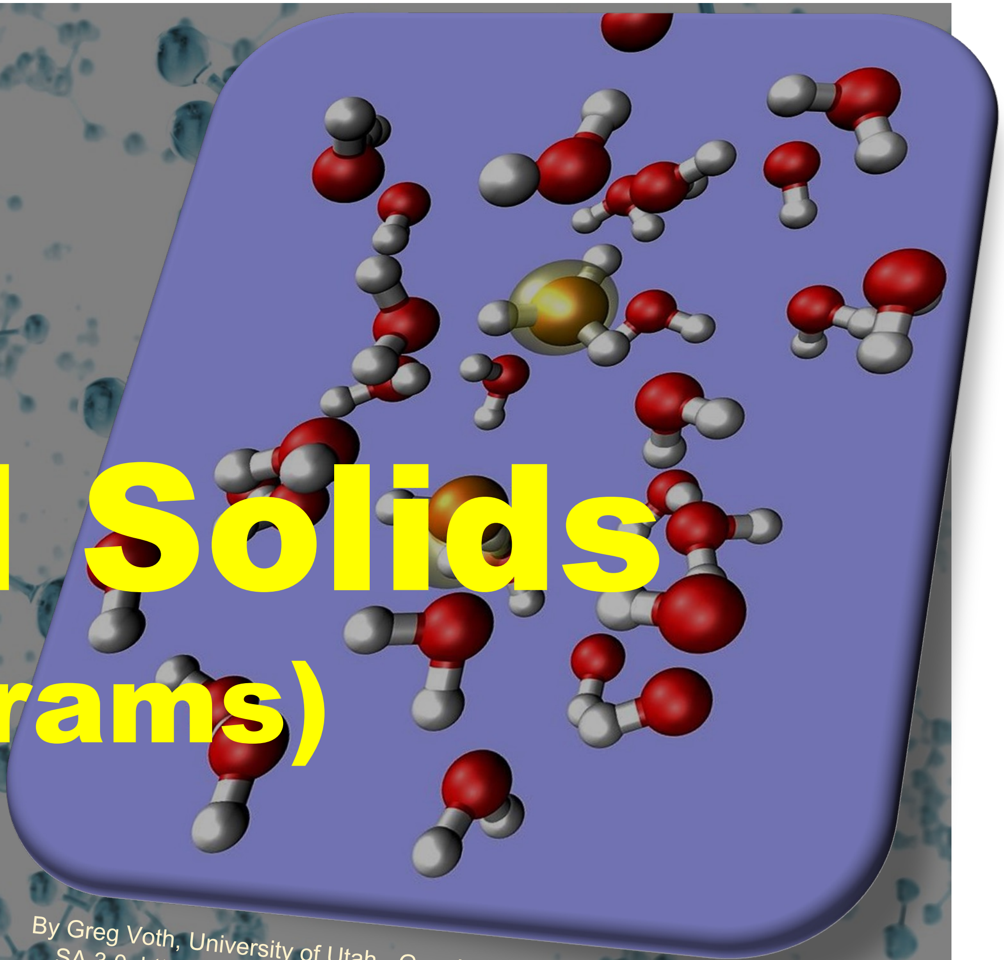
higher atmospheric pressure

higher boiling point
(100 °C)



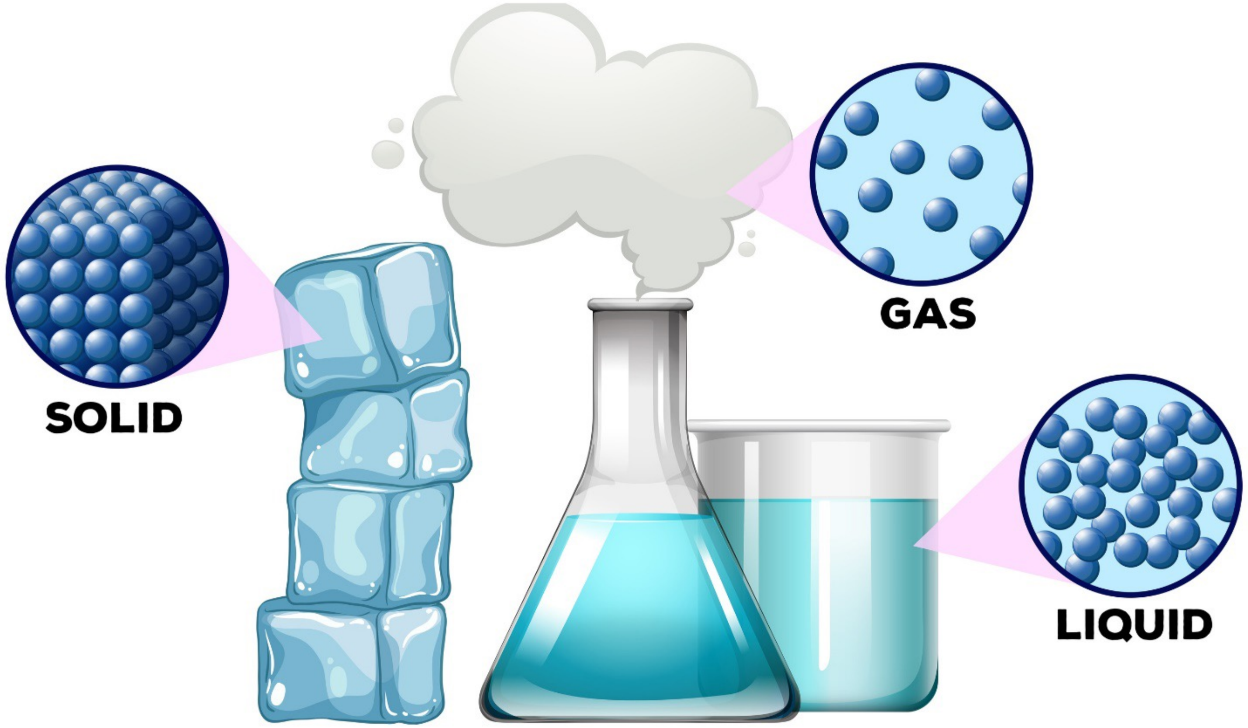
Liquids and Solids

(Phase Diagrams)



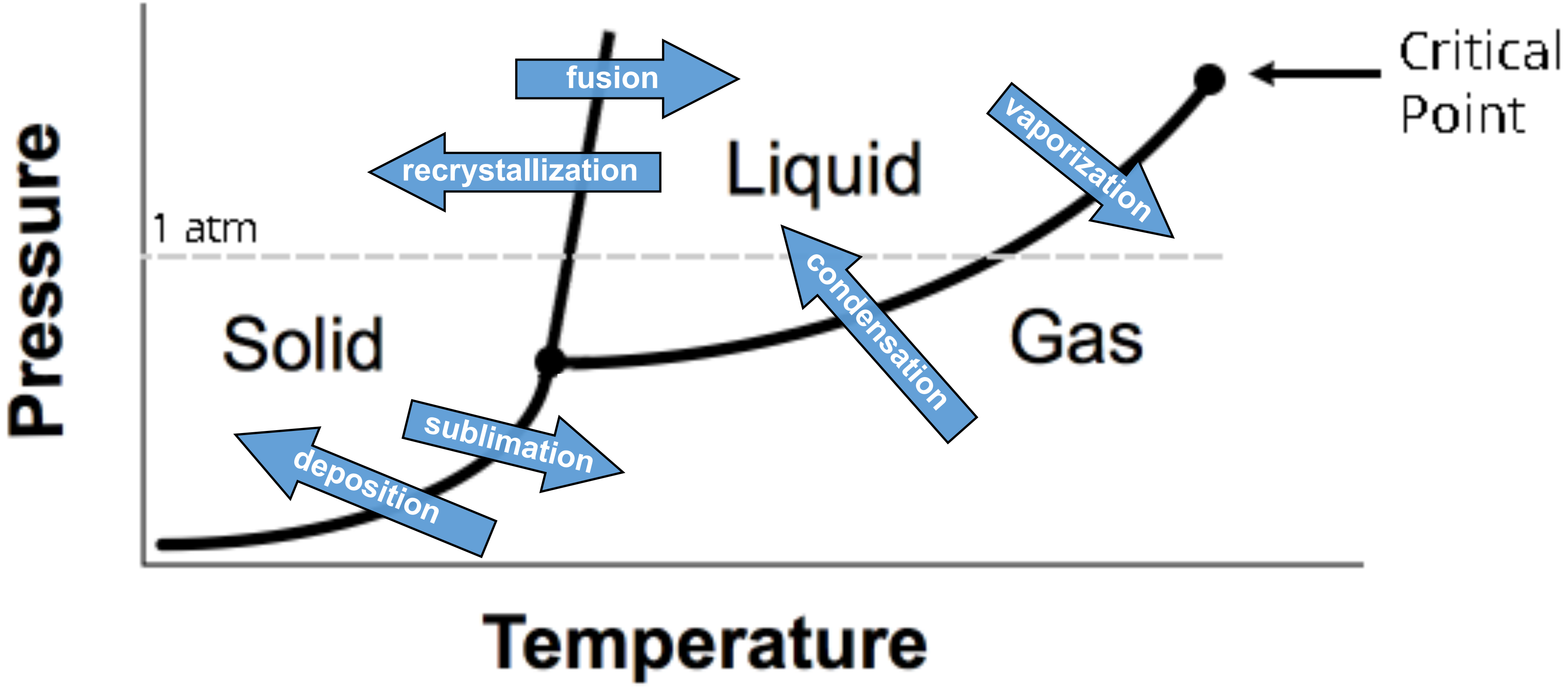
What is a Phase Diagram?

A ***phase diagram*** is a graphical way to show the pressures and temperatures at which a substance will exist as either a ***solid***, a ***liquid***, or a ***gas***, or in some kind of equilibrium in-between two or more of these states.



What is a Phase Diagram?

For example, this is what a fairly typical ***phase diagram*** looks like:



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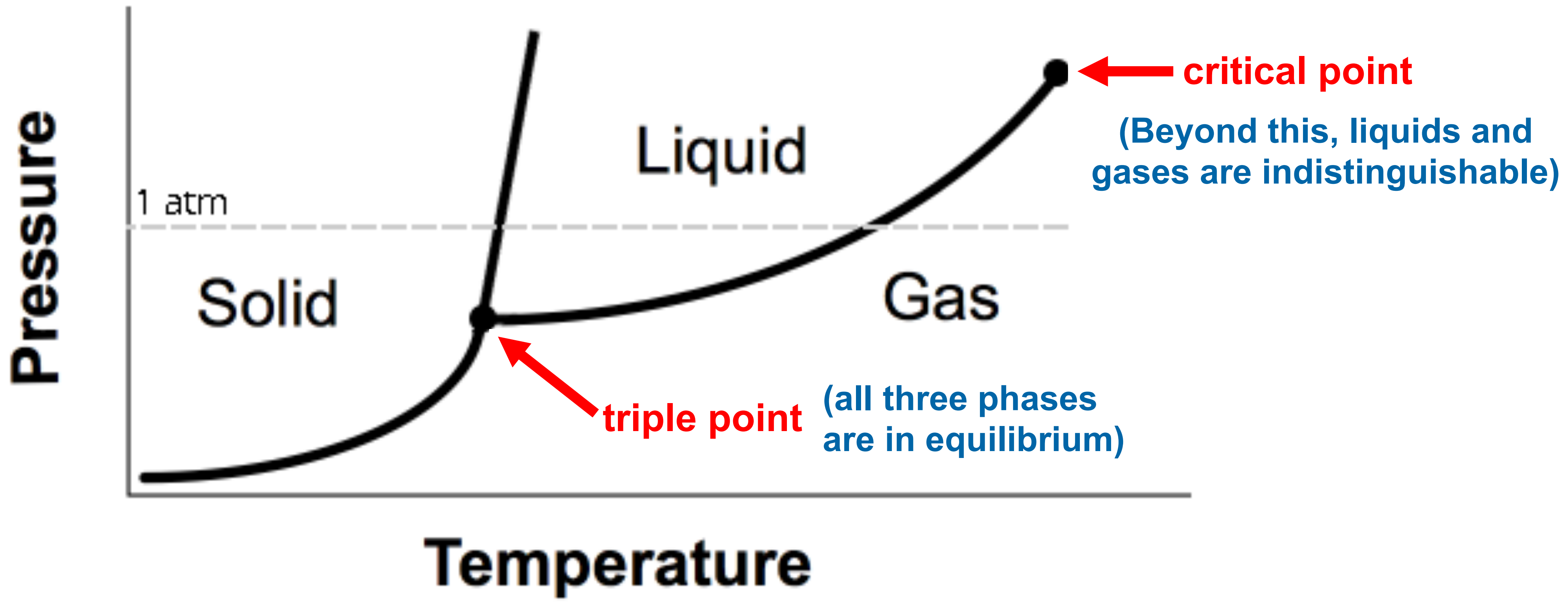


Lines of Equilibrium

(Things You Should Remember)

- The line between a solid and liquid is where solid/liquid can exist at the same time. This is where the phase change occurs.
- Going from a solid to a liquid is called fusion, and that occurs if you increase the temperature at a high enough pressure.
- If your pressure is not high enough (below the ***triple point***), then increasing the temperature will never get you a liquid, you'll just go from a solid to a gas, which is called ***sublimation***.
- You should be able to assign all the 6 phase changes on the phase diagram like we did for the phase changes chart.

Triple and Critical Points

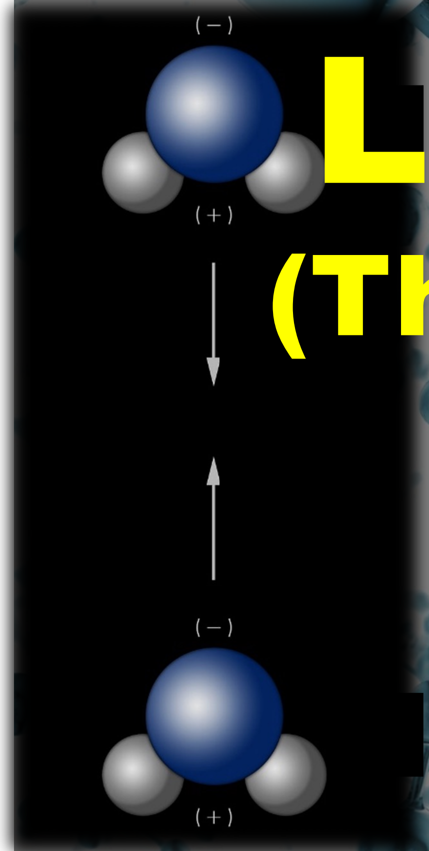
(Things You Should Remember)

Triple point

- The pressure/temperature combination at which all three phases exist at the same time, in equilibrium with each other

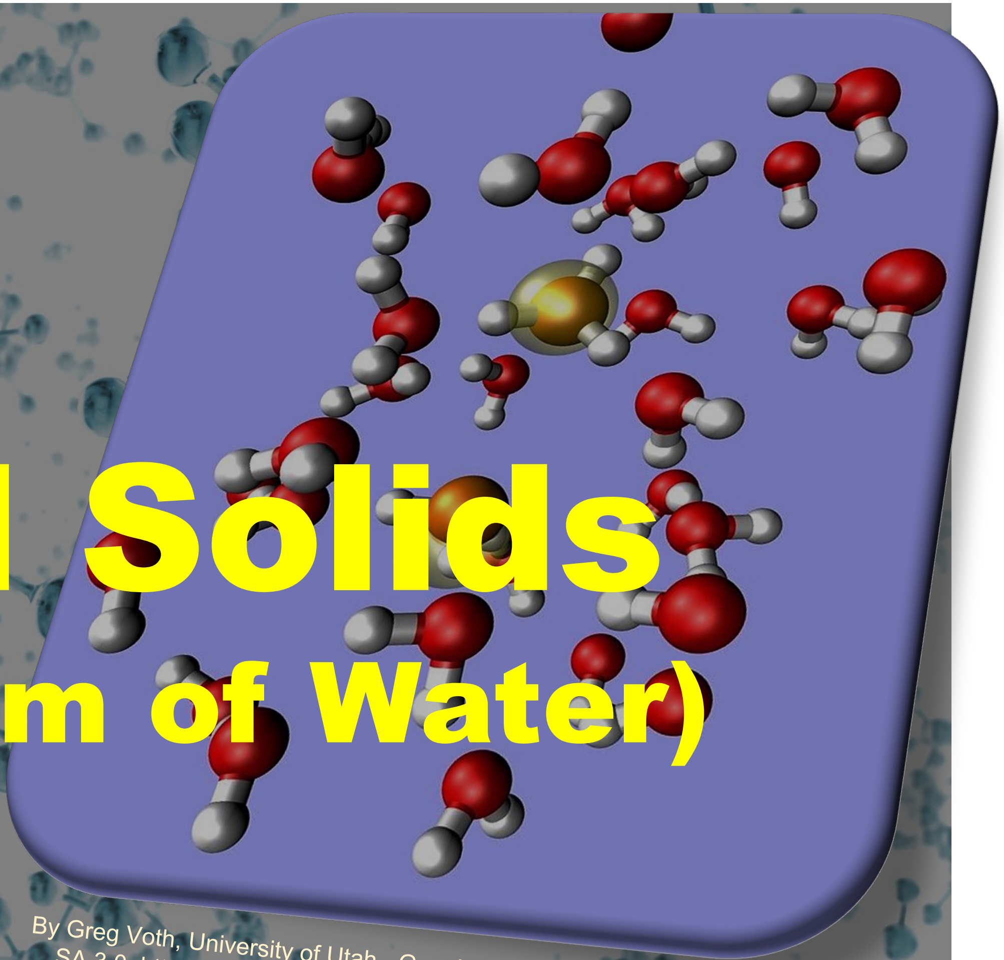
Critical point

- The pressure/temperature combination beyond which liquid and gas coexist at the same time.
- Unlike the solid/liquid line that continues forever (as far as the EXAM is concerned), the ***critical point*** is a point at which the liquid/gas equilibrium line no longer exists.



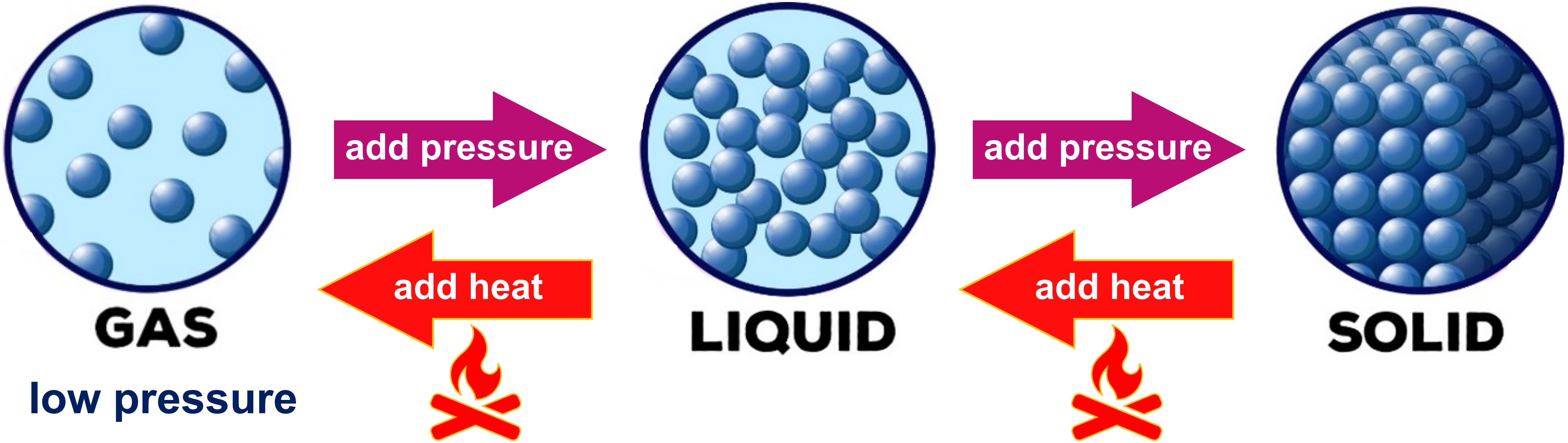
Liquids and Solids

(The Phase Diagram of Water)



Pressure's Effect

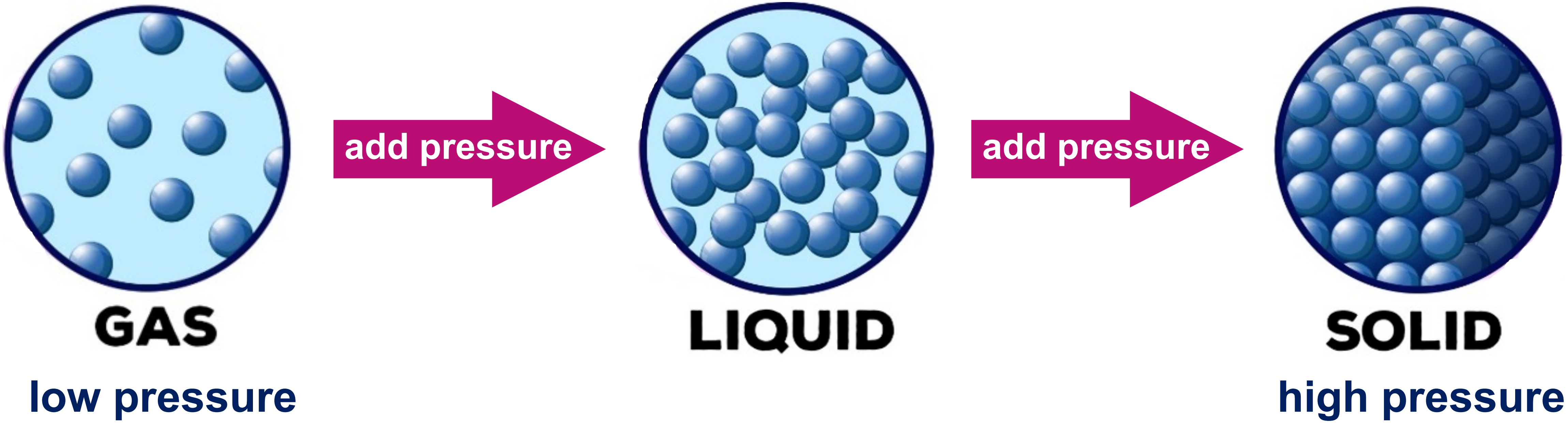
For *most* compounds:



low pressure

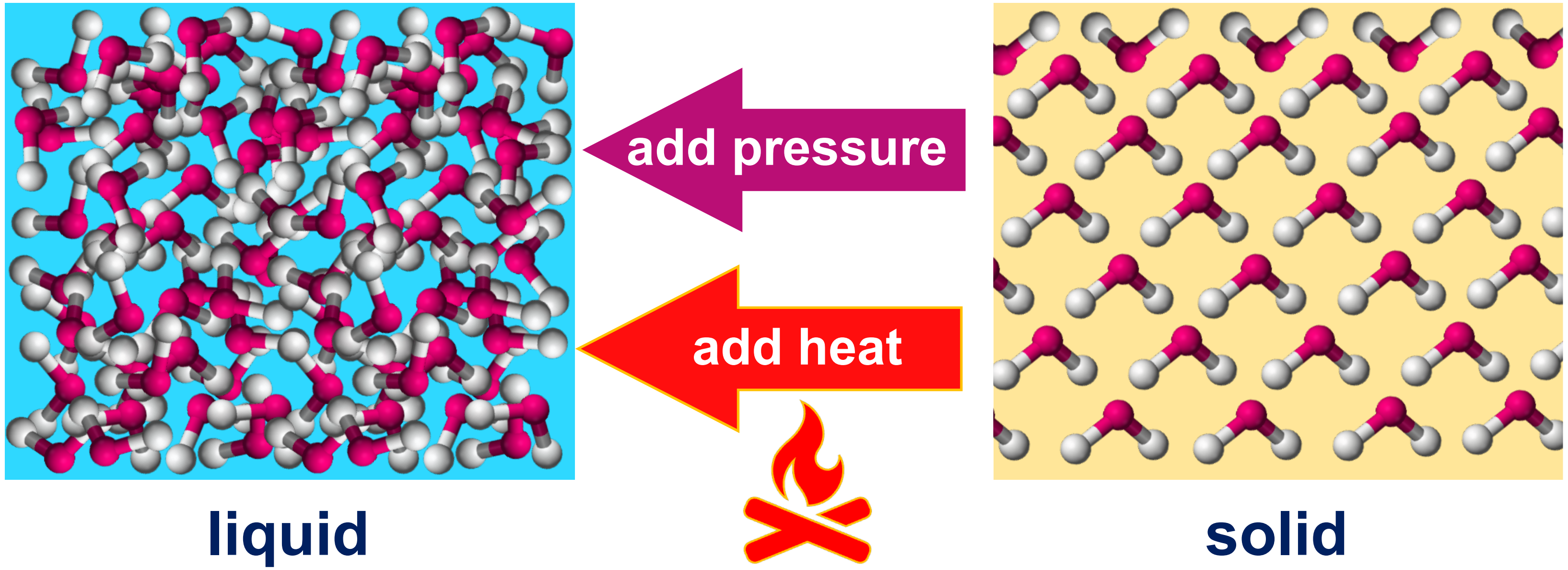
Pressure’s Effect

For *most* compounds:



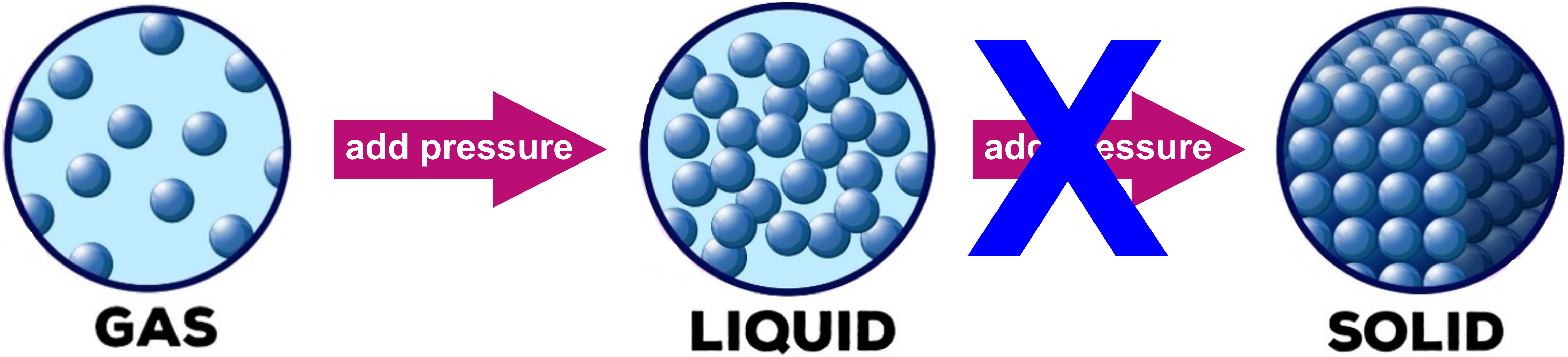
Water is Unusual

Water is unusual because *<u>it's denser as a liquid than as a solid</u>*.



Water is Unusual

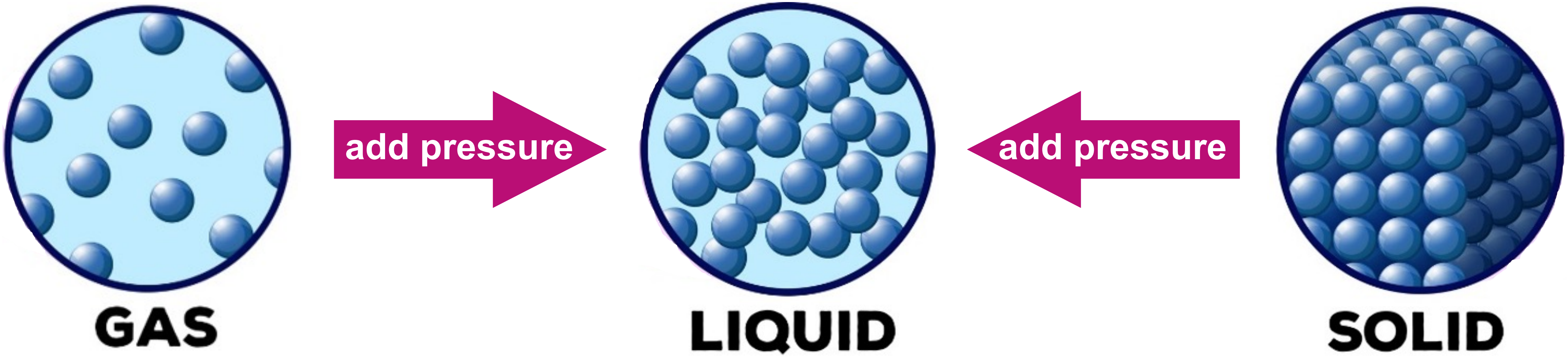
For *water* :



low pressure

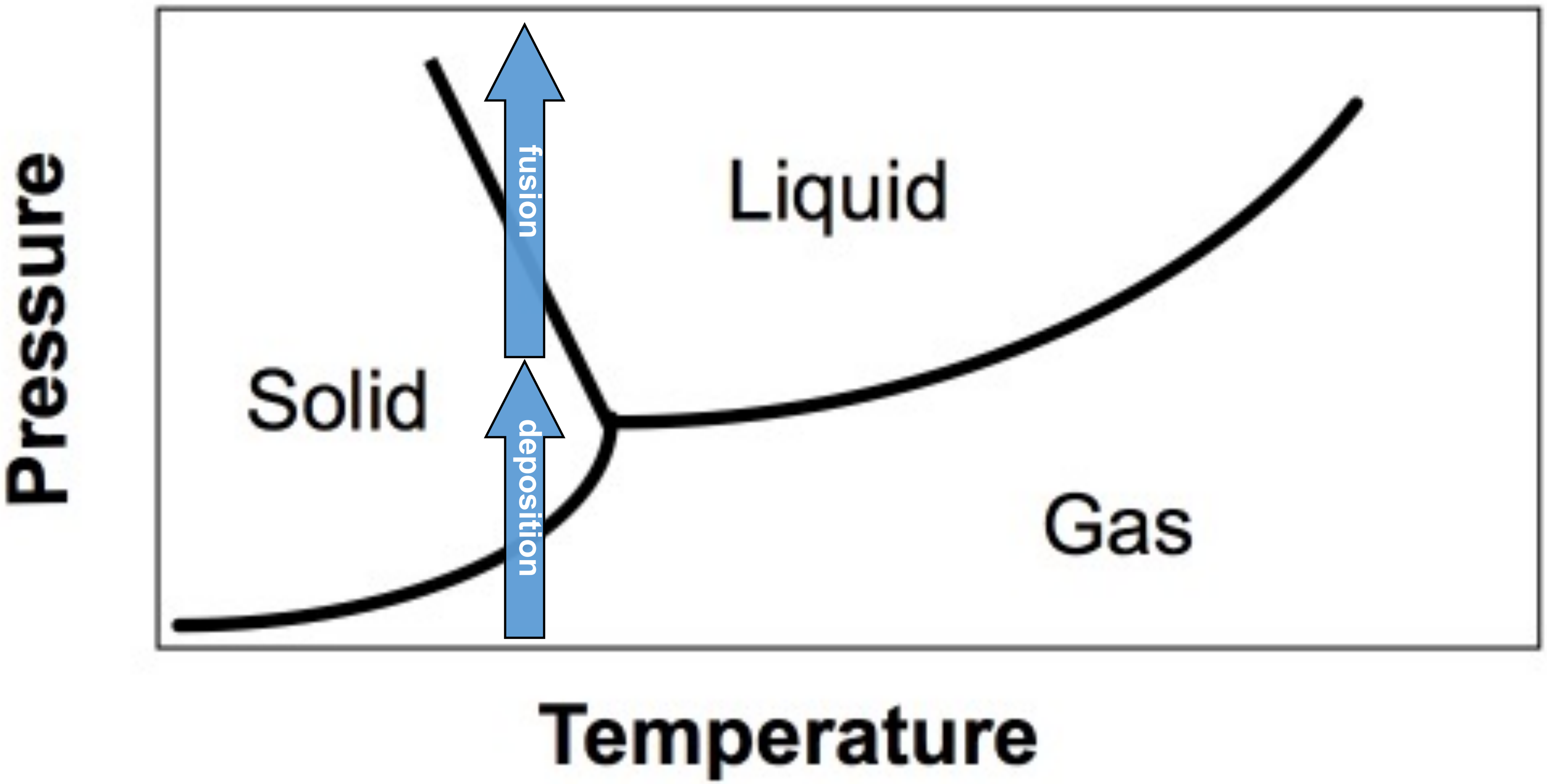
Water is Unusual

For *water* :

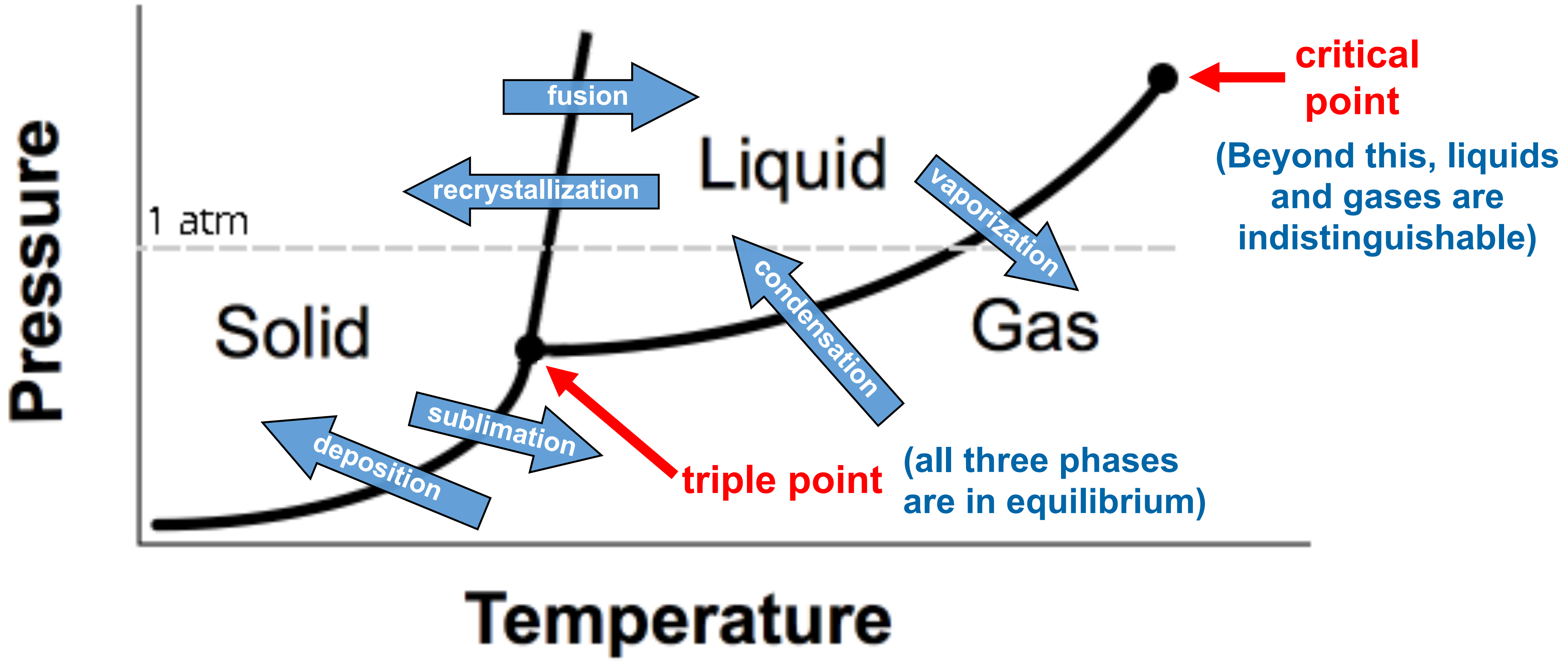


low pressure

Water's Phase Diagram



Typical Phase Diagrams



To Summarize

- Because water is denser as a liquid than a solid, the solid/liquid equilibrium line in water's ***phase diagram*** has a negative slope, instead of a positive one.

- For most compounds, such as CO_2, solids are usually *denser* than liquids. Thus, for most compounds, increased pressure favors the ***solid phase***. But in water, the ***liquid phase*** is denser.

- Thus, in water, increasing the pressure favors the ***liquid phase***, instead of its ***solid phase***.