Chapter 11 Intermolecular Forces and Liquids and Solids

11.1 The Kinetic Molecular Theory of Liquids and Solids

Gases were all about empty space. Solids and liquids are explained in terms of the forces that keep the particles (molecules, atoms, or ions) together.

11.2 Intermolecular Forces – the forces that cause molecules to stick together to form molecular solids and liquids.

Intramolecular attractions are the covalent bonds, the attractions (sigma and pi bonds) **between atoms** that make molecules.

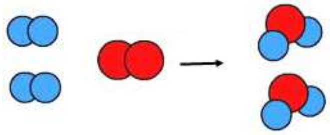
An example of an **intra**molecular change is the formation of water from hydrogen and oxygen:

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$$

Diatomic hydrogen and oxygen's covalent bonds are broken, and new covalent bonds between oxygen and hydrogen are formed.

The change in potential energy is the $\Delta H°_{rxn}$ = - 242 kJ/mol H_2O.

$$\text{H–H} + \text{H–H} + \text{O=O} \rightarrow \text{H–O–H} \quad + \quad \text{H–O–H}$$

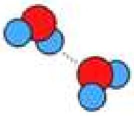


Intermolecular attractions are **weaker** Coulombic attractions **between molecules**.

Intermolecular attractions account for the liquid and solid phases of molecules and noble gases.

Intermolecular forces are weaker than covalent bonds.
The Δ*H*'s for phase changes will be in the tens of kJ rather than hundreds of kJ for chemical changes.

An example of an **inter**molecular change is the phased change involved in the condensation of steam:

$H_2O(g)$	→	$H_2O(l)$
 Separate molecules		 Intermolecular force keeps molecules together.

Condensing steam is a change in physical state. No change occurs in the formula. The intermolecular forces are weaker than the covalent bonds. The change in potential energy for the formation of these intermolecular force attractions is smaller than the formation of water's covalent intramolecular bonds. In this case, one fifth as much, $\Delta H^\circ_{condensation}$ = -44 kJ/mol

Intermolecular forces questions will deal with boiling, melting, and vapor pressure.

Do **not use the term van der Waals forces in any of your answers in FRQ's**.

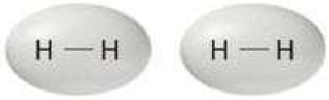
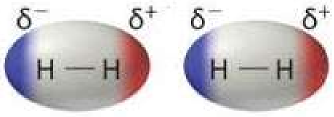
There are **four categories of intermolecular forces** that cause molecules to stick together:

London Dispersion Forces
Dipole-dipole
Ion-dipole
Hydrogen Bonding IMF's

London Dispersion Forces – attractive forces **between molecules.**
All molecules are capable of producing London Dispersion forces.

London dispersion forces are induced dipoles.
Oscillations in electron density of a molecule in the valence electrons will produce charges on one molecule which then induces an opposite charge on an adjacent molecule.

These four drawings explain how induced charges form.

	Nonpolar diatomic hydrogen molecules
	A natural fluctuation in electron density occurs on the left hydrogen molecule. The electron's greater distribution density increases on its one side, creating a slight negative charge, δ^-. This results in a slight positive charge, δ^+, on the other side of the molecule.
	The left molecule's δ^+ charge induces the δ^- charge to form on the right molecule.
	The induced charges are instantaneous, and they fluctuate around the atom.

London dispersion forces increase with the surface area of the electron clouds around atoms.

The larger the electron cloud around the molecule, the more **polarizable** the molecule becomes which will lead to greater dispersion forces. Large molecules have greater dispersion forces because they have a larger number of electrons. The larger the molecule, the greater its polarizability. **Polarizability is also increased by pi bonding.**

A symmetrical molecule's only intermolecular attraction is the London dispersion force, LDF.
Symmetrical molecules and monatomic gases such as He, H_2, SF_6 and CH_4 (and any hydrocarbon) can only have induced LDF charges.

Helium is symmetrical and, with the lowest electron surface area of any substance, it is the least polarizable. As a result, helium has the lowest LDF and lowest boiling temperature of any substance (only a few K above absolute zero). Liquid helium baths are used to cool substances to close to absolute zero.

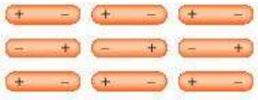
While LDF's are often generalized as the weakest intermolecular attractions, LDF's increase with molecular size and as a result **LDF's can have stronger intermolecular attractions than dipole-dipole or even hydrogen bonding IMF's.**

Two caveats when answering LDF questions on the AP Chem exam!

1. **It is possible for a substance that has only LDF's to have higher boiling temps and lower vapor pressures than substances with other types of intermolecular attractions.**

2. **Do not use molecular mass in explaining the magnitude of the LDF's!** While many textbooks indicate that molecular mass is an index for the degree of polarizability, AP grading guidlines **do not allow molecular mass** as an answer! Only use the electron surface area of the molecule in comparisons of LDF's. Large electron surface areas allow for greater perturbations. A larger electron surface area is **more polarizable and thus can have greater LDF's.** When comparing LDF forces on FRQ questions, use the term polarizability.

Dipole-Dipole Forces – attractive forces between **polar** molecules

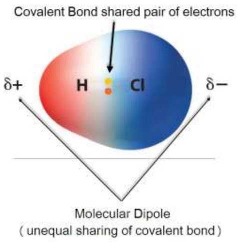
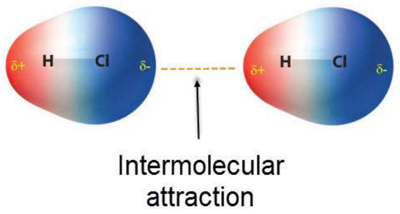


Molecules that have a permanent dipole moment tend to align with opposite polarities in the solid phase for maximum attractive interaction.

Permanent polar charges on molecules (dipoles) produce intermolecular attractions.

Asymmetrical molecules have permanent dipole-dipole forces

HCl, H_2S, SO_2 and O_3 are all asymmetrical and will have permanent dipoles. These polar molecules condense into liquids because of dipole-dipole intermolecular attractions. A dipole moment is the measurement of the magnitude of the polarity of a molecule.

	Covalent bonds are attractions of two nuclei to a pair of electrons between atoms, in this case, H:Cl. Since the hydrogen atom has a lower electronegativity than the chlorine atom, the sharing is unequal, and the chlorine side of the molecule will have a partial negative charge, δ-. The hydrogen atom will have less control of the electron pair. Therefore, the hydrogen side of the molecule will have a slight positive charge, δ+. A dipole is caused by an imbalance in the electronegativities of the atoms in a molecule.
	The dipole partial charges will provide the Coulombic attractions to cause the molecules in a gas to condense into a liquid or solid. The intermolecular attraction is often shown with a dotted line between the molecules since the intermolecular dipole-dipole attraction energy is usually much smaller than the intramolecular covalent bond energies which are shown as solid lines.

NOTE!

If a question asks for all the intermolecular forces between a substance with dipole-dipole be sure to include LDF as well since London dispersion forces will also contribute to the intermolecular attractions.

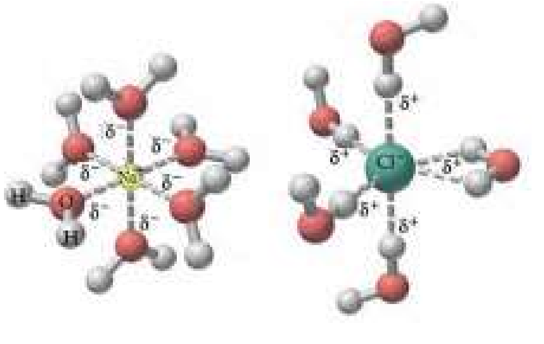
Ion-Dipole Forces - attractions of an ion to one of the dipoles of a polar molecule. This occurs in solutions. The ion-dipole force is the major reason that ionic compounds dissociate in water.

Water has a very strong dipole.

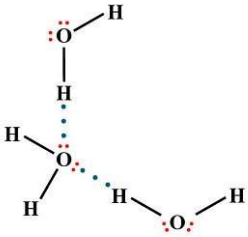
Water's negative portion of the dipole, δ-, is on the oxygen atom. The δ- attracts cations (positive ions) of an ionic substance.

Water's positive portion of the dipole, δ⊕, is on the hydrogen atoms. The δ⊕ attracts anions (negative ions) of an ionic substance.

The water's dipole charges can neutralize the ion charges, causing the ionic substance to dissolve in water. This attraction and type of diagram is commonly found on the exam!



Hydrogen "Bond" IMF's - a special type of intermolecular force between the intensely **positive charged hydrogen atom** and another molecule's nitrogen, oxygen or fluorine negative dipole.



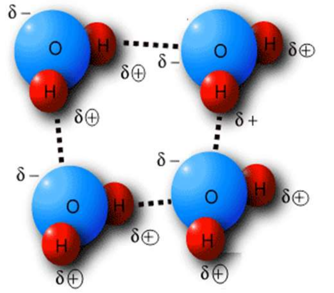
The hydrogen atom can only attain this concentrated positive charge in a molecule when it is attracted to one of three highly electronegative atoms:

H covalently bonded to N	**-N-H**δ⊕··· -δX
H covalently bonded to O	**-O-H**δ⊕··· -δX
H covalently bonded to F	**F-H**δ⊕··· -δX

The ··· represents the **inter**molecular attraction that is called the hydrogen bond.
The -δX is the negative dipole (pair of electrons) of an N, O or F atom.

The high electronegativity of the N, O, and F atoms are the only atoms that can produce the special focused partial positive charge (δ⊕) on the H atom that can produce the special intermolecular attraction called hydrogen bonding.

Since a hydrogen atom has only one electron, there are no other underlying electrons in lower energy levels to mitigate the positive charge of the proton in the nucleus of the hydrogen atom. This "exposed" proton is what makes the hydrogen "bond" such a strong intermolecular attraction. Despite the term bond in hydrogen bond, this is still an intermolecular attraction. Chemistry teachers wish the name could be changed to "special hydrogen attraction".

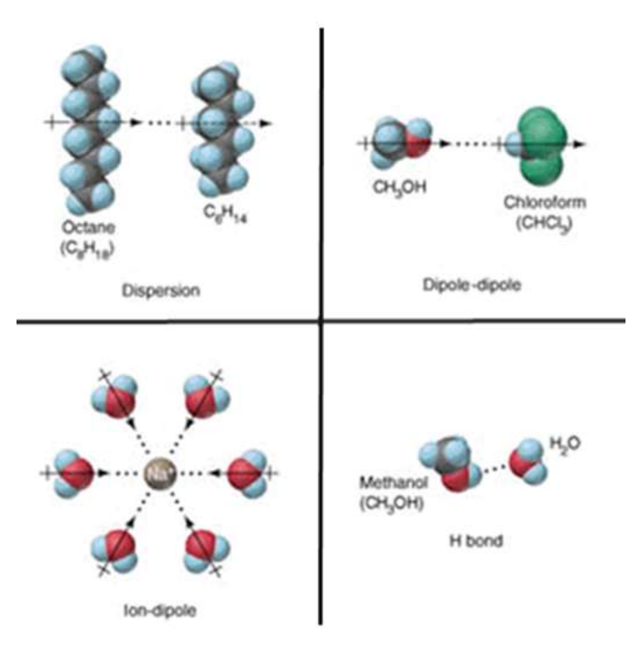


The H(δ⊕) must also be attracted to the lone pair of electrons of :N, :O, or :F

A substance with hydrogen bonding will also have dipole-dipole attractions and LDF's.

If a question asks for all the intermolecular attractions when hydrogen bonding is involved, you must also list LDF and dipole-dipole in addition to hydrogen bonding.

Every AP Chemistry test has questions on the four types of intermolecular attractions.
LDF, Dipole-Dipole, Ion-Dipole, Hydrogen Bond IMF's



Special note! When answering FRQ's that involve breaking or forming any one of these IMF's, **do not use the terms forming or breaking bonds**. The reader would mark your response as incorrect as forming or breaking **bonds** implies forming or breaking covalent intramolecular bonds. Instead say forming or breaking IMF's. Even when referring to hydrogen bonding, write forming or breaking hydrogen bond IMF's.

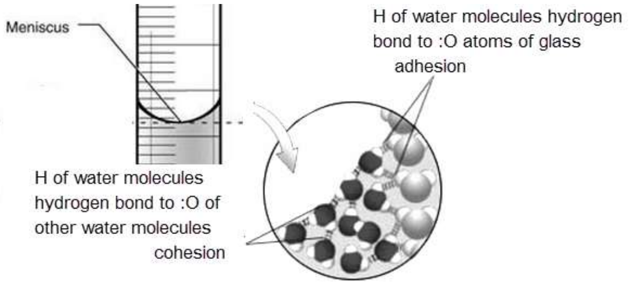
11.3 Properties of Liquids

Surface tension and viscosity are not part of the AP Chemistry curriculum

Capillary is the process of a liquid flowing in narrow spaces in opposition to gravity. In glass tubes, adhesion (intermolecular attractions of one substance to another) can cause water to move up the tube noticeable distances. This is what causes a meniscus.

Water will "crawl" up the side of the glass because of the lone pairs of electrons of oxygen, Si-O: δ-, in the glass.

The lone pair electrons on the glass molecules oxygen atoms will attract the special H⊕ of the water molecules.



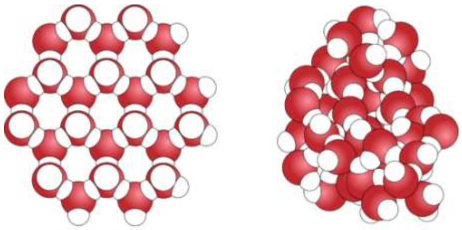
The terms hydrophilic and hydrophobic are often used in references to capillary action. However, remember that **hydrophobic does not mean that water is repelled**. The "phobic" is a misleading term.
The "hydrophobic" property is the result of water having **greater intermolecular attractions to its own molecules** compared to its attraction to the other substance.

The Structure and Properties of Water

The “open” crystal structure of ice caused by the angles of the hydrogen bond IMF’s in ice makes ice less dense than the randomly packed molecules of liquid water.

The density of ice is 0.92 g/ml vs the density of water 1.0 g/mL

This is an anomaly as most crystalline arrangements of substances are more compact than the random arrangements of the liquid phase.



$H_2O(s)$ $H_2O(l)$

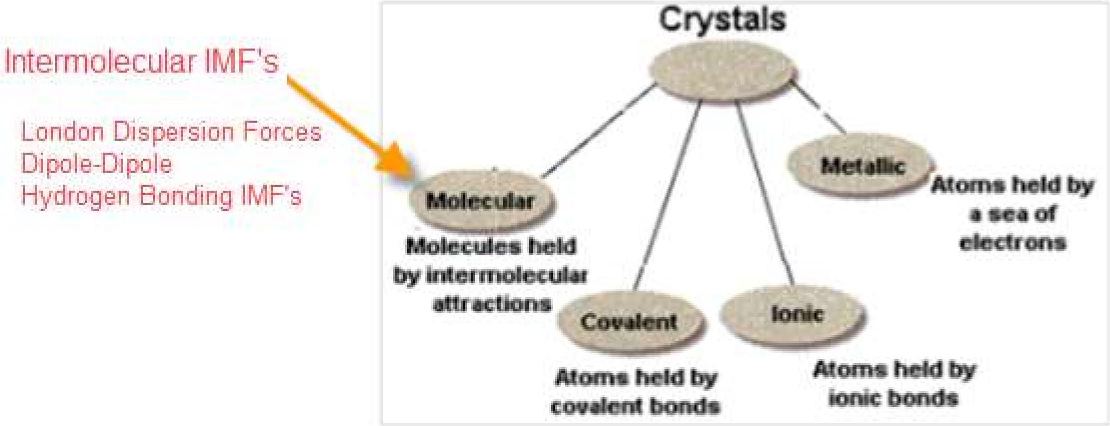
11.4 Crystal Structure *Not in the AP curriculum*

Solids that have a regular arrangement are called crystalline and are composed of unit cells. The smallest unit of the regular pattern is a unit cell. Unit cells and atomic packing are *not part of the AP curriculum*.
Some solids have no regular pattern and are called amorphous solids.

11.5 X-Ray Diffraction *Not in the AP curriculum*…You may skip this topic also.

11.6 Types of Crystals

In addition to molecular solids with its four types of intermolecular attractions, there are three other types of substances each of which have a specific type of bonding.

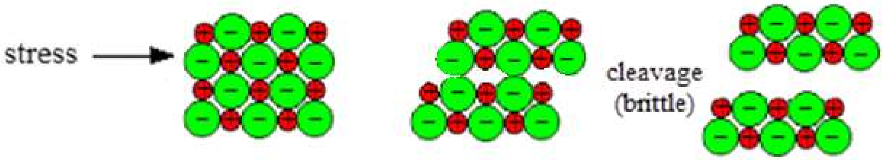


Ionic Crystals – atoms held by ionic bonds (these are classified as bonds)

No need to learn about unit cells or packing.
Ionic Crystals are three dimensional arrays of cations and anions.

The Coulombic attractions of ions are stronger than the partial charges of dipoles. As a result, the melting and boiling temperatures of ionic compounds are high. No ionic compound is a liquid at room temperature. Melting temperatures are typically in the hundreds of degrees Celsius and boiling temperatures are measured in the thousands of degrees Celsius.

Ionic crystals are brittle. They cleave (split) when a force is applied to the crystal because of disruptions to the crystal lattice. The opposite charges that cause the ions to stick together become misaligned causing the solid to shatter.



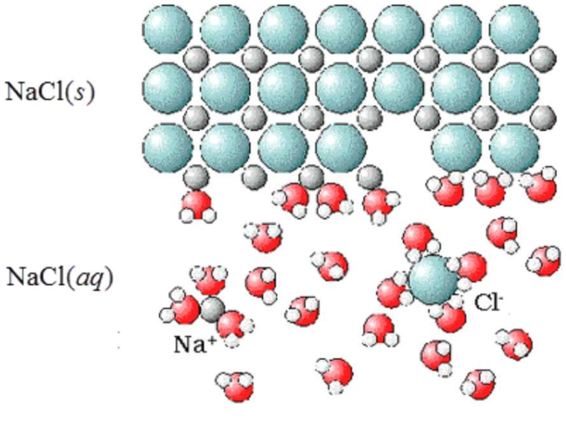
Smaller ions and ions with larger charges will have higher lattice energies and higher melting and boiling points.

e.g. MgO (Mg^{2+} and O^{2-}) will have greater interionic attractions than KBr (K^+ and Br^-). As a result, MgO has a higher melting temperature than KBr. Smaller ions also have higher Coulombic attractions because the Coulombic forces increase as the ions get closer to one another.

An important, unique feature of ionic compounds:

Ionic compounds do not conduct electricity as solids since the ions are locked in place
Ionic compounds do conduct electricity when molten via the movement of ions.

Ionic compounds will not dissolve in nonpolar liquids because London dispersion forces in nonpolar solvents are not strong enough to compete with the strong cohesion of the ionic attractions.

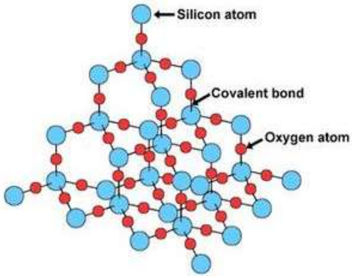
Some ionic compounds dissolve in water because the concentrated positive dipole of the hydrogen atoms and the negative dipole of the oxygen atom in water can compete with the ionic charges. The small, polar water molecules surround and cloak the ions forming ion-dipole attractions. This was mentioned before as being ion-dipole attractions. Ionic solutions conduct electricity because the dissociated ions can move in the solution. You are expected to be able to draw a solvated ion of the solute with the +δ hydrogen of the water molecules surrounding the anions and the -δ oxygens next to the cation as in this drawing.	

Covalent Crystal - Covalent Network Solids is the official AP terminology

The empirical formulas of these substances are either a single element or two elements. The element(s) may be nonmetal or metalloid. The atoms in the covalent network solid form an extensive, macroscopic two or three-dimensional system of covalent bonds. A single crystal would be a giant covalent molecule.

Memorize these common covalent network solids:

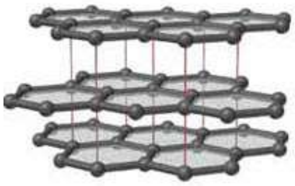
C as diamond in a 3-D network of C atoms.
C as graphite in 2-D sheets in a planar network.
Si (used in almost all computer chips)
Ge (just like Si)
SiO_2 (as quartz in 3-D network and asbestos fibers in 2 D string network)
SiC (silicon carbide)
BN (boron nitride)

Covalent network solids are often hard to recognize from their formulas since the formula is an empirical formula. SiO_2, quartz, looks much like a molecular formula (especially since it looks just like carbon dioxide). However, there are no individual SiO_2 molecules. SiO_2 is an empirical formula where the silicon atoms and oxygen atoms form a giant three-dimensional molecule with twice as many oxygen atoms as silicon atoms.	

Covalent network solids have very high melting temperatures (thousands of degrees Celsius) since melting the solid requires breaking covalent bonds.

Covalent network solids usually do not conduct electricity because their valence electrons are locked in covalent bonds.

Carbon is the poster child of network covalent solids. It has several forms, the most notable are diamond and graphite.

	Diamond has carbon atoms with four *sp*^{3} orbitals forming covalent bonds in three dimensions. This forms one of the hardest substances known. A diamond is the best-known conductor of heat as an oscillation in one atom will transfer to all the attached atoms. There is no mobility of the shared pairs of electrons. A diamond will not conduct electricity.
	Graphite has carbon atoms with three *sp*^{2} orbitals forming covalent bonds in two dimensional sheets. The only major intermolecular force between the two-dimensional sheets is the London dispersion force. Since the network of covalent bonds is only along 2 dimensional planes, graphite is a soft network solid and is used as a high temperature lubricant because the molecularly bonded sheets can readily slide by one another, much like the individual cards in a deck of cards. Also, the delocalized *p* orbitals allow for electrical conductivity along the axes of the plane.

Molecular Crystals

These have already been explained in the sections on intermolecular attractions.
Molecular crystals, molecules held together by dispersion forces, dipole-dipole, and hydrogen bond IMF's.

Molecular crystal physical properties differ from the other types of solids.

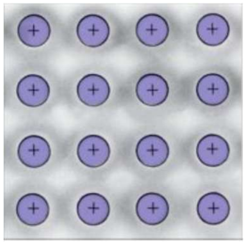
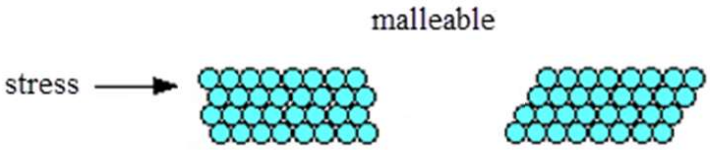
Lower melting temperatures
Normally **do not conduct electricity as solids or liquids**.

Most molecular crystals, except for larger organic molecules or polymers, melt at temperatures below 200°C.

If a substance is a gas or a liquid[1] at room temperature, odds are that it is a molecular substance.

Metallic Crystals

Metallic solids are good conductors of heat and electricity. They have a wide range of melting points and are shiny. Metals are described as malleable (can be beaten into sheets) and ductile (can be pulled out into wires).

A metallic solid can be represented as positive cores consisting of the nucleus and inner electrons of each atom surrounded by a sea of mobile valence electrons. The electrons are delocalized. This model explains electrical conduction because the electrons are mobile, increased temperatures decrease electrical conductivity due to the interference by the core atom vibrations.	
This model explains the malleability and ductility of metals since, as the core atoms are moved, the electrons can fill in so there is no change in the Coulombic attractions. This allows the atoms of a metal to roll over each other into new positions without breaking the metallic bond. This is in contrast to brittle ionic compounds whose fixed charges would not allow this.  	

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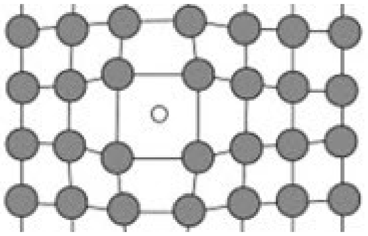
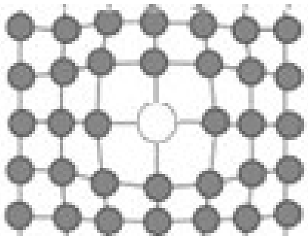
[1] Gallium and mercury and their alloys are exceptions.

Special AP Chem material not in Chang or most college texts,

"…Metallic solids are often pure substances but may also be mixtures called alloys."

1. Some properties of alloys can be understood in terms of the size of the component atoms. Be able to draw these models of alloys.

-**Interstitial alloys** form between atoms with different radii. The smaller atoms are inserted in the interstitial spaces between the larger atoms. (Steel is an example in which carbon occupies the interstices in iron.) The interstitial atoms make the lattice more rigid, decreasing malleability and ductility. The most important example of an interstitial element is the carbon in steel. Hydrogen, boron, and nitrogen are also used in interstitial alloys because these atoms are typically smaller than most metal atoms.	

-**Substitutional alloys** form when atoms of comparable radii substitute for the other atoms in the lattice. (Brass is an example in which some copper atoms are substituted with a different element, usually zinc.) The alloy remains malleable and ductile but may have changes in properties such as hardness. Copper in sterling silver is another example of a substitutional alloy.	

2. Alloys typically retain a sea of mobile electrons and remain conductors of electricity.

3. In some cases, alloy formation alters the chemistry of the surface. An example is the formation of a nonreactive oxide layer in stainless steel.

The key idea of alloys is that adding extra elements with different atomic sizes to a pure metal disrupts the regular crystal structure. Thus, it is harder for atoms to slip past each other. The greater the difference in atomic size between the atoms of the alloy, the harder and less ductile the alloy will be.

Metallurgy, the chemistry of metals, is complex and the generalizations made in the previous alloy statements don't hold up to close examination, however they are the expected answers and explanations for AP Chem questions.

A summary of the properties of the different types of crystalline solids:

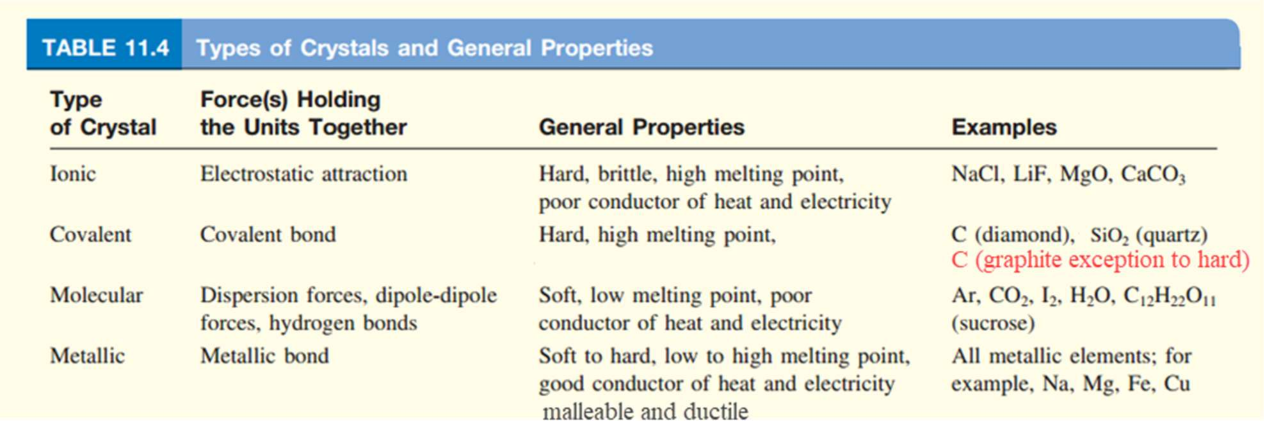
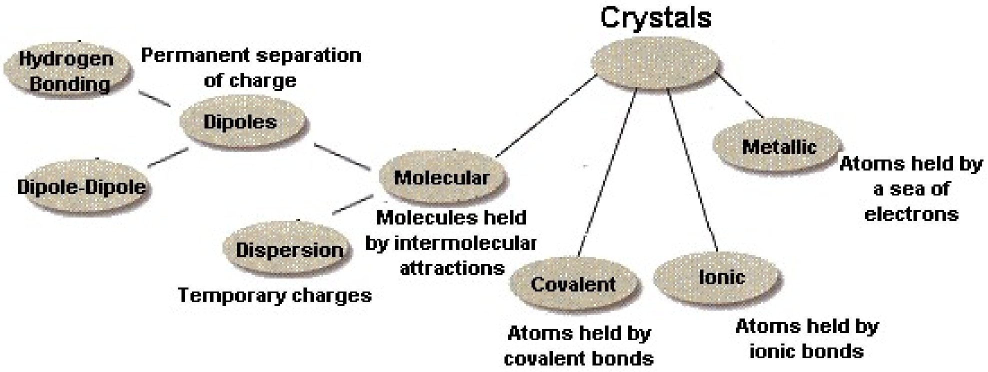


TABLE 11.4 Types of Crystals and General Properties

Type of Crystal	Force(s) Holding the Units Together	General Properties	Examples
Ionic	Electrostatic attraction	Hard, brittle, high melting point, poor conductor of heat and electricity	NaCl, LiF, MgO, $CaCO_3$
Covalent	Covalent bond	Hard, high melting point,	C (diamond), SiO_2 (quartz) C (graphite exception to hard)
Molecular	Dispersion forces, dipole-dipole forces, hydrogen bonds	Soft, low melting point, poor conductor of heat and electricity	Ar, CO_2, I_2, H_2O, $C_{12}H_{22}O_{11}$ (sucrose)
Metallic	Metallic bond	Soft to hard, low to high melting point, good conductor of heat and electricity malleable and ductile	All metallic elements; for example, Na, Mg, Fe, Cu

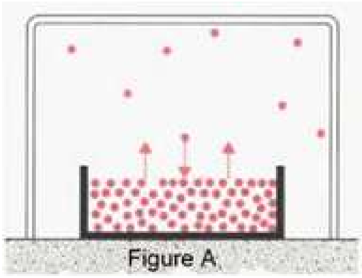
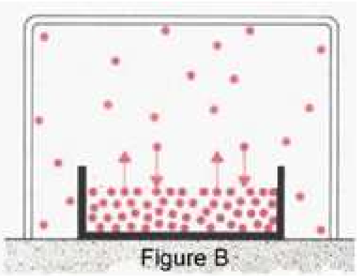


11.7 Amorphous Solids

Amorphous solids, such as glass, lack a regular three-dimensional arrangement of atoms. That’s all you need to know about amorphous solids.

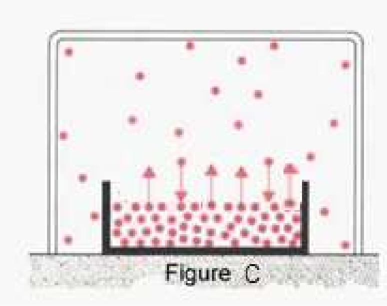
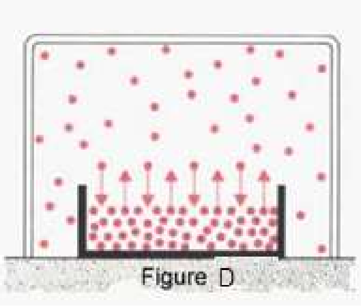
11.8 Phase Changes

Liquid-Vapor Equilibrium …know and understand these statements
When liquid is sealed in a container with air, the vapor pressure inside will rise as some of the liquid molecules evaporate (Figure A)

	
Initially: Evaporation > Condensation	Final Equilibrium: Evaporation = Condensation

The vapor pressure will level off when the gaseous molecules become sufficiently concentrated, and the vapor condenses at the same rate that the liquid evaporates (Figure B). This is the vapor pressure of the liquid at this temperature.

If the liquid is heated, the rate of evaporation will increase (Figure C). The molecules in the gas phase will become more concentrated. As a result, there will be a new final equilibrium with a higher vapor pressure concentration (Figure D)

	
Higher Temperature increases evaporation	Final Higher temperature Equilibrium

- The **greater the intermolecular attractions**, the **lower the vapor pressure (often on the AP Exam)**.
- The vapor pressure of a substance is constant at a given temperature.
    - **The amount of liquid or type of container will not change the vapor pressure**.
        - The increase in surface area will allow more liquid to evaporate, but also will allow more liquid to condense, so there is no net change in the concentration of vapor.
- **The vapor pressure of a substance increases as temperature increases.**
- **Boiling** occurs when the **vapor pressure of a liquid equals the surrounding pressure**.
- At a given pressure, the boiling temperature of a substance remains constant.
- The **greater the intermolecular attractions**, the **higher the boiling temperature (often on the AP Exam)**.

The Clausius Clapeyron equation is not part of the AP Syllabus.

Critical Temperature and Pressure **--** the outer limits of liquids and gases and are not in the AP curriculum. However, they are part of the CLEP Chemistry exam.

Solid – Liquid - Gas Equilibrium and Heating Curves (always on AP Exams)

Go through each of the five segments of a pure substance heating curve.

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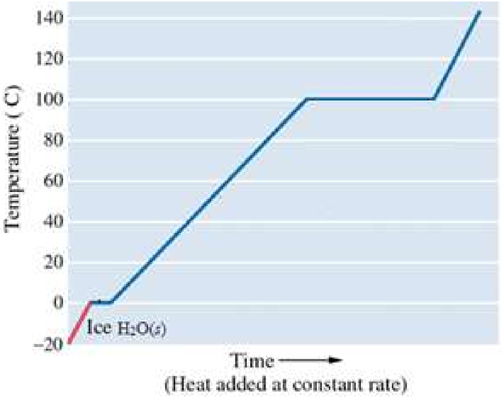

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<td>
Ice $H_2O(s)$ *Heating* (increase in KE)

Temperature increases as heat is added.

The slope / of the heating curve correlates to the specific heat of the substance. The steeper the slope the lower the specific heat.
Ice has a specific heat of 2.1 J/g°C,
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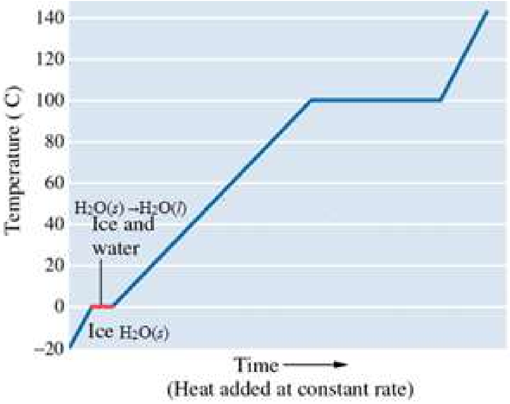

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Ice and Water $H_2O(s) \rightarrow H_2O(l)$ *Phase Change* (increase in PE)
Temperature remains constant as heat is added: 0°C

The Ice-Water plateau is where the heat is used to break the ice crystal lattice. ‘

Melting is always endothermic: $\Delta H_{fusion} = +$

The average kinetic energy constant while the stored energy, enthalpy, increases.

The length of the line correlates to the heat of fusion.
Heat of fusion of ice, ΔH_{fusion} = 6.1 kJ/mol.
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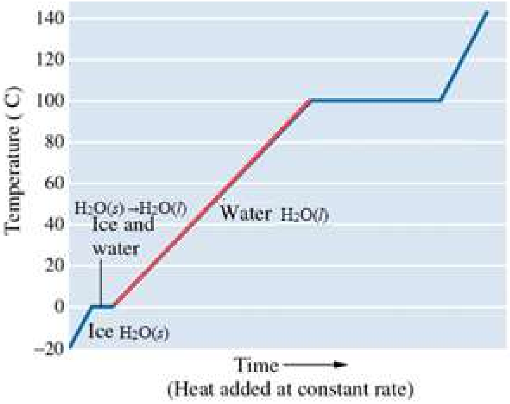

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<td>
Water $H_2O(l)$ *Heating* (increase in KE)

Temperature increases as heat is added.

Since the specific heat of water is greater than the specific heat of ice, the slope of heating water line is less than that of ice.

Water a specific heat of 4.18 J/g°C.
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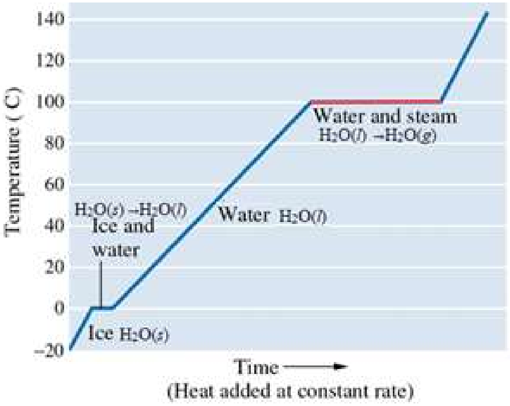
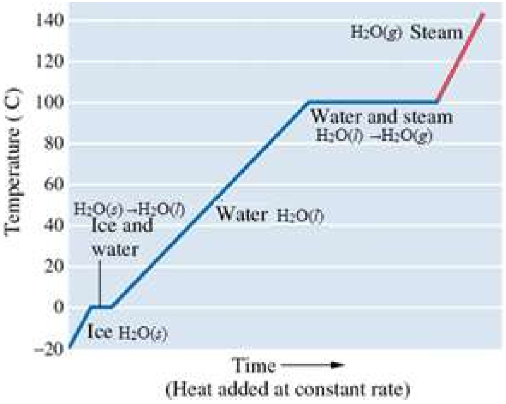
	$H_2O(s) \rightarrow H_2O(g)$ *Phase Change* (increase in PE) Temperature remains constant as heat is added: T = 100°C **Vaporization is always endothermic:** $\Delta \boldsymbol{H}_{\boldsymbol{vaporizion}} = +$ The Water- Steam plateau is longer than the Ice-Water Plateau. It takes more energy to separate molecules (break the intermolecular forces) than to break up their crystalline arrangement $\Delta H_{\text{vaporization}} > \Delta H_{fusion}$. Heat of vaporization of water, $\Delta H_{\text{vaporization}} = 40.$ kJ/mol.
	$H_2O(g)$ *Heating* (increase in KE) Temperature increases as heat is added. Steam has a specific heat of 2.0 J/g°C and a steeper slope than water or ice.

11.9 Phase Diagrams are not part of AP Chemistry.

Phase diagrams are used in the CLEP Chemistry exam**.**

CLEP also includes the special phase, *super critical fluid*, that forms at the critical point of the phase diagram.