

Video  
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(10:09)

## Geometry and Intermolecular Forces

Name: \_\_\_\_\_

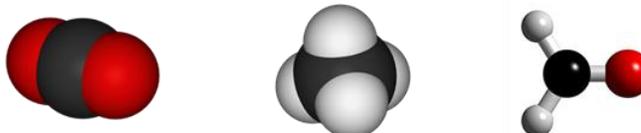
*AP Chemistry Lecture Outline*

The properties of a molecule depend on its shape and the nature of its bonds.

**VSEPR (valence-shell electron-pair repulsion) theory:**



bond angles: the angles made by the lines joining the nuclei of a molecule's atoms



**VSEPR essentials**

electron domain: a region in which at least two electrons are found

-- they repel each other because...

bonding domain: 2-to-6  $e^-$  that are shared by two atoms; they form a...

nonbonding domain: 2  $e^-$  that are located on a single atom; also called a...

For ammonia, there are three bonding domains and one nonbonding domain.

Domains arrange themselves so as to minimize their repulsions.

The electron-domain geometry is one of five basic arrangements of domains.

-- it depends only on the total # of  $e^-$  domains, NOT the kind of each domain

The molecular geometry describes the orientation of the atoms in space.

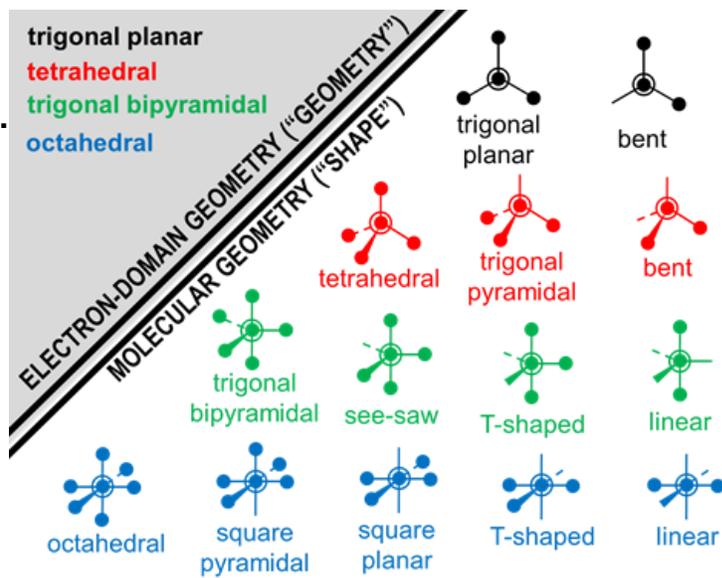
-- it depends on how many of each kind of  $e^-$  domain

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Total # of Domains	Electron-Domain Geometry	Possible Molecular Geometries
2		
3		
4		
5		
6		

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Summary of  
selected EDGs and MGs.....



To find the electron-domain geometry (EDG) and/or molecular geometry (MG), draw the Lewis structure. Multiple bonds count as a single domain.

EX. Predict the EDG and MG of each of the following.



For molecules with more than one central atom, simply apply the VSEPR model to each part.

EX. Predict the EDG and MG around the three interior atoms of ethanoic (acetic) acid.

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Nonbonding domains are attracted to only one nucleus; therefore, they are more spread out than are bonding domains. The effect is that nonbonding domains (i.e., "lone pairs") compress bond angles. Domains for multiple bonds have a similar effect.

e.g., the ideal bond angle for the tetrahedral EDG is  $109.5^\circ$



Video 91115 (5:38)

### Polarity of Molecules

A molecule's polarity depends on its overall dipole, which is the vector sum of the molecule's bond dipoles. Consider  $\text{CO}_2$  v.  $\text{H}_2\text{S}$ ...



EX. Classify as polar or nonpolar:



**Valence-Bond Theory:** merges Lewis structures w/the idea of atomic orbitals (2s, 3p, etc.)

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Lewis theory says...

covalent bonding occurs when atoms share electrons

V-B theory says...

covalent bonding occurs when valence orbitals of adjacent atoms overlap; then, two e<sup>-</sup>s of opposite spin (one from each atom) combine to form a bond

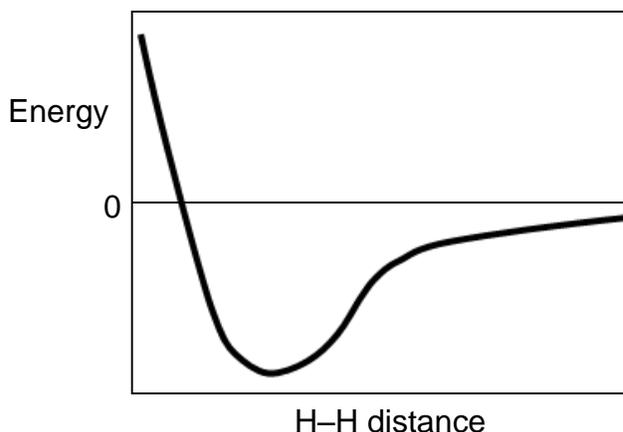
Consider H<sub>2</sub>, Cl<sub>2</sub>, and HCl...

H<sub>2</sub>

Cl<sub>2</sub>

HCl

There is always an optimum distance between two bonded nuclei. At this optimum distance, attractive (+/-) and repulsive (+/+ and -/-) forces balance.



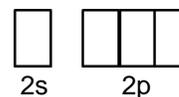
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### Hybridized Orbitals

V-B theory can't explain some observations about molecular compounds without the concept of hybridized orbitals.

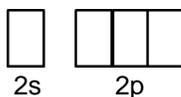
Consider methane:

Expected valence orbitals of central atom:



Problem:

What about...?



New problem:

Solution:

**KEY:**

linear →  
trig. planar →

tetrahedral →  
trig. bipy. →  
octahedral →

Video 91124 (9:31)

### $\sigma$ Bonds, $\pi$ Bonds, and Multiple Bonds

$\sigma$  (sigma) bonds are bonds in which the  $e^-$  density is along the internuclear axis.

- These are the single bonds we have considered up to this point.
- Produced by the orbital-overlap combos of: s-s, s-p, p-p (head-to-head), s- $sp^2$ , and p- $sp^2$

Multiple bonds result from the sideways overlap of two p orbitals (one from each atom) that are oriented perpendicularly to the internuclear axis. These are  $\pi$  (pi) bonds.

$\pi$  bonds are generally weaker than  $\sigma$  bonds because  $\pi$  bonds have less overlap.

Single bonds are  $\sigma$  bonds, e.g.,

Double bonds consist of one  $\sigma$  and one  $\pi$ , e.g.,

Triple bonds consist of one  $\sigma$  and two  $\pi$ , e.g.,

Experiments indicate that all of  $C_2H_4$ 's atoms lie in the same plane.

This suggests that  $\pi$  bonds introduce rigidity (i.e., a reluctance to rotate) into molecules.

- $\pi$  bonding does NOT occur with  $sp^3$  hybridization, only  $sp$  and  $sp^2$
- $\pi$  bonding is more prevalent with small atoms (e.g., C, N, O)

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### Delocalized $\pi$ Bonding

Localized  $\pi$  bonds are between...

- e.g.,

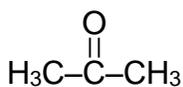
Delocalized  $\pi$  bonds are "smeared out" and shared among...

- these are common for molecules with...
- The electrons involved in these bonds are delocalized electrons.

Consider benzene, C<sub>6</sub>H<sub>6</sub>.

- Each carbon atom is \_\_\_\_\_ hybridized.
- This leaves...

EX. Which of the following exhibit delocalized bonding?



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### A Closer Look at Matter

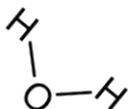
Chemical properties are due only to chemical composition; physical properties are due to chemical composition AND the state of matter.

### Intermolecular Forces (IMFs):

- largely determine the physical properties of molecular liquids and solids

For a given substance, i.e., H<sub>2</sub>O, the strengths of IMFs go...

	GASES	LIQUIDS	SOLIDS
How much KE?			
Particles how close together?			



IMFs are much weaker than ionic or covalent bonds.

- In vaporizing water, we overcome the IMFs between water molecules, but...

BP and FP/MP depend on IMFs.

- strong IMFs →
- weak IMFs →

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## Types of IMFs

When ions are present: ion-dipole forces  
For neutral molecules: dipole-dipole forces  
London dispersion forces  
hydrogen bonding forces } electrostatic forces

Ion-Dipole Forces (IDFs) -- exist between an ion and a partial charge on the end of a polar molecule  
-- important for...

Dipole-Dipole Forces (DDFs) -- exist between neutral polar molecules  
--  
-- as dipole moment  $\mu$  (i.e., the polarity) increases...

## London Dispersion Forces (LDFs)

- exist between ALL molecules, but are the ONLY forces between *nonpolar* molecules
- 
- polarizability: the ease with which the charge distribution in a molecule can be distorted by an external magnetic field
- 

## Hydrogen Bonding Forces (HBFs)

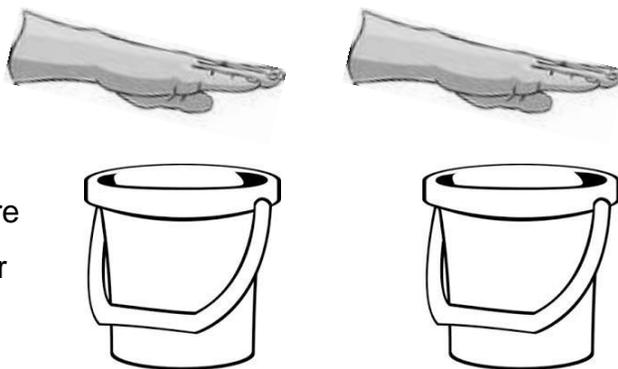
- 
- exist between a hydrogen atom in a polar bond and an unshared electron pair on a nearby, small, highly electronegative atom or ion
- 
- important in structures of proteins and DNA

### IMF SUMMARY

<b>ion-dipole forces</b> -- btwn ions and solvent molecules for salts dissolved in polar liquids	<b>dipole-dipole forces</b> -- btwn polar molecules (but NOT for polar molecules with H-F or H-O or H-N bonds)
<b>London dispersion forces</b> -- btwn ALL molecules, but are the ONLY IMFs btwn nonpolar molecules -- increase w/increasing molecular mass (i.e., w/increasing # of e <sup>-</sup> )	<b>hydrogen bonding</b> -- btwn polar molecules containing H-F or H-O or H-N bonds

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## Vapor Pressure



\_\_\_\_\_ vapor pressure  
\_\_\_\_\_ intermolecular  
forces (IMFs)

\_\_\_\_\_ vapor pressure  
\_\_\_\_\_ intermolecular  
forces (IMFs)

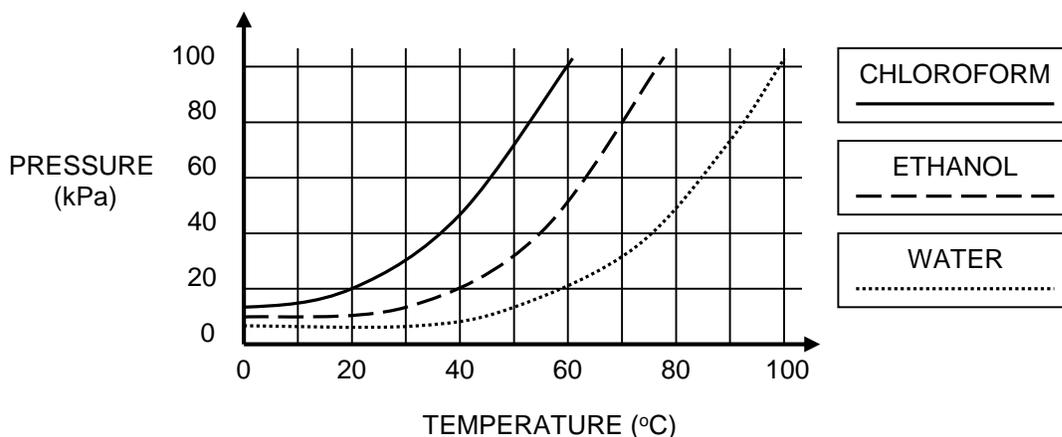
Vapor pressure is a measure of the tendency for liquid particles to enter the gas phase, i.e., it is the pressure exerted by a vapor in dynamic equilibrium with its liquid or solid phase

Examples of substances with high vapor pressures, i.e., \_\_\_\_\_ substances:

--

As temp.  $\uparrow$  /  $\downarrow$ , VP / .

Because of its strong IMFs (i.e., \_\_\_\_\_), water has a relatively low VP.



BOILING →

-- normal boiling point (NBP): the boiling temp. of a liquid at 1 atm of c.p.



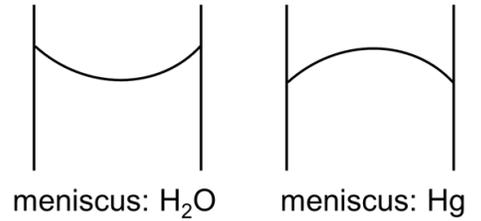
i.e., at NBP...

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cohesive forces: IMFs that bind...

adhesive forces: IMFs that bind...

--



capillary action: the rise of liquids up narrow tubes

-- adhesion " \_\_\_\_\_ " the liquid, while cohesion...

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viscosity: a liquid's resistance to flow

-- high viscosity =

-- depends on IMFs

--

surface tension M'cules on a liquid's surface experience a net inward force due to IMFs.

--

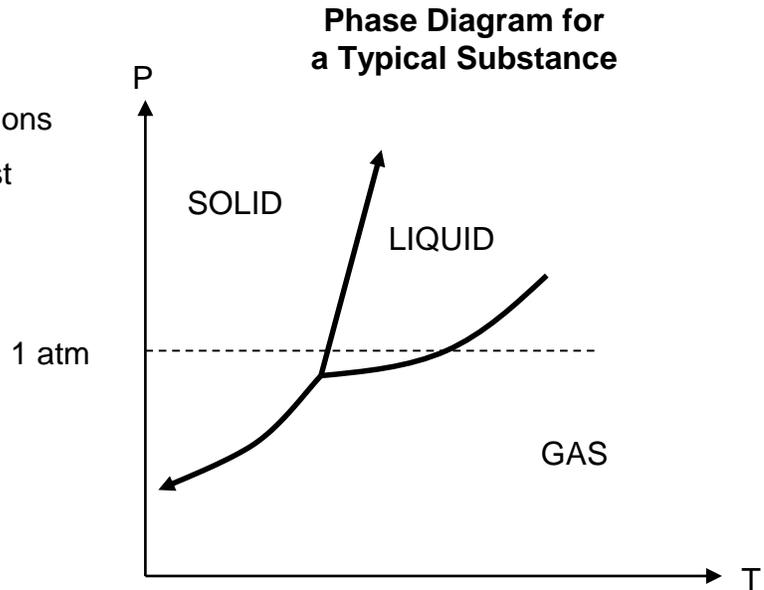
-- Surface tension is...

--

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### Phase Diagrams

-- graphs showing the conditions under which equilibria exist between different states of matter



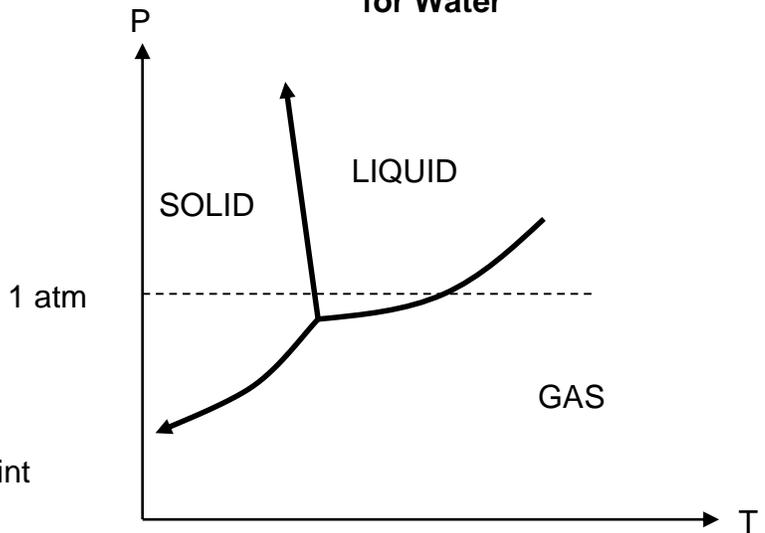
critical temperature: the highest temperature at which a substance can be a liquid

-- as IMFs increase, crit. temp...

critical pressure: the pressure required to bring about liquefaction at the critical temp.

Water is NOT a typical substance. Its phase diagram differs slightly, as shown here.

Phase Diagram for Water



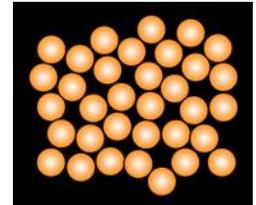
supercritical fluid: how we describe a substance at or beyond its critical point

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**Structures of Solids**

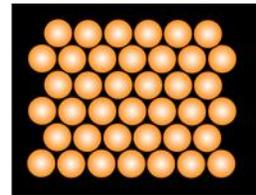
amorphous solid: the particles have no orderly structure

- e.g.,
- IMFs are highly variable, so these solids have no specific...



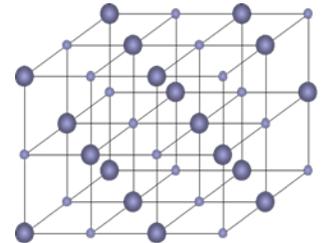
crystalline solid: the particles are in well-defined arrangements

- e.g.,
- 

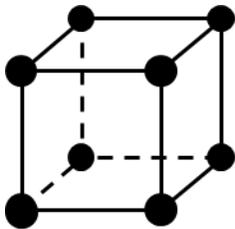


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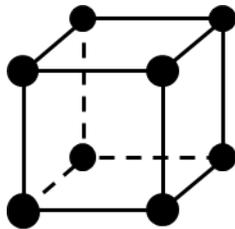
crystal lattice: a 3-D array of points showing the crystal's structure



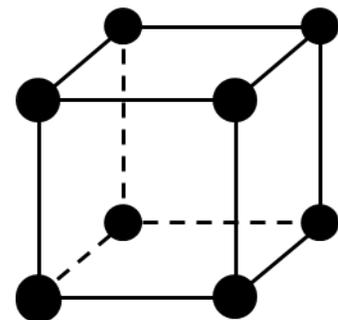
unit cells: the repeating units of a crystalline solid



primitive (or simple) cubic



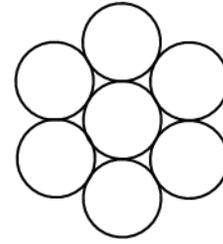
body-centered cubic



face-centered cubic

Roughly equal-sized spheres, such as those in metallic solids, are arranged in one of several configurations. These configurations are collectively called the close packing of spheres.

-- In a given layer, the atoms are arranged such that each atom in that layer is surrounded by six others. This is called a...

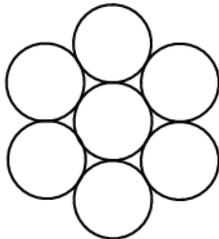


FCC is equivalent to a close-packed, repeating configuration of A-B-C-A-B-C (rather than A-B-A-B).

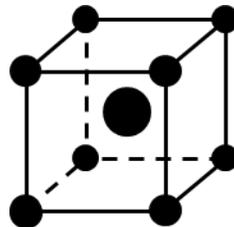
The coordination number for a packing pattern is equal to the number of equidistant, **nearest** neighbors for any atom within the matrix.

-- for particular packing arrangements:

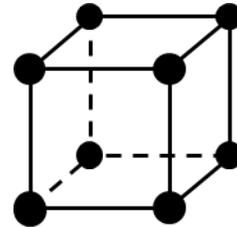
FCC:



BCC:



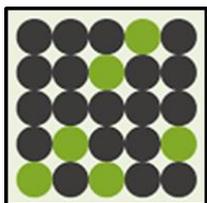
P/SC:



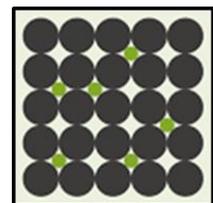
For unequal-sized spheres, sometimes the larger spheres assume a close-packed arrangement, and then the smaller particles fit into the spaces in between.

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(4:22)

alloy: a mixture of elements (w/at least one metal)  
formed by cooling the molten mixture



The mixture is usually used in the \_\_\_\_\_ state of matter and always has at least some of the properties of...



In substitutional alloys, the different types of atoms...

In interstitial alloys, the different types of atoms...

-- The less-numerous atoms of the one type...

-- No substituting takes place; the secondary-component atoms...

substitutional



interstitial

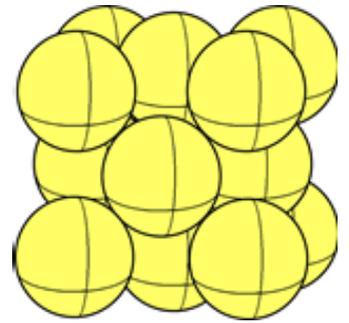


Predict which type of alloy tends to...

- ...be MORE rigid than the primary metal constituent
- ...have 'nearby' METAL atoms as a secondary constituent
- ...have NONMETAL atoms (like C) as a secondary constituent
- ...maintain the ductility of the primary constituent

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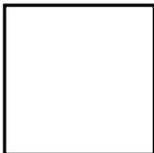
Gold exhibits a face-centered cubic unit cell that is  $4.08 \text{ \AA}$  on a side. Estimate gold's density, in  $\text{g/cm}^3$ .



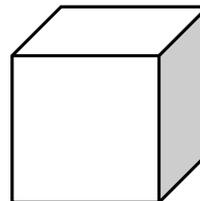
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Obviously, the side length of a unit cell is related to the atomic radius of the cell's atoms.

FCC



BCC



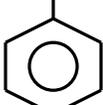
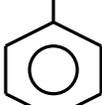
EX. Assume that molybdenum exhibits a body-centered cubic unit cell and has a density of  $10.0 \text{ g/cm}^3$ . Determine the metallic radius of molybdenum, in pm.

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### Bonding in Solids

In molecular solids, the particles are held together by IMFs.

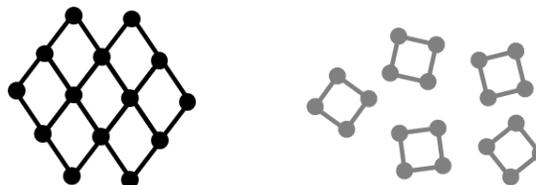
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	benzene 	toluene CH <sub>3</sub> 	phenol OH 
BP (°C)			
MP (°C)			
Why?			

In covalent-network solids, particles are held together in large networks by covalent bonds.

-- e.g.,

--



NOTE: Graphite has layers of covalently-bonded C atoms <sup>w</sup>/delocalized,  $\pi$  e<sup>-</sup>s (similar to benzene).

The layers are held to each other by...

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Ionic solids consist of ions held together by ionic bonds.

- MPs depend largely on magnitude of charges.
  - e.g., MP of KCl = \_\_\_\_\_; MP of CaO = \_\_\_\_\_
- 

Ionic solids are also brittle and don't conduct elec.

Metallic solids consist entirely of metal atoms.

- these have various structures, <sup>w</sup>/each atom touching 8 or 12 others
- bonding is due to delocalized valence  $e^-$  that are free to move throughout solid

\*\*

- metallic bond strength increases <sup>w</sup>/# of v.  $e^-$
- e.g. MP of Li = \_\_\_\_\_; MP of Fe = \_\_\_\_\_

### Metallic Properties

- heat and elec. conductivity
- 
- 
- ductility/malleability

