

## Intermolecular Forces

Love & Hate in the Molecular Realm



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If I put 2 molecules into a sealed flask, what could happen?

1. They ignore each other.
2. They LOVE each other – they're attracted to each other
3. They HATE each other – they repel each other



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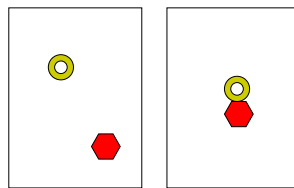
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If they LOVE each other, what would that look like?



Initially

Later



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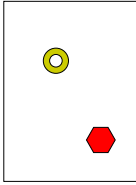
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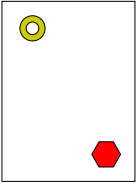
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**If they HATE each other, what would that look like?**





Initially



Later

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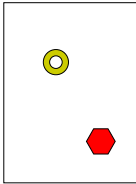
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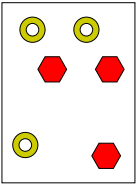
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**If they IGNORE each other, what would that look like?**





Initially



Later

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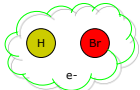
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**What determines LOVE or HATE?**



The structure of the molecule.

What is the structure of a molecule?



What's in the nuclei?  
Protons!

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## Molecular structure is all about...



POSITIVE & NEGATIVE CHARGES!

So Love & Hate is all about...

Opposites attract, like repel!

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## Types of Intermolecular Forces



1. London Dispersion forces, aka Van der Waal's forces, aka Instantaneous dipole-induced dipole forces.
2. Dipole-Dipole interactions: either permanent or temporary
3. Hydrogen bonding – particularly strong case of dipole-dipole interaction

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## London Dispersion forces, aka Van der Waal's forces, aka Instantaneous dipole-induced dipole forces.



This is NOT the strongest, but it is the primary intermolecular force.

All atoms or molecules with electrons have Van der Waal's forces – so ALL atoms or molecules have Van der Waal's forces

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### Instantaneous dipole-induced dipole forces

Induced dipole

Instantaneous dipole

The electron cloud is mobile. Charge density is constantly moving around

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### How Great is THAT!?!?!

Induced dipole

Instantaneous dipole

Because the induced dipole is ALWAYS a mirror image of the instantaneous dipole, dispersion forces are ALWAYS attractive

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### Dispersion Forces are ALWAYS ATTRACTIVE

All molecules like each other, at least a little bit. So all molecules stick together, at least a little bit.

If they didn't...  
 ...the universe would be a much more chaotic place!  
 Universal repulsion would have things flying apart all over the place!

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### Van der Waal's forces



Van der Waal's forces get stronger as the temporary dipole gets stronger.

The temporary dipole is caused by electron mobility, so the more electrons the stronger the Van der Waal's forces.

# electrons increases as # protons, so the heavier the molecule the stronger the Van der Waal's forces.

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### Alkanes



Methane –  $\text{CH}_4$

Ethane –  $\text{CH}_3\text{CH}_3$

Propane –  $\text{CH}_3\text{CH}_2\text{CH}_3$

Butane -  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

Pentane -  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

Hexane -  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

Heptane -  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

Octane -  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

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### What do you know about these molecules?



Methane –  $\text{CH}_4$

Ethane –  $\text{CH}_3\text{CH}_3$

Propane –  $\text{CH}_3\text{CH}_2\text{CH}_3$

Butane -  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

Pentane -  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

Hexane -  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

Heptane -  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

Octane -  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

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### What do you know about these molecules?



- Methane – gas at standard T & P
- Ethane – gas at standard T & P
- Propane – gas at standard T & P – Liquid under slight pressure
- Butane - gas at standard T & P – Liquid under slight pressure
- Pentane - Liquid
- Hexane - Liquid
- Heptane - Liquid
- Octane - Liquid

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### Solids, Liquids, and Gases



What is the difference between a solid, a liquid, and a gas microscopically?

How tightly stuck together the molecules are!!!

Solids are stuck together more than liquids that are stuck together more than gases

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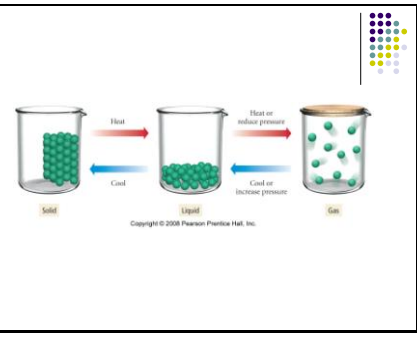
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### Solids, Liquids, and Gases & Heat



What happens when you heat up a solid?

Eventually it melts – why?

Adding heat adds energy to the molecules, when they have enough energy they can escape their attraction to their neighbors!

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### Which has a higher boiling point?



- A.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{-Br}$
- B.  $\text{CH}_3\text{CH}_2\text{CH}_3$
- C. They are the same
- D. I don't know without more structure information.

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### Which has a higher boiling point?



- A.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{-Br}$
- B.  $\text{CH}_3\text{CH}_2\text{CH}_3$
- C. They are the same
- D. I don't know without more structure information.

It has a higher molar mass, so it has larger van der Waal's forces, so it has a higher boiling point – takes more energy to separate the molecules.

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## Van der Waal's Forces are...

...the first consideration – but not the last!



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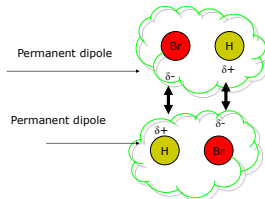
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## Dipole – Dipole Interactions



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## Dipole – Dipole interactions

A molecule with a permanent dipole is called a "polar molecule".

All polar molecules have Dipole-Dipole interactions in ADDITION TO Van der Waal's forces.



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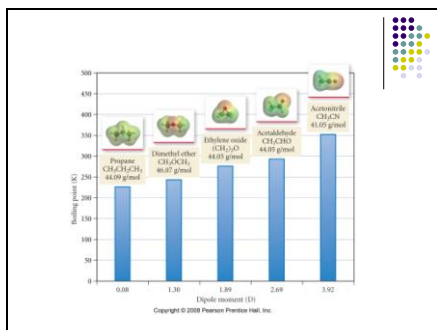
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**EXAMPLE 11.1** Dipole-Dipole Forces  
 Which of the following molecules have dipole-dipole forces?  
 (a) CO<sub>2</sub> (b) CH<sub>2</sub>Cl<sub>2</sub> (c) CH<sub>4</sub>

continued...

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(c) CH<sub>4</sub>  
 (1) Since the electronegativity of C is 2.5 and that of hydrogen is 2.1 the C—H bonds are nearly nonpolar.  
 (2) In addition, since the geometry of the molecule is tetrahedral, any slight polarities that the bonds might have will cancel. CH<sub>4</sub> is therefore nonpolar and does not have dipole-dipole forces.

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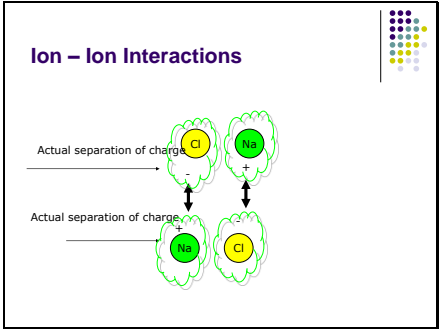
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### Ion-Ion interactions

The strongest possible interaction.

The complete charge separation makes it a HUGE dipole-dipole type interaction.

This is why most ionic compounds are solids at room temperature.

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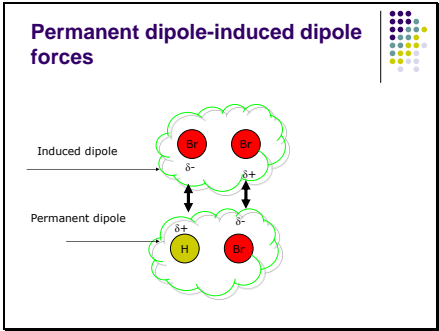
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### Dipole – Induced Dipole interactions



This is a special case of a Dipole – Dipole interaction where there are 2 different molecules involved and only 1 of them is polar.

Generally weaker than a permanent Dipole-Dipole interaction, it is still IN ADDITION TO Van der Waal's forces.

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### NaF vs. F<sub>2</sub>



What do you know about these 2 molecules?

NaF is an ionic solid

F<sub>2</sub> is a gas at room temp

NaF has a molar mass of 42 g/mol, F<sub>2</sub> has a molar mass of 38 g/mol.

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### Ion-ion interactions are the strongest



Based on Van der Waal's forces, you'd expect NaF and F<sub>2</sub> to be similar.

The powerful ionic forces of NaF make it a solid – trumping the Van der Waal's interaction.

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## HBr vs. Cl<sub>2</sub>



What do you know about these 2 molecules?

HBr is a gas at room temp

Cl<sub>2</sub> is a gas at room temp

HBr has a molar mass of 81 g/mol

Cl<sub>2</sub> has a molar mass of 71 g/mol

HBr is polar, Cl<sub>2</sub> is non-polar

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## HBr boils at 207 K, Cl<sub>2</sub> boils at 239 K



Based on Van der Waal's forces, you'd expect HBR and Cl<sub>2</sub> to be similar, but HBR should have the higher boiling point since it has the higher molecular weight AND it is polar so dipole-dipole would push it over the top.

This is why it is dangerous to compare dissimilar molecules. Dipole interactions are a tie-breaker if everything else is the same.

In this case, however, we have a geometry problem...

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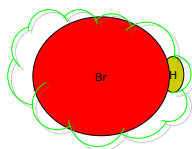
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## Why doesn't it work here?



HBr is almost a perfect sphere.



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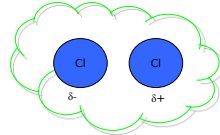
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## Cl<sub>2</sub> is a dumbbell

Van der Waal's forces require formation of a dipole.  
Hard to do if you are completely round like HBr.  
Much easier if you are a dumbbell like Cl<sub>2</sub>.



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## Beware shape

As you might imagine, this shape dependence  
can become significant for large molecules  
like proteins.

It is best to make the comparison of  
intermolecular forces between molecules of a  
homologous series.

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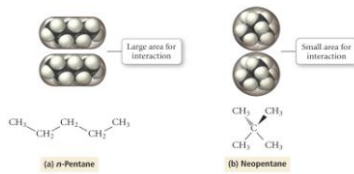
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## Identical mass. No dipole.



n-pentane boils at 36.1°C, Neopentane boils at 9.5 °C

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### Hydrogen Bonding – just a special case of dipole-dipole interactions



Hydrogen bonding is a dipole-dipole interaction that occurs when hydrogen is bonded to something very electronegative like F, O, or N.

It is just a very strong dipole-dipole interaction because of the very polar nature of the H-F, H-O, or H-N bond.

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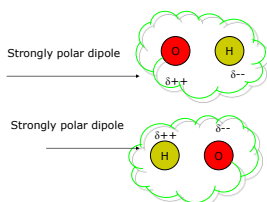
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### Hydrogen Bonding – just a special case of dipole-dipole interactions



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### Compare H<sub>2</sub>O to H<sub>2</sub>S



Which would you expect to have the higher boiling point?

H<sub>2</sub>O has a molar mass of 18 g/mol  
H<sub>2</sub>S has a molar mass of 34 g/mol

Based on Van der Waal's forces alone, H<sub>2</sub>S should have the higher boiling point.

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### Compare H<sub>2</sub>O to H<sub>2</sub>S

The boiling point of water is 373 K.

The boiling point of H<sub>2</sub>S is 213 K.

H<sub>2</sub>S is a gas at room temperature while water is a liquid!

No FON, no Hydrogen bonding



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#### EXAMPLE 11.2 Hydrogen Bonding

One of the following compounds is a liquid at room temperature. Which one and why?



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List the following compounds in order of INCREASING boiling point: NH<sub>3</sub>, CH<sub>4</sub>, CH<sub>3</sub>OH

- A. NH<sub>3</sub>, CH<sub>4</sub>, CH<sub>3</sub>OH
- B. CH<sub>4</sub>, CH<sub>3</sub>OH, NH<sub>3</sub>
- C. NH<sub>3</sub>, CH<sub>3</sub>OH, CH<sub>4</sub>
- D. CH<sub>4</sub>, NH<sub>3</sub>, CH<sub>3</sub>OH



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### Here's some...



Physical properties that show "intermolecular forces":

1. Boiling point
2. Melting point
3. Surface tension
4. Viscosity
5. Capillary action
6. Evaporation

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### Phase changes



Intermolecular Forces are attractions between molecules.

Temperature is a measure of kinetic energy.

Boiling Point (or Freezing Point) are measures of the strength of intermolecular forces: the higher the temperature, the more kinetic energy required to separate the molecules.

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### Not just temperature...



We mentioned TWO things that affected molecules and their interactions:

1. Energy
2. Space

Another way of looking at "space" is pressure.

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**What is "pressure"?**

Pressure =  $\frac{\text{Force}}{\text{Area}}$

Pressure is squeezing the molecules together!



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**Propane under Pressure**



$\text{C}_3\text{H}_8(\text{g})$

$\text{C}_3\text{H}_8(\text{l})$

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**Phase Changes**


You can create a phase change, by changing the temperature.

Consider a flask full of steam at 200°C.

If I start cooling it down, what happens?

It condenses into liquid water. When?

NOT (necessarily) 100°C.



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## Normal Boiling Point



100°C is the "normal boiling point" of water.  
What's the "normal" for?

Normal means at standard pressure, 1 atm.

One way to condense steam is to decrease the temperature, another way is to increase the pressure.

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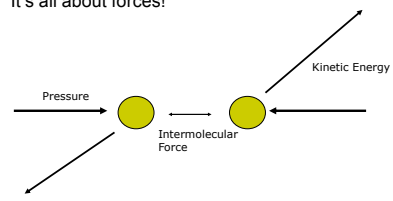
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It's all about forces!



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## Phase Diagrams



A "phase diagram" collects all the P, T and phase information and displays it in one simple graph.

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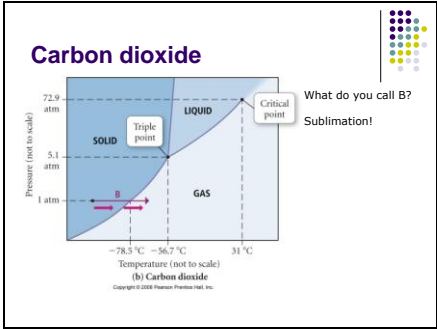
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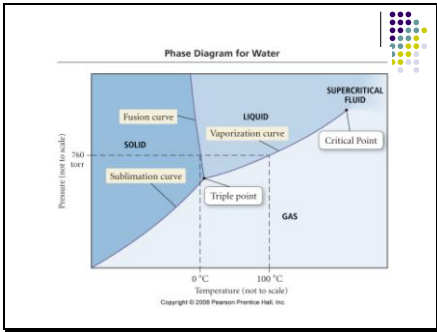
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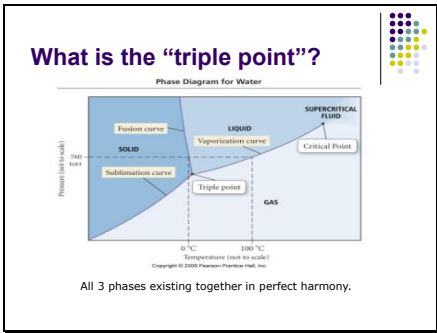
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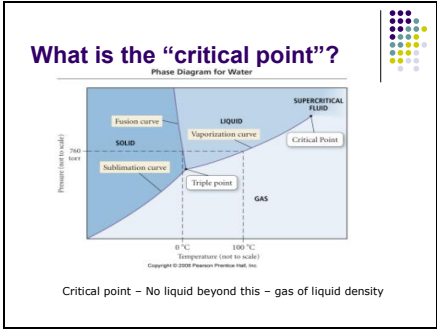
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### Energy of Phase Changes

How do you define "boiling"?

Vapor pressure = atmospheric pressure

What's vapor pressure?

It's the pressure exerted by the vapor above a liquid.

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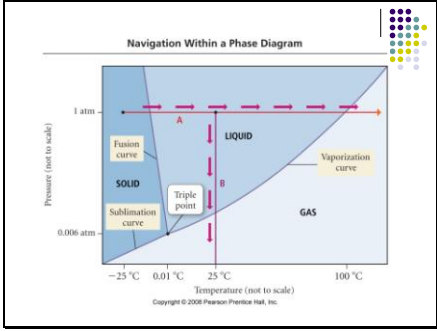
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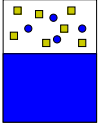
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As you raise T, you raise  $P_{\text{vap}}$  until  $P_{\text{vap}} = P_{\text{atm}}$



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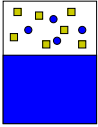
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What do you have to do to become "vapor"?  
You have to go from a liquid to a gas!



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**Making a phase change...**

Suppose I start with 100 g of ice at  $-40^{\circ}\text{C}$  (1 atm) and start heating it up, what happens?

The ice gets warmer and warmer until...melting point!

Suppose I am ice at  $0^{\circ}\text{C}$ , do I just spontaneously melt?

Not exactly. I am warm enough, but I'm still a solid and my molecules are still "associated" with each other. I need to get ripped away from my brothers.



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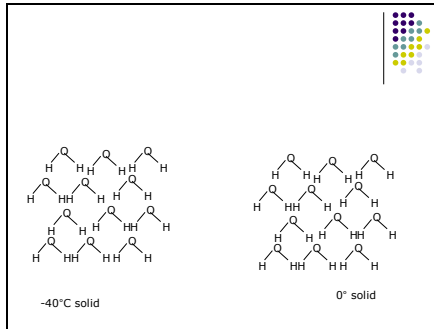
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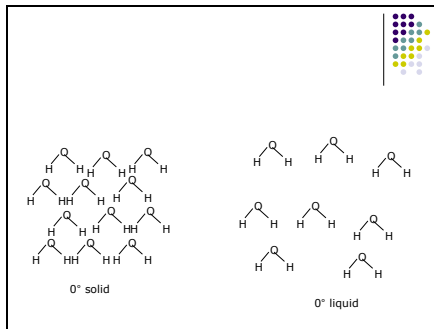
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**At the phase transition temperature...**

...you still need energy to make the transition.

Going from solid to liquid, this is called the "heat of fusion" ( $\Delta H_{fus}^\circ$ )

Going from liquid to gas, this is called "heat of vaporization" ( $\Delta H_{vap}^\circ$ )

Going from solid to gas, this is called the "heat of sublimation" ( $\Delta H_{sub}^\circ$ )

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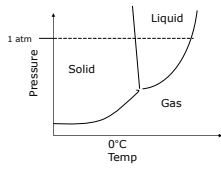
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## Phase Diagram for H<sub>2</sub>O

The "°" in the  $\Delta H^\circ$  means standard conditions.



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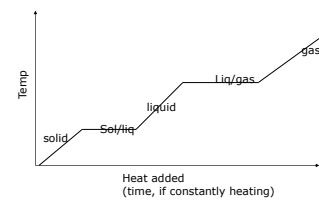
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## Heating/cooling curves



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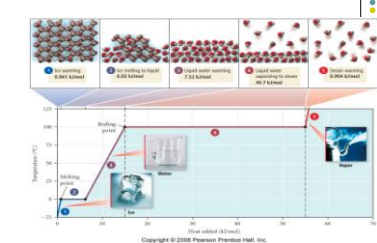
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**EXAMPLE 11.3** Using the Heat of Vaporization in Calculations  
Calculate the mass of water (in g) that can be vaporized at its boiling point with 155 kJ of heat.

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**Animation**

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**Heating/cooling curves**

Temp

gas

Liq/gas

liquid

solid/liq

solid

Heat removed  
(time, if constantly heating)

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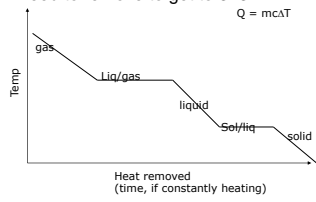
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### Could we quantify the energy?

If I have steam at 500 K, how much energy do I need to remove to get to 373 K?




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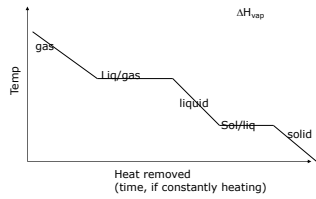
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### Could we quantify the energy?

Once my steam is down to 373 K, how much energy do I need to remove to turn it into a liquid?




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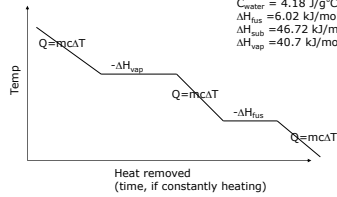
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### Just follow the curve.

For water:  
 $C_{steam} = 1.84 \text{ J/g}^\circ\text{C}$   
 $C_{ice} = 2.09 \text{ J/g}^\circ\text{C}$   
 $C_{water} = 4.18 \text{ J/g}^\circ\text{C}$   
 $\Delta H_{fus} = 6.02 \text{ kJ/mol}$   
 $\Delta H_{sub} = 46.72 \text{ kJ/mol}$   
 $\Delta H_{vap} = 40.7 \text{ kJ/mol}$




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### A little problem

I have 50 g of ice at 100 K. How much energy would I need to add to get steam at 500 K?




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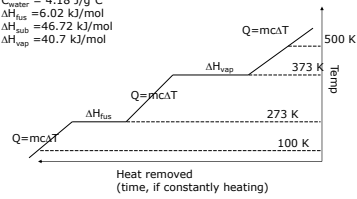
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### Just follow the curve.

For water:  
 $C_{\text{steam}} = 1.84 \text{ J/g}^\circ\text{C}$   
 $C_{\text{ice}} = 2.09 \text{ J/g}^\circ\text{C}$   
 $C_{\text{water}} = 4.18 \text{ J/g}^\circ\text{C}$   
 $\Delta H_{\text{fus}} = 6.02 \text{ kJ/mol}$   
 $\Delta H_{\text{sub}} = 46.72 \text{ kJ/mol}$   
 $\Delta H_{\text{vap}} = 40.7 \text{ kJ/mol}$




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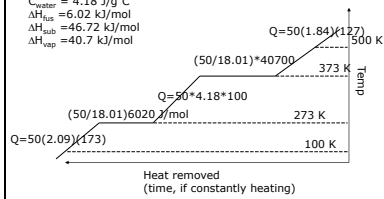
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### Just follow the curve.

For water:  
 $C_{\text{steam}} = 1.84 \text{ J/g}^\circ\text{C}$   
 $C_{\text{ice}} = 2.09 \text{ J/g}^\circ\text{C}$   
 $C_{\text{water}} = 4.18 \text{ J/g}^\circ\text{C}$   
 $\Delta H_{\text{fus}} = 6.02 \text{ kJ/mol}$   
 $\Delta H_{\text{sub}} = 46.72 \text{ kJ/mol}$   
 $\Delta H_{\text{vap}} = 40.7 \text{ kJ/mol}$




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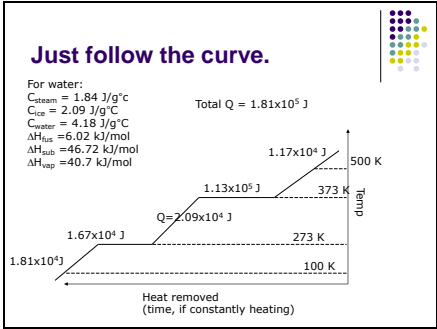
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**Vapor Pressure**

What is "vapor pressure"?

It's the "pressure" exerted by the "vapor" of a liquid in a closed container that is in equilibrium with the liquid.

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**Vapor Pressure**

- [\\_16-15-2010\Chapter\\_11\Present\Media\water evap.swf](#)

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### What does it do?



Vapor pressure explains evaporation of water: you must satisfy the equilibrium. In an open container, the water vapor keeps drifting away from the surface and you never reach equilibrium (unless it is really humid).

Vapor pressure explains “boiling” – the spontaneous change from liquid phase to gas phase. Boiling occurs when the vapor pressure = atmospheric pressure.

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### Vapor Pressure



Vapor pressure depends on temperature. Vapor pressure also depends on  $\Delta H_{\text{vap}}$

Clausius-Clapeyron equation:

$$\ln P_{\text{vap}} = -\frac{\Delta H_{\text{vap}}}{R} \frac{1}{T} + C$$

Where C is a constant, R is the ideal gas constant.

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**EXAMPLE 11.4** Using the Clausius-Clapeyron Equation to Determine Heat of Vaporization from Experimental Measurements of Vapor Pressure  
The vapor pressure of dichloromethane was measured as a function of temperature, and the following results were obtained:

Temperature (K)	Vapor Pressure (torr)
240	6.8
220	4.3
240	23
260	73
280	197
300	393

Determine the heat of vaporization of dichloromethane.

continued...

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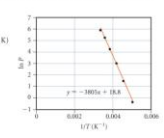
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**Solution**

To find the heat of vaporization, use an Excel spreadsheet or a graphing calculator to make a plot of the natural log of vapor pressure (ln P) as a function of the inverse of the temperature in kelvins (1/T). Then fit the points to a line and determine the slope of the line. The slope of the best fitting line is  $-3805 \text{ K}$ . Since the slope equals  $-\Delta H_{\text{vap}}/R$ , we find the heat of vaporization as follows:

$$\begin{aligned} \text{slope} &= -\Delta H_{\text{vap}}/R \\ \Delta H_{\text{vap}} &= -\text{slope} \times R \\ &= -(-3805 \text{ K})(8.314 \text{ J/mol}\cdot\text{K}) \\ &= 31.6 \times 10^3 \text{ J/mol} \\ &= 31.6 \text{ kJ/mol} \end{aligned}$$


continued...

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**A little algebra:**

$$\ln P_{\text{vap}} = -\frac{\Delta H_{\text{vap}}}{R} \frac{1}{T} + C$$

Suppose you are interested in the boiling point at two different pressures:

$$\ln P_{\text{vap},1} = -\frac{\Delta H_{\text{vap}}}{R} \frac{1}{T_1} + C$$

$$\ln P_{\text{vap},2} = -\frac{\Delta H_{\text{vap}}}{R} \frac{1}{T_2} + C$$

I can compare them by subtracting them:

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**Subtract the 2<sup>nd</sup> equation from the 1st**

$$\ln P_{\text{vap},1} = -\frac{\Delta H_{\text{vap}}}{R} \frac{1}{T_1} + C$$

$$\ln P_{\text{vap},2} = -\frac{\Delta H_{\text{vap}}}{R} \frac{1}{T_2} + C$$

$$\ln P_{\text{vap},1} - \ln P_{\text{vap},2} = -\frac{\Delta H_{\text{vap}}}{R} \frac{1}{T_1} - \left(-\frac{\Delta H_{\text{vap}}}{R} \frac{1}{T_2}\right)$$


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## Vapor Pressure



More helpful form – find the  $P_{\text{vap}}$  at 2 different temperatures:

$$\ln \frac{P_{\text{vap}1}}{P_{\text{vap}2}} = \frac{-\Delta H_{\text{vap}}}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

Must know  $\Delta H_{\text{vap}}$  for this to be helpful.

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**EXAMPLE 11.5** Using the Two-Point Form of the Clausius–Clapeyron Equation to Predict the Vapor Pressure at a Given Temperature

Methanol has a normal boiling point of 64.6 °C and a heat of vaporization ( $\Delta H_{\text{vap}}$ ) of 35.2 kJ/mol. What is the vapor pressure of methanol at 12.0 °C?

continued...

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**Solve** First, convert  $T_1$  and  $T_2$  from °C to K.

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### Other manifestations of intermolecular forces:

Surface Tension

Capillary action

Viscosity



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### Surface Tension

• surface tension is a property of liquids that results from the tendency of liquids to minimize their surface area

- in order to minimize their surface area, liquids form drops that are spherical
  - as long as there is no gravity
- the layer of molecules on the surface behave differently than the interior
  - because the cohesive forces on the surface molecules have a net pull into the liquid interior
- the surface layer acts like an elastic skin



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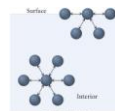
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### Surface Tension

- because they have fewer neighbors to attract them, the surface molecules are less stable than those in the interior
  - have a higher potential energy
- the surface tension of a liquid is the energy required to increase the surface area a given amount
  - at room temp, surface tension of  $H_2O$  =  $72.8 \text{ mJ/m}^2$



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## Factors Affecting Surface Tension



- the stronger the intermolecular attractive forces, the higher the surface tension will be
- raising the temperature of a liquid reduces its surface tension
  - raising the temperature of the liquid increases the average kinetic energy of the molecules
  - the increased molecular motion makes it easier to stretch the surface

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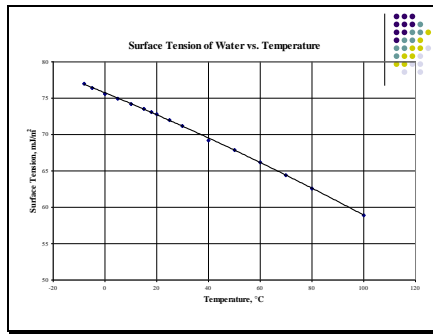
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## Capillary Action



- **capillary action** is the ability of a liquid to flow up a thin tube against the influence of gravity
  - the narrower the tube, the higher the liquid rises
- capillary action is the result of the two forces working in conjunction, the cohesive and adhesive forces
  - cohesive forces attract the molecules together
  - adhesive forces attract the molecules on the edge to the tube's surface

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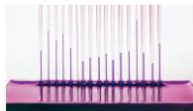
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## Capillary Action

- the adhesive forces pull the surface liquid up the side of the tube, while the cohesive forces pull the interior liquid with it
- the liquid rises up the tube until the force of gravity counteracts the capillary action forces



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## Meniscus

- the curving of the liquid surface in a thin tube is due to the competition between adhesive and cohesive forces
- the meniscus of water is concave in a glass tube because its adhesion to the glass is stronger than its cohesion for itself
- the meniscus of mercury is convex in a glass tube because its cohesion for itself is stronger than its adhesion for the glass
  - metallic bonds stronger than intermolecular attractions



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## Viscosity

viscosity is the resistance of a liquid to flow

- 1 poise = 1 P = 1 g/cm·s
- often given in centipoise, cP
- larger intermolecular attractions = larger viscosity
- higher temperature = lower viscosity

TABLE 11.5 Viscosity of Several Hydrocarbons at 20 °C

Hydrocarbon	Molar Mass (g/mol)	Formula	Viscosity (cP)
N-Pentane	72.15	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	0.240
N-Hexane	86.17	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	0.326
N-Heptane	100.2	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	0.409
N-Octane	114.2	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	0.542
N-Nonane	128.3	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	0.711



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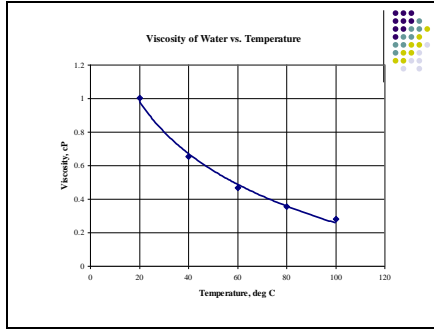
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**What about solutions?**

Still thinking about energy, what happens if I put sugar in water?

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**What about solutions?**

I need to pull apart all the sugar molecules, I need to pull apart the water molecules enough to insert the sugar molecules, then the sugar molecules relax and attract the water molecules.

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## What about solutions?

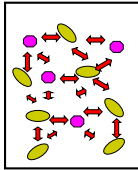
The energy change is, as always,  
simply the sum of the processes:

$$\Delta H_{\text{soln}} = \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} + \Delta H_{\text{mix}}$$

$\Delta H_{\text{solute}}$  = endothermic (pull apart solute)

$\Delta H_{\text{solvent}}$  = endothermic (pull apart solvent)

$\Delta H_{\text{mix}}$  = exothermic (solvent/solute attract each other)



## Sometimes its endo, sometimes its exo

$$\Delta H_{\text{soln}} = \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} + \Delta H_{\text{mix}}$$

$\Delta H_{\text{solute}}$  = endothermic (pull apart solute)

$\Delta H_{\text{solvent}}$  = endothermic (pull apart solvent)

$\Delta H_{\text{mix}}$  = exothermic (solvent/solute attract each other)

So  $\Delta H_{\text{soln}} = (\Delta H_{\text{solute}} + \Delta H_{\text{solvent}}) + \Delta H_{\text{mix}}$   
= (+ pull Joules) + (-mix Joules)  
Hot pack/Cold pack!

## Animation of dissolution

[..16-15-2010\Chapter\\_11\Present\Media\dissolve.mov](#)

## Solid State structures



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## Determining Crystal Structure

- crystalline solids have a very regular geometric arrangement of their particles
- the arrangement of the particles and distances between them is determined by **x-ray diffraction**
- in this technique, a crystal is struck by beams of x-rays, which then are reflected
- the wavelength is adjusted to result in an interference pattern – at which point the wavelength is an integral multiple of the distances between the particles



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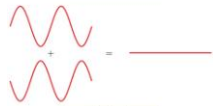
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Constructive interference



Destructive interference

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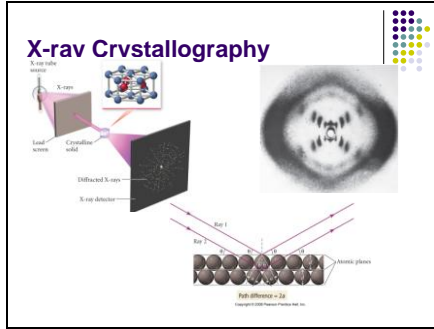
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### Crystal Lattice

- when allowed to cool slowly, the particles in a liquid will arrange themselves to give the maximum attractive forces
  - therefore minimize the energy
- the result will generally be a crystalline solid
- the arrangement of the particles in a crystalline solid is called the **crystal lattice**
- the smallest unit that shows the pattern of arrangement for all the particles is called the **unit cell**

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### Unit Cells

Unit cells are 3-dimensional,

- usually containing 2 or 3 layers of particles
- unit cells are repeated over and over to give the macroscopic crystal structure of the solid
- starting anywhere within the crystal results in the same unit cell
- each particle in the unit cell is called a **lattice point**
- **lattice planes** are planes connecting equivalent points in unit cells throughout the lattice

The diagram shows a 3D lattice of yellow spheres. Red lines connect the spheres to form a grid of unit cells, illustrating how they repeat to form the macroscopic crystal structure.

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Cubic Cell Name	Atoms per Unit Cell	Structure	Coordination Number	Edge Length in terms of r	Packing Efficiency (fraction of volume occupied)
Simple Cubic	1		6	$2r$	52%
Body-centered Cubic	2		8	$\frac{4}{\sqrt{3}}r$	68%
Face-centered Cubic	4		12	$2\sqrt{2}r$	74%

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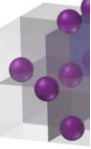
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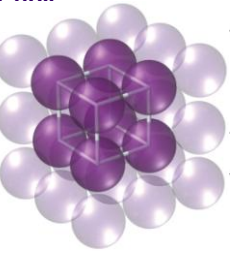

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### Simple Cubic

Coordination number: 

Atoms per unit cell =  $\frac{1}{8} \times 8 = 1$   
 $\frac{1}{8}$  atom at each of 8 corners


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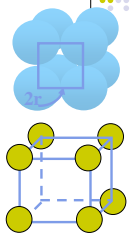
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### Cubic Unit Cells - Simple Cubic

- 8 particles, one at each corner of a cube
- $\frac{1}{8}$  of each particle lies in the unit cell
  - each particle part of 8 cells
  - 1 particle in each unit cell
  - 8 corners x  $\frac{1}{8}$
- edge of unit cell = twice the radius
- coordination number of 6




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### Body-Centered Cubic

Body-Centered Cubic Unit Cell

Coordination number = 8

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

$\frac{1}{8}$  atom at each of 8 corners

1 atom at center

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$$l = \frac{4r}{\sqrt{3}}$$


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### Cubic Unit Cells - Body-Centered Cubic

- 9 particles, one at each corner of a cube + one in center
- $\frac{1}{8}$ th of each corner particle lies in the unit cell
  - 2 particles in each unit cell
  - 8 corners  $\times \frac{1}{8} + 1$  center
- edge of unit cell =  $(4/\sqrt{3})$  times the radius of the particle
- coordination number of 8

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### Face-Centered Cubic

Face-Centered Cubic extended structure

Coordination number

Face-centered cubic unit cell =  $(\frac{1}{8} \times 8) + (\frac{1}{2} \times 6) = 4$

1/2 atoms at 6 faces

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### Cubic Unit Cells - Face-Centered Cubic

- 14 particles, one at each corner of a cube + one in center of each face
- $1/8^{\text{th}}$  of each corner particle +  $1/2$  of face particle lies in the unit cell
- 4 particles in each unit cell
  - 8 corners  $\times 1/8$  + 6 faces  $\times 1/2$
- edge of unit cell =  $2\sqrt{2}$  times the radius of the particle
- coordination number of 12

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### Example 11.7 – Calculate the density of Al if it crystallizes in a fcc and has a radius of 143 pm

<b>Given:</b>	face-centered cubic, $r = 143 \text{ pm} = 1.43 \times 10^{-8} \text{ cm}$ , $m = 1.792 \times 10^{-22} \text{ g}$
<b>Find:</b>	density, $\text{g/cm}^3$
<b>Concept Plan:</b>	$\text{density, g/cm}^3 \leftarrow \frac{\text{mass}}{\text{volume}}$ $\text{fcc} \rightarrow \text{mass} \rightarrow \text{atoms} \times \text{mass 1 atom}$ $\text{fcc} \rightarrow \text{volume} \rightarrow \text{edge length} \rightarrow \text{radius}$ $\text{mass} \leftarrow \frac{\text{molar mass}}{\text{atoms per mol}}$ $\text{edge length} \leftarrow \frac{\text{radius}}{2\sqrt{2}}$ $\text{volume} \leftarrow \text{edge length}^3$
<b>Relationships:</b>	$d = m/V$ $1 \text{ cm} = 10^{10} \text{ m}$ , $1 \text{ pm} = 10^{-12} \text{ m}$ $V = l^3$ , $l = 2r\sqrt{2}$ , $d = m/V$ $\text{fcc} = 4 \text{ atoms/uc}$ , $\text{Al} = 26.982 \text{ g/mol}$ , $1 \text{ mol} = 6.022 \times 10^{23} \text{ atoms}$
<b>Solution:</b>	$d = \frac{4 \text{ atoms/uc} \times 26.982 \text{ g/mol}}{6.022 \times 10^{23} \text{ atoms/mol} \times (2 \times 143 \text{ pm} \times \sqrt{2})^3}$ $d = \frac{4 \times 26.982 \text{ g/mol}}{6.022 \times 10^{23} \times (403.1 \text{ pm})^3}$ $d = \frac{107.928 \text{ g/mol}}{6.022 \times 10^{23} \times 6.51 \times 10^7 \text{ pm}^3}$ $d = \frac{107.928 \text{ g/mol}}{3.92 \times 10^{31} \text{ pm}^3}$ $d = \frac{107.928 \text{ g/mol}}{3.92 \times 10^{31} \times 10^{-30} \text{ cm}^3} = 2.71 \text{ g/cm}^3$
<b>Check:</b>	the accepted density of Al at $20^\circ\text{C}$ is $2.71 \text{ g/cm}^3$ , so the answer makes sense.

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### Closest-Packed Structures First Layer

- with spheres, it is more efficient to offset each row in the gaps of the previous row than to line-up rows and columns

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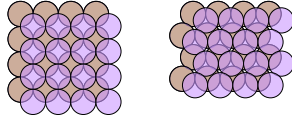
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### Closest-Packed Structures Second Layer

- the second layer atoms can sit directly over the atoms in the first – called an **AA** pattern
- or the second layer can sit over the holes in the first – called an **AB** pattern




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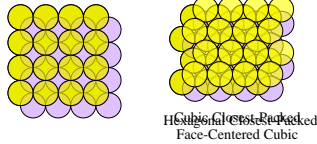
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### Closest-Packed Structures Third Layer – with Offset 2<sup>nd</sup> Layer

- the third layer atoms can align directly over the atoms in the first – called an **ABA** pattern
- or the third layer can sit over the uncovered holes in the first – called an **ABC** pattern




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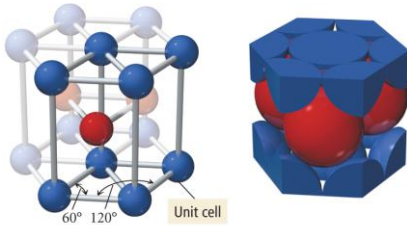
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### Hexagonal Close Packing




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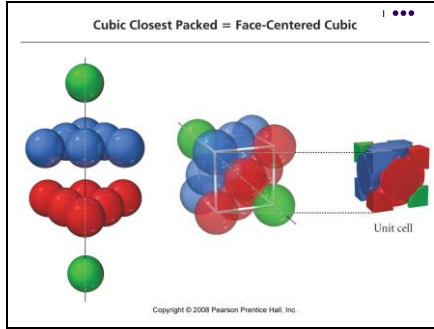
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### Classifying Crystalline Solids

- classified by the kinds of units found
- sub-classified by the kinds of attractive forces holding the units together
- **molecular solids** are solids whose composite units are molecules
- **ionic solids** are solids whose composite units are ions
- **atomic solids** are solids whose composite units are atoms
  - **nonbonding atomic solids** are held together by dispersion forces
  - **metallic atomic solids** are held together by metallic bonds
  - **network covalent atomic solids** are held together by covalent bonds

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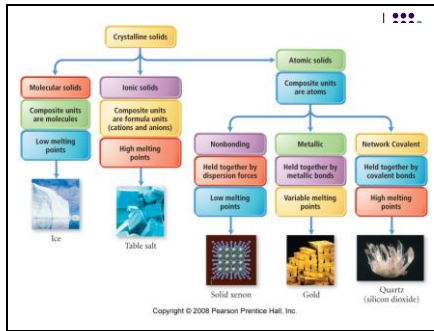
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## Molecular Solids



- the lattice sites are occupied by molecules
- the molecules are held together by intermolecular attractive forces
  - dispersion forces, dipole attractions, and H-bonds
- because the attractive forces are weak, they tend to have low melting point
  - generally  $< 300^{\circ}\text{C}$

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## Ionic Solids Attractive Forces



- held together by attractions between opposite charges
  - nondirectional
  - therefore every cation attracts all anions around it, and vice versa
- the coordination number represents the number of close cation-anion interactions in the crystal
- the higher the coordination number, the more stable the solid
  - lowers the potential energy of the solid
- the coordination number depends on the relative sizes of the cations and anions
  - generally, anions are larger than cations
  - the number of anions that can surround the cation limited by the size of the cation
  - the closer in size the ions are, the higher the coordination number is

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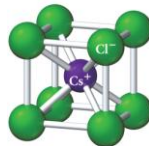
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## Ionic Crystals

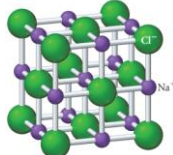


Cesium chloride ( $\text{CsCl}$ )



coordination number = 8  
 $\text{Cs}^+ = 167 \text{ pm}$   
 $\text{Cl}^- = 181 \text{ pm}$

Sodium chloride ( $\text{NaCl}$ )



coordination number = 6  
 $\text{Na}^+ = 97 \text{ pm}$   
 $\text{Cl}^- = 181 \text{ pm}$

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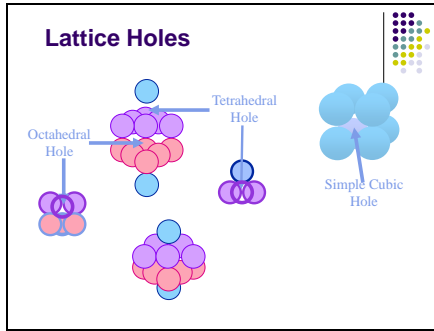
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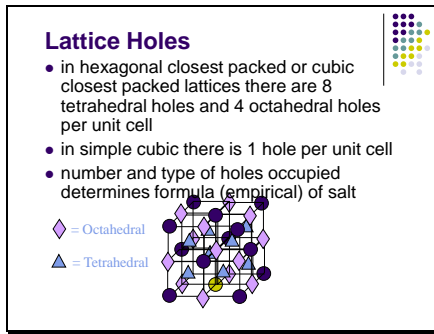
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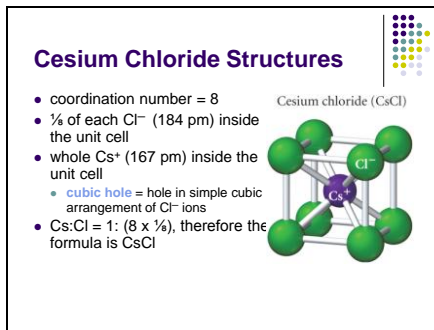
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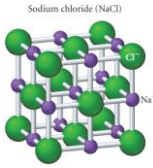
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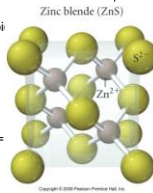
## Rock Salt Structures

- coordination number = 6
- $\text{Cl}^-$  ions (181 pm) in a face-centered cubic arrangement
  - $\frac{1}{8}$  of each corner  $\text{Cl}^-$  inside the unit cell
  - $\frac{1}{2}$  of each face  $\text{Cl}^-$  inside the unit cell
- each  $\text{Na}^+$  (97 pm) in holes between  $\text{Cl}^-$ 
  - octahedral holes
  - 1 in center of unit cell
  - $\frac{1}{4}$  of each edge  $\text{Na}^+$  inside the unit cell
- $\text{Na}:\text{Cl} = (\frac{1}{8} \times 12) + 1; (\frac{1}{4} \times 8) + (\frac{1}{2} \times 6) = 4:4 = 1:1$ ,
- therefore the formula is NaCl



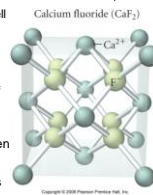
## Zinc Blende Structures

- coordination number = 4
- $\text{S}^{2-}$  ions (184 pm) in a face-centered cubic arrangement
  - $\frac{1}{8}$  of each corner  $\text{S}^{2-}$  inside the unit cell
  - $\frac{1}{2}$  of each face  $\text{S}^{2-}$  inside the unit cell
- each  $\text{Zn}^{2+}$  (74 pm) in holes between  $\text{S}^{2-}$ 
  - tetrahedral holes
  - 1 whole in  $\frac{1}{2}$  the holes
- $\text{Zn}:\text{S} = (4 \times 1); (\frac{1}{8} \times 8) + (\frac{1}{2} \times 6) = 4:4 = 1:1$ ,
- therefore the formula is ZnS



## Fluorite Structures

- coordination number = 4
- $\text{Ca}^{2+}$  ions (99 pm) in a face-centered cubic arrangement
  - $\frac{1}{8}$  of each corner  $\text{Ca}^{2+}$  inside the unit cell
  - $\frac{1}{2}$  of each face  $\text{Ca}^{2+}$  inside the unit cell
- each  $\text{F}^-$  (133 pm) in holes between  $\text{Ca}^{2+}$ 
  - tetrahedral holes
  - 1 whole in all the holes
- $\text{Ca}:\text{F} = (\frac{1}{8} \times 8) + (\frac{1}{2} \times 6); (8 \times 1) = 4:8 = 1:2$ ,
- therefore the formula is  $\text{CaF}_2$ 
  - fluorite structure common for 1:2 ratio
- usually get the **antifluorite** structure when the cation:anion ratio is 2:1
  - the anions occupy the lattice sites and the cations occupy the tetrahedral holes



### Nonbonding Atomic Solids



- noble gases in solid form
- solid held together by weak dispersion forces
  - very low melting
- tend to arrange atoms in closest-packed structure
  - either hexagonal cp or cubic cp
  - maximizes attractive forces and minimizes energy

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### Metallic Atomic Solids



- solid held together by metallic bonds
  - strength varies with sizes and charges of cations
    - coulombic attractions
- melting point varies
- mostly closest packed arrangements of the lattice points
  - cations

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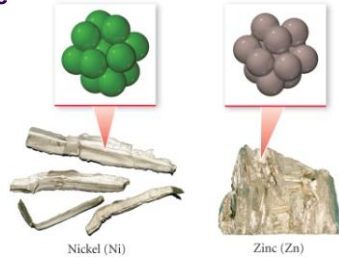
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### Metallic Structure



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### Metallic Bonding

- metal atoms release their valence electrons
- metal cation "islands" fixed in a "sea" of mobile electrons

The diagram shows two representations of metallic bonding. On the left, a 4x6 grid of grey spheres with '+' signs represents metal cations. On the right, a blue rectangular area contains several blue spheres with '+' signs and a large number of small yellow and green dots representing a sea of mobile electrons.

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### Crystal Structure of Metals at Room Temperature

- body-centered cubic
- hexagonal closest packed
- other
- cubic cp, face-centered
- diamond

The periodic table is color-coded to show the crystal structure of elements at room temperature. A legend identifies the colors: dark purple for body-centered cubic, red for hexagonal closest packed, black with a grid pattern for other structures, blue for cubic close-packed (face-centered), and orange for diamond. The structures are distributed across the periodic table, with body-centered cubic in the middle-left, hexagonal closest packed in the bottom-left, cubic close-packed in the middle-right, and diamond in the top-right.

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### Network Covalent Solids

- atoms attached to its nearest neighbors by covalent bonds
- because of the directionality of the covalent bonds, these do not tend to form closest-packed arrangements in the crystal
- because of the strength of the covalent bonds, these have very high melting points
  - generally > 1000°C
- dimensionality of the network affects other physical properties

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### The Diamond Structure: a 3-Dimensional Network



- the carbon atoms in a diamond each have 4 covalent bonds to surrounding atoms
  - $sp^3$
  - tetrahedral geometry
- this effectively makes each crystal one giant molecule held together by covalent bonds
  - you can follow a path of covalent bonds from any atom to every other atom

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### Properties of Diamond

- very high melting,  $-3800^\circ\text{C}$ 
  - need to overcome some covalent bonds
- very rigid
  - due to the directionality of the covalent bonds
- very hard
  - due to the strong covalent bonds holding the atoms in position
  - used as abrasives
- electrical insulator
- thermal conductor
  - best known
- chemically very nonreactive



(a) Diamond



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### The Graphite Structure: a 2-Dimensional Network



- in graphite, the carbon atoms in a sheet are covalently bonded together
  - forming 6-member flat rings fused together
    - similar to benzene
    - bond length = 142 pm
  - $sp^2$ 
    - each C has 3 sigma and 1 pi bond
  - trigonal-planar geometry
  - each sheet a giant molecule
- the sheets are then stacked and held together by dispersion forces
  - sheets are 341 pm apart

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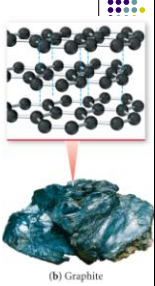
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### Properties of Graphite

- hexagonal crystals
- high melting, ~3800°C
  - need to overcome some covalent bonding
- slippery feel
  - because there are only dispersion forces holding the sheets together, they can slide past each other
    - glide planes
  - lubricants
- electrical conductor
  - parallel to sheets
- thermal insulator
- chemically very nonreactive



(b) Graphite

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### Silicates

- ~90% of earth's crust
- extended arrays of Si-O
  - sometimes with Al substituted for Si – aluminosilicates
- glass is the amorphous form

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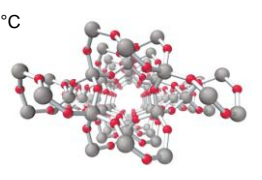
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### Quartz

- 3-dimensional array of Si covalently bonded to 4 O
  - tetrahedral
- melts at ~1600°C
- very hard




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## Micas



- minerals that are mainly 2-dimensional arrays of Si bonded to O
  - hexagonal arrangement of atoms
- sheets
- chemically stable
- thermal and electrical insulator

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## Band Theory



- the structures of metals and covalent network solids result in every atom's orbitals being shared by the entire structure
- for large numbers of atoms, this results in a large number of molecular orbitals that have approximately the same energy, we call this an **energy band**

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## Band Theory



- when 2 atomic orbitals combine they produce both a bonding and an antibonding molecular orbital
- when many atomic orbitals combine they produce a band of bonding molecular orbitals and a band of antibonding molecular orbitals
- the band of bonding molecular orbitals is called the **valence band**
- the band of antibonding molecular orbitals is called the **conduction band**

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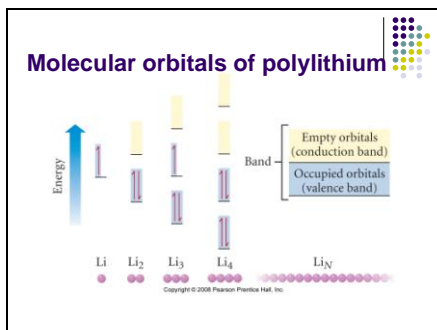
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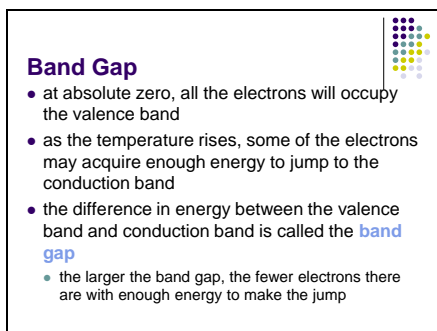
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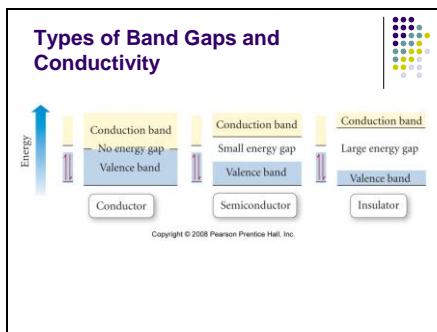
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## Band Gap and Conductivity



- the more electrons at any one time that a substance has in the conduction band, the better conductor of electricity it is
- if the band gap is  $\sim 0$ , then the electrons will be almost as likely to be in the conduction band as the valence band and the material will be a **conductor**
  - metals
  - the conductivity of a metal decreases with temperature
- if the band gap is small, then a significant number of the electrons will be in the conduction band at normal temperatures and the material will be a **semiconductor**
  - graphite
  - the conductivity of a semiconductor increases with temperature
- if the band gap is large, then effectively no electrons will be in the conduction band at normal temperatures and the material will be an **insulator**

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## Doping Semiconductors



- **doping** is adding impurities to the semiconductor's crystal to increase its conductivity
- goal is to increase the number of electrons in the conduction band
- **n-type semiconductors** do not have enough electrons themselves to add to the conduction band, so they are doped by adding electron rich impurities
- **p-type semiconductors** are doped with an electron deficient impurity, resulting in electron "holes" in the valence band. Electrons can jump between these holes in the valence band, allowing conduction of electricity

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## Diodes



- when a p-type semiconductor adjoins an n-type semiconductor, the result is an **p-n junction**
- electricity can flow across the p-n junction in only one direction – this is called a **diode**
- this also allows the accumulation of electrical energy – called an **amplifier**

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**EXAMPLE 11.6** Using Bragg's Law

When an X-ray beam of  $\lambda = 154 \text{ pm}$  was incident on the surface of an iron crystal, it produced a maximum reflection at an angle of  $\theta = 32.0^\circ$ . Assuming  $n = 1$ , calculate the separation between layers of iron atoms in the crystal.

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**EXAMPLE 11.7** Relating Density to Crystal Structure

Aluminum crystallizes with a face-centered cubic unit cell. The radius of an aluminum atom is  $143 \text{ pm}$ . Calculate the density of solid crystalline aluminum in  $\text{g/cm}^3$ .

continued...

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**Solve!** Begin by finding the mass of the unit cell. Obtain the mass of an aluminum atom from its molar mass. Since the face-centered cubic unit cell contains four atoms per unit cell, multiply the mass of aluminum by 4 to get the mass of a unit cell.

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