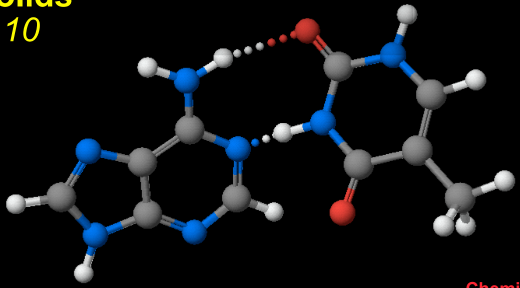
Intermolecular Forces, Liquids and Solids

Chap. 10



Chemistry 222
Professor Michael Russell

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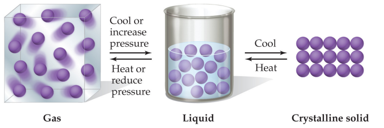
Last update: 4/29/24

States of Matter

The fundamental difference between states of matter is the distance between particles.



Total disorder; much empty space; particles have complete freedom of motion; particles far apart

Disorder; particles or clusters of particles are free to move relative to each other; particles close together

Ordered arrangement; particles are essentially in fixed positions; particles close together

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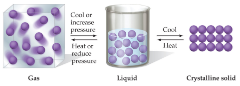
Solids and liquids often referred to as "condensed phases"

The States of Matter



Some Characteristic Properties of the States of Matter

Gas	Assumes both the volume and shape of its container Is compressible Flows readily Diffusion within a gas occurs rapidly
Liquid	Assumes the shape of the portion of the container it occupies Does not expand to fill container Is virtually incompressible Flows readily Diffusion within a liquid occurs slowly
Solid	Retains its own shape and volume Is virtually incompressible Does not flow Diffusion within a solid occurs extremely slowly

The state a substance is in at a particular temperature and pressure depends on two antagonistic entities:

- **the kinetic energy of the particles;**
- **the strength of the attractions between the particles.**

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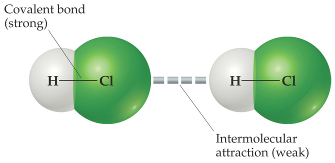
Intermolecular Forces



The attractions between molecules (*inter*molecular forces) are not nearly as strong as the *intra*molecular attractions that hold compounds together.

Intramolecular forces: **ionic, covalent, metallic**

Intermolecular forces are *not* chemical bonds!

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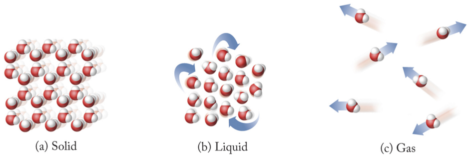
Intermolecular Forces

Kinetic Energy (E_k) vs. Attractive (IM) Force

E_K = lowest intermediate highest


(a) Solid (b) Liquid (c) Gas

Intermolecular (IM) Attraction:

highest intermediate lowest

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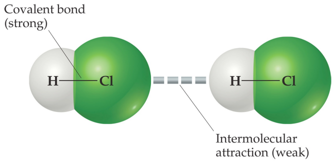
We will assume gases have no IM force in CH 222

Intermolecular Forces



Intermolecular forces are strong enough to affect physical properties such as boiling and melting points, vapor pressures, and viscosities.

See the IM Forces Guide

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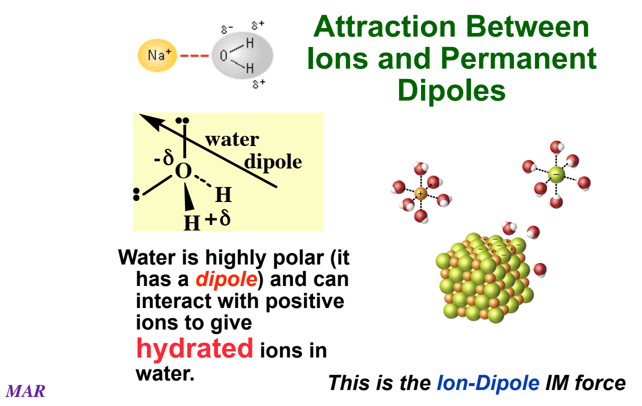

Attraction Between Ions and Permanent Dipoles

Water is highly polar (it has a *dipole*) and can interact with positive ions to give **hydrated** ions in water.

This is the Ion-Dipole IM force

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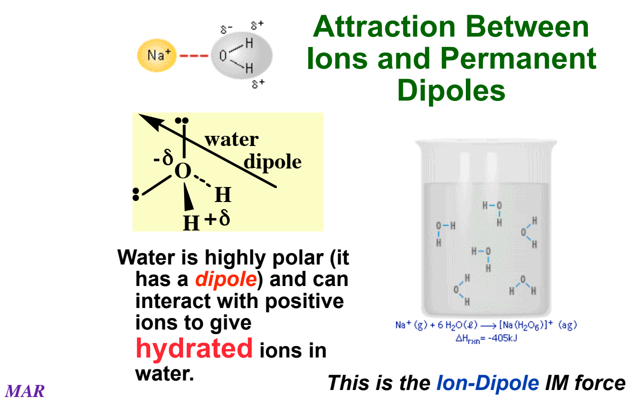

Attraction Between Ions and Permanent Dipoles

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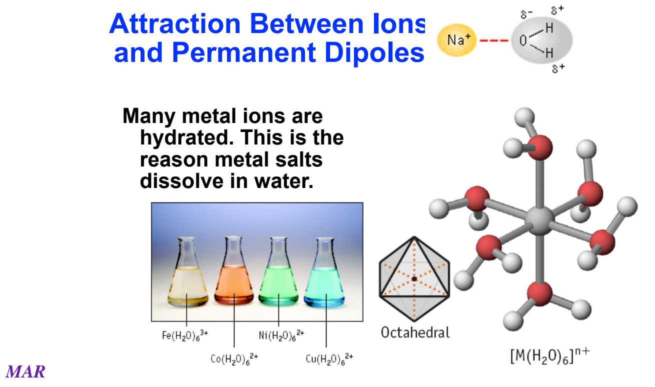

Attraction Between Ions and Permanent Dipoles

Many metal ions are hydrated. This is the reason metal salts dissolve in water.

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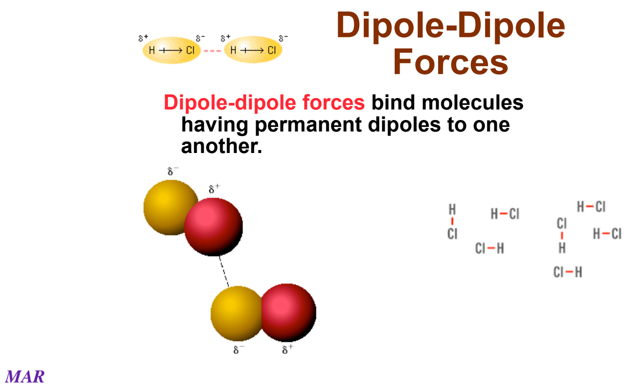

Dipole-Dipole Forces

Dipole-dipole forces bind molecules having permanent dipoles to one another.

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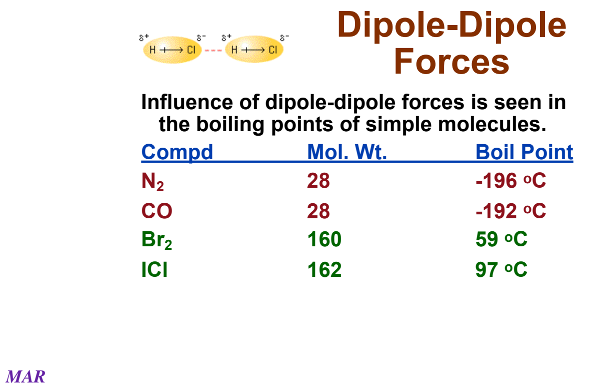

Dipole-Dipole Forces

Influence of dipole-dipole forces is seen in the boiling points of simple molecules.

Compd	Mol. Wt.	Boil Point
N_2	28	-196 °C
CO	28	-192 °C
Br_2	160	59 °C
ICl	162	97 °C

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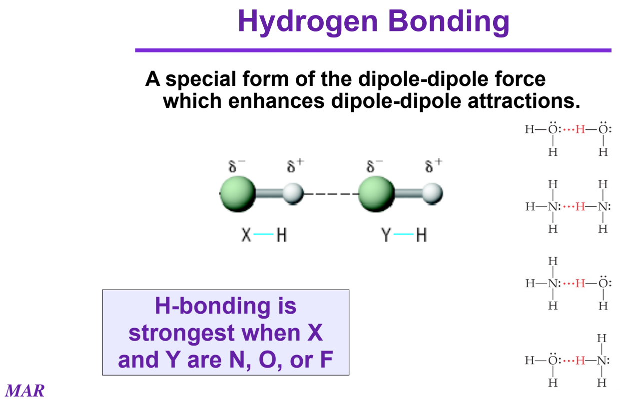

Hydrogen Bonding

A special form of the dipole-dipole force which enhances dipole-dipole attractions.

H-bonding is strongest when X and Y are N, O, or F

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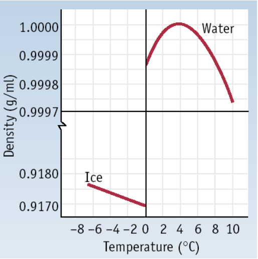
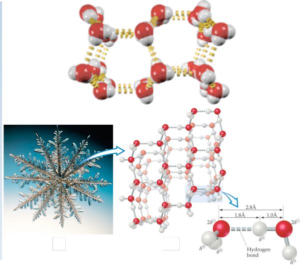
Hydrogen Bonding in H_2O

Ice has open lattice-like structure.
Ice density is < liquid and so solid floats on water.





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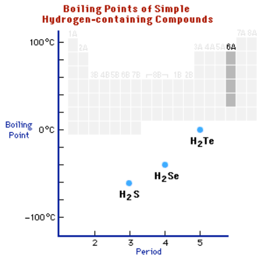
Hydrogen Bonding

H bonds ---> abnormally high boiling point of water.



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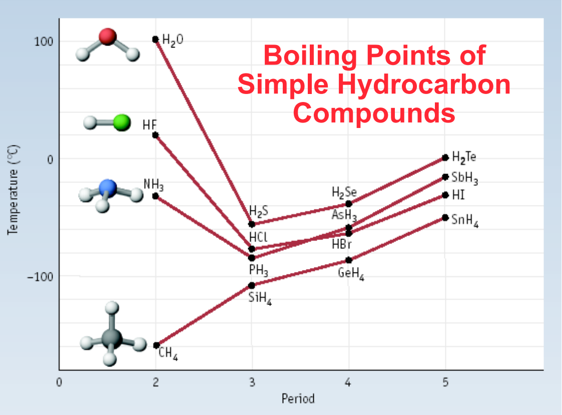
Boiling Points of Simple Hydrocarbon Compounds



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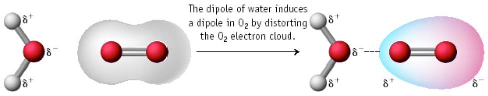
FORCES INVOLVING INDUCED DIPOLES

How can non-polar molecules such as O_2 and I_2 dissolve in water?



The water dipole INDUCES a dipole in the O_2 electric cloud.

Dipole-induced dipole

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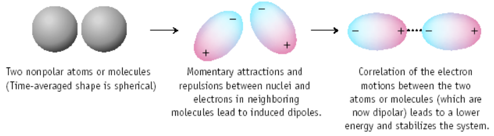
FORCES INVOLVING INDUCED DIPOLES

Formation of a dipole in two nonpolar I_2 molecules.

Induced dipole-induced dipole (ID-ID)



"Induced Dipole-Induced Dipole" is also known as "London Dispersion", same thing

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FORCES INVOLVING INDUCED DIPOLES

The induced forces between I_2 molecules are very weak, so solid I_2 sublimes (goes from a solid to gaseous molecules).

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FORCES INVOLVING INDUCED DIPOLES

The magnitude of the induced dipole depends on the tendency to be distorted.

Higher molar mass ---> larger induced dipoles.

Larger atoms have larger electron clouds which are easier to polarize

Halogen	Molecular Weight (amu)	Boiling Point (K)	Noble Gas	Molecular Weight (amu)	Boiling Point (K)
F_2	38.0	85.1	He	4.0	4.6
Cl_2	71.0	238.6	Ne	20.2	27.3
Br_2	159.8	332.0	Ar	39.9	87.5
I_2	253.8	457.6	Kr	83.8	120.9
			Xe	131.3	166.1

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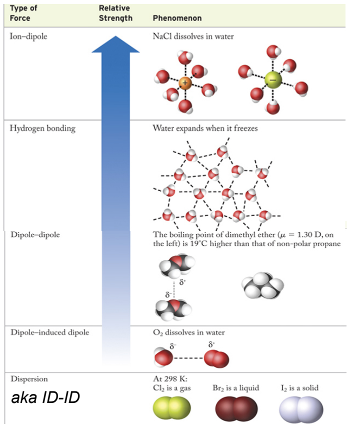
Intermolecular Forces Strength Summary



Type of Force	Relative Strength	Phenomenon
Ion–dipole		NaCl dissolves in water
Hydrogen bonding		Water expands when it freezes
Dipole–dipole		The boiling point of dimethyl ether (μ = 1.30 D, on the left) is 19°C higher than that of non-polar propane
Dipole–induced dipole		O_2 dissolves in water
Dispersion *aka ID-ID*		At 298 K: Cl_2 is a gas Br_2 is a liquid I_2 is a solid

Ion-ion / metallic force strongest of all

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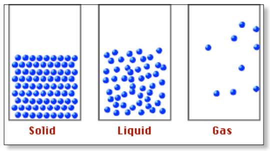
Liquids



In a liquid

- molecules are in constant motion
- there are appreciable intermolecular forces
- molecules close together
- Liquids are almost incompressible
- Liquids do not fill the container

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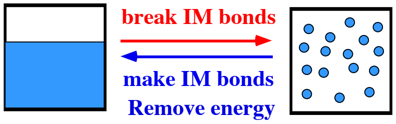
Liquids

The two key properties we need to describe are EVAPORATION and its opposite- CONDENSATION



evaporation--->

LIQUID

Add energy

break IM bonds

VAPOR

make IM bonds

Remove energy

<---condensation

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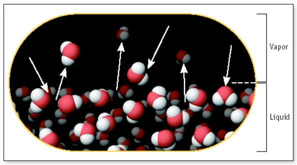
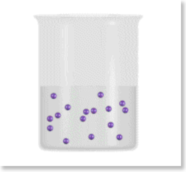
Liquids

To evaporate, molecules must have sufficient energy to break IM forces.





Breaking IM forces requires energy. The process of evaporation is endothermic.

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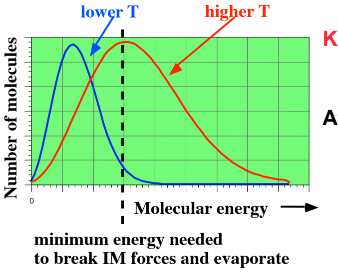
Liquids



Distribution of molecular energies in a liquid.

Kinetic Energy proportional to Temperature

At higher T a much larger number of molecules has high enough energy to break IM forces and move from liquid to vapor state.

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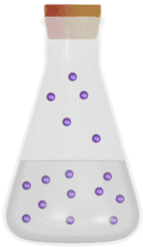
Liquids

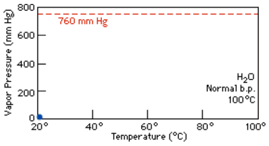
When molecules of liquid are in the vapor state, they exert a VAPOR PRESSURE

EQUILIBRIUM VAPOR PRESSURE is the pressure exerted by a vapor over a liquid in a closed container when the rate of evaporation = the rate of condensation.



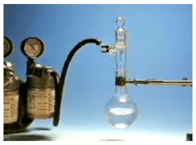
Vapor Pressure

Boiling Liquids



Liquid boils when its vapor pressure equals atmospheric pressure.

Boiling Point at Lower Pressure



When pressure is lowered, the vapor pressure can equal the external pressure at a lower temperature.

Consequences of Vapor Pressure Changes

When can cools, vp of water drops. Pressure in the can is less than that of atmosphere, so can is crushed.

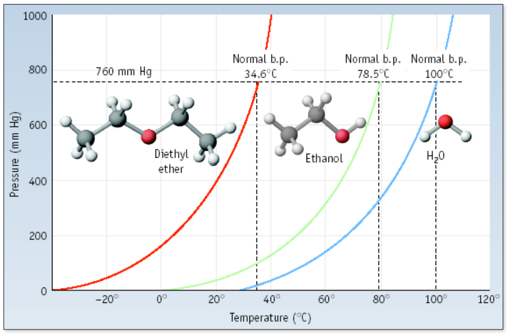
Consequences of Vapor Pressure Changes - *Whoops!*

http://www.DOCTORSLIME.COM

Photo s from http://www.DOCTORSLIME.COM

When car cools on hot day (i.e. cleaning with cold water), vp of fumes inside drops. Pressure in the car is less than that of atmosphere, so car is crushed!

Equilibrium Vapor Pressure



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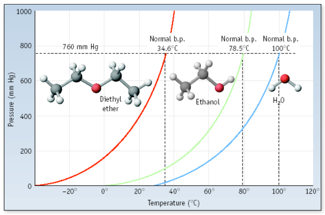
Liquids



The curves show all conditions of P and T where LIQ and VAP are in EQUILIBRIUM.

The VP rises with T.

When VP = external P, the liquid boils.

This means that BPs of liquids change with altitude.

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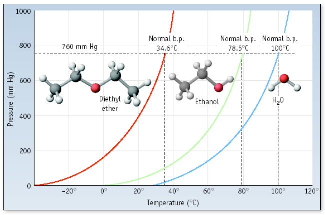
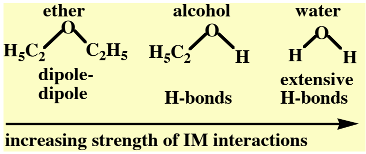
Liquids



If external P = 760 mm Hg, T of boiling is the NORMAL BOILING POINT

VP of a given molecule at a given T depends on IM forces. Here the VPs are in the order:



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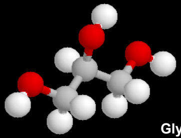
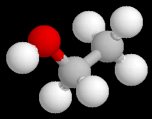
Viscosity

VISCOSITY is the tendency or resistance of liquids to flow.

Liquids "flow" differently due to the strength of their intermolecular bonds





Viscosity results from several factors, including IM interactions, molecular shape and size

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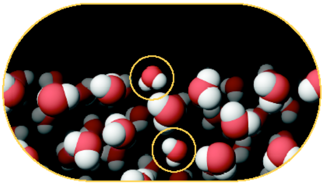
Liquids

Molecules at surface behave differently than those in the interior.



Molecules at surface experience net INWARD force of attraction.
This leads to SURFACE TENSION - the energy required to break the surface.

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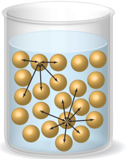
Surface Tension



SURFACE TENSION also leads to spherical liquid droplets.

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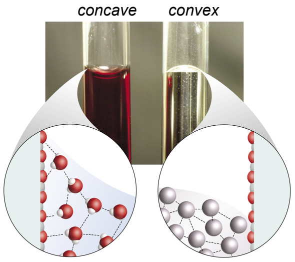
Liquids

IM forces also lead to CAPILLARY action

Cohesive forces: interactions between like particles.

Adhesive forces: interactions between unlike particles.



"Concave up is like a cup, concave down is like a frown"

Concave *(concave up)* Meniscus: adhesive forces ≥ cohesive forces (H_2O on glass)

Convex *(concave down)* Meniscus: Cohesive forces > adhesive forces (Hg on glass).

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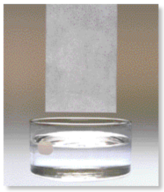
Capillary Action



Movement of water up a piece of paper depends on H-bonds between H_2O and the OH groups of the cellulose in the paper.

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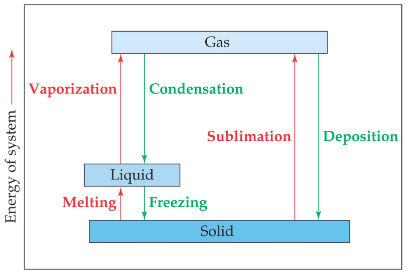
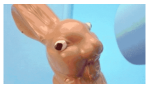
Heat Transfer with Phase Change

Overall patterns:

solid → liquid → gas = *endothermic reaction*
gas → liquid → solid = exothermic reaction





Chapter 5: Heat Transfer with no Phase Change ($q = mC\Delta T$)

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Heat Transfer with Phase Change

HEAT OF VAPORIZATION is the heat required (at constant P) to *vaporize* a liquid.

LIQ + heat ---> *VAP*

Compd.	ΔH_{vap} (kJ/mol)	IM Force
H_2O	40.7 (100 °C)	H-bonds
SO_2	26.8 (-47 °C)	dipole
Xe	12.6 (-107 °C)	induced dipole

HEAT OF FUSION is the heat required (at constant P) to *melt* a solid.

SOL + heat ---> LIQ

Temperature constant during phase change

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Clausius-Clapeyron

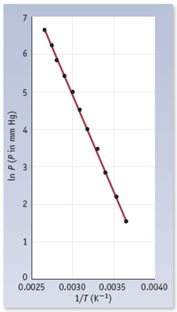
The **Clausius–Clapeyron Equation** provides a link between **vapor pressure (*P*), temperature (in *K*),** and **molar heat of vaporization (ΔH_{vap}):**

$$\ln P = -\frac{\Delta H^\circ_{vap}}{RT} + C$$

Perform a ***linear regression*** (**ln P** *vs.* **1/T(K)**) to get best values, or, with only two temps:

$$\ln \frac{P_1}{P_2} = \frac{\Delta H^\circ_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

R = 8.3145 J mol^{-1} K^{-1}



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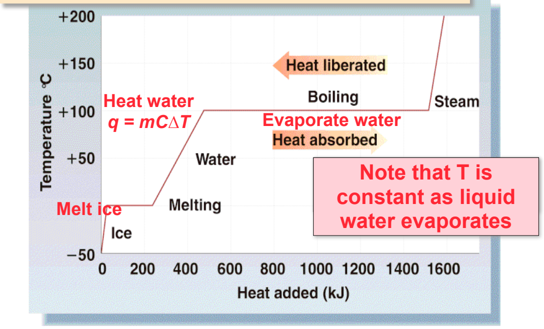
Heating/Cooling Curve for Water



Note that T is constant as liquid water evaporates

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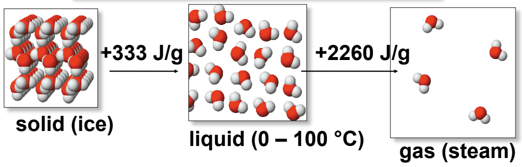
Heat & Changes of State

What quantity of heat is required to melt 500. g of ice at 0.0 ^{o}C and heat the water to steam at 100. ^{o}C?

Heat of fusion of ice = 333 J/g
Specific heat of water = 4.184 J/g•K
Heat of vaporization = 2260 J/g



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Heat & Changes of State

What quantity of heat is required to melt 500. g of ice at 0.0 ^{o}C and heat the water to steam at 100. ^{o}C?

1. To melt ice

q = (500. g)(333 J/g) = 1.67×10^{5} J

2. To raise water from 0.0 ^{o}C to 100. ^{o}C

q = (500. g)(4.184 J/g•K)(100. - 0)K = 2.09×10^{5} J

3. To evaporate water at 100. ^{o}C

q = (500. g)(2260 J/g) = 1.13×10^{6} J

4. Total heat energy = 1.51×10^{6} J = 1510 kJ

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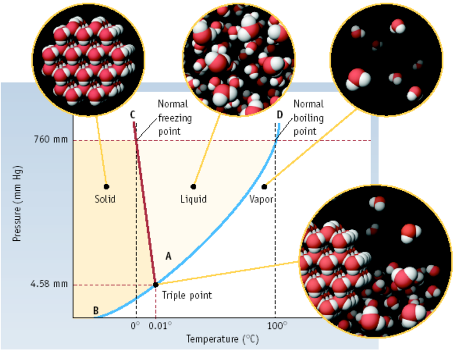
Phase Diagrams



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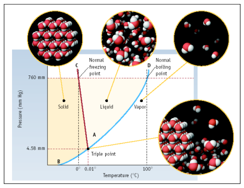

TRANSITIONS BETWEEN PHASES

See the phase diagram for water in text

Lines connect all conditions of T and P where EQUILIBRIUM exists between the phases on either side of the line.

At equilibrium particles move from liquid to gas as fast as they move from gas to liquid.

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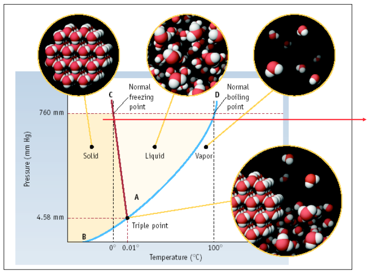
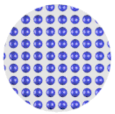
Phase Diagram for Water





Animation of solid phase.

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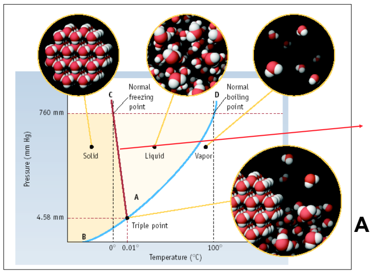
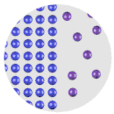
Phase Diagram for Water

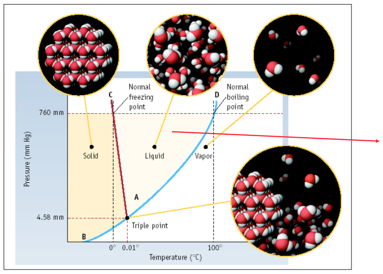


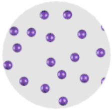


Animation of equilibrium between solid and liquid phases.

MAR

Phase Diagram for Water





Animation of liquid phase.

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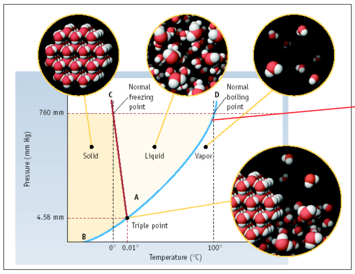
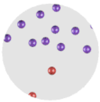
Phase Diagram for Water





Animation of equilibrium between liquid and gas phases.

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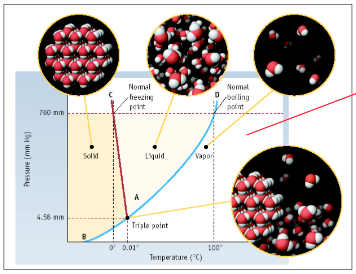
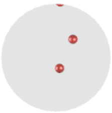
Phase Diagram for Water





Animation of gas phase.

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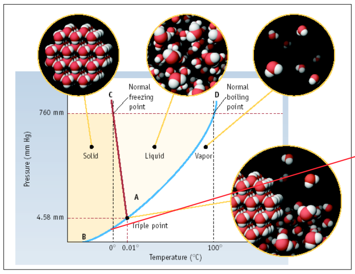
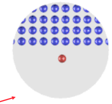
Phase Diagram for Water





Animation of equilibrium between solid and gas phases.

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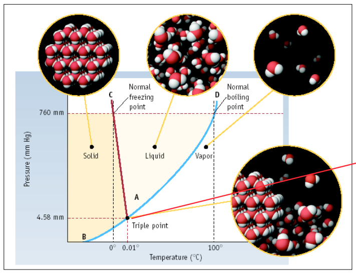
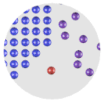
Phase Diagram for Water



Animation of triple point.



At the TRIPLE POINT all three phases are in equilibrium.

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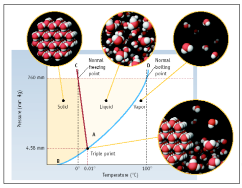

Phases Diagrams-
Important Points for Water

	T(˚C)	P(mm Hg)
Normal boil point	100	760
Normal freeze point	0	760
Triple point	0.0098	4.58

Water at the Triple Point

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An Introduction to Solids

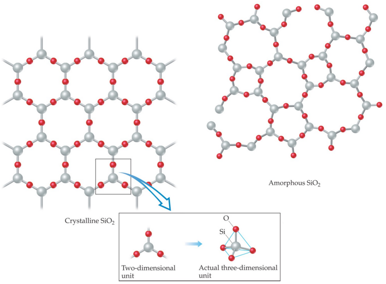
We can think of solids as falling into two groups:

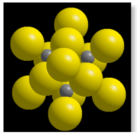
- **crystalline**: particles in highly ordered arrangements
- **amorphous**: no particular order in arrangement of particles.

We will focus on crystalline solids in CH 222.

Molecules, atoms or ions locked into a **CRYSTAL LATTICE**

Particles are close together with very strong IM forces. They are highly ordered, rigid, incompressible





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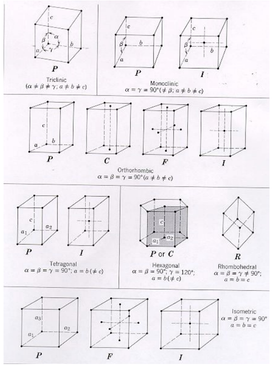
A **UNIT CELL** is the smallest repeating unit in a crystal lattice



Crystal Lattices

7 Brevais lattice (unit cell) types:

- **Triclinic**
- **Monoclinic**
- **Orthorhombic**
- **Tetragonal**
- **Hexagonal**
- **Rhombohedral**
- **Cubic (Isometric)**

We will use just the **cubic** system in CH 222

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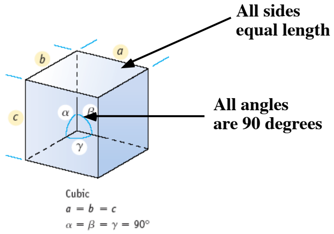
Cubic Unit Cells

There are 7 basic crystal systems, but we are only concerned with **CUBIC** (*isometric*) in CH 222.



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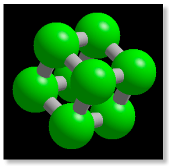
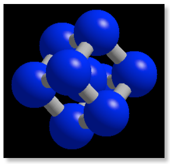
Cubic Unit Cells

Three types of Cubic Unit Cells:

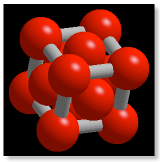
Simple cubic (SC)



Body-centered cubic (BCC)



Face-centered cubic (FCC)



See *Cubic Unit Cells Guide*

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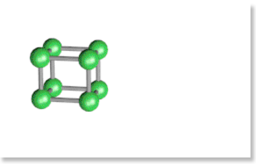
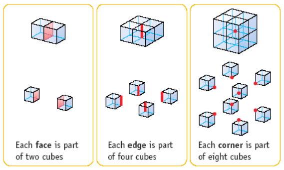
Simple Cubic Unit Cell





Simple cubic unit cell.

Note that each atom is at a corner of a unit cell and is shared among 8 unit cells.

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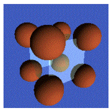
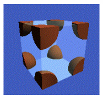
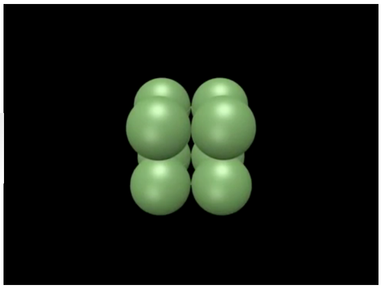
The Simple Cubic Unit Cell



edge = 2r
r = radius





Atom at each corner,
Only 1 net atom per simple cubic cell

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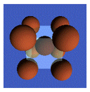
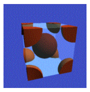
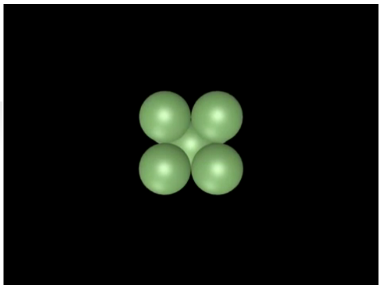
Body-Centered Cubic Unit Cell



edge = $4r/\sqrt{3}$
r = radius

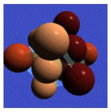




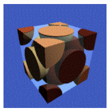
Atom at each cube corner plus one in center
Two net atoms per bcc unit cell

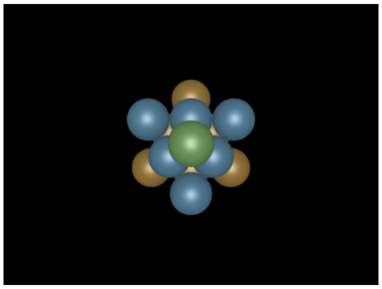
Face-Centered Cubic Unit Cell

also known as cubic close packing



edge = $4r/\sqrt{2}$
r = radius





Atom in each cube corner plus atom in each cube face, four net atoms per fcc unit cell

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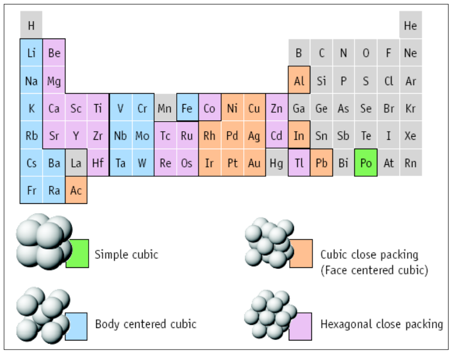
Unit Cells for Metals



H																	He
Li 🟦	Be 🟪											B	C	N	O	F	Ne
Na 🟦	Mg 🟪											Al 🟧	Si	P	S	Cl	Ar
K 🟦	Ca 🟪	Sc 🟪	Ti 🟪	V 🟦	Cr 🟦	Mn	Fe 🟦	Co 🟪	Ni 🟧	Cu 🟧	Zn 🟪	Ga	Ge	As	Se	Br	Kr
Rb 🟦	Sr 🟪	Y 🟪	Zr 🟪	Nb 🟦	Mo 🟦	Tc 🟪	Ru 🟪	Rh 🟧	Pd 🟧	Ag 🟧	Cd 🟪	In 🟧	Sn	Sb	Te	I	Xe
Cs 🟦	Ba 🟦	La	Hf 🟪	Ta 🟦	W 🟦	Re 🟪	Os 🟪	Ir 🟧	Pt 🟧	Au 🟧	Hg	Tl 🟪	Pb 🟧	Bi	Po 🟩	At	Rn
Fr 🟦	Ra 🟦	Ac 🟧															

🟩 Simple cubic
🟧 Cubic close packing (Face centered cubic)
🟦 Body centered cubic
🟪 Hexagonal close packing

Finding the Lattice Type

To find out if a metal is SC, BCC or FCC, use the known radius and density of an atom to calc. no. of atoms per unit cell.

PROBLEM **Al has density = 2.699 g/cm^3 and Al radius = 143 pm. Verify that Al is FCC.**

SOLUTION

1. Calc. unit cell edge (cm)

***see <u>handout</u>*: edge = 4 * radius / √2**

edge = 4 * 143 pm / √2 = 404 pm

404 pm * (10^{-10} cm / pm) = 4.04 * 10^{-8} cm

Finding the Lattice Type

PROBLEM **Al has density = 2.699 g/cm^3 and Al radius = 143 pm. Verify that Al is FCC.**

SOLUTION

2. Calc. unit cell volume

edge = 4.04 x 10^{-8} cm *(previous slide)*

V = (cell edge)^3 = (4.04 x 10^{-8} cm)^3

V = 6.62 x 10^{-23} cm^3

3. Now use density to find mass

mass = (6.62 x 10^{-23} cm^3)(2.699 g/cm^3)

= 1.79 x 10^{-22} g/unit cell

Finding the Lattice Type

PROBLEM **Al has density = 2.699 g/cm^3 and Al radius = 143 pm. Verify that Al is FCC.**

SOLUTION

4. Calculate number of Al per unit cell from mass of unit cell.

$$\text{Mass 1 Al atom} = \frac{26.98\text{ g}}{\text{mol}} \bullet \frac{1\text{ mol}}{6.022 \times 10^{23}\text{ atoms}}$$

1 atom = 4.480 x 10^{-23} g, *so*

$$\frac{1.79 \times 10^{-22}\text{ g}}{\text{unit cell}} \bullet \frac{1\text{ atom}}{4.480 \times 10^{-23}\text{ g}} = 3.99\text{ Al atoms/unit cell}$$

...more in lab and problem set

Other Types of Crystalline Solids

Type of Solid	Form of Unit Particles	Forces Between Particles	Properties	Examples
Molecular	Atoms or molecules	London dispersion forces, dipole–dipole forces, hydrogen bonds	Fairly soft, low to moderately high melting point, poor thermal and electrical conduction	Argon, Ar; methane, CH_4; sucrose, $C_{12}H_{22}O_{11}$; Dry Ice, CO_2
Covalent-network	Atoms connected in a network of covalent bonds	Covalent bonds	Very hard, very high melting point, variable thermal and electrical conduction	Diamond, C; quartz, SiO_2
Ionic	Positive and negative ions	Electrostatic attractions	Hard and brittle, high melting point, poor thermal and electrical conduction	Typical salts—for example, NaCl, $Ca(NO_3)_2$
Metallic	Atoms	Metallic bonds	Soft to very hard, low to very high melting point, excellent thermal and electrical conduction, malleable and ductile	All metallic elements—for example, Cu, Fe, Al, Pt

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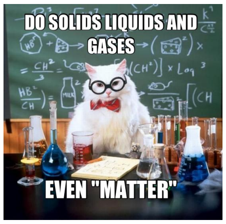
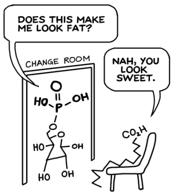
End of Chapter 10

See:

- *Chapter Ten Study Guide*
- *Chapter Ten Concept Guide*
- *Important Equations (following this slide)*
- *End of Chapter Problems (following this slide)*





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Important Equations, Constants, and Handouts from this Chapter:

Intermolecular (IM) Forces: *know* **when** *they apply,* **strength** *(strongest to weakest)***:**

- **metallic/ion-ion**
- **ion-dipole**
- **dipole-dipole** (*with* **Hydrogen bonding** *for* **O, F** *and* **N** *to* **H)**
- **dipole-induced dipole**
- **induced dipole-induced dipole (ID-ID)**

Solids: *unit cell type:*

- **simple cubic (SC)**
- **body centered cubic (BCC)**
- **face centered cubic (FCC)**

States of Matter: solids, liquids, gases, phase diagrams, triple point, "normal" boiling and freezing points, the slope of the solid-liquid line in a phase diagram, q = mC∆T and q = "mass*heat", vapor pressure

sc: 1 atom, $d_0 = 2r$
bcc: 2 atoms, $d_0 = 4r/\sqrt{3}$
fcc: 4 atoms, $d_0 = 4r/\sqrt{2}$
mole = 6.022×10^{23}

r ⇔ d_0 ⇔ Volume < *density* > **mass** < *molar mass* > **mols** < *avogadro's number* > **atoms/molecules**

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End of Chapter Problems: *Test Yourself*

1. What type of intermolecular force must be overcome in converting each of the following from a liquid to a gas? **liquid O_2, H_2O, CH_3I, CH_3CH_2OH**
2. Ethanol, CH_3CH_2OH, has a vapor pressure of 59 mm Hg at 25 °C. What quantity of heat energy is required to evaporate 125 mL of the alcohol at 25 °C? The enthalpy of vaporization of the alcohol at 25 °C is 42.32 kJ/mol. The density of the liquid is 0.7849 g/mL.
3. Liquid ammonia, $NH_3(l)$, was once used in home refrigerators as the heat transfer fluid. The specific heat of the liquid is 4.7 J/g • K and that of the vapor is 2.2 J/g • K. The enthalpy of vaporization is 23.33 kJ/mol at the boiling point. If you heat 12 kg of liquid ammonia from -50.0 °C to its boiling point of -33.3 °C, allow it to evaporate, and then continue warming to 0.0 °C, how much heat energy must you supply?
4. Aluminum has a face centered cubic crystal lattice and a density of 2.699 g/cm^3. What is the radius of an aluminum atom?
5. Iron has a body centered cubic unit cell and a radius of 126 pm. Find the density of iron.

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End of Chapter Problems: *Answers*

1. **liquid O_2**: ID-ID, **H_2O**: Hydrogen bonding, **CH_3I**: Dipole-dipole, **CH_3CH_2OH**: Hydrogen bonding
2. 90.1 kJ
3. The total heat required is the sum of the heat required to (1) heat the liquid from –50.0 ºC to its boiling point, (2) vaporize the gas, and (3) heat the vapor to 0.0 ºC. Answer (1) = 940 kJ, Answer (2) = 16000 kJ, Answer (3) = 880 kJ, and total energy = 18000 kJ
4. 143.2 pm
5. 7.8740 g/cm^3

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