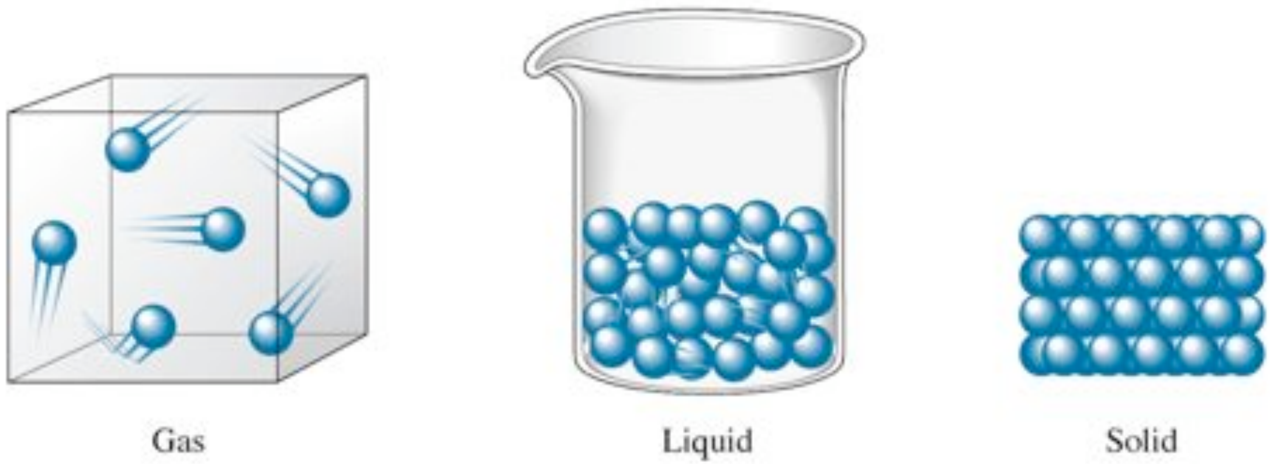
The kinetic Molecular Theory of Liquids and solids

Characteristic properties of gases, liquids,and solids



	Gas	Liquid	Solid
Definite volume	no	yes	yes
Definite shape	no	no	yes
density	low	high	high
compressibility	high	very slight	no
Molecular motion	free	slide	vibrate

States of matter

solid

Liquid

Gas

Plasma

- examine attractive forces between molecules

Intermolecular Forces

Attractive forces between molecules

Intermolecular Forces

ion-ion $NH_4^+ \leftrightarrow NO_3^-$

ion-dipole $K^+ \leftrightarrow HCl$

ion-induced dipole $K^+ \leftrightarrow Cl\text{-}Cl$

dipole-dipole $HCl \leftrightarrow HCl$

dipole-induced dipole $HCl \leftrightarrow Cl\text{-}Cl$

induced dipole-induced dipole $Cl\text{-}Cl \leftrightarrow Cl\text{-}Cl$

Intermolecular Forces

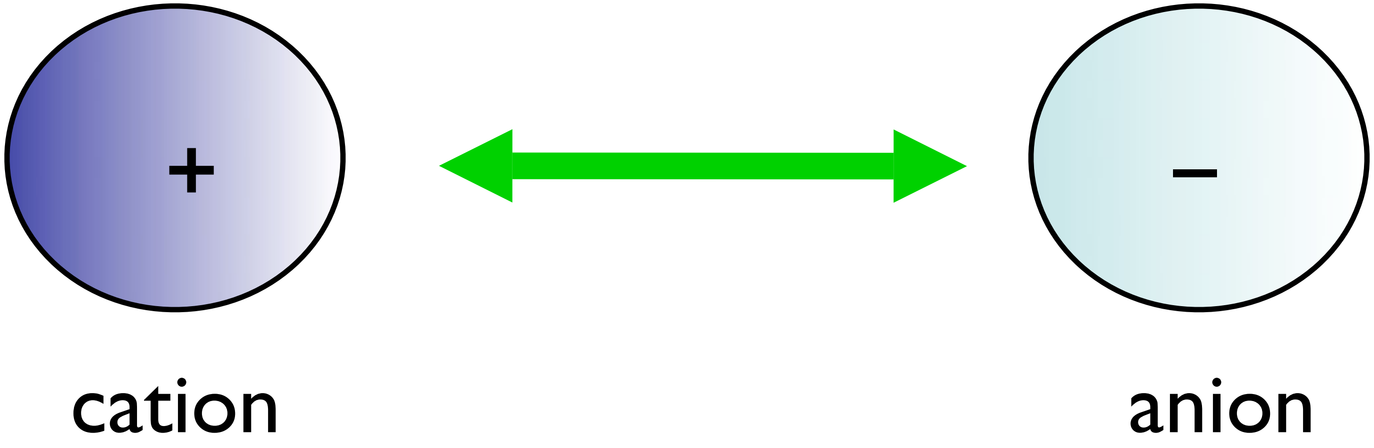
Van der Waals forces

dipole-dipole **HCl ↔ HCl**

dipole-induced dipole **HCl ↔ Cl-Cl**

induced dipole-induced dipole **Cl-Cl ↔ Cl-Cl**

Ion-ion attractive force



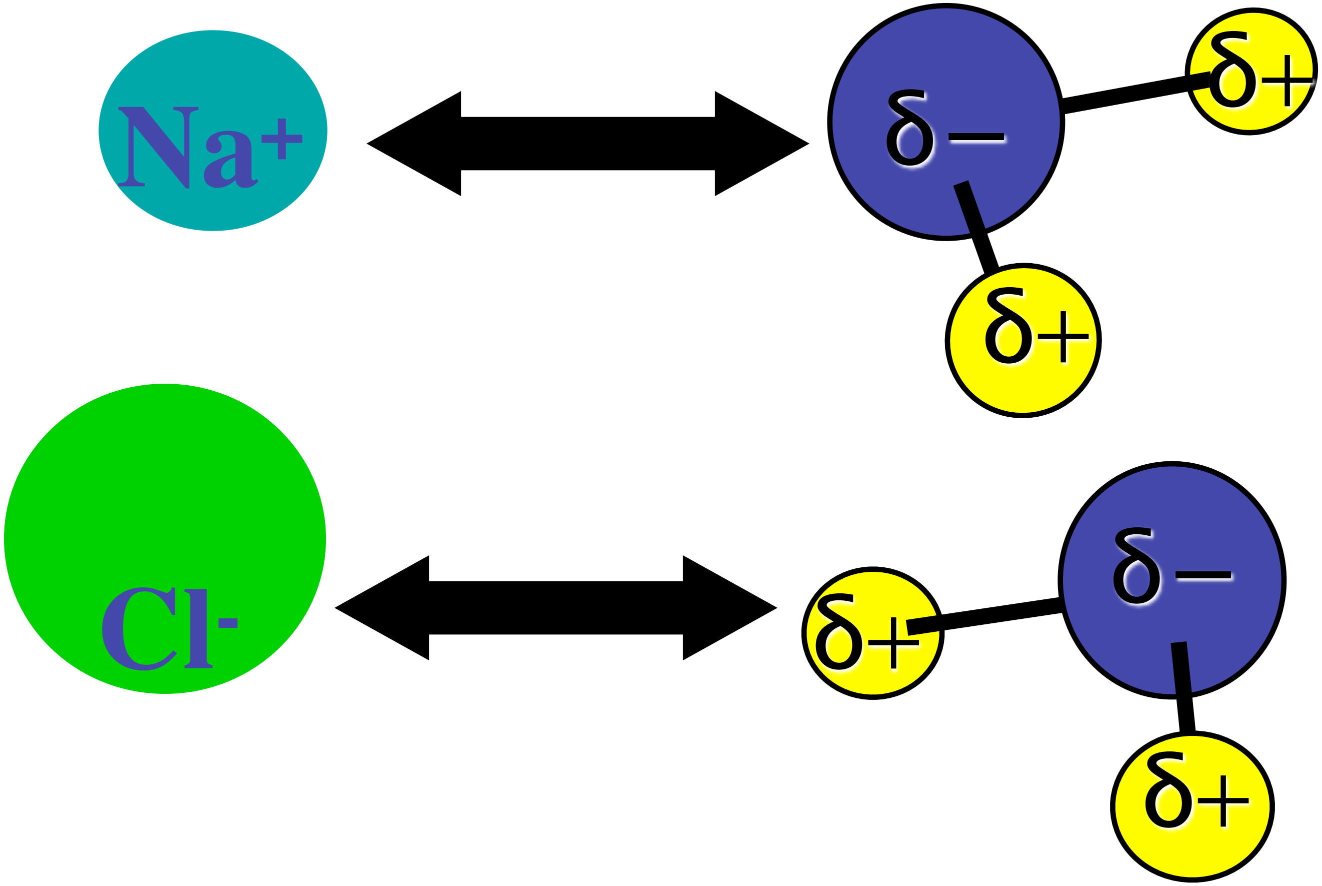
- is an ionic bond
- very strong

ion-dipole attractive forces

attractive forces between an ion and a polar molecule

ion-dipole attractive force

(eg. Water dissolving NaCl crystal)

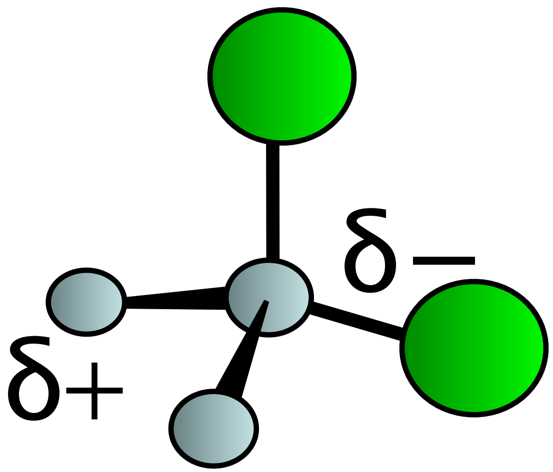


Demo - Odyssey Molecular Stockroom "Sodium Halide"

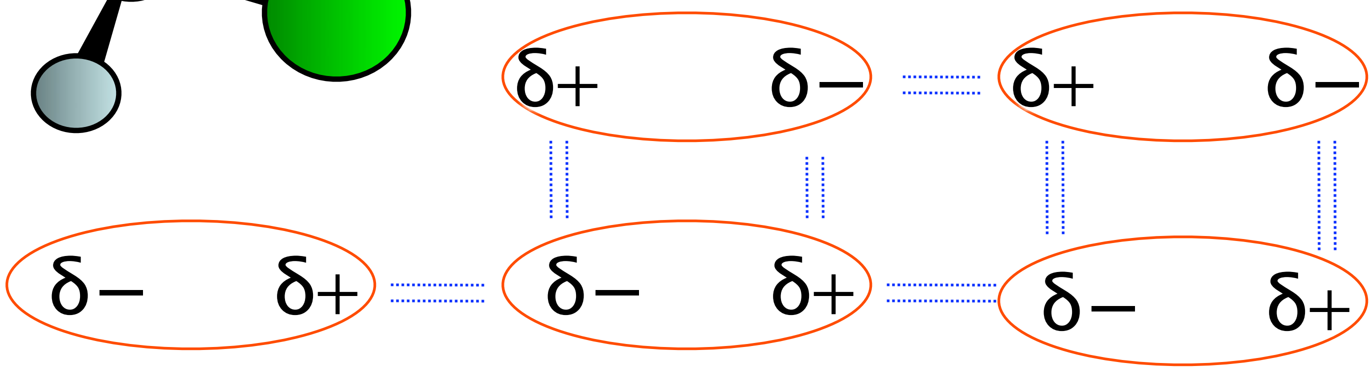
dipole -dipole attractive forces

attractive forces between polar molecules

dipole-dipole attractive force



CH_2Cl_2



(UC-IMFDipoleDipole)

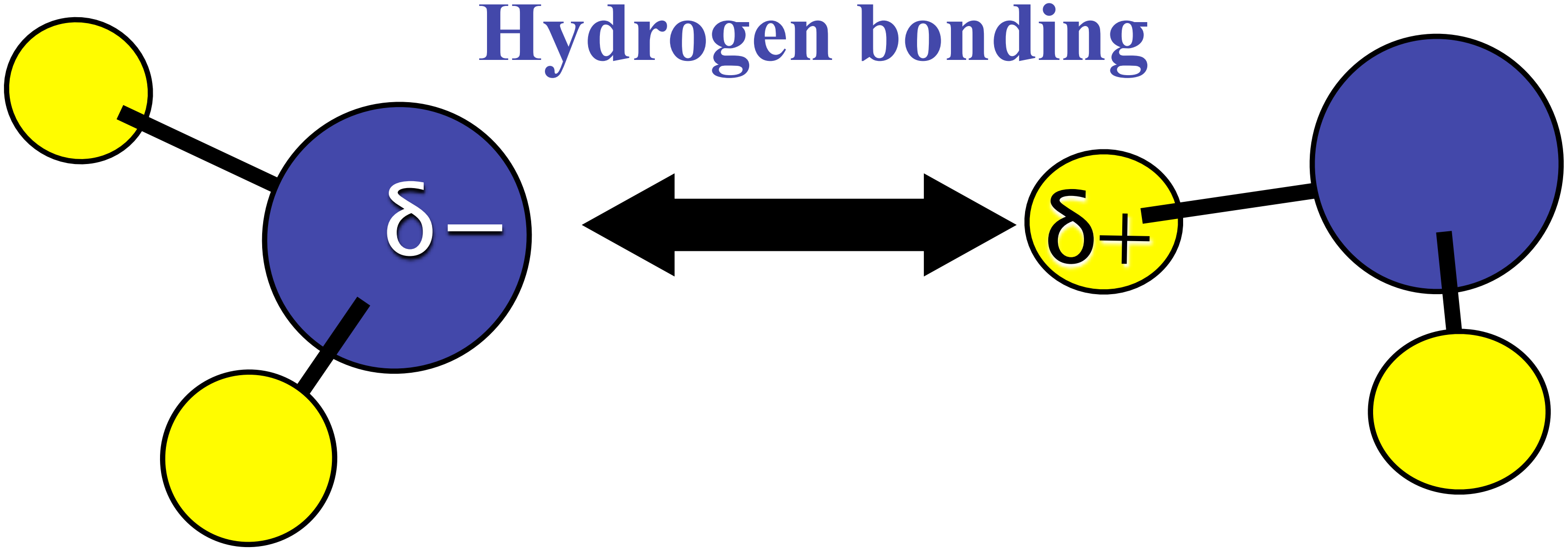
Hydrogen bonding

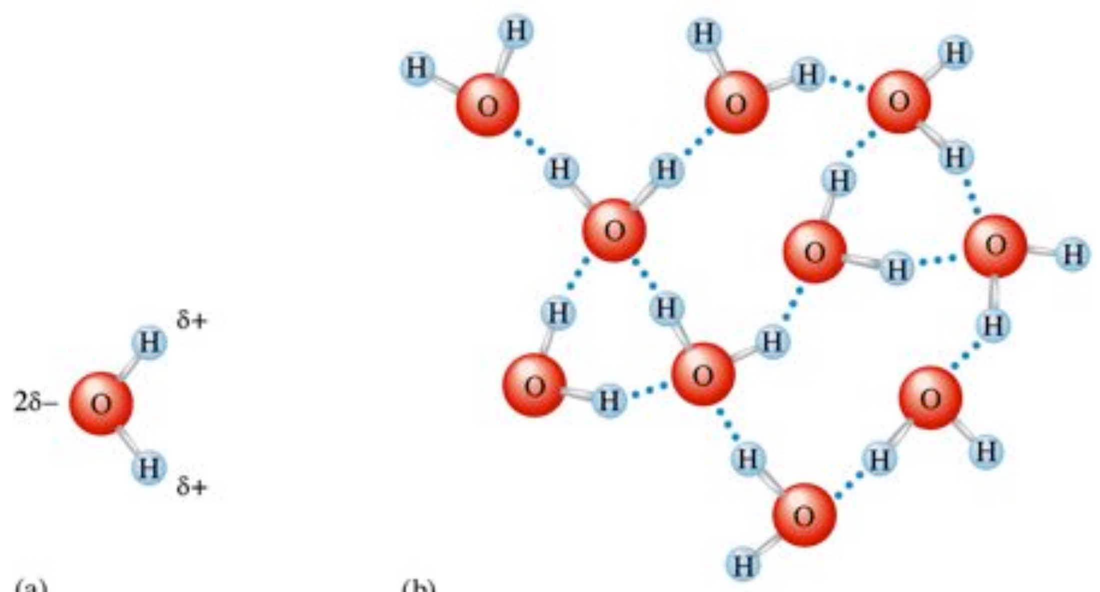
A special type of dipole- dipole interaction

A very strong dipole interaction

dipole-dipole attractive force

Hydrogen bonding



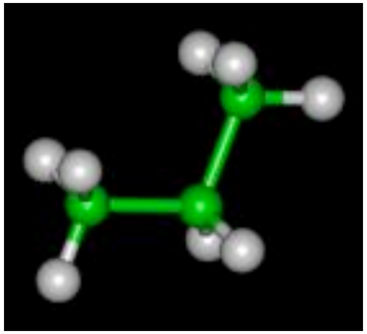


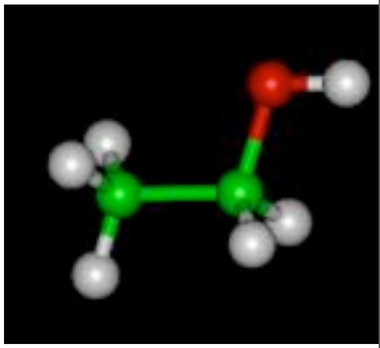
Demo - Odyssey Experiment "Melting Transition"

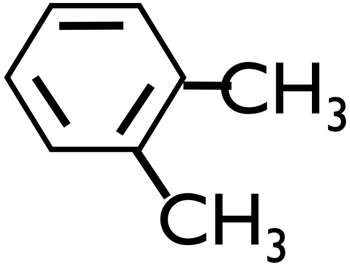
Importance of Hydrogen Bonding

- boiling point depends on intermolecular forces in liquid state

compound	MW	μ	Bp, °C
$CH_3CH_2CH_3$	44	0	–42
CH_3CH_2OH	46	1.7	+78

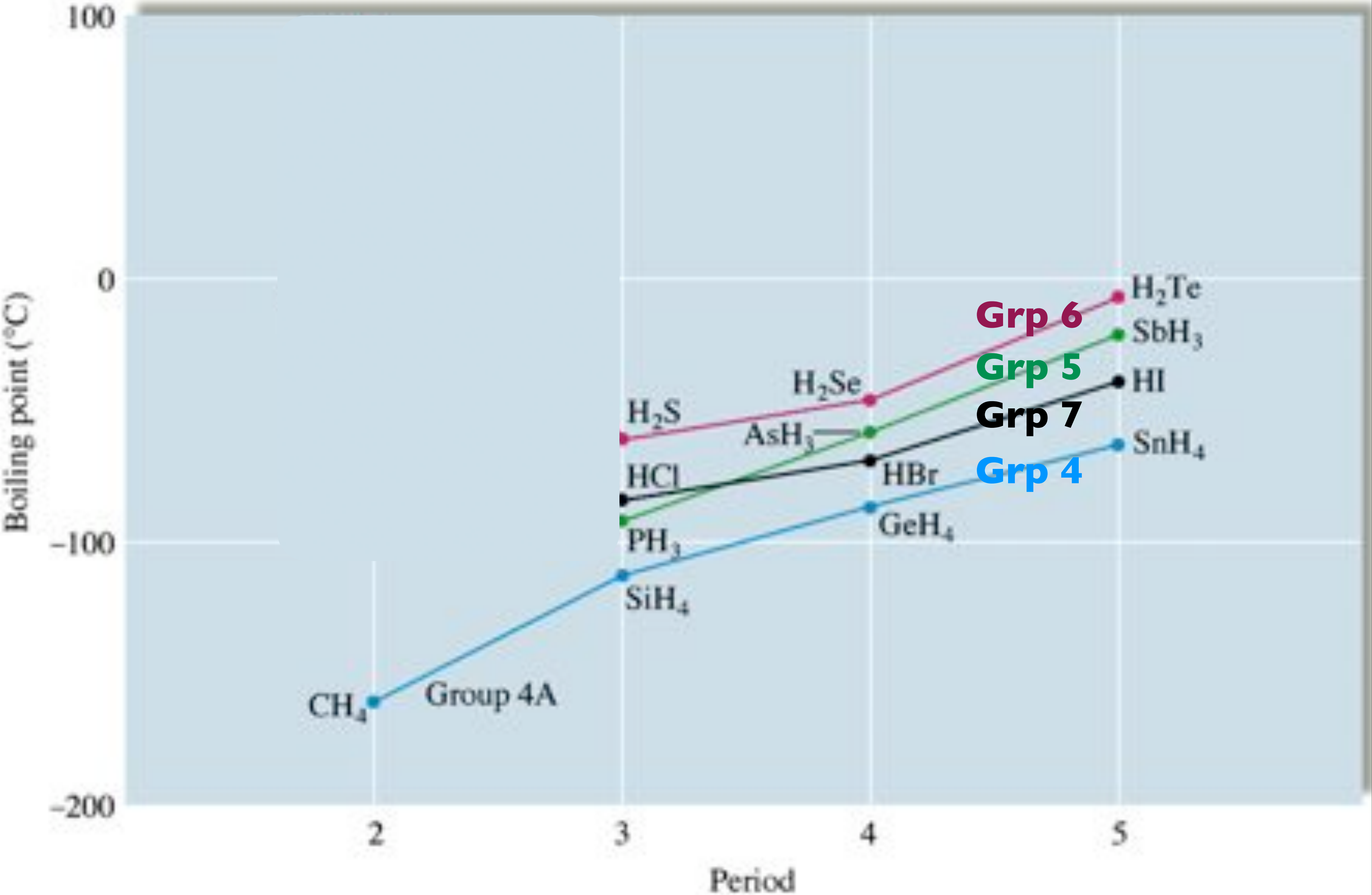






Demo - xylene/ GoofOff Bp

Boiling Point Trends for Hydrides



Hydrogen bonding is possible in compounds with H bound to an electronegative atom like:

OH groups

water, alcohols, acids, carbohydrates

NH groups

ammonia, amines, peptides, proteins, nucleic acids

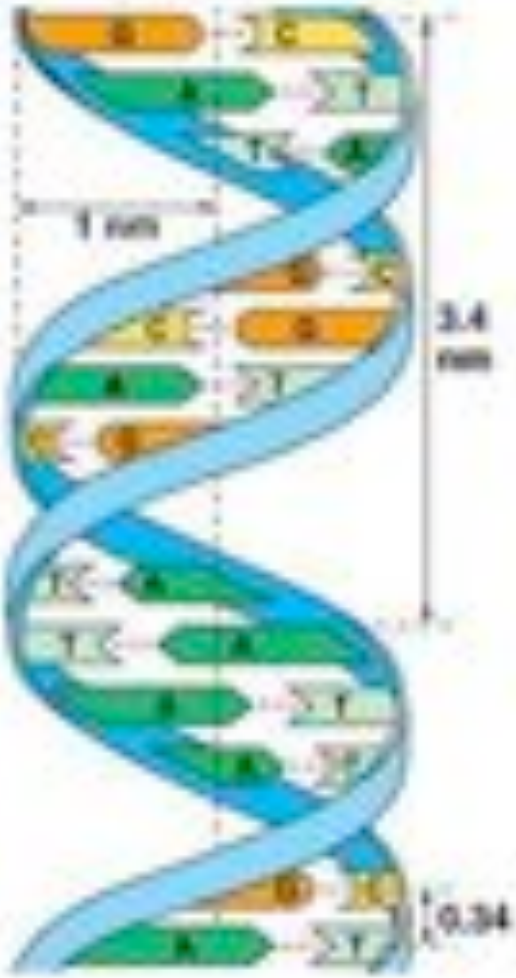
HF (hydrogen fluoride)

(IMFhydrogenbondingforces)

Importance of Hydrogen Bonding

- hydrogen bonding in
  - proteins
  - nucleic acids (DNA and RNA)

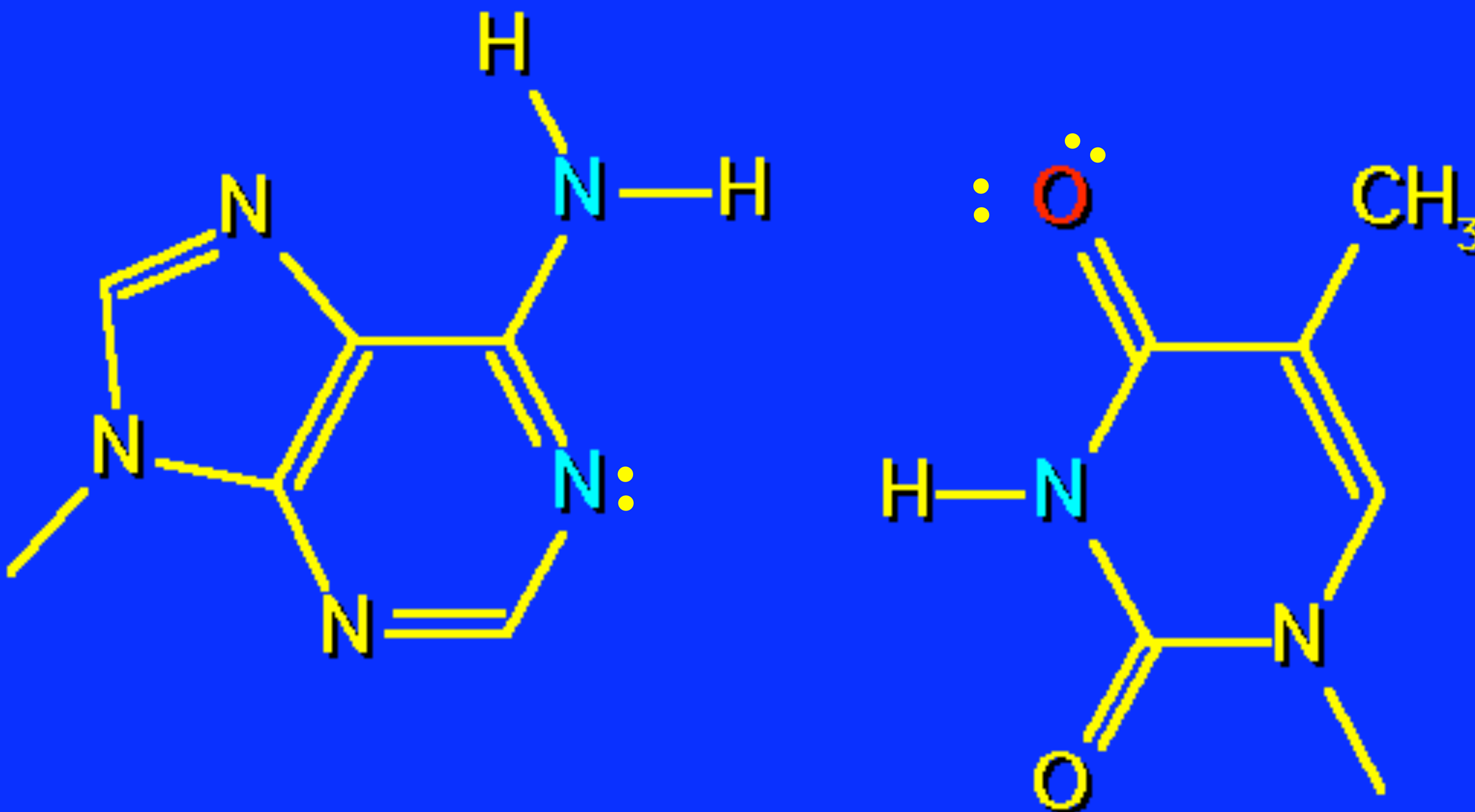
H-bonding in DNA



(a)

(c)

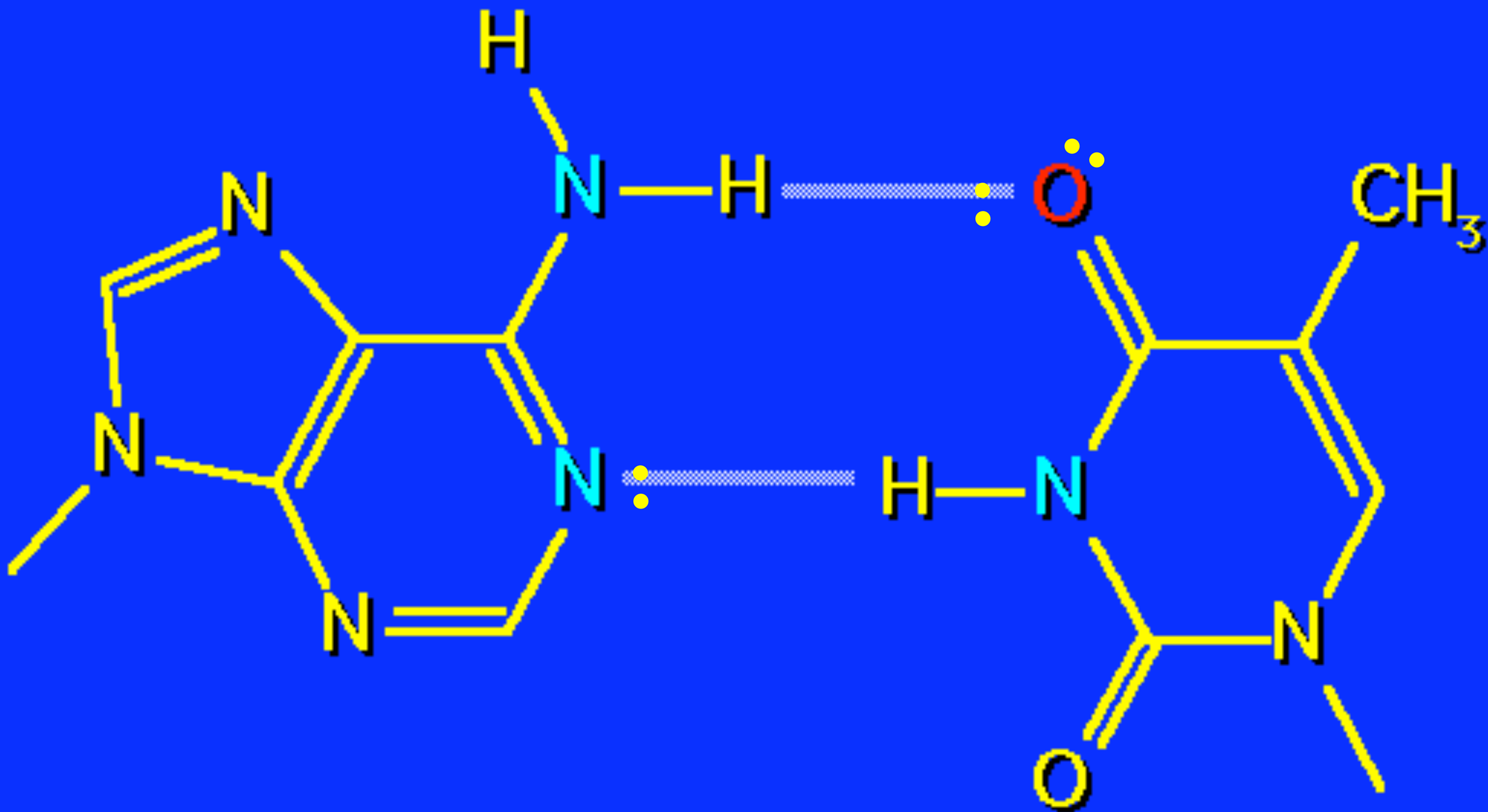
Base pairing in nucleic acid bases



Adenine

Thymine

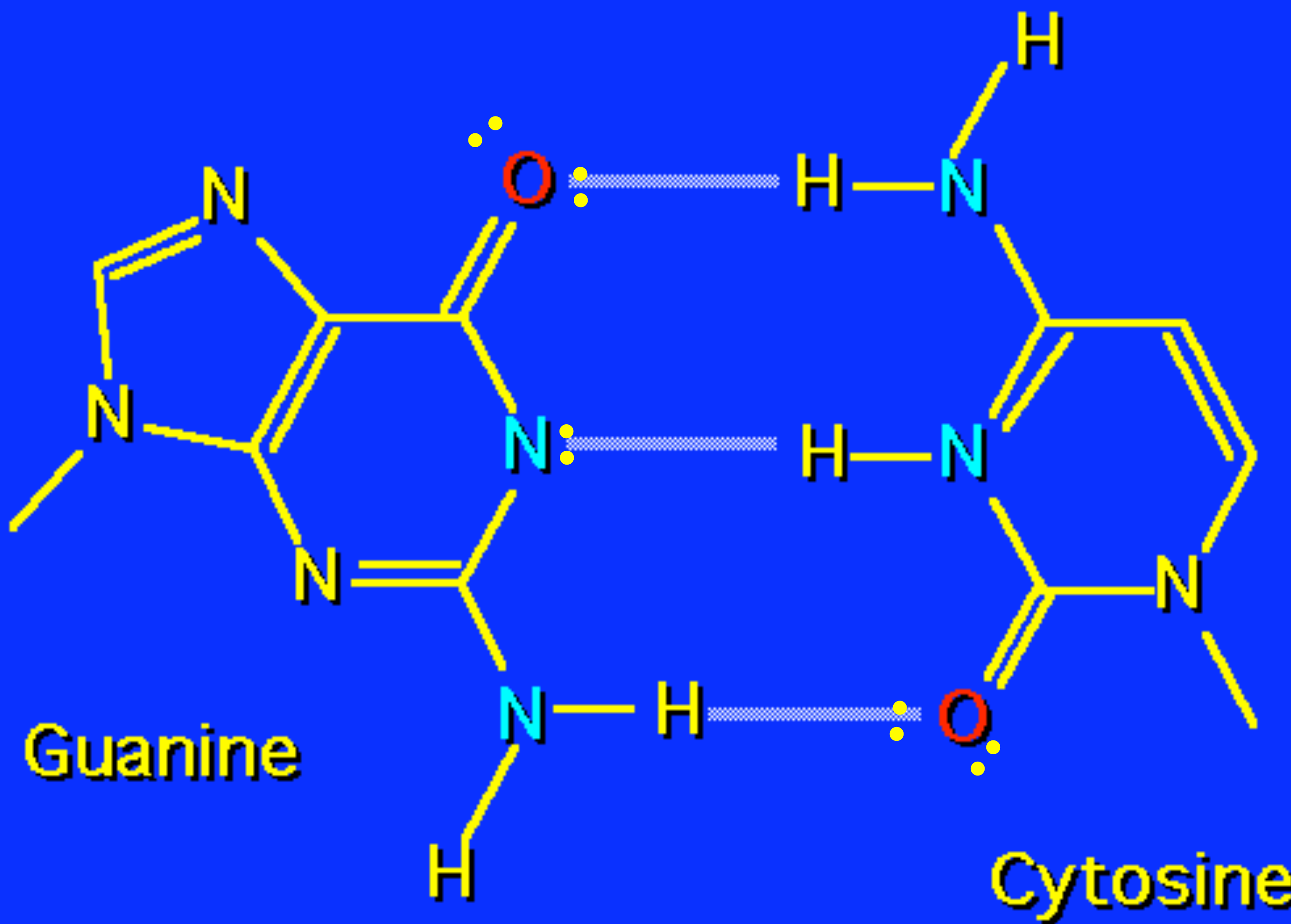
Base pairing in nucleic acid bases



Adenine

Thymine

Base pairing in nucleic acid bases



Dispersion forces

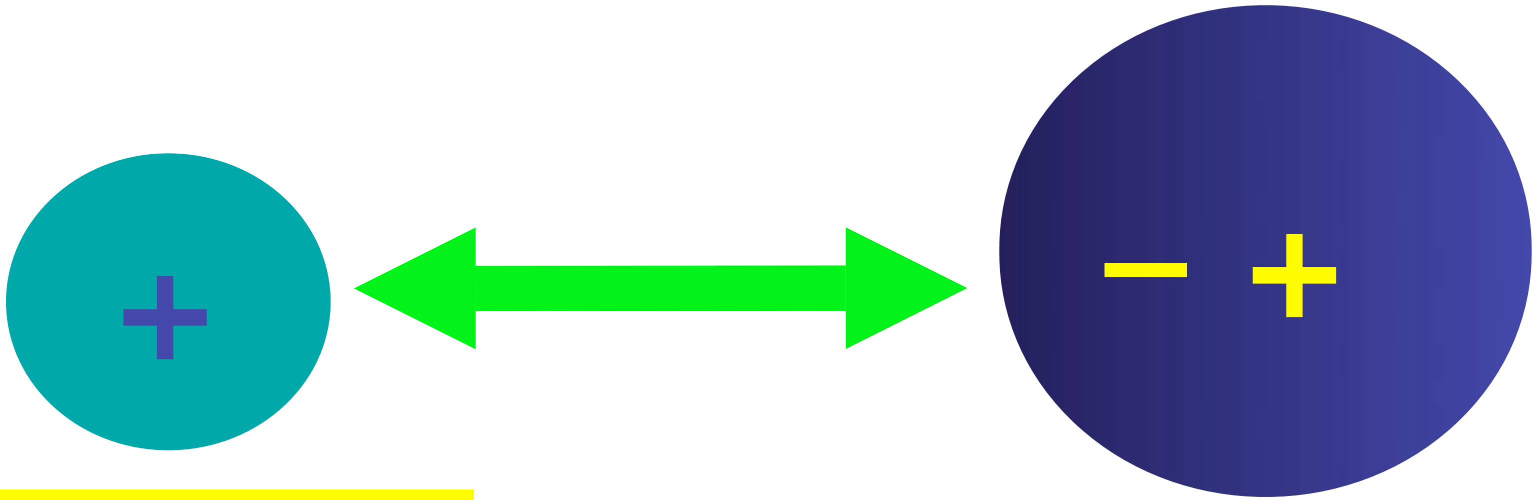
attractive forces from induced temporary dipoles

States of Matter for Halogens

depend only on London forces

Example:	State at STP
F_2	gas
Cl_2	gas
Br_2	liquid
I_2	solid

ion-induced dipole attractive force



Polarizability: the ease with which the electron distribution surrounding an atom is distorted by an external electric field

balloon-wall demo

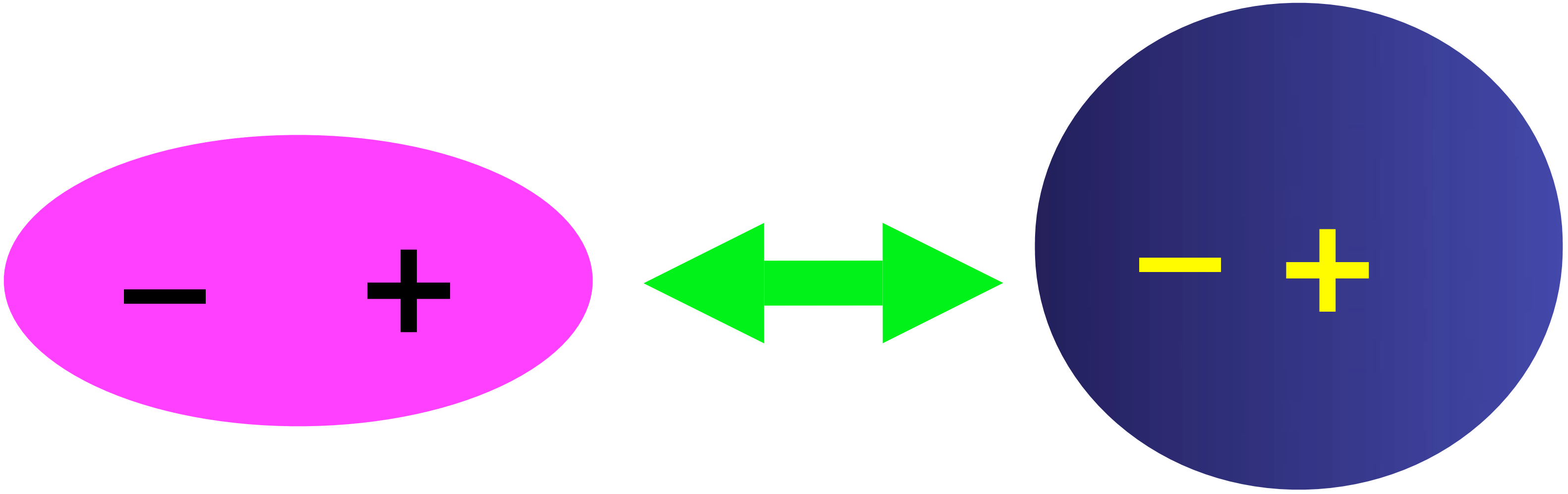
Polarizability

- increases with size of atom

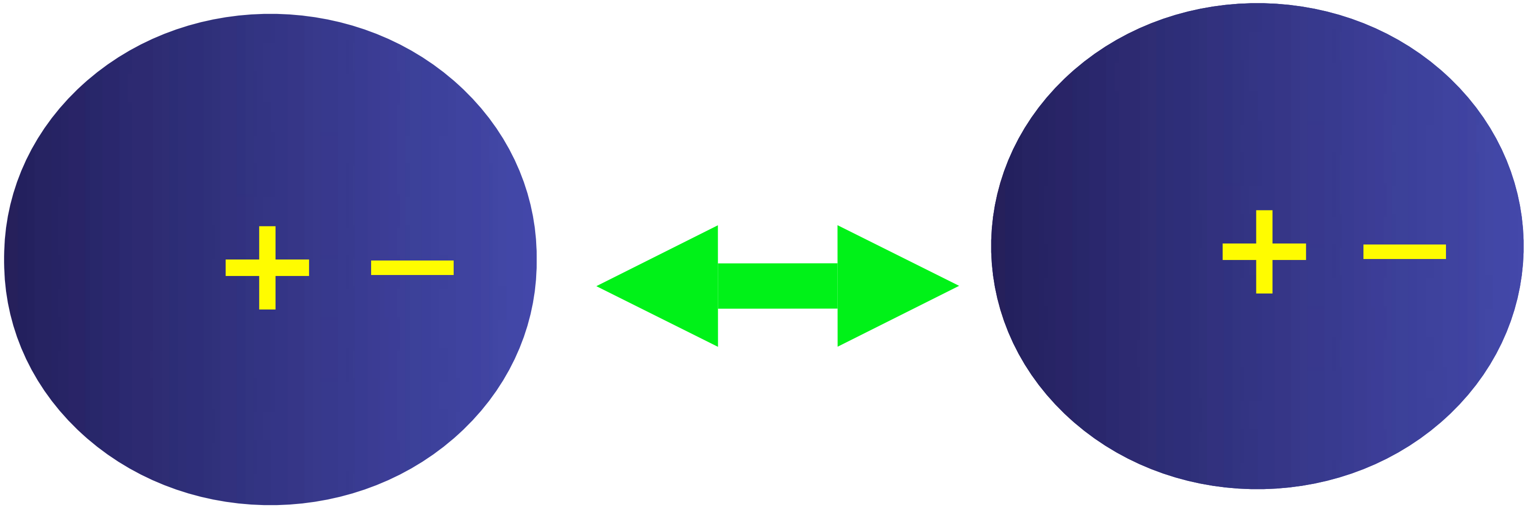
fluorine very nonpolarizable (“hard”)

iodine very polarizable (“soft”)

Dipole-induced dipole attractive forces



Induced dipole-induced dipole attractive forces (*London Forces*)



No polarization

No polarization

Boiling Points

depend on intermolecular attractive forces in liquid state

Example:

	State at STP	BP
F_2	gas	85 K
Cl_2	gas	239 K
Br_2	liquid	332 K
I_2	solid	458 K

$$I_2\,(s) \longrightarrow I_2\,(g)$$

$\Delta H^\circ = 62$ kJ/mol

This is a direct measure of the induced dipole-induced dipole attractions between I_2 molecules in the solid state

Melting points of similar nonpolar molecules

compound	Melting Point, °C
CF_4	–150
CCl_4	–23
CBr_4	90
CI_4	171

More electrons, more polarizable, stronger dispersion forces

What about Disperion forces as a function of molecule size/length?

Name	*Molecular Formula*	*Melting Point (°C)*	*Boiling Point (°C)*	*State at 25°C*
methane	CH_4	-183	-164	gas
ethane	C_2H_6	-183	-89	
propane	C_3H_8	-190	-42	
butane	C_4H_{10}	-138	-0.5	
pentane	C_5H_{12}	-130	36	
hexane	C_6H_{14}	-95	69	
heptane	C_7H_{16}	-91	98	
octane	C_8H_{18}	-57	125	
nonane	C_9H_{20}	-51	151	liquid
decane	$C_{10}H_{22}$	-30	174	
undecane	$C_{11}H_{24}$	-25	196	
dodecane	$C_{12}H_{26}$	-10	216	
eicosane	$C_{20}H_{42}$	37	343	
triacontane	$C_{30}H_{62}$	66	450	solid

Approximate magnitudes of intermolecular forces

Force	Energy, kJ/mol
ion-ion	500–1000
ion-dipole	40–600
ion-induced dipole	
dipole-dipole	5–25
dipole-induced dipole	2–10
induced dipole–induced dipole	0.05–40

Properties of Liquids

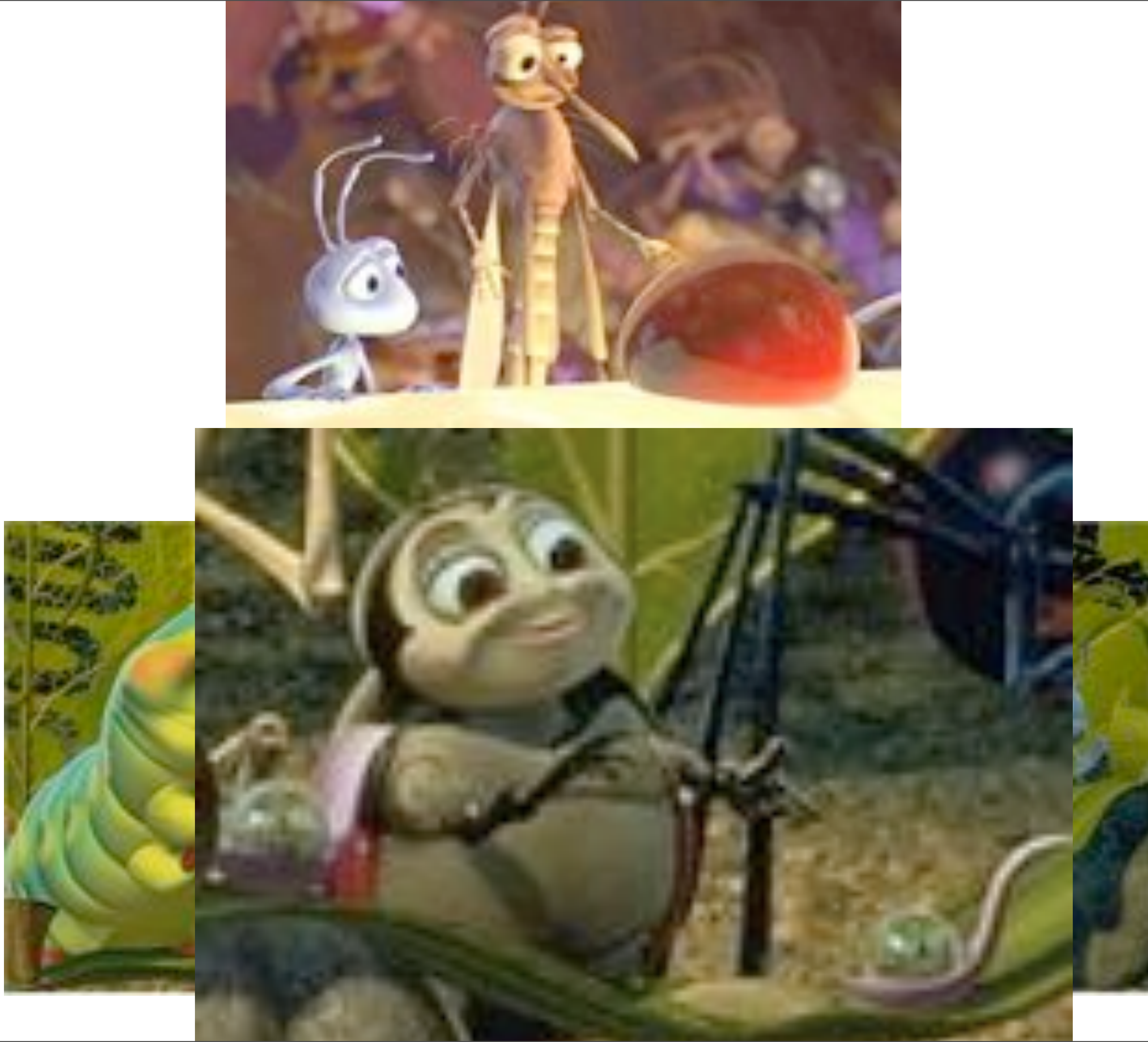
surface tension **viscosity**

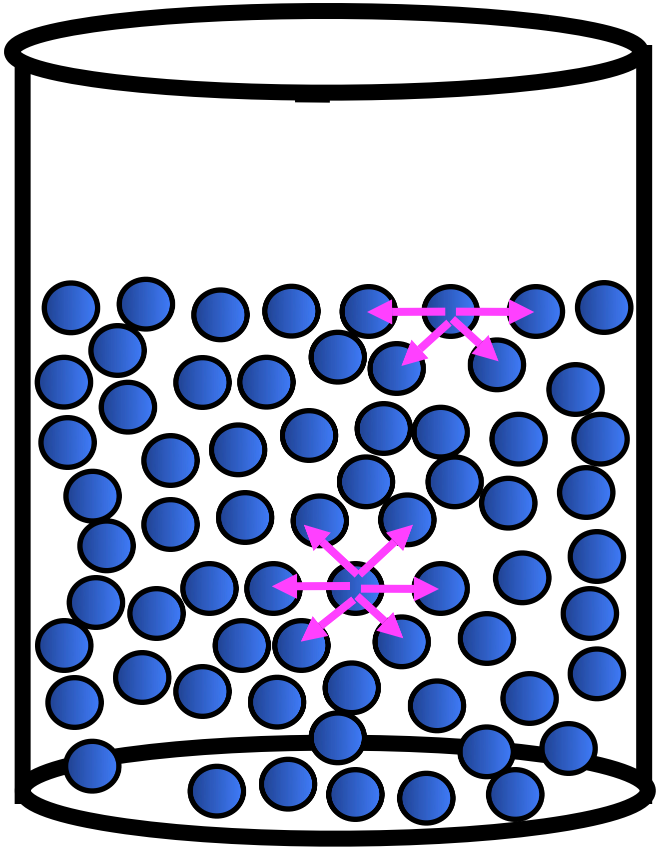
Surface tension

the tendency of a liquid to minimize its surface area

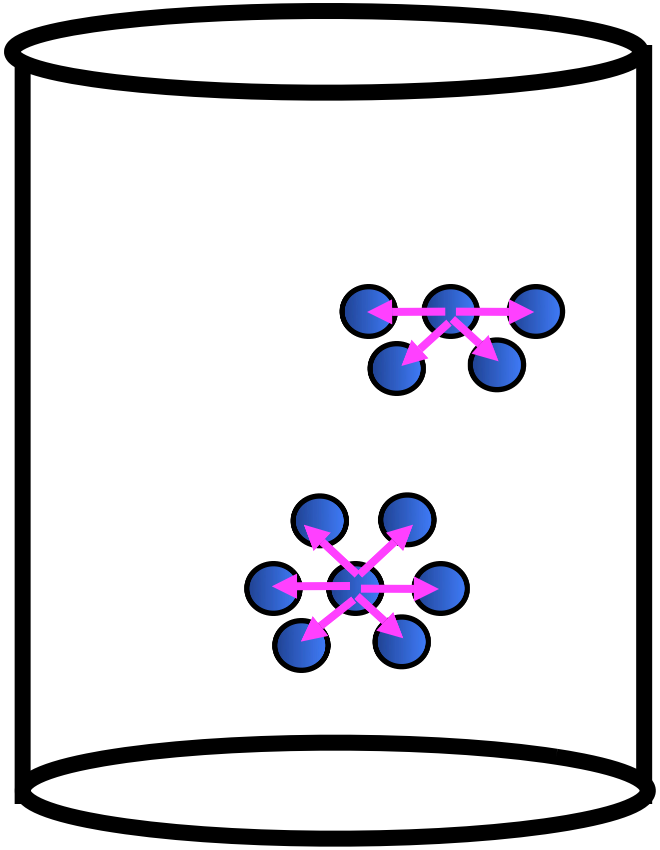
or

the effort needed to stretch or increase the surface area





Intermolecular forces acting on a molecule in the surface layer of a liquid and the interior region of the liquid



Intermolecular forces acting on a molecule in the surface layer of a liquid and the interior region of the liquid are different

What affects surface tension?

High surface tension is related to strong intermolecular forces

Water: 73 dynes/cm

principal intermolecular force is hydrogen bonding

http://www.sciencefriday.com/videos/watch/10177/

Octane(C_8H_{18}): 22 dynes/cm

principal intermolecular force is induced dipole- induced dipole

Capillary Action

is a manifestation of surface tension

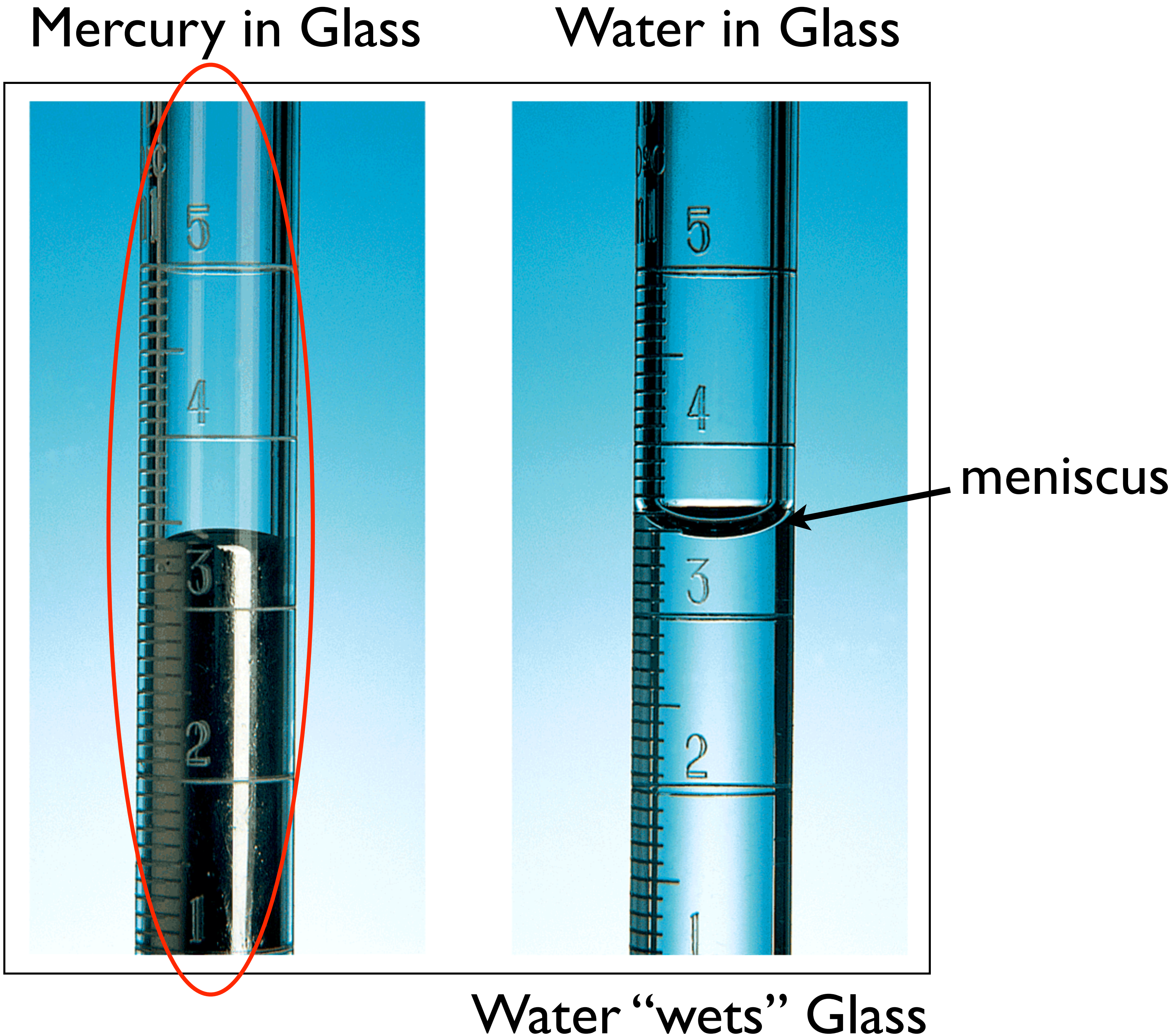
an example is water rising in a narrow tube

two forces (cohesion and adhesion) are involved

Cohesion: is the attraction between molecules of the liquid

Adhesion : attractive forces between the liquid and the glass

Which exhibits stronger cohesive forces than adhesive forces: Hg on glass or H_2O on glass?



viscosity

a measure of a liquid's resistance to flow

The stronger the intermolecular bonds, the higher the viscocity

Crystal Structure

Crystalline Solids

Possess rigid and long-range order; atoms, molecules, or ions occupy specific positions

maximize attractive, minimize repulsive forces

Ex: metals (Al), ionic compounds (NaCl), molecular crystals (sugar, water ice)

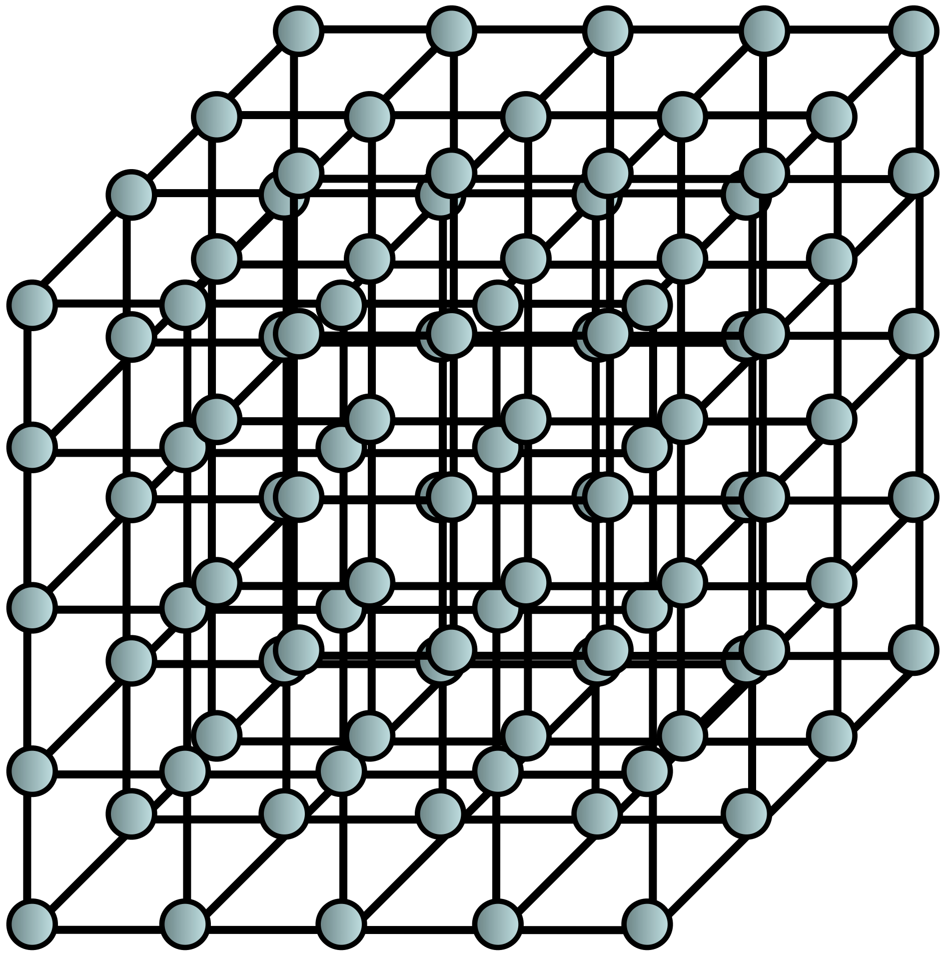
Amorphous Solids

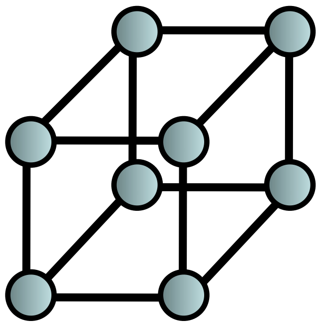
lack long-range order

Ex: soot, glass, paper

Cell Unit

the basic repeating unit of a crystalline solid.

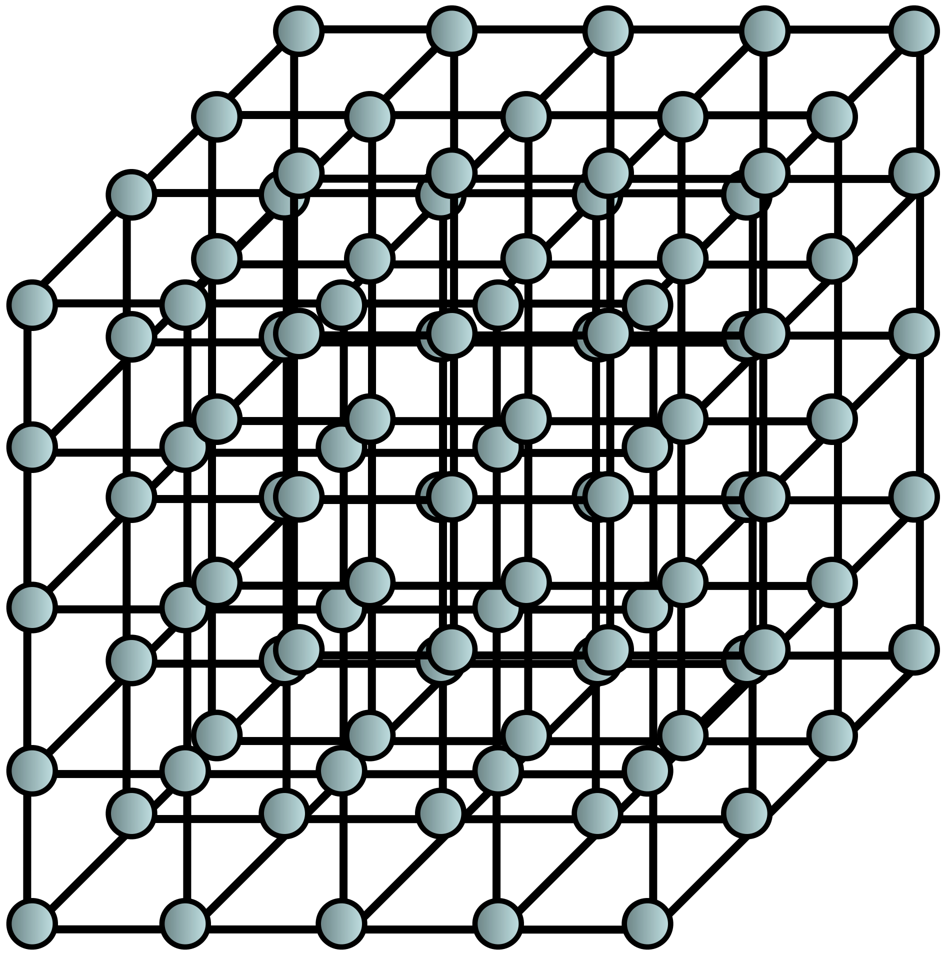


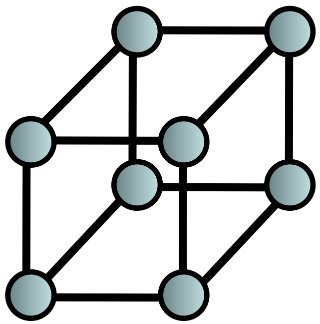


Odyssey Expt 53 Crystal Lattices

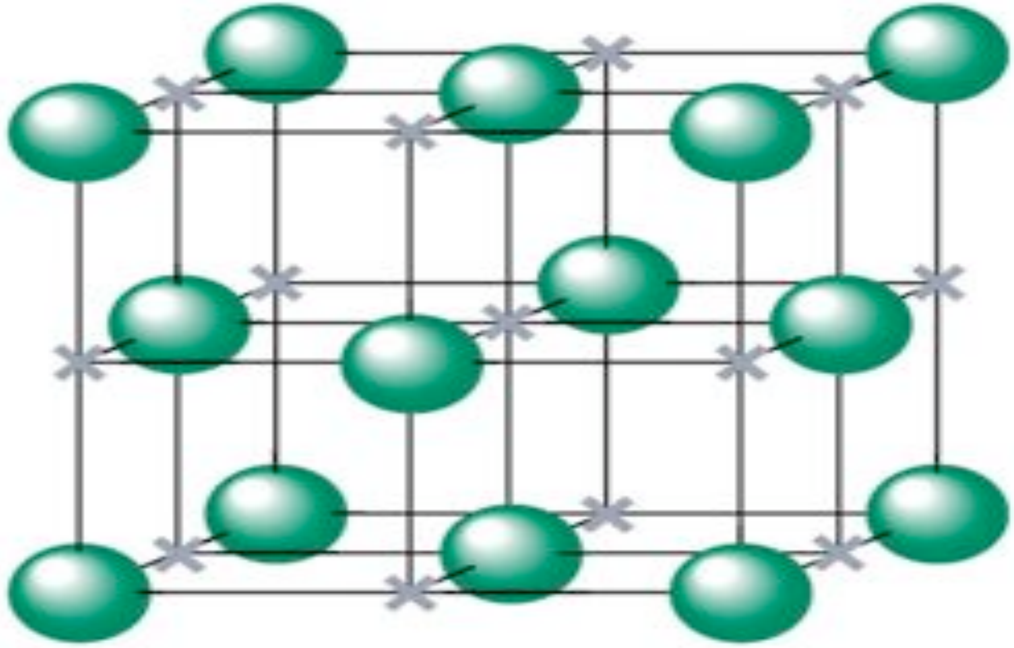
Lattice Points

each sphere represents a lattice point





the spheres represent atoms, ions or molecules



(a)

(b)

Crystal Lattice

graphical depiction of atomic positions

(lines shown in a lattice are not necessarily covalent bonds; they simply trace the shape of the lattice and locate the atoms more clearly)

all crystal lattices are built of unit cells

There are seven kinds of crystal lattices

cubic

tetragonal

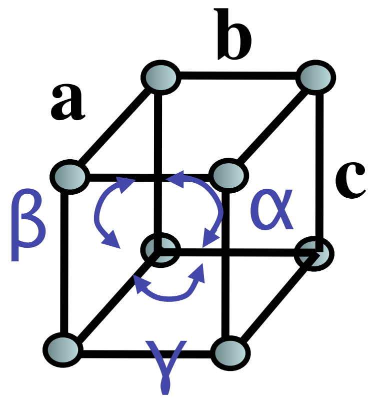
orthorombic

monoclinic

Triclinic

hexagonal

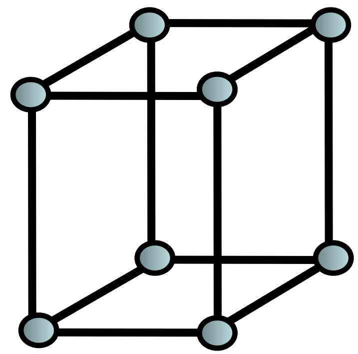
rhombohedral



simple cubic

a = b = c

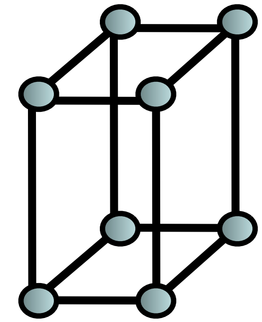
α = β = γ = 90°



tetragonal

a = b ≠ c

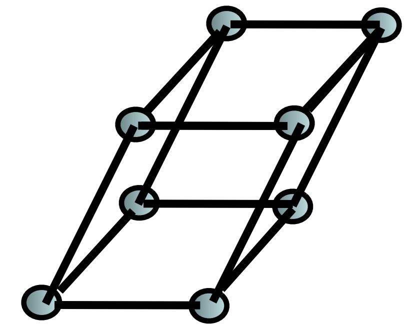
α = β = γ = 90°



orthorhombic

a ≠ b ≠ c

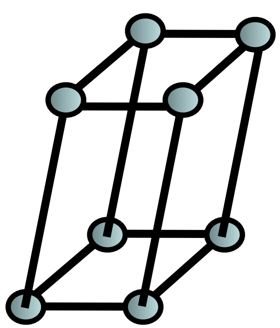
α = β = γ = 90°



rhombohedral

a = b = c

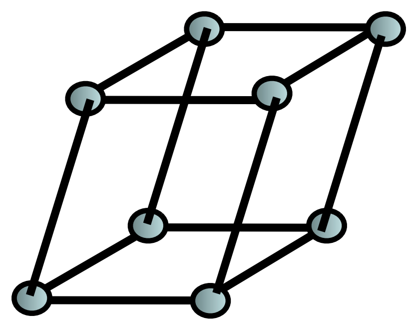
α = β   γ ≠ 90°



monoclinic

a ≠ b ≠ c

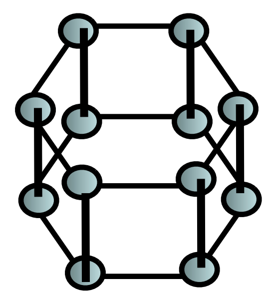
α = γ   β ≠ 90°



triclinic

a ≠ b ≠ c

α = β   γ ≠ 90°



hexagonal

a = b ≠ c

α = β = 90°   γ = 120°

Types of Crystals

Types of Crystalline Solids

Determined by the kinds of forces that hold the particles together

Ionic

covalent

molecular

metallic

Ionic Crystals

composed of charged species

are hard and brittle, have high melting points, and are poor conductors of heat and electricity

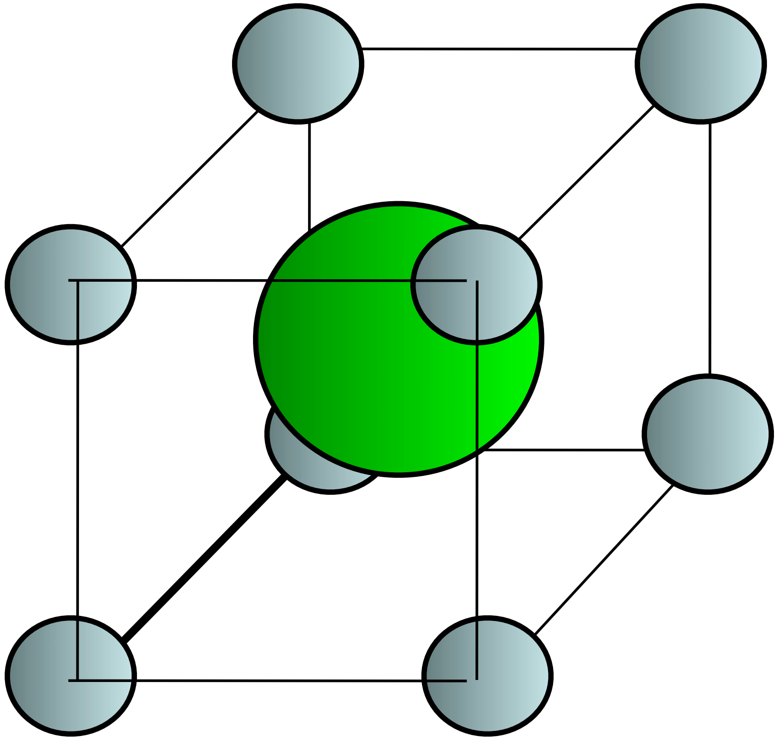
Packing of ionic solids

ions at lattice points

maximize electrostatic attraction between oppositely charged ions

minimize electrostatic repulsion between ions of same charge

Crystal structures of cesium chloride



CsCl

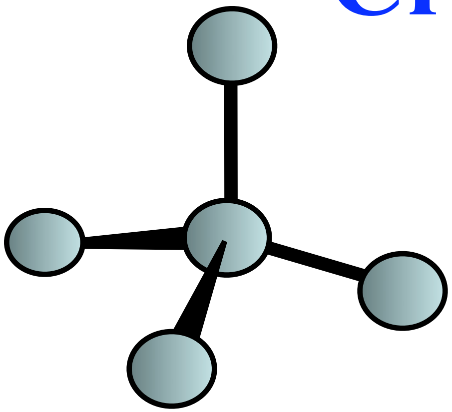
Covalent Crystals/ Network Solids

atoms occupy lattice points

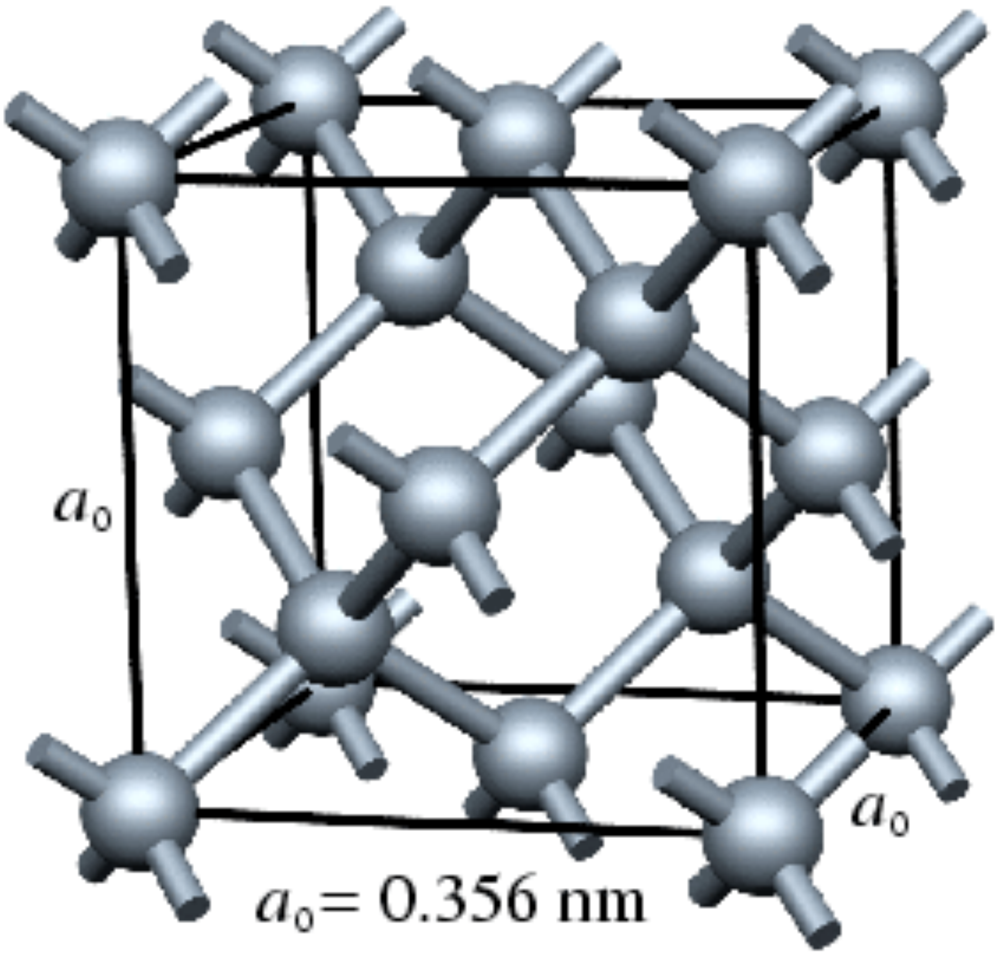
atoms held together by covalent bonds

properties: hard, high melting point, poor conductors of heat and electricity

Carbon as Diamond - a Covalent Crystal/Network Solid



Tetrahedral sp^3 Carbon in a 3D Lattice

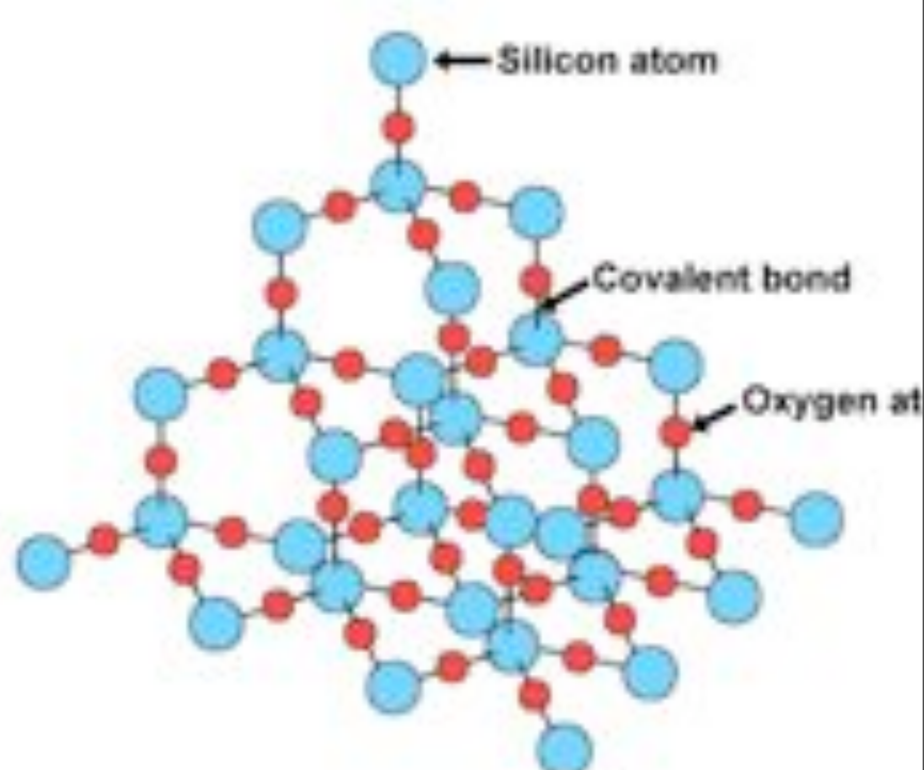


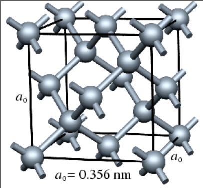
The whole crystal is one giant molecule

Odyssey: Stockroom/Carbon/Diamond

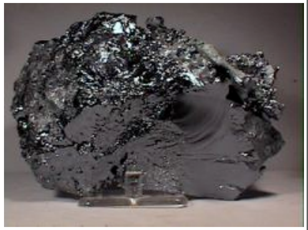
Silicon Dioxide - a Covalent Crystal/Network Solid

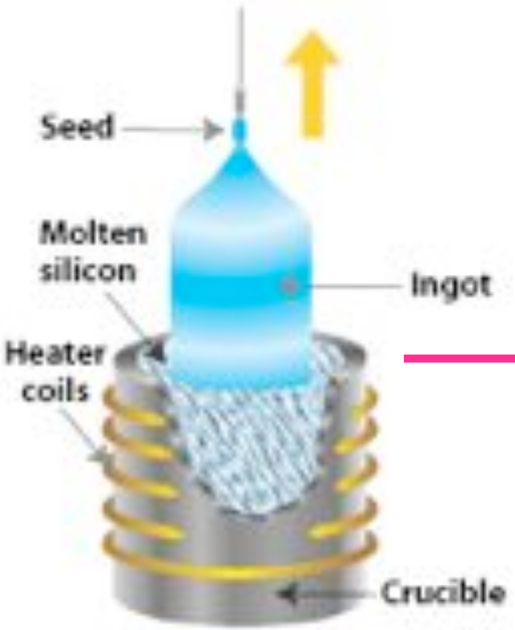
Formula	SiO_2
Molar Mass	60.0843 g
Melting Point	1710 (°C)
Boiling Point	2230 (°C)

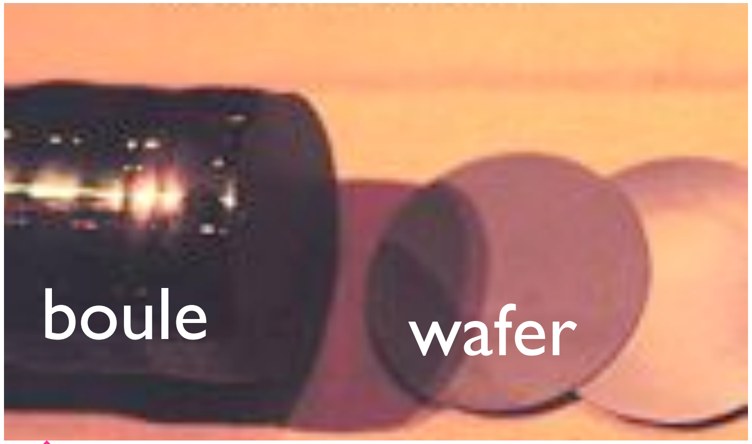




Silicon - a Covalent Crystal/Network Solid







Molecular Crystals

species at lattice points are covalent molecules

lattice is held together by van der Waals forces

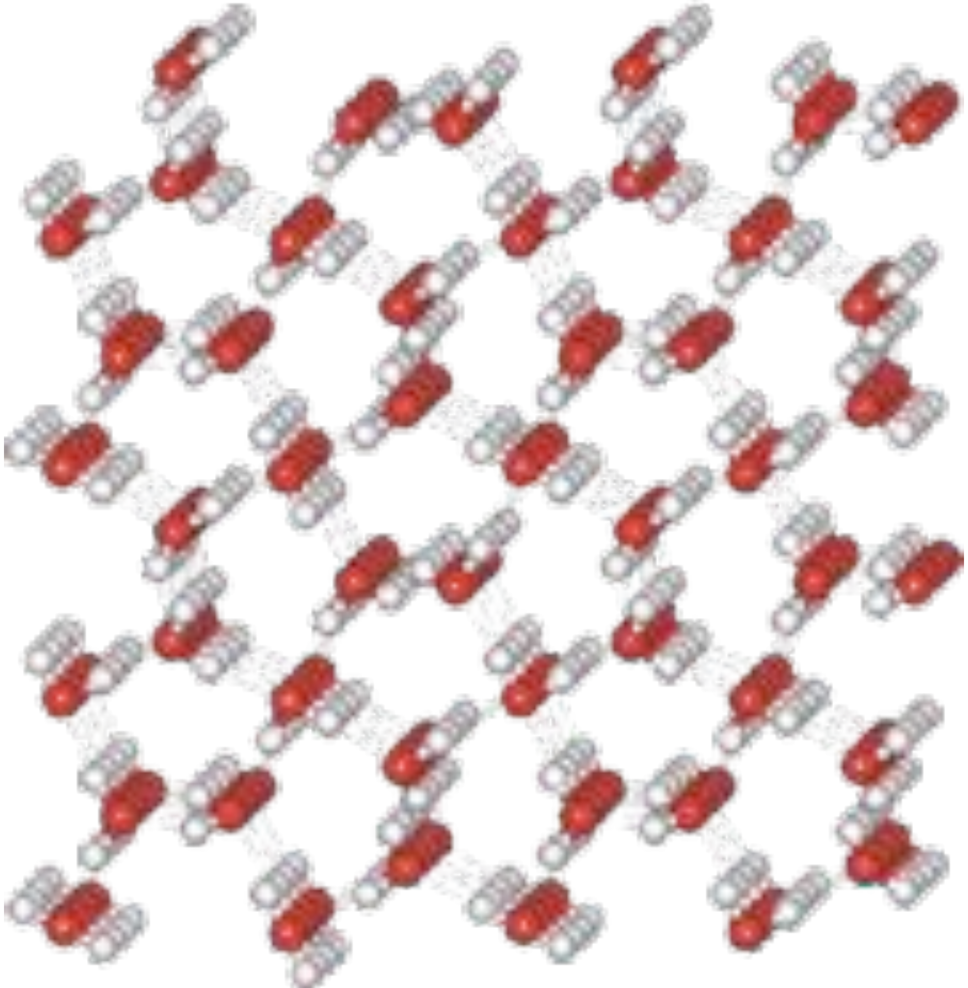
are soft, low melting, and poor conductors of heat and electricity

examples include ice, sucrose, sulfur, solid carbon dioxide

Molecular Crystals

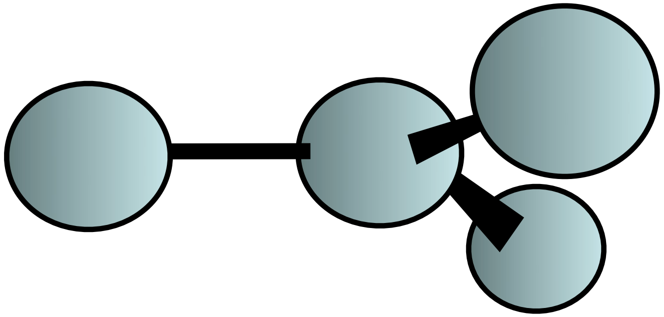
sugar

water ice



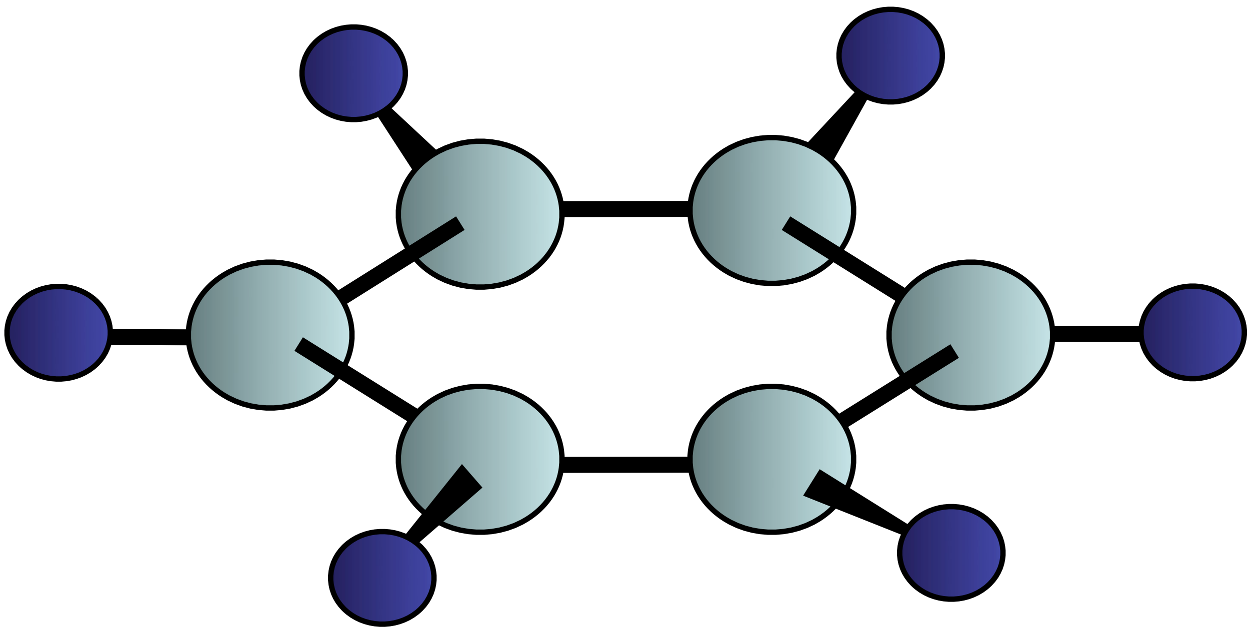
Carbon in Graphite
Trigonal Planar Lattice

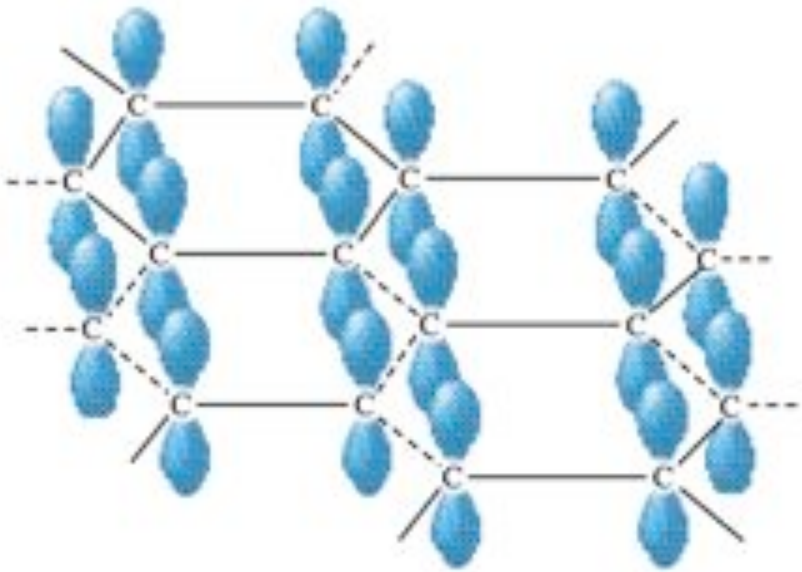
Carbon bonded to three other atoms is sp^2 hybridized



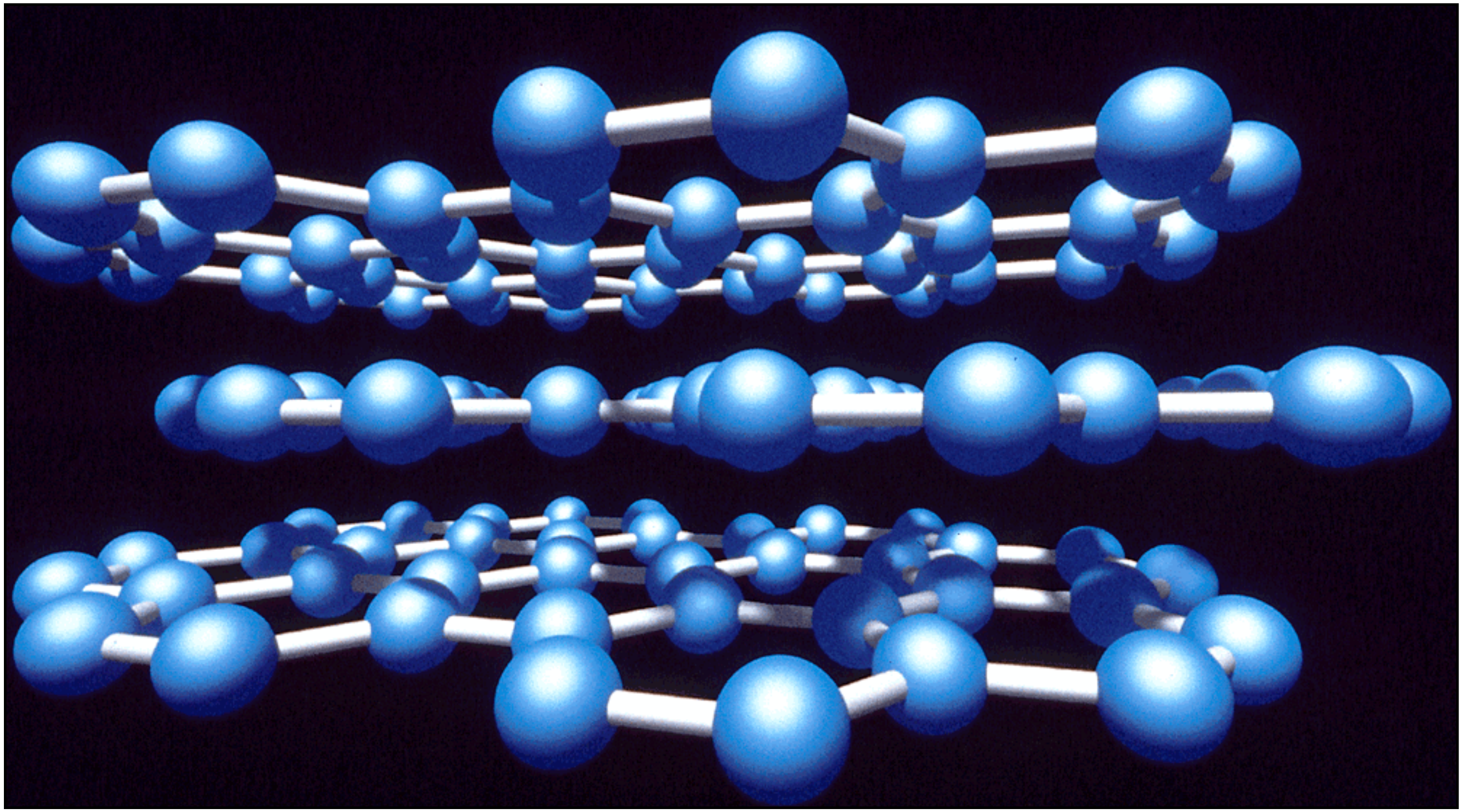
Benzene (C_6H_6)

All C's are sp2 hybridized

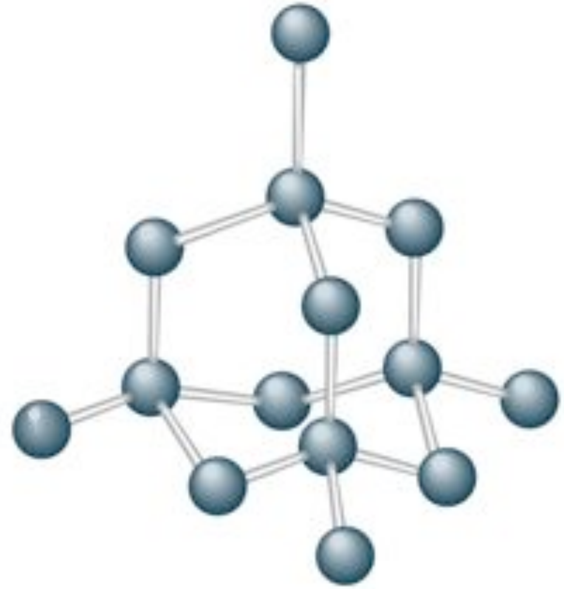




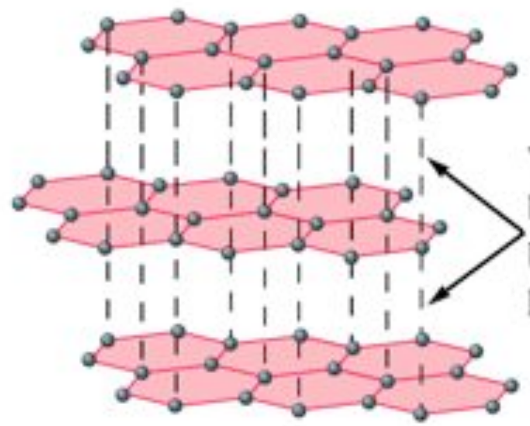
(a)



Odyssey: Stockroom/Carbon/Graphite/Tube vs. Space Filling



(a) Diamond



(b) Graphite

sp^3
covalen
t

sp^2
London
forces

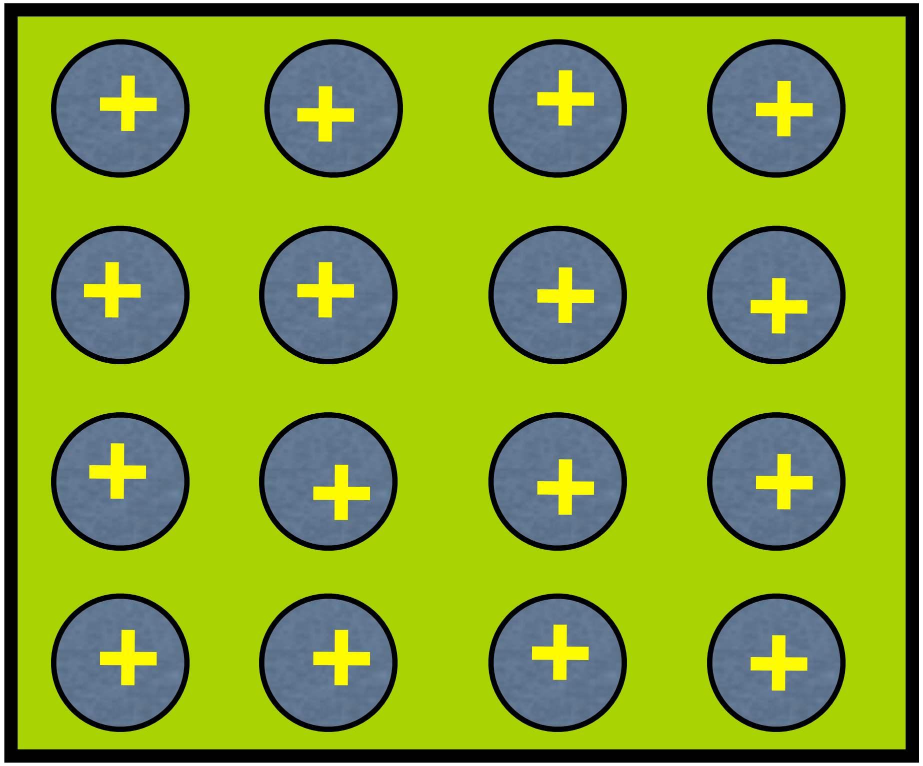
Metallic crystals

lattice points occupied by metal atoms

nuclei and core electrons occupy lattice sites, valence electrons move throughout the lattice

valence electrons delocalized over many, if not all, atoms in the lattice. Like a delocalized pi bond, they are attracted to the nuclei of many (many!) atoms and are the "glue" that holds the crystal together.

Metallic crystals



Each circled positive charge represents the nucleus and inner electrons of a metal atom. The green area indicates a sea of mobile electrons

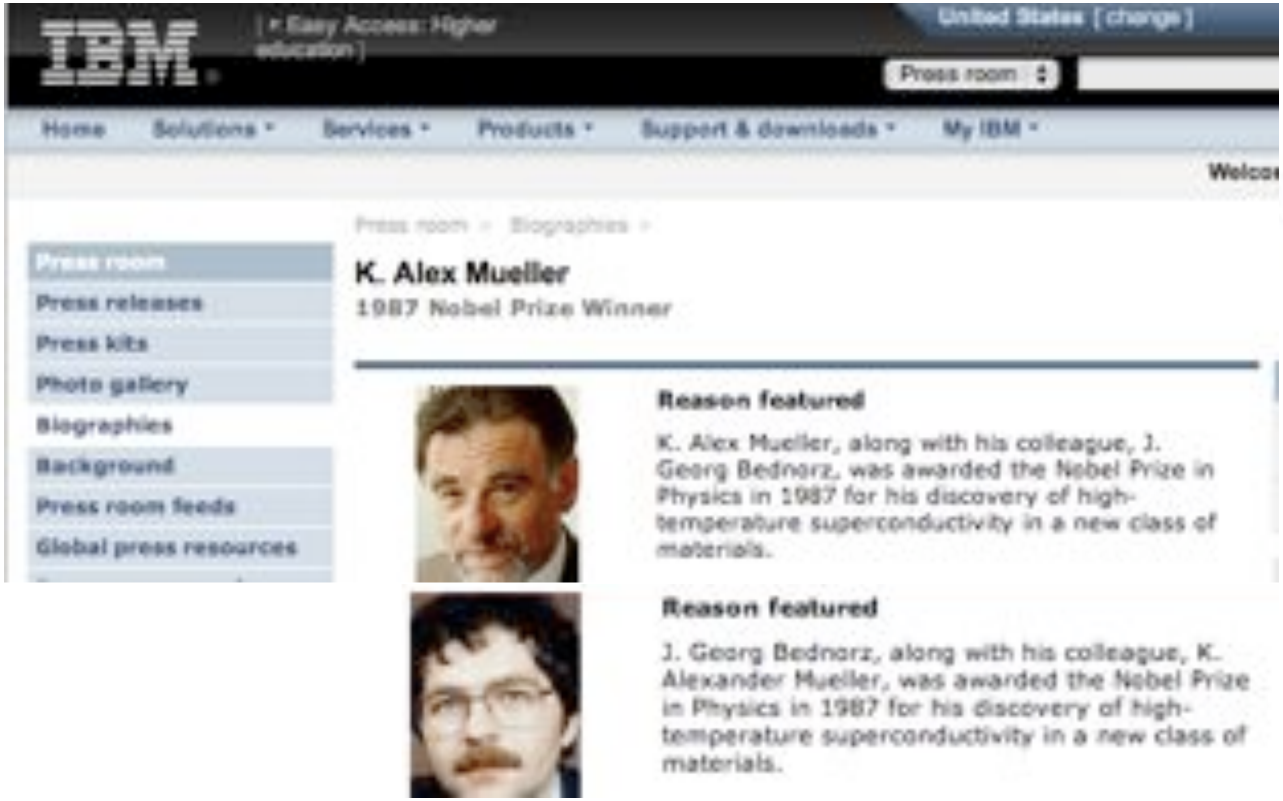
Properties of Metals

Conduct electricity

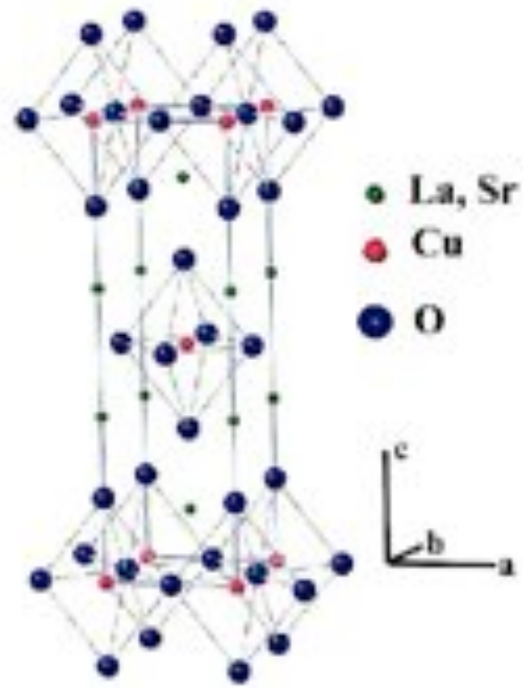
malleable

ductile

High Temperature Superconductors and Ductility



Unit Cell!



Good news: Discovered new materials which are superconductive at the highest temperatures ever. (around 77 K, liquid nitrogen temp).
Nobel prize 1987.

Bad news: The materials are brittle like ceramics, and are not ductile!
These superconductors are super tricky to pull into wires....

Metal Alloys

Contain a mixture of elements and have metallic properties

2 types:

Substitution

Interstitial

Substitution Alloys

Some of the host metal atoms are replaced by other metal atoms of similar size

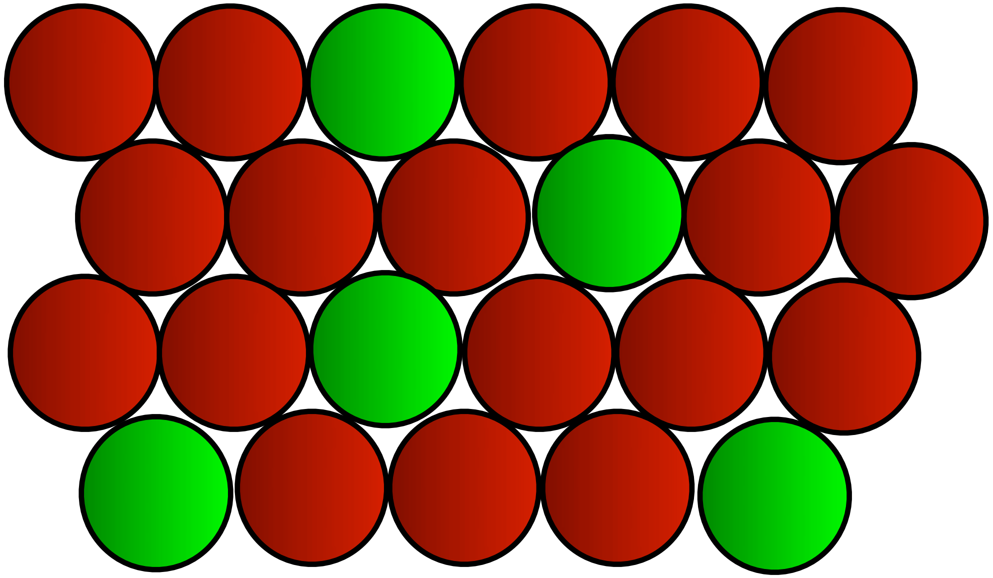
Brass

copper and 33.3% zinc

Sterling silver

Silver and 7% copper

Substitution Alloys



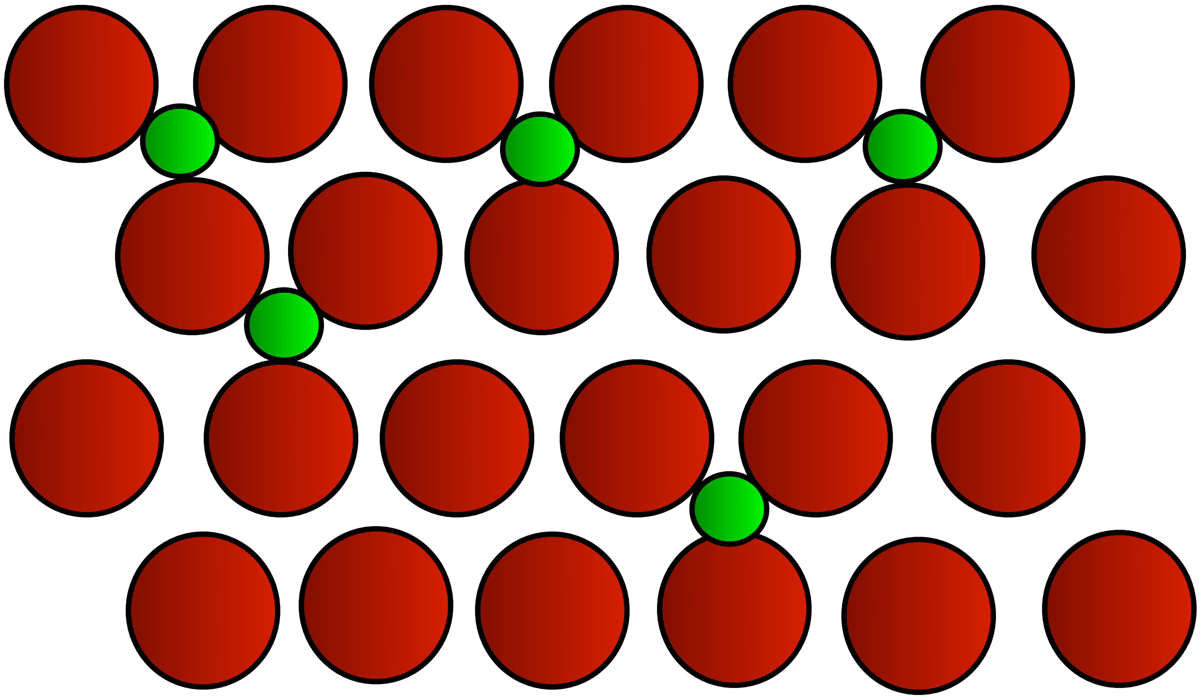
interstitial Alloys

Formed when some of the interstices (holes) in the closest packed metal structure are occupied by small atoms

Steel

	% carbon in the holes of iron	
low	**.2%**	**some what malleable**
medium	**.2 - .6%**	**harder**
high	**.6 - 1.5%**	**tool grade**

interstitial Alloys



Phase Changes

Liquid-Vapor Equilibrium

vaporization

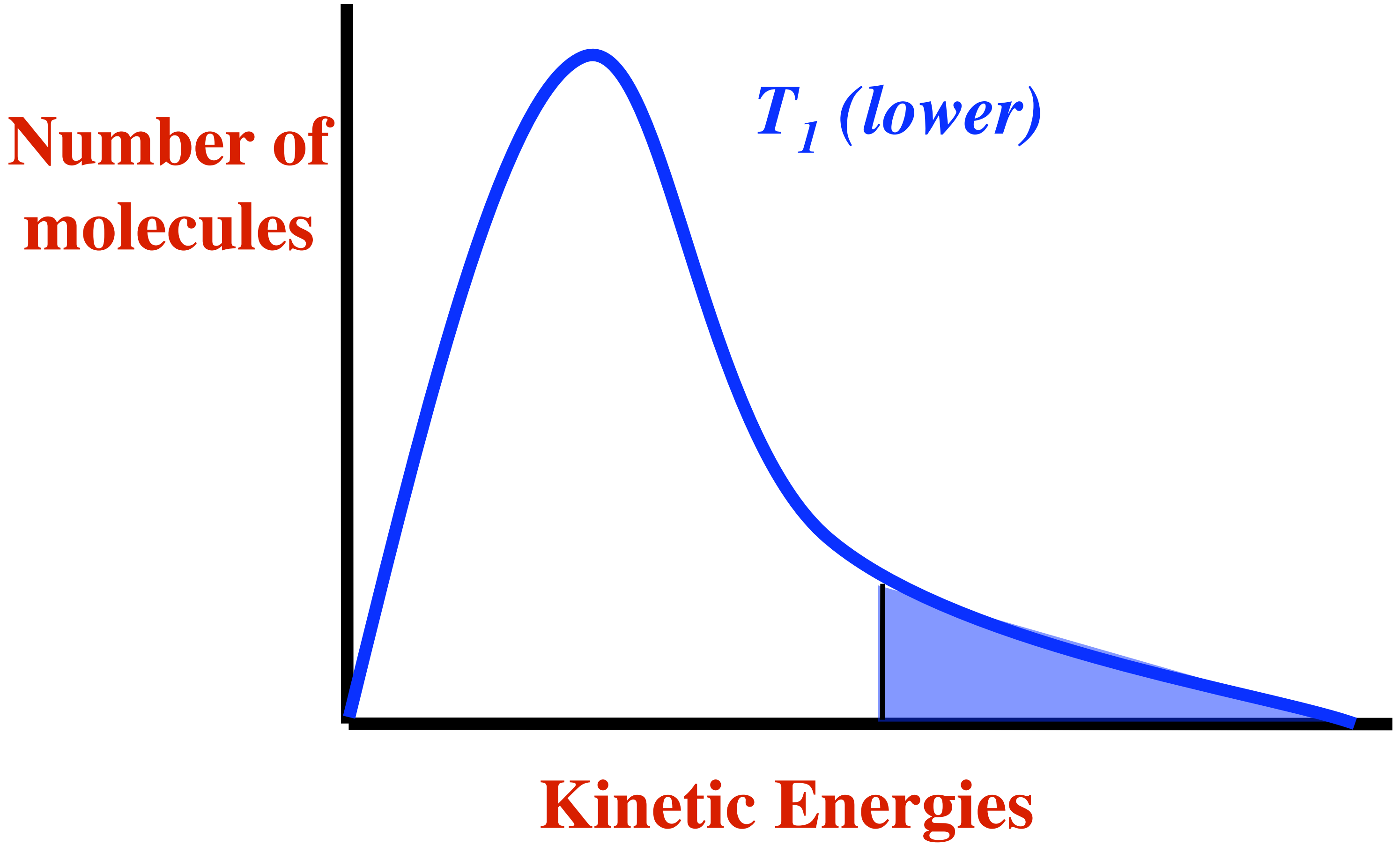
liquid $\rightleftharpoons$ **gas**

condensation

Say you cool down a gas. The condensation point (a temp) is the same as what other temp?

Boiling point!

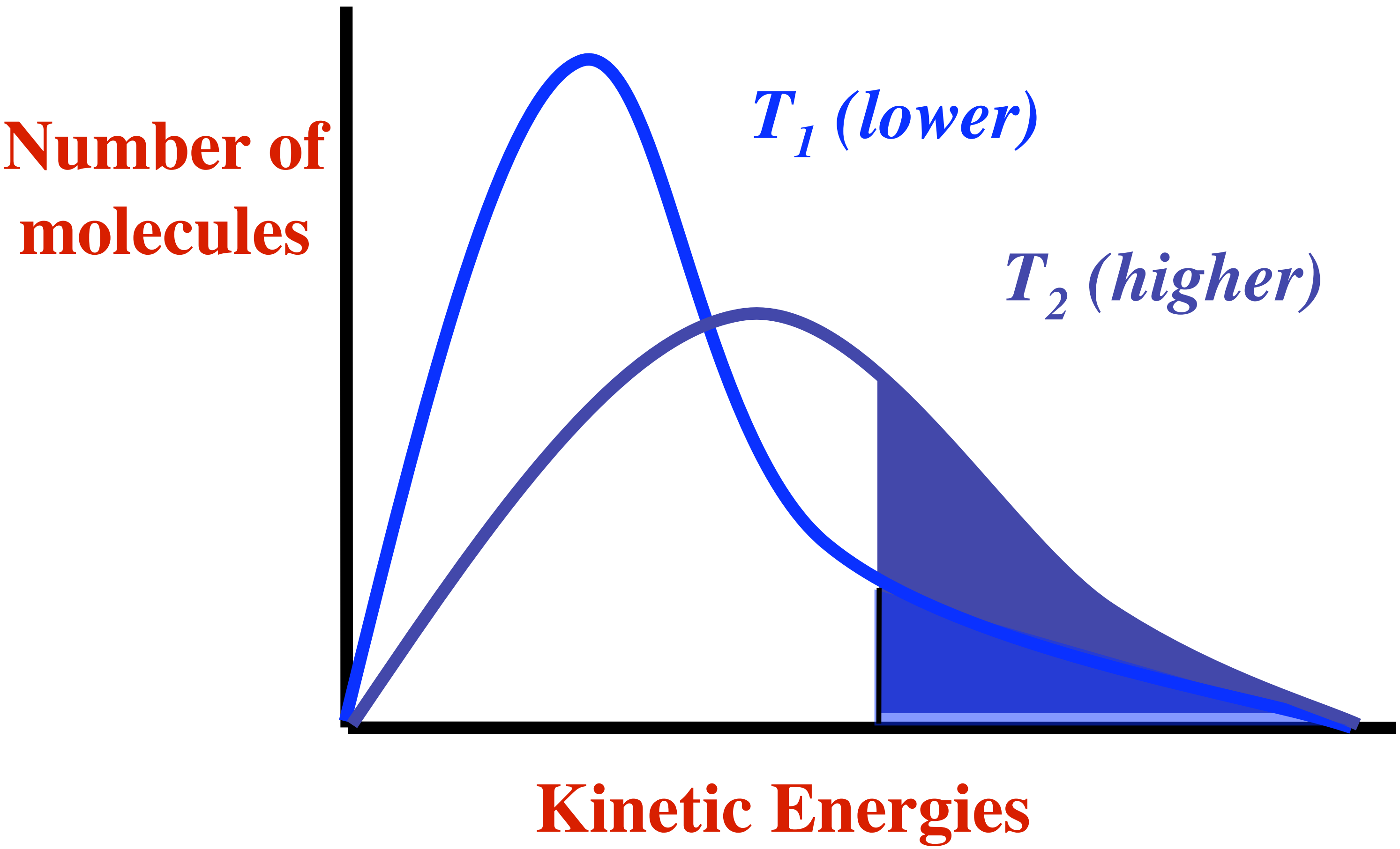
Distribution of kinetic Energies



At any given temperature a certain number of molecules in a liquid possess sufficient kinetic energy to escape from the surface

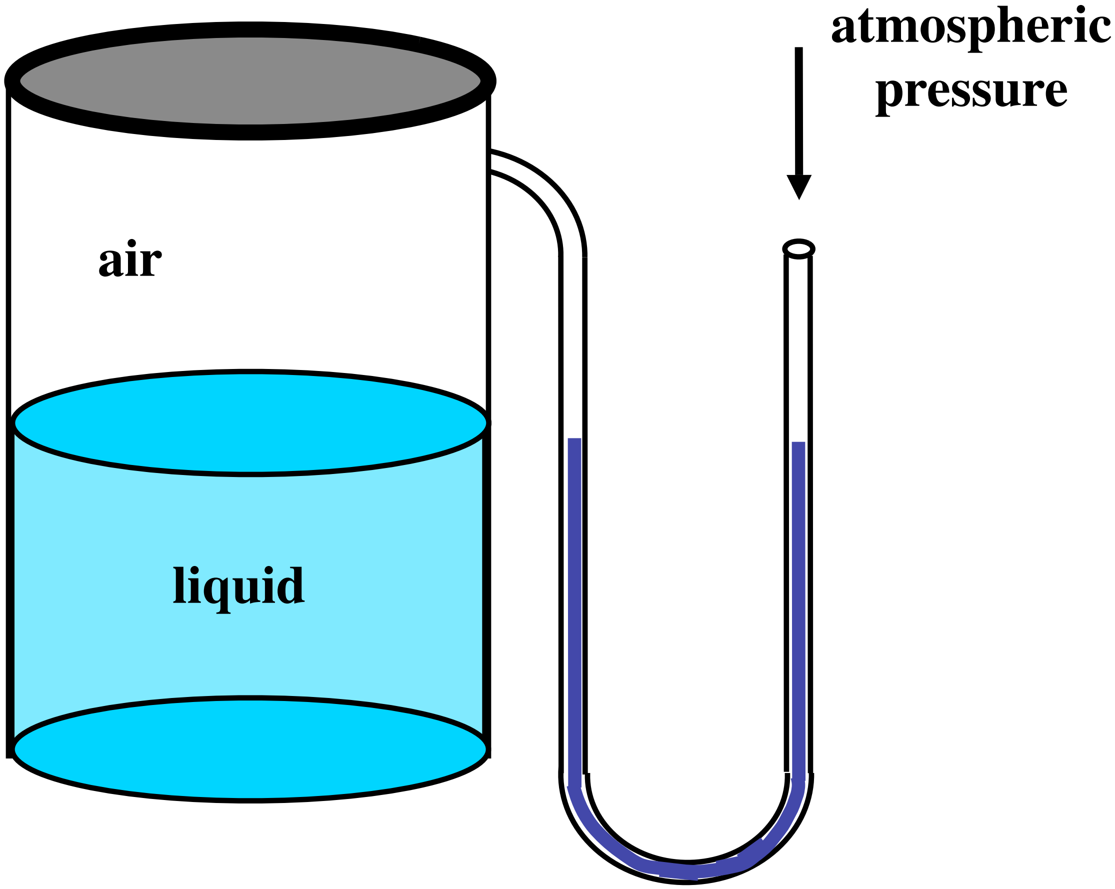
Odyssey #37, Temp Dependence

Distribution of kinetic Energies

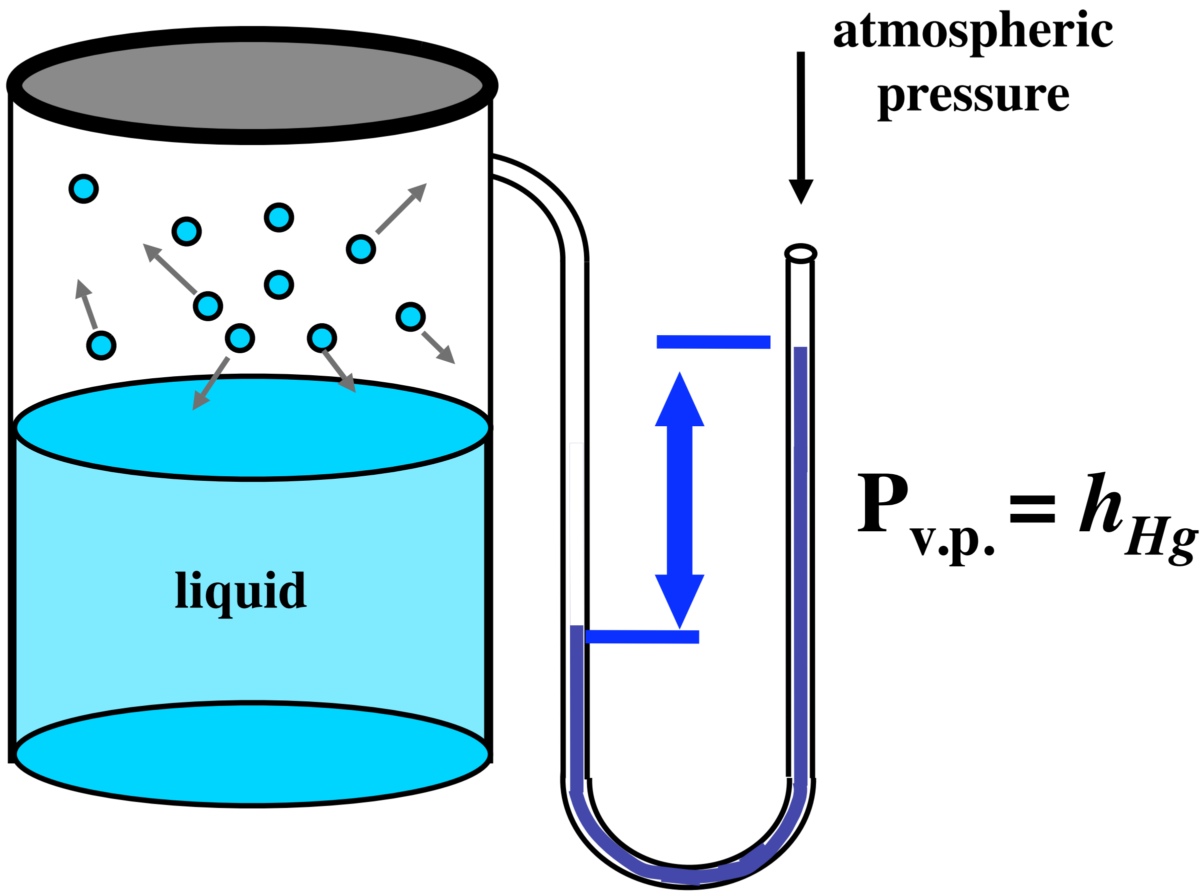


At higher temperatures more molecules in a liquid possess sufficient kinetic energy to escape from the surface

Vapor Pressure



before evaporation

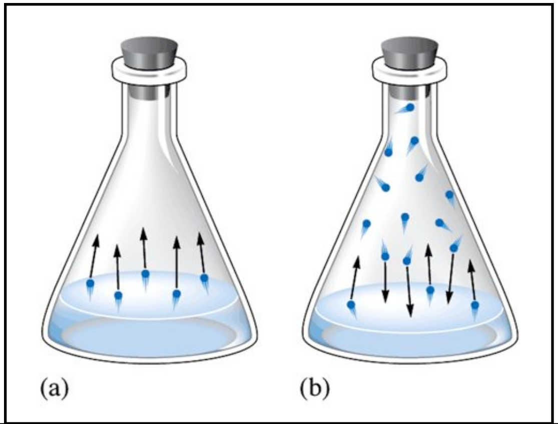


at equilibrium

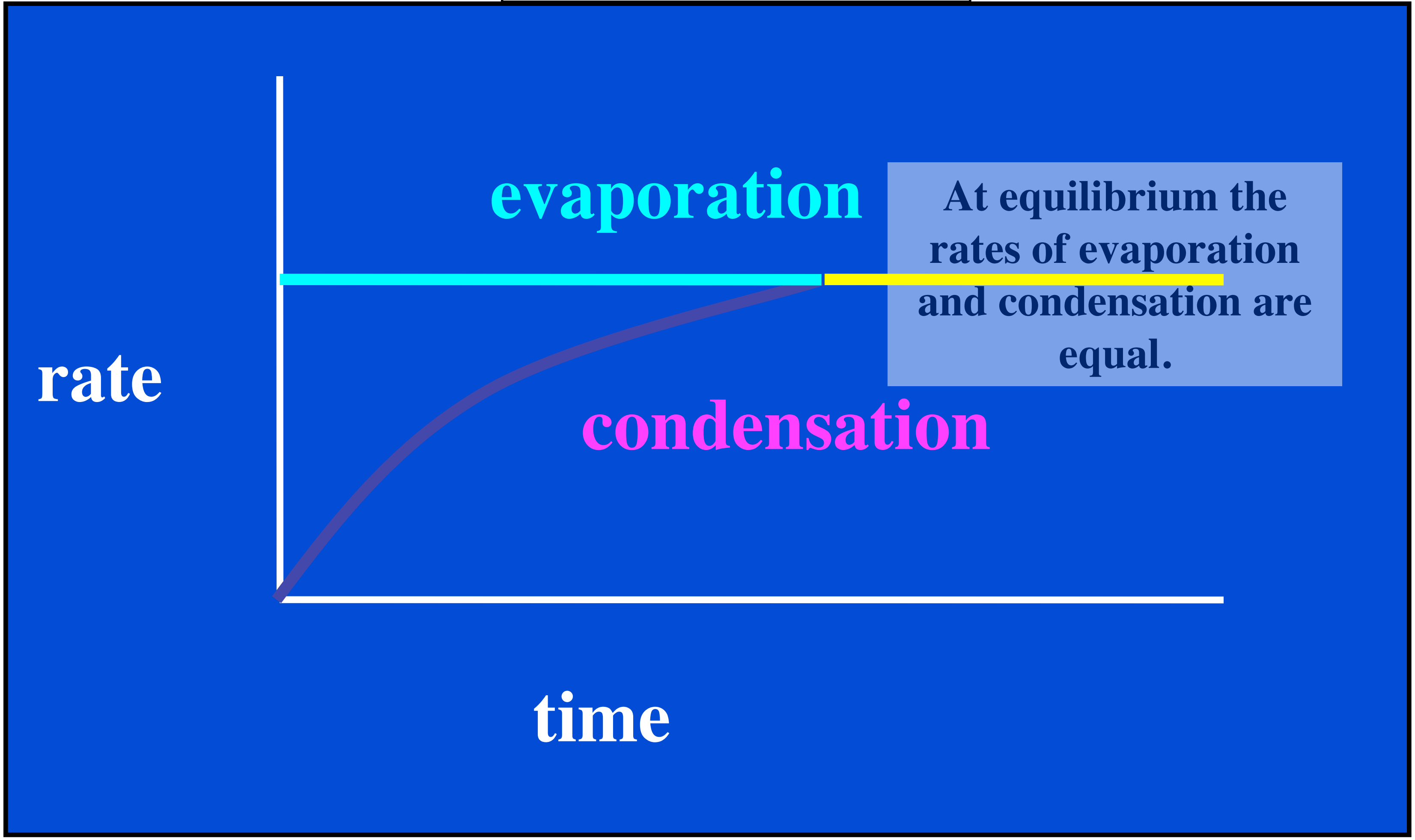
Demo :States of Matter w/ gravity on, 60 atoms, IMFs=2.0

What happens over time to the rates of

- condensation?
- evaporation?



$H_2O(l) \Leftrightarrow H_2O(g)$



Condensation and Evaporation

evaporation and condensation are dynamic processes

evaporation and condensation occur simultaneously

the rate of evaporation depends on the temperature and the surface area

the rate of condensation increases as the number of molecules in the gas phase increases

a system is at equilibrium when the rates of the forward and reverse processes are equal

Vapor Pressure

pressure of the vapor, when vapor and liquid are in equilibrium with one another

vapor pressure is a characteristic property of a particular substance

Increases with temperature

Definition of Boiling Point

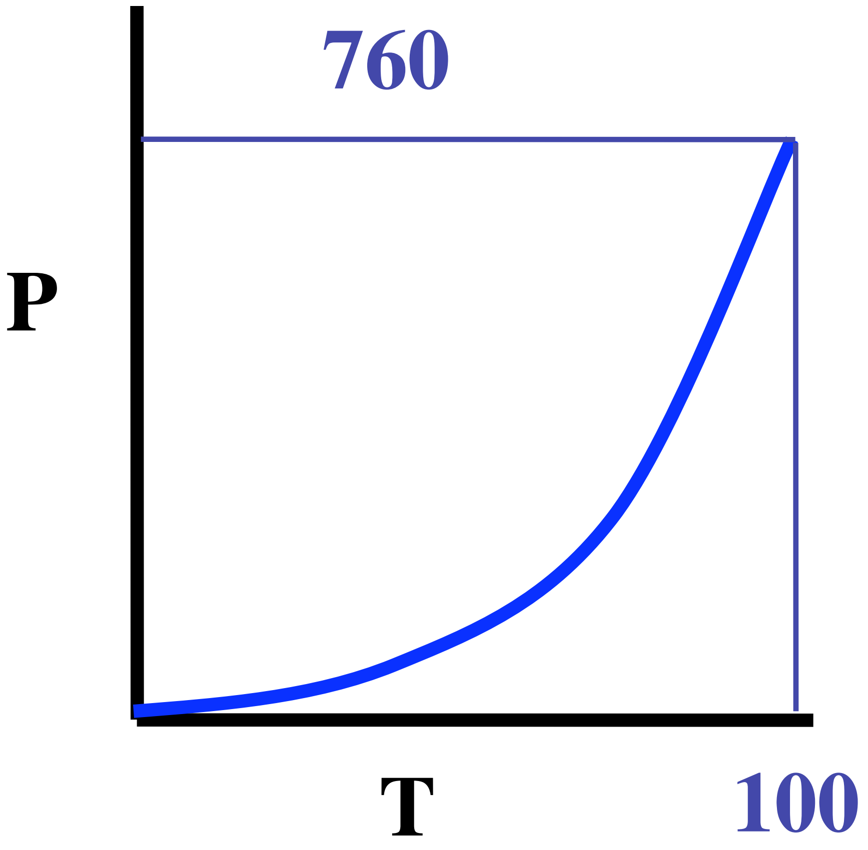
temperature at which vapor pressure of a substance equals external pressure

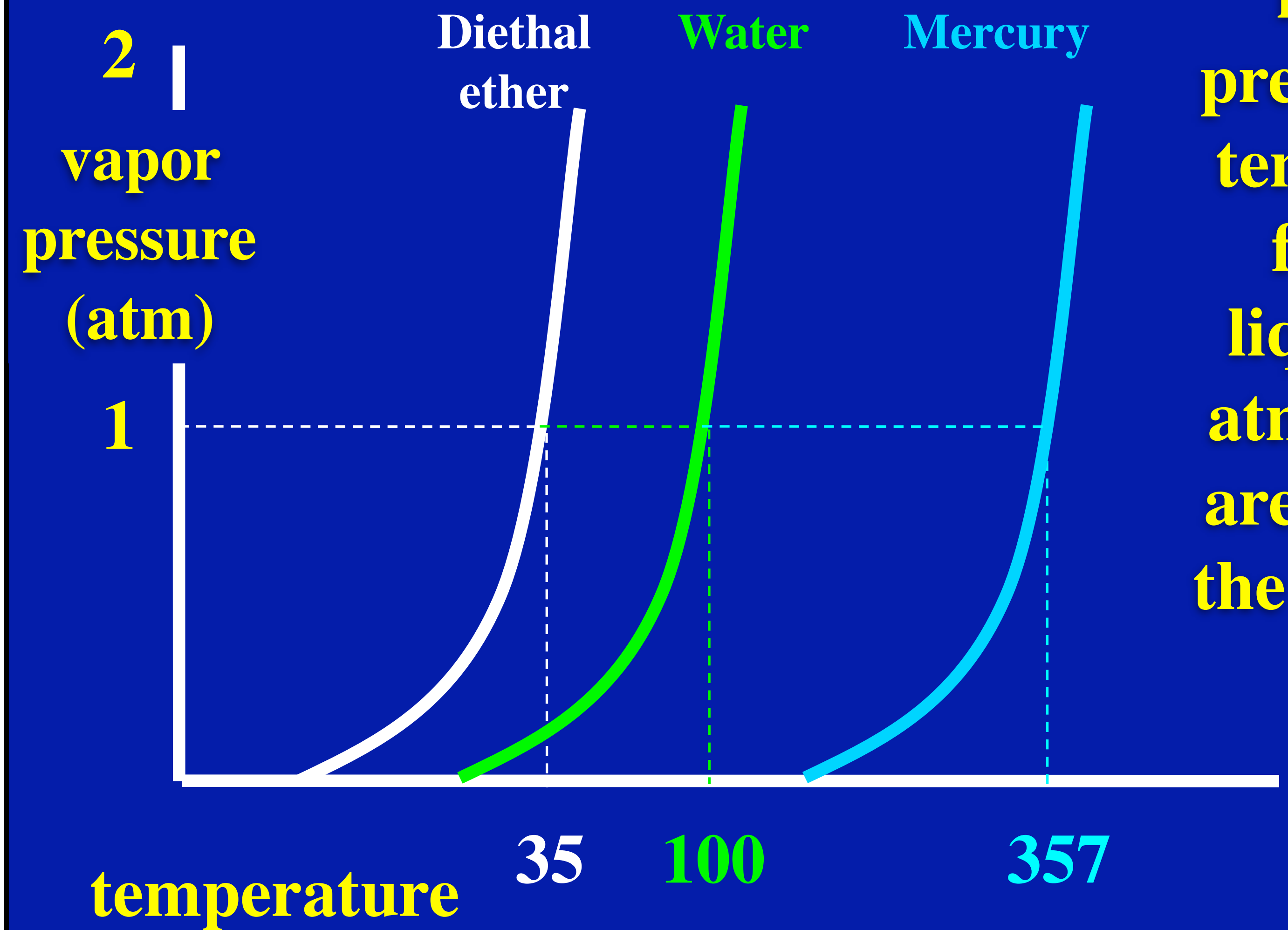
***normal boiling point*: boiling point when the external pressure equals 1 atmosphere**

Demo: Warm water in vacuum chamber

Vapor Pressure of Water

T (C°)	P (torr)
0.0	4.579
10.0	9.209
20.0	17.535
25.0	23.756
30.0	31.824
40.0	55.324
60.0	149.4
70.0	233.7
90.0	525.8





The increase in vapor pressure with temperature for three liquids at 1 atm pressure are shown on the horizontal axis.

Heat of Vaporization and Boiling Point

Molar heats of vaporization for selected liquids

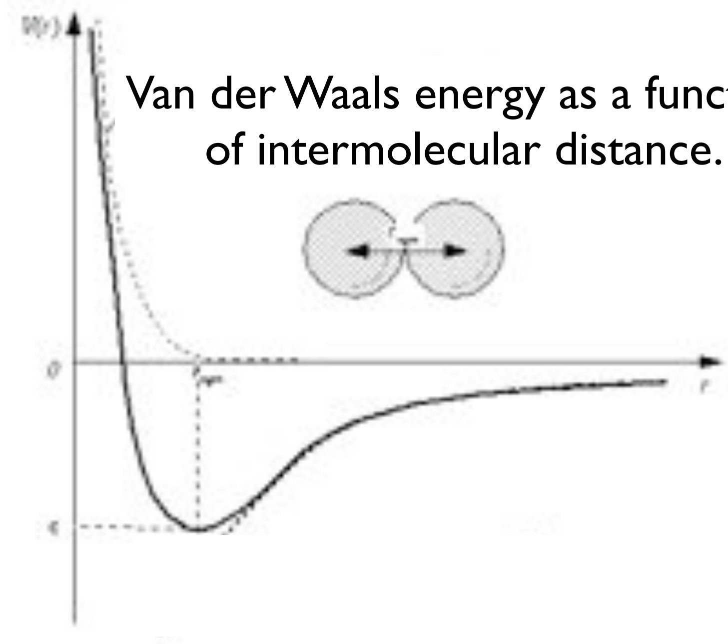
substance		B.Pt. °C	ΔH_{vap} kJ/mol
Argon	Ar	- 186	6.3
Methane	CH_4	- 164	9.2
Diethyl ether	$CH_3CH_2OCH_2CH_3$	34.6	26.0
Ethanol	CH_3CH_2OH	78.3	39.3
Benzene	C_6H_6	80.1	31.0
Water	H_2O	100	40.79
Mercury	Hg	357	59.0

Critical Temperature and Pressure

Critical Points

critical temperature: temperature above which gas cannot be liquefied no matter how great the applied pressure (is the highest temperature at which a substance can exist as a liquid)

critical pressure: the minimum pressure required to bring about liquefaction at the critical temperature



Van der Waals energy as a function of intermolecular distance.

Critical Pressures and Temperatures for selected compounds

substance		T_c (°C)	P_c (atm)
Argon	Ar	- 186	6.3
Methane	CH_4	- 83.0	45.6
Carbon dioxide	CO_2	31.0	73.0
Ethanol	CH_3CH_2OH	243	63
Benzene	C_6H_6	288.9	47.9
Water	H_2O	374.4	219.5
Mercury	Hg	1462	1036

Liquid-Solid Equilibrium

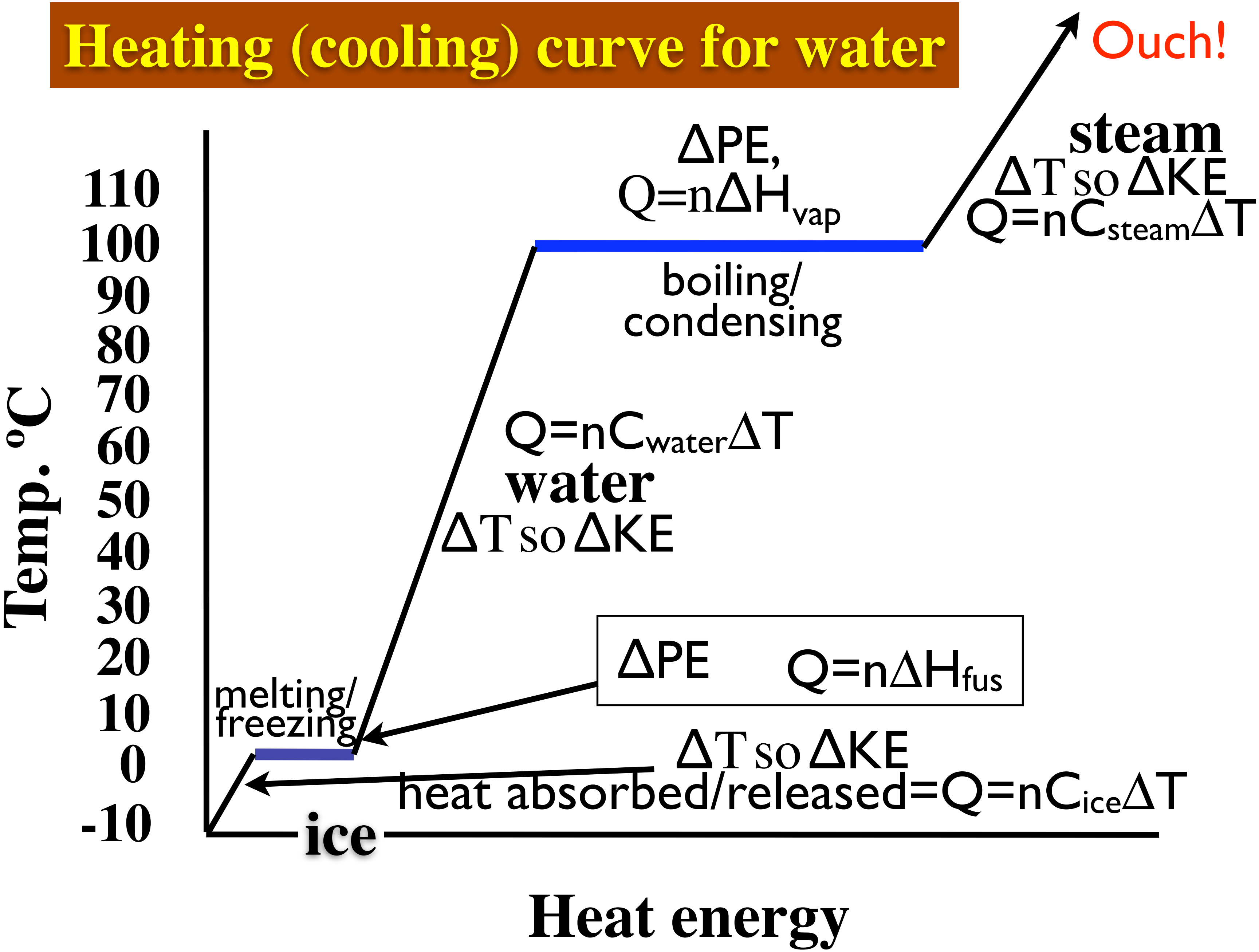
Liquid-Solid Equilibrium

melting point

temperature at which solid and liquid phases coexist in equilibrium

***normal melting point*: melting point at a pressure of 1 atmosphere**

Heating (cooling) curve for water



How much heat is required to raise the temp of 9.0 g of ice from -15 °C to steam at +150 °C?

Warm up the ice

$Q = nC_{ice}\Delta T = 9.0g(2.11\ J/g°C)[0-(-15°C)] = 285\ J$

Melt the ice

$Q = n\Delta H_{fus} = 9.0g(334\ J/g) = 3006\ J$

Warm up the water

$Q = nC_{water}\Delta T = 9.0g(4.18J/g°C)[100-0°C] = 3762\ J$

Boil the water

$Q = n\Delta H_{vap} = 9.0g(2258\ J/g) = 20322\ J$

Warm up the steam

$Q = nC_{steam}\Delta T = 9.0g(2.08\ J/g°C)[150°C-100°C] = 936\ J$

$Q_{TOT} = 285\ J + 3006\ J + 3762\ J + 20322\ J + 936\ J =$ **28311 J**
= **28.3 kJ**

Changes of State

solid

ΔH_{fusion} $\downarrow\uparrow$ $-\Delta H_{fusion}$

liquid

$\Delta H_{vaporization}$ $\downarrow\uparrow$ $-\Delta H_{vaporization}$

gas

Molar heats of fusion for selected liquids

substance		M.Pt. °C	ΔH_{fusion} kJ/mol
Argon	Ar	- 190	1.3
Methane	CH_4	- 183	0.84
Diethyl ether	$CH_3CH_2OCH_2CH_3$	- 116.2	6.90
Ethanol	CH_3CH_2OH	- 117.3	7.61
Benzene	C_6H_6	5.5	10.9
Water	H_2O	0	6.01
Mercury	Hg	- 39	23.4

Trends in melting point temps and heat of fusion #s?

Molar heats of vaporization and fusion for selected liquids

substance		ΔH_{vap} kJ/mol	ΔH_{fusion} kJ/mol
Argon	Ar	6.3	1.3
Methane	CH_4	9.2	0.84
Diethyl ether	$CH_3CH_2OCH_2CH_3$	26.0	6.90
Ethanol	CH_3CH_2OH	39.3	7.61
Benzene	C_6H_6	31.0	10.9
Water	H_2O	40.79	6.01
Mercury	Mg	59.0	23.4

Trends in heat of vaporization and heat of fusion #s?

Solid-Vapor Equilibrium

Solid -Vapor Equilibrium

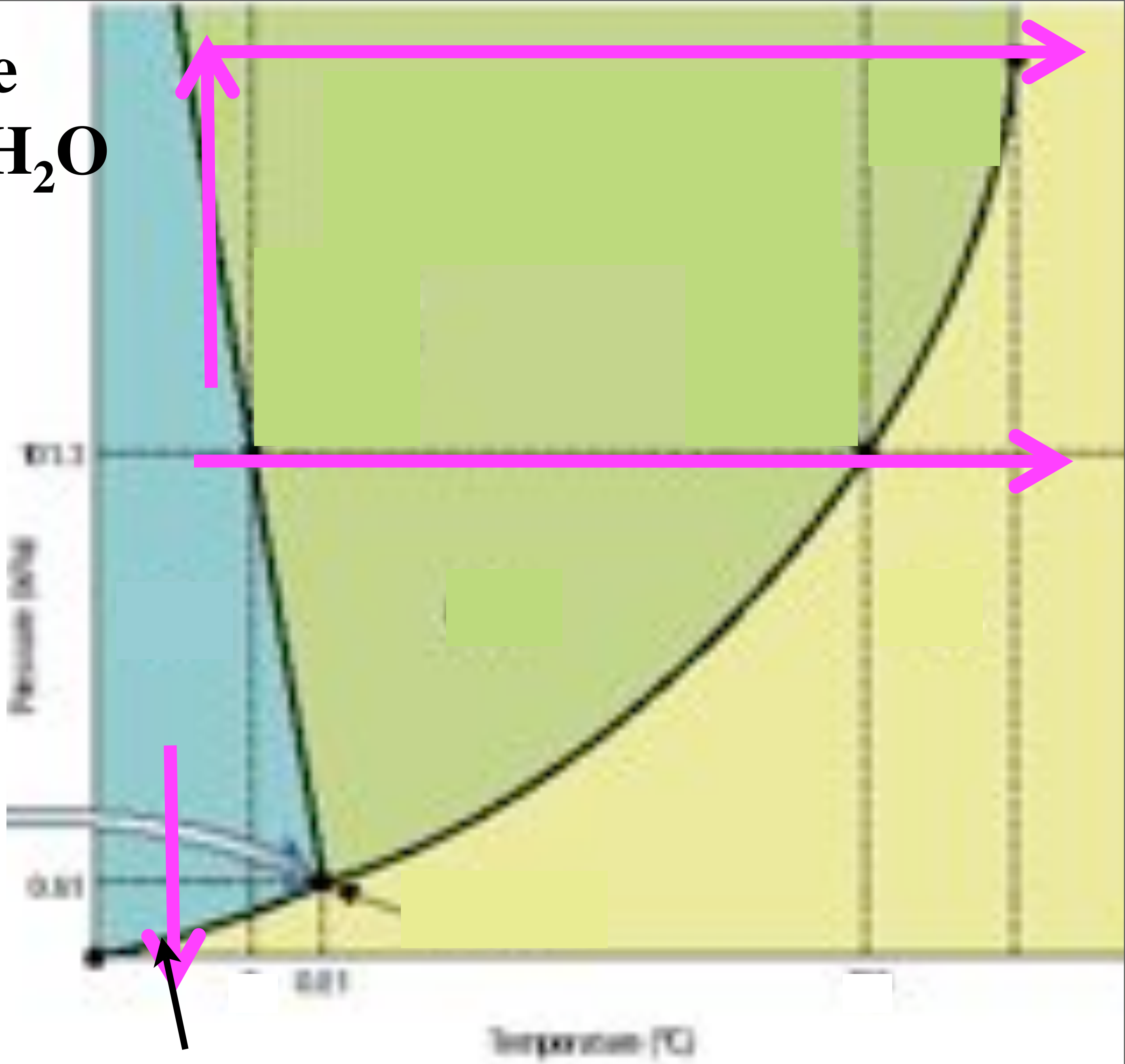
$$\text{solid} \rightleftharpoons \text{gas}$$

sublimation

Phase Diagrams

Phase diagrams are graphs that summarize conditions (temperature, pressure) under which a substance exists as a solid, liquid, or gas.

P - T Phase Diagram for H_2O



Carbon dioxide phase diagram