Chapter 12

Intermolecular Forces and Physical Properties of Liquids and Solids

Topics

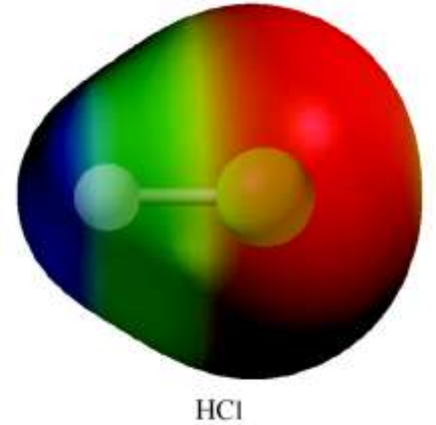
- Intermolecular forces
- Properties of liquids
- Crystal structure
- Types of crystals
- Amorphous solids
- Phase changes
- Phase diagrams

12.1 Intermolecular Forces

- *Intermolecular forces* are the attractive forces holding particles(molecules, atoms or ions) together in the *condensed* (liquid and solid) *phases* of matter
- Ionic bonding mentioned previously is a sort of strong cuolombic forces between oppositely charged particles that make up the ionic compound.
    - That is why all of these compounds are solids

Intermolecular Forces

- Intermolecular forces in this chapter are those resulting from coulombic attractions between partially charged species
- Weaker than forces of ionic bonding
- Coulombic attractions depend upon:
  - the magnitude of the charge
  - the distance between charges



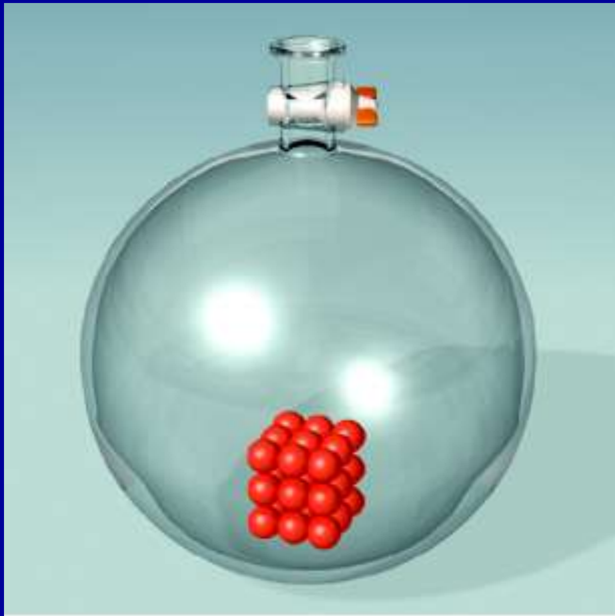
Intra- vs. Inter-molecular forces

- intramolecular forces
  - – inside molecules (bonding)
  - – hold atoms together into molecule
- intermolecular forces
  - – These are what hold the molecules together in the condensed states.
  - – Forces between molecules
  - – They get weaker as phase changes from S – L – G
- When a substance changes state, molecules stay together but intermolecular forces are ***weakened***

The Three Phases of Matter

Gas

Liquid



Solid

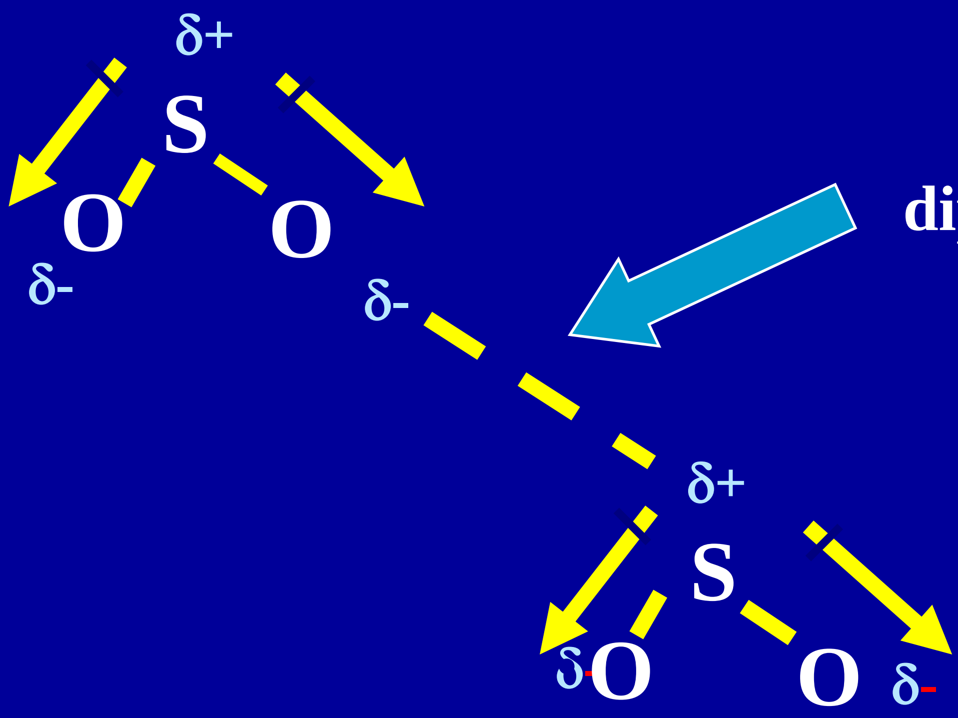
condensed phases

Types of Intermolecular Forces

- ***Intermolecular forces are known collectively as van der Waals forces***
- ***van der Waals forces*** **–between atoms and molecules of pure substances include the following:**
  - – ***Dipole-dipole interactions*** **– attractive forces between polar molecules**
  - – ***Hydrogen bonding*** **– attractive force in polar molecules containing a H atom bonded to a small, highly electronegative element (N, O and F)**
  - – **(*London*) Dispersion forces – attractive forces arising from instantaneous dipoles and induced dipoles**

Dipole-dipole interactions

- **Intermolecular forces** between molecules that posses dipole moment
- **The opposite ends of the dipole can attract each other so the molecules stay close together.**

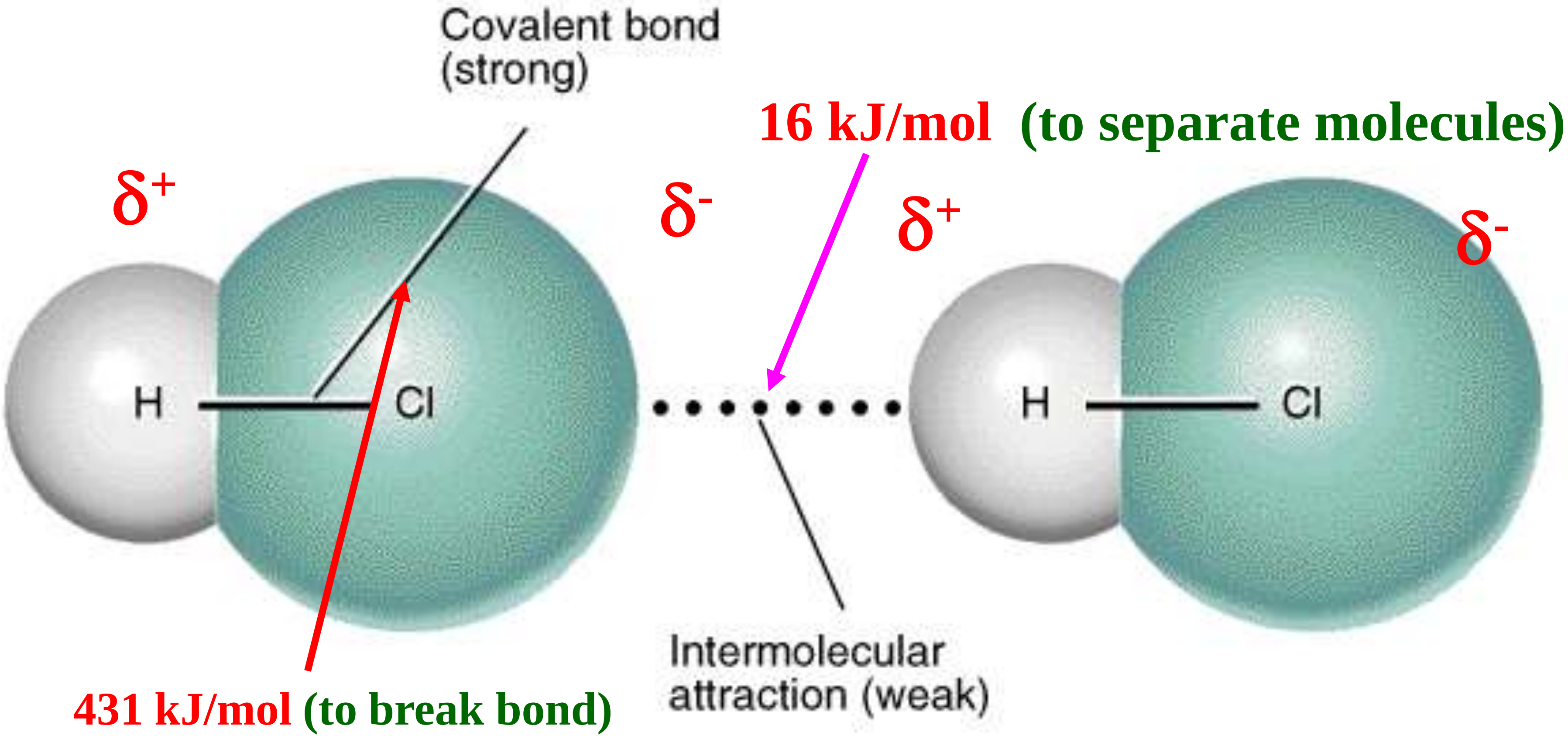


dipole-dipole attraction

What effect does this attraction have on the boiling point?

The strengths of ***intermolecular forces*** are generally weaker than either ionic or covalent bonds.

Polar molecules have dipole-dipole attractions for one another.



16 kJ/mol (to separate molecules)

431 kJ/mol (to break bond)

- Molecules with dipole-dipole interactions possess higher melting points and boiling points than nonpolar molecules of comparable molar mass

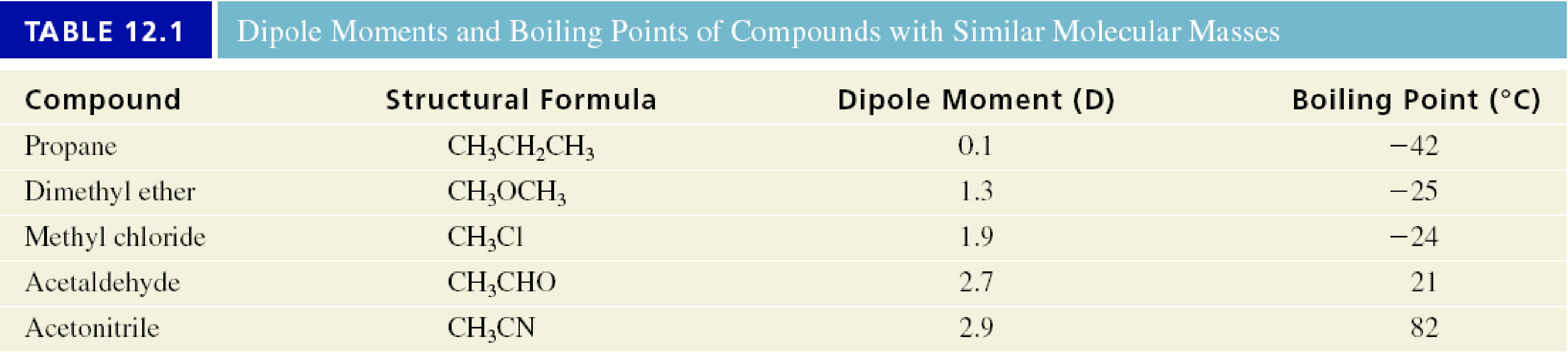


TABLE 12.1 Dipole Moments and Boiling Points of Compounds with Similar Molecular Masses

Compound	Structural Formula	Dipole Moment (D)	Boiling Point (°C)
Propane	$CH_3CH_2CH_3$	0.1	−42
Dimethyl ether	CH_3OCH_3	1.3	−25
Methyl chloride	CH_3Cl	1.9	−24
Acetaldehyde	CH_3CHO	2.7	21
Acetonitrile	CH_3CN	2.9	82

- Substance with larger intermolecular attractions will require more energy to separate the particles and will therefore boil at higher temperature

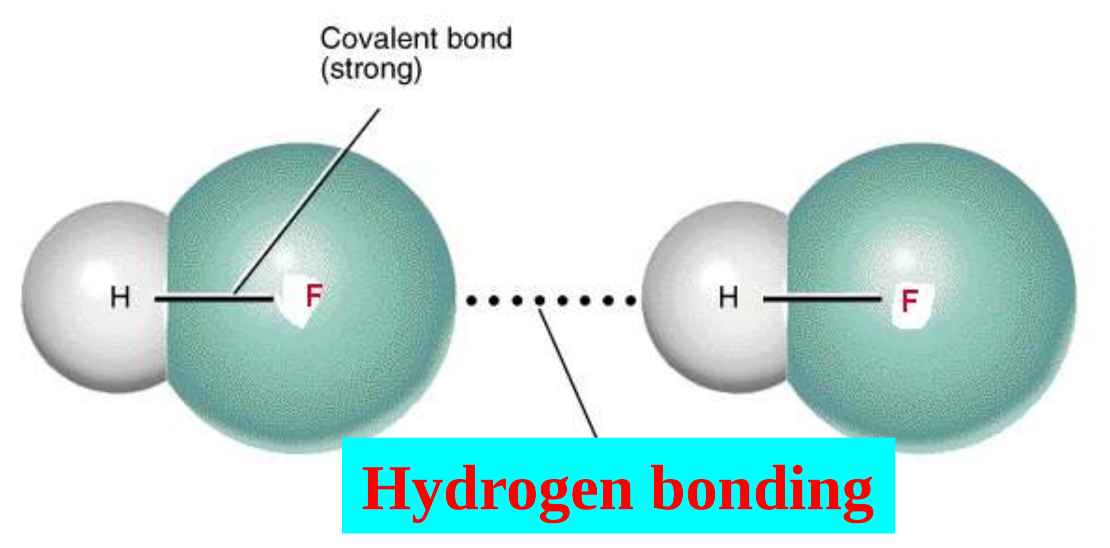
Hydrogen Bonding

- A hydrogen bond is an intermolecular force in which a ***hydrogen atom*** covalently bonded to a ***nonmetal atom*** in one molecule is simultaneously ***attracted*** to a ***nonmetal*** atom of a ***neighboring molecule***

- The *strongest hydrogen* bonds are formed if the nonmetal atoms are *small* and *highly electronegative* – e.g., ***N, O, F***
  - very strong type of dipole-dipole attraction
    - because bond is so polar
    - because atoms are so small

Hydrogen Bonding in HF

$$H\text{-}F^{\delta-} \text{ --- } {}^{\delta+}H\text{-}F$$



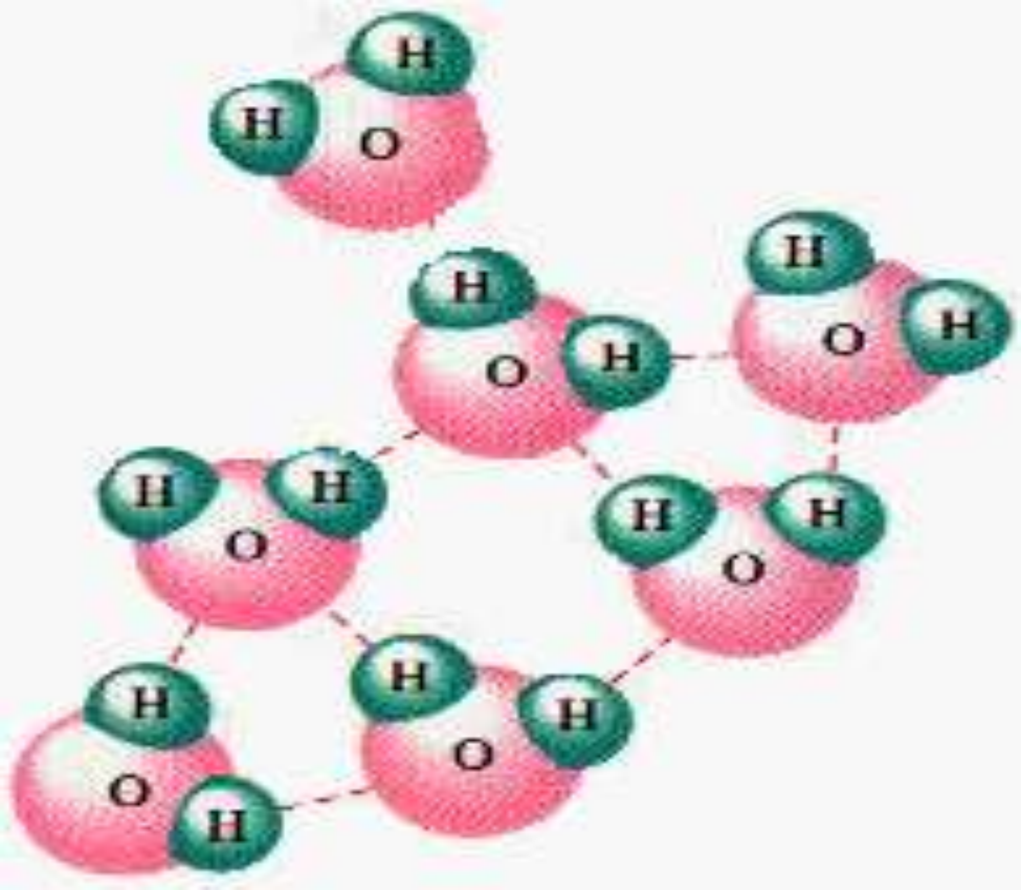
- Hydrogen bond is 5-10% as strong as the covalent bond

Hydrogen bonding between water molecules

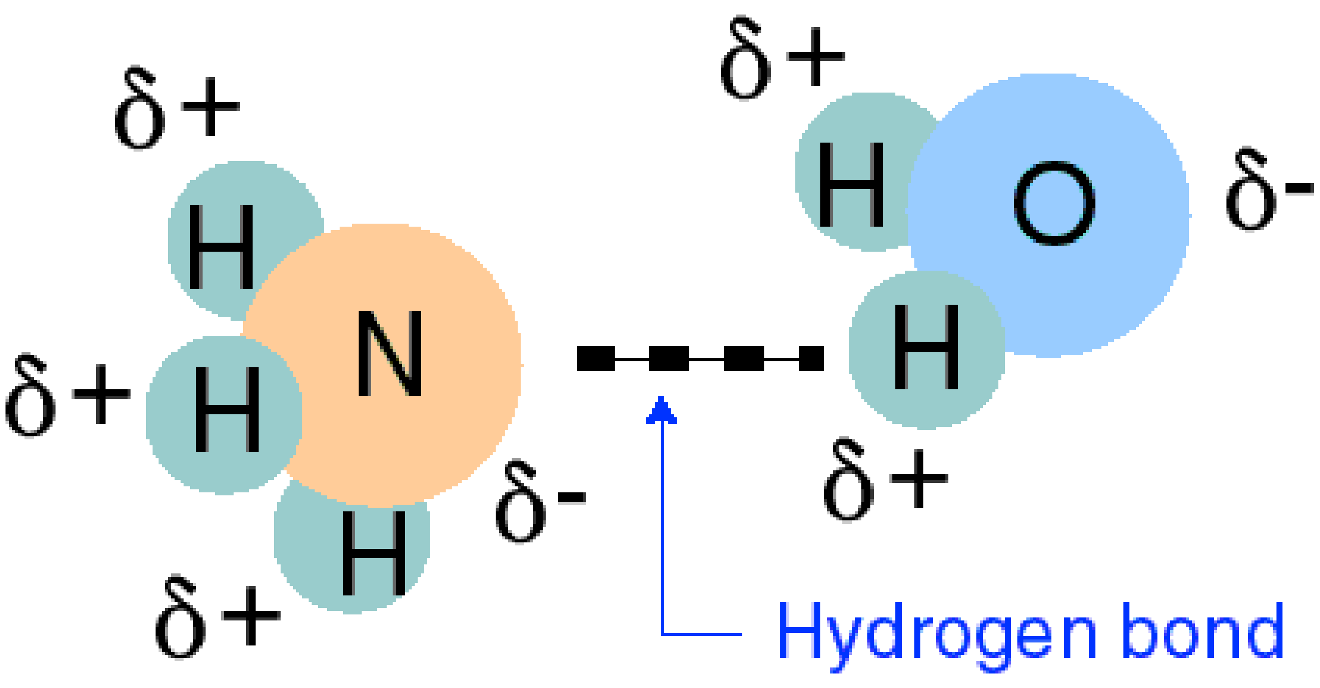
δ+

δ-

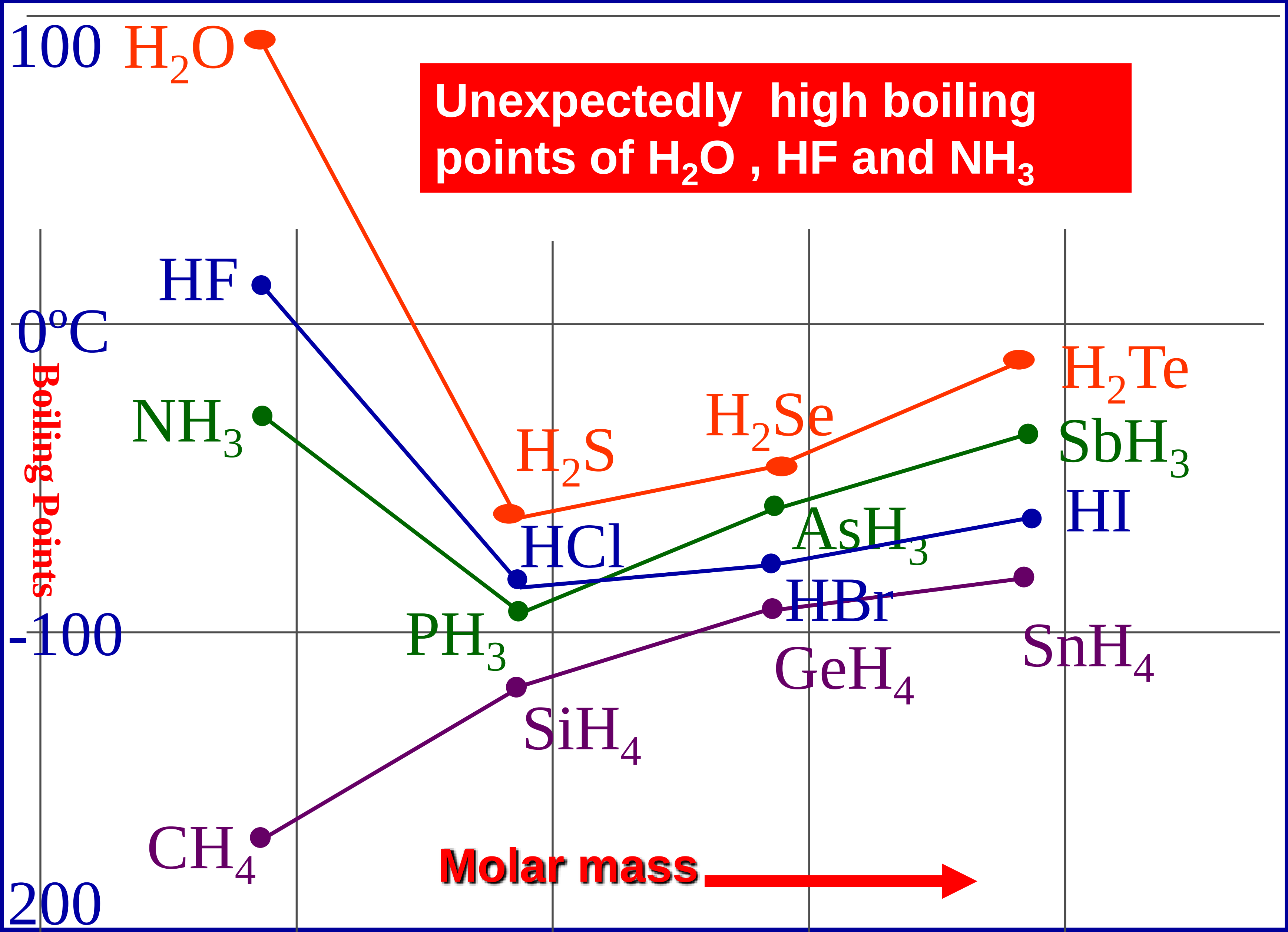
δ+



Hydrogen bonding between ammonia and water



Effect of Molar Mass and Hydrogen Bonding on boiling points

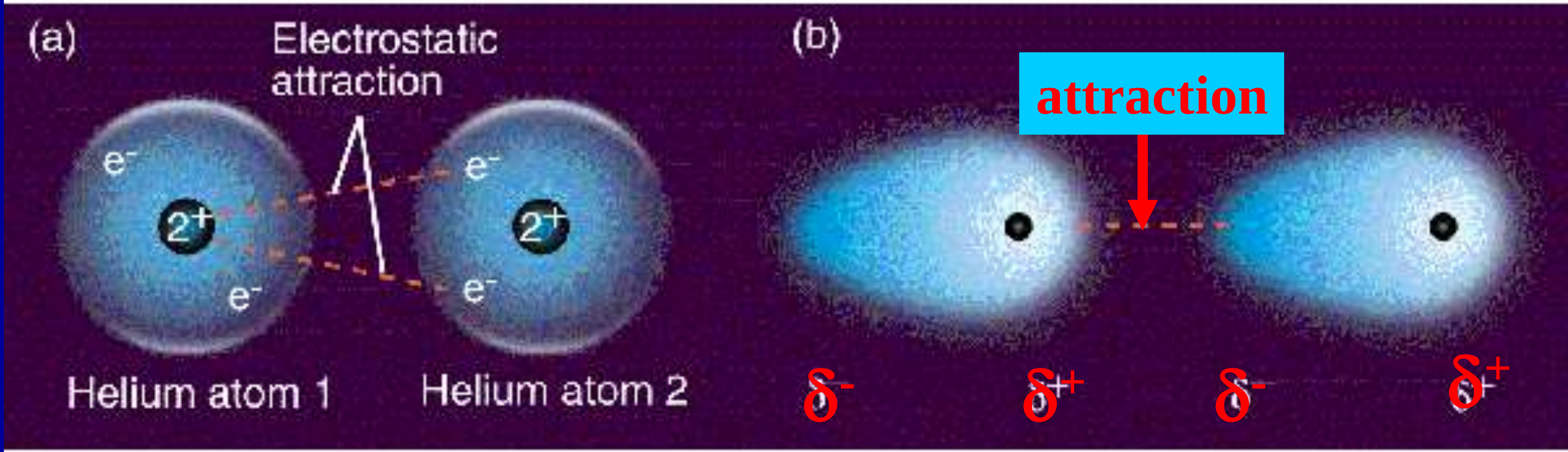


Unexpectedly high boiling points of H_2O , HF and NH_3

London Dispersion Forces

- N_2 and O_2 can be liquefied under certain pressure and temperature. So nonpolar molecules must also exhibit attractive intermolecular forces
- These forces are coulombic in nature but they arise from the movement of electrons in nonpolar molecules
- Instantaneous dipoles arise from the movement of electrons that disturbs the uniformity of the distribution of electrons in the nonpolar molecules

- Consequently electrons are not evenly distributed at every instant in time.
- Thus, they will have an instantaneous dipole.
- Atom with instantaneous dipole induces a dipole in the atom next to it.
- attractive forces arise from instantaneous dipoles and induced dipoles

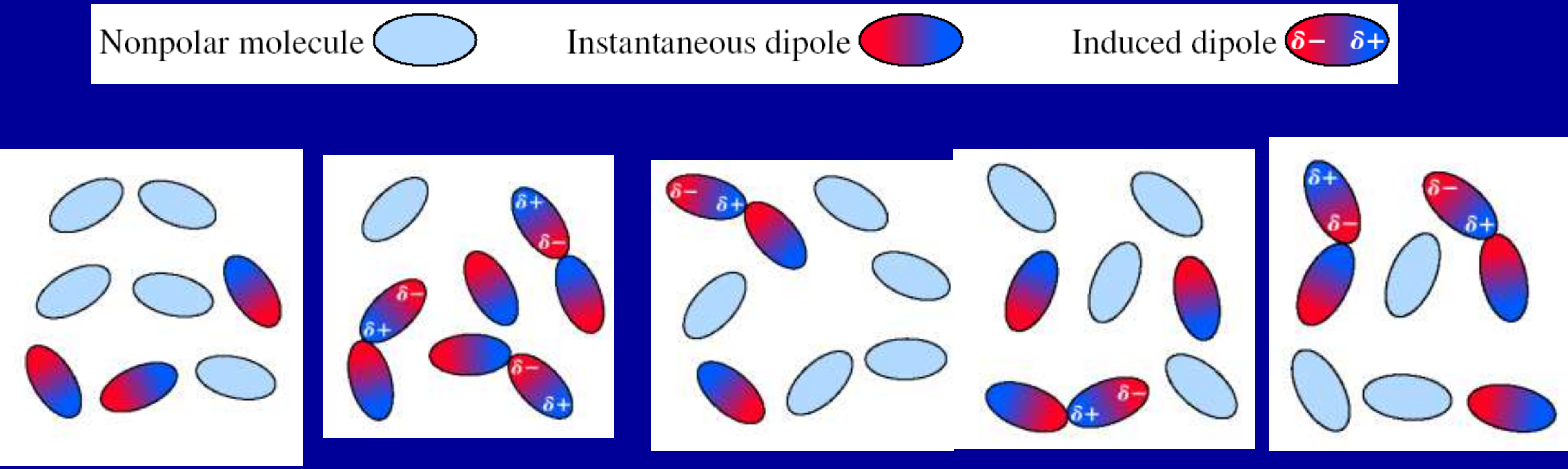


“Electrons are shifted to overload one side of an atom or molecule”.

Polarizability: the ease with which an atom or molecule can be distorted to have an instantaneous dipole.

In general big molecules are more easily polarized than little ones.

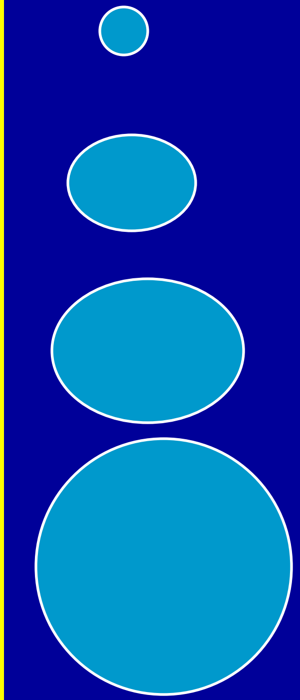
Instantaneous and Induced Dipoles



- Magnitude depends on the ability to be *polarized* which is greater for larger molecules.
- In small molecules electrons are close to the nuclei therefore they cannot move freely
- In large molecules electrons are farther away from the nuclei thus they move freely

nuclei therefore they cannot move freely

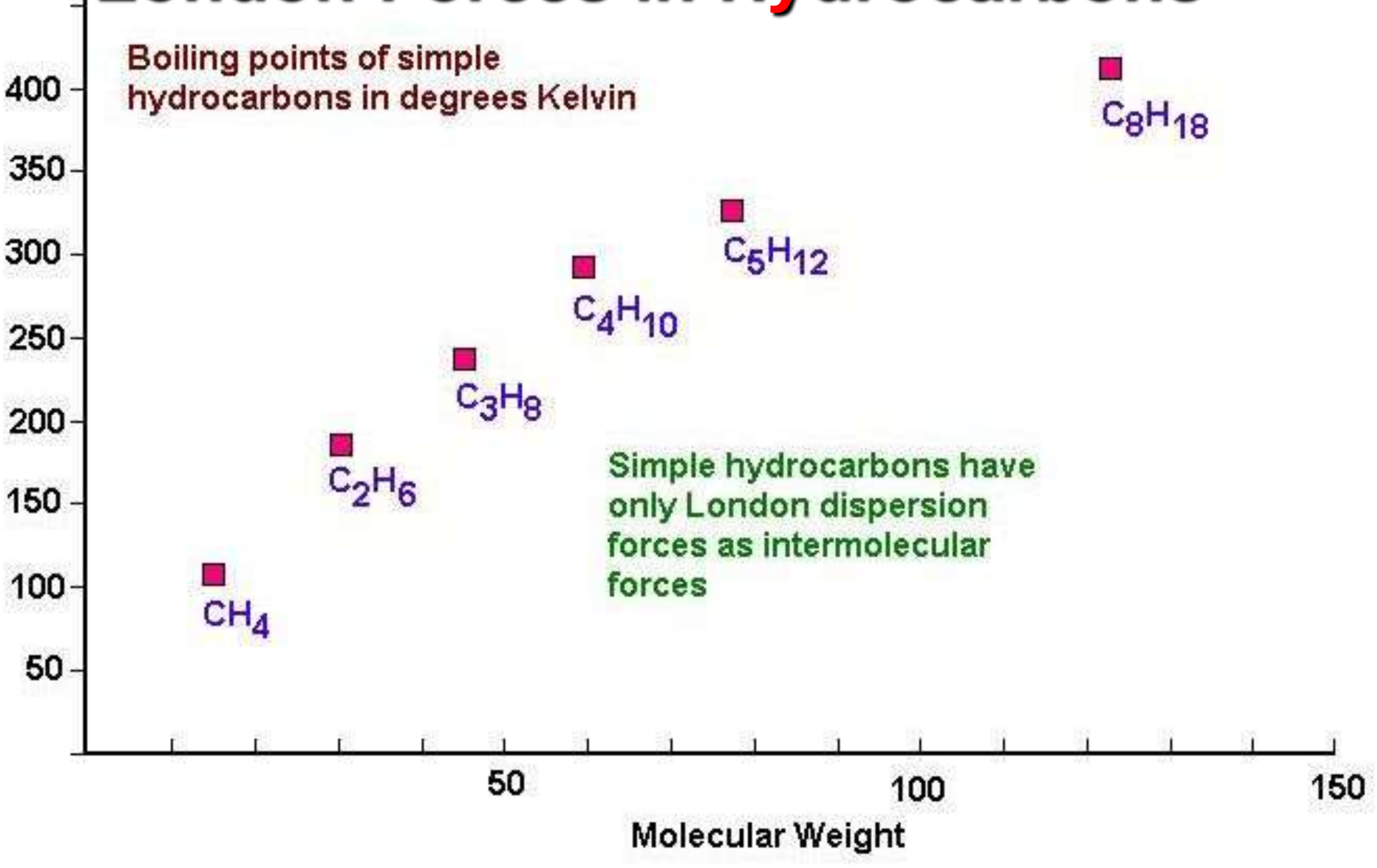
Halogen	Boiling Pt (K)	Noble Gas	Boiling Pt (K)
F_2	85.1	He	4.6
Cl_2	238.6	Ne	27.3
Br_2	332.0	Ar	87.5
I_2	457.6	Kr	120.9



Which one(s) of the above are most polarizable?

Hint: look at the relative sizes.

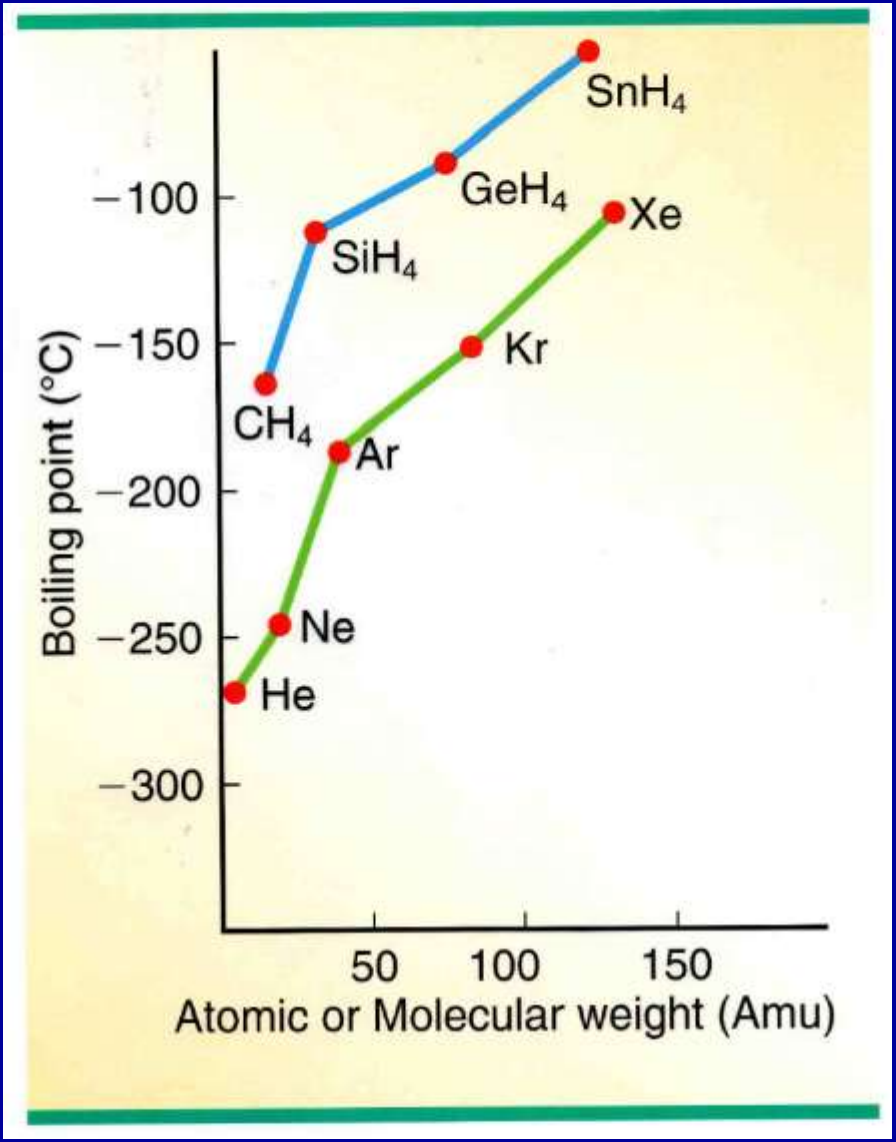
London Forces in Hydrocarbons



Boiling Points for Some Non Polar Molecules

The larger the molecule the larger the London forces due to more electrons in the molecule.

The stronger the attraction, the higher the boiling point.



London Dispersion Forces

- They exist in every molecular compound
- They are significant only for nonpolar molecules and noble gas atoms
- They are much weaker than other forces.

Relative Magnitudes of Forces

The types of bonding forces vary in their strength as measured by average bond energy.

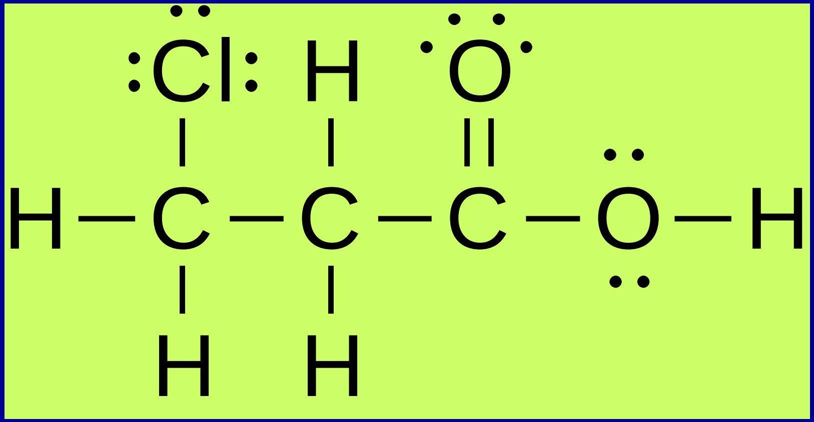
Strongest

Weakest

Covalent bonds	400 kcal/mol
Hydrogen bonding	12-16 kcal/mol
Dipole-dipole interactions	2-0.5 kcal/mol
London forces	less than 1 kcal/mol

What kind(s) of intermolecular forces exist in

$CH_2ClCH_2COOH(l)$



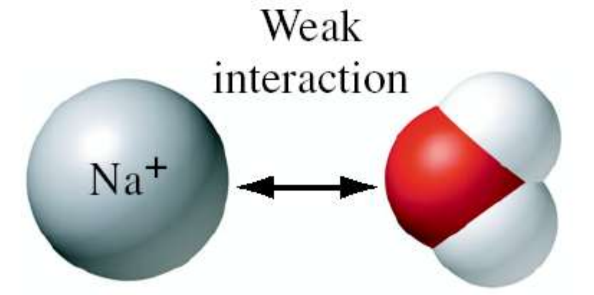
dispersion forces

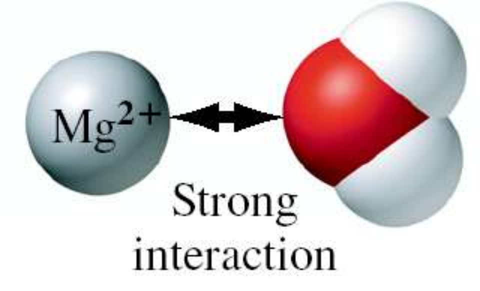
dipole-dipole interactions

hydrogen bonding

Ion-dipole Interactions

- Occur in mixtures of ionic and polar species
- Coulombic attraction between ions and polar molecules
- Dependent upon
  - Size and charge of ion
  - Dipole moment of the molecule
  - Size of the molecule
- Can also be repulsive
- Hydration of cations is an example





12.2 Properties of Liquids

- Low compressibility
- Lack of rigidity
- High density compared to gases
- Surface tension
- Viscosity
- Vapor pressure

Stronger intermolecular forces cause each of these to increase.

Surface Tension

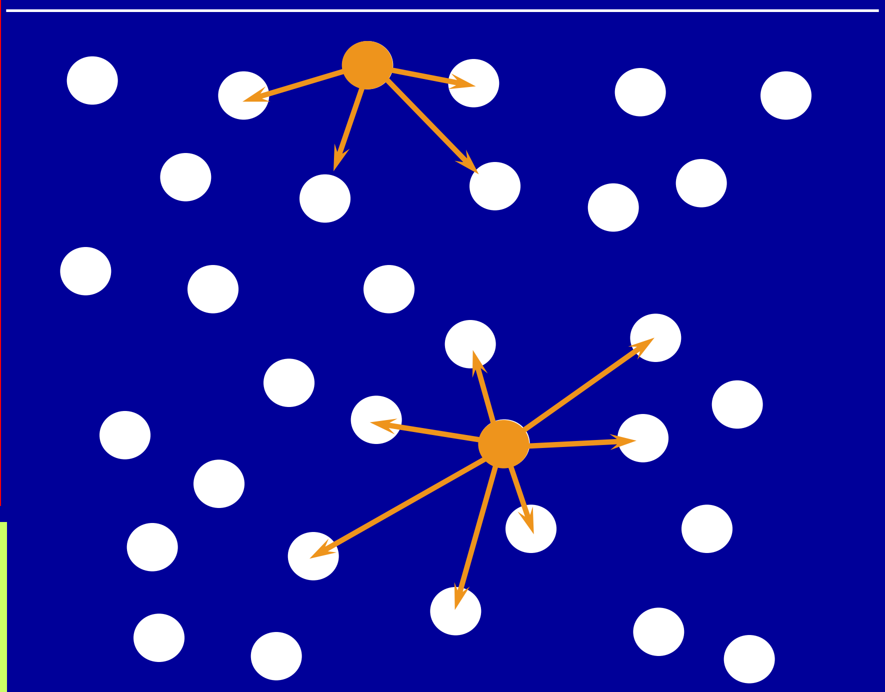
- **Surface tension is a quantitative measure of the elastic force at the surface of a liquid**

- **Manifestations of surface tension**
  - **Beading (beading of water on a freshly waxed car)**
  - **Formation of a *meniscus* *(Concave like water and convex like mercury)***
  - ***Capillary action* which results from a combination of**
    - ***Cohesion* (attractions between like molecules, cohesive forces)**
    - ***Adhesion* (attractions between unlike molecules, adhesive forces)**

Surface tension

- Molecules at the top are only pulled inside by other molecules
- There is no upward pull to balance the downward pull
- This results in a net pull inward on surfaced molecules

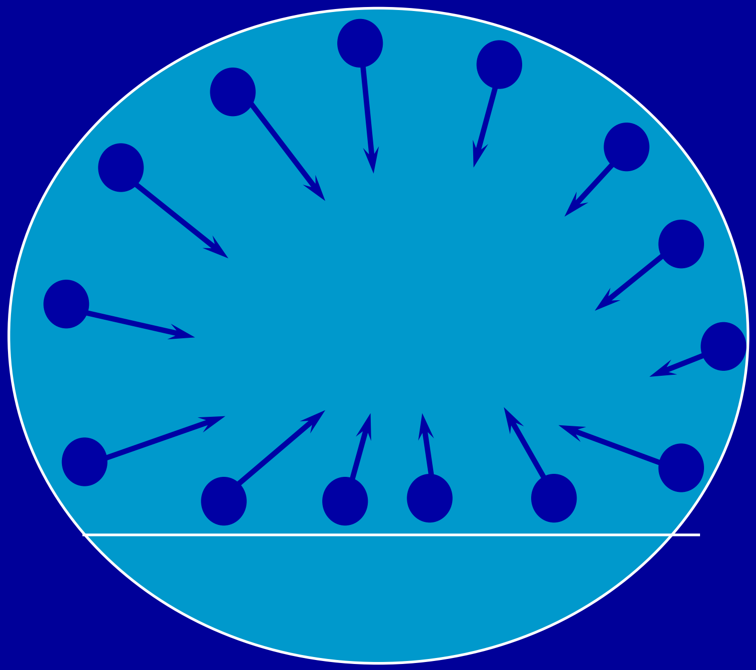
- Molecules in the middle are attracted in all directions.



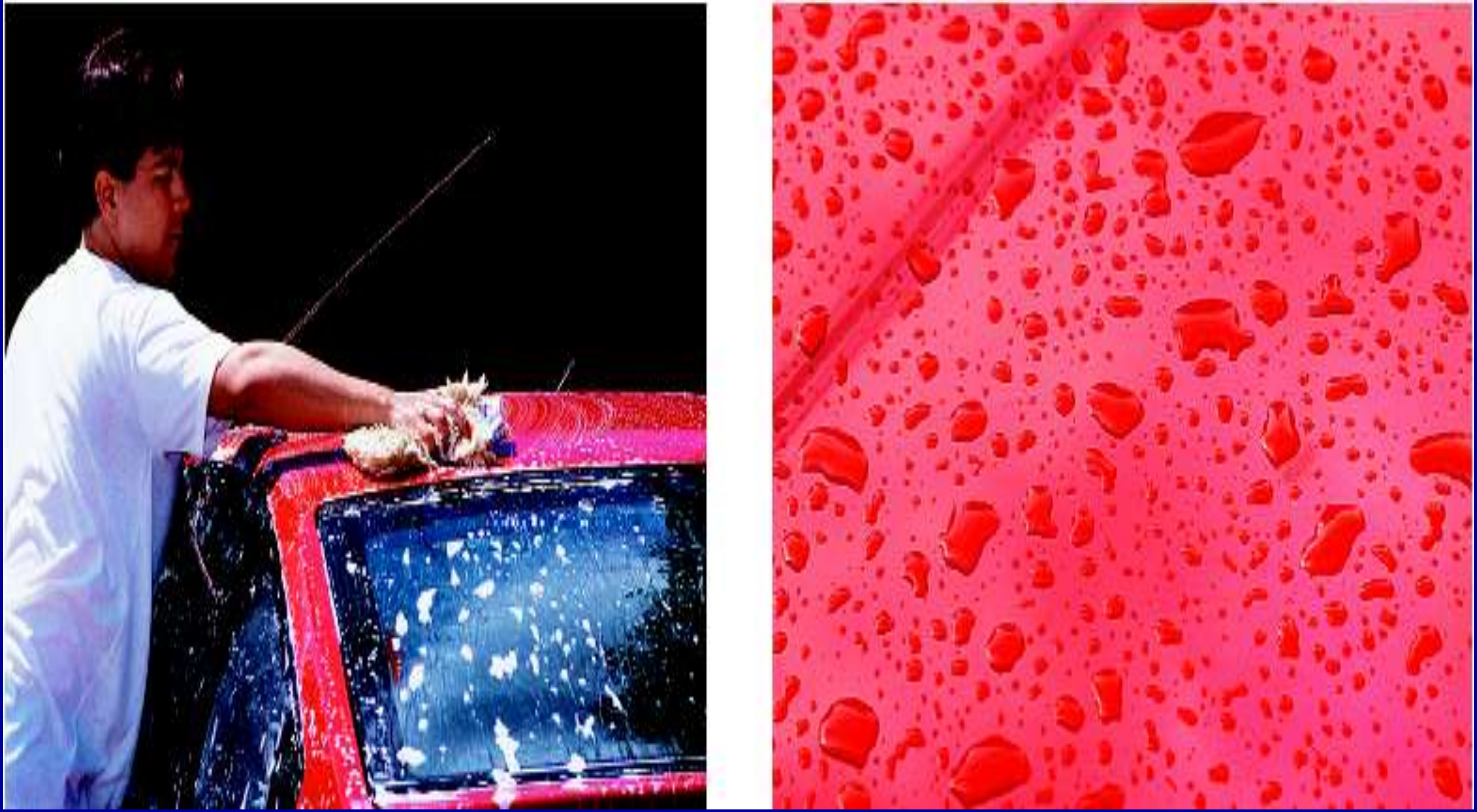
- Minimizes surface area.

Beading

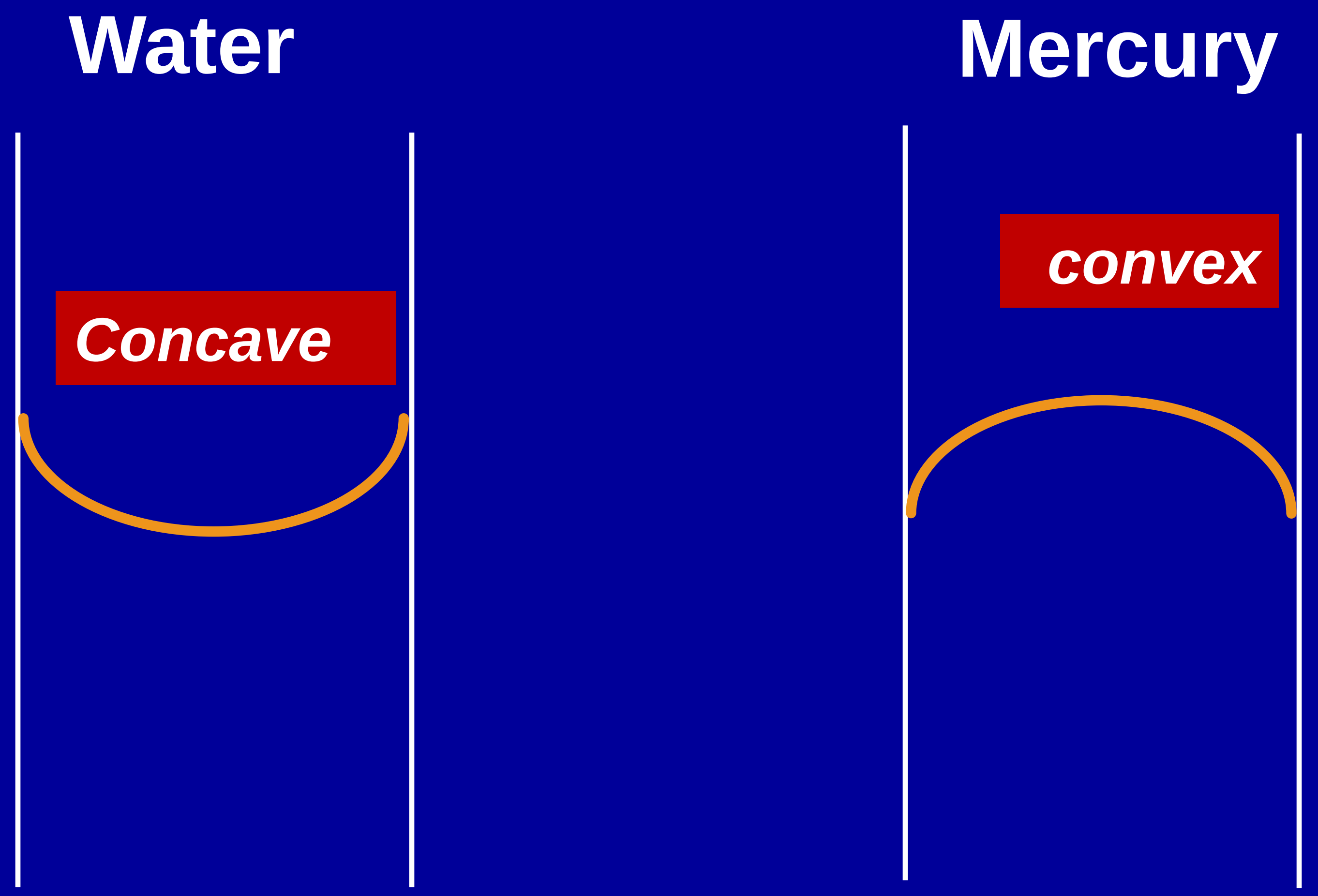
- A polar substance is placed on a non-polar surface.



Effect of Surface Tension



Meniscus



Water

Concave

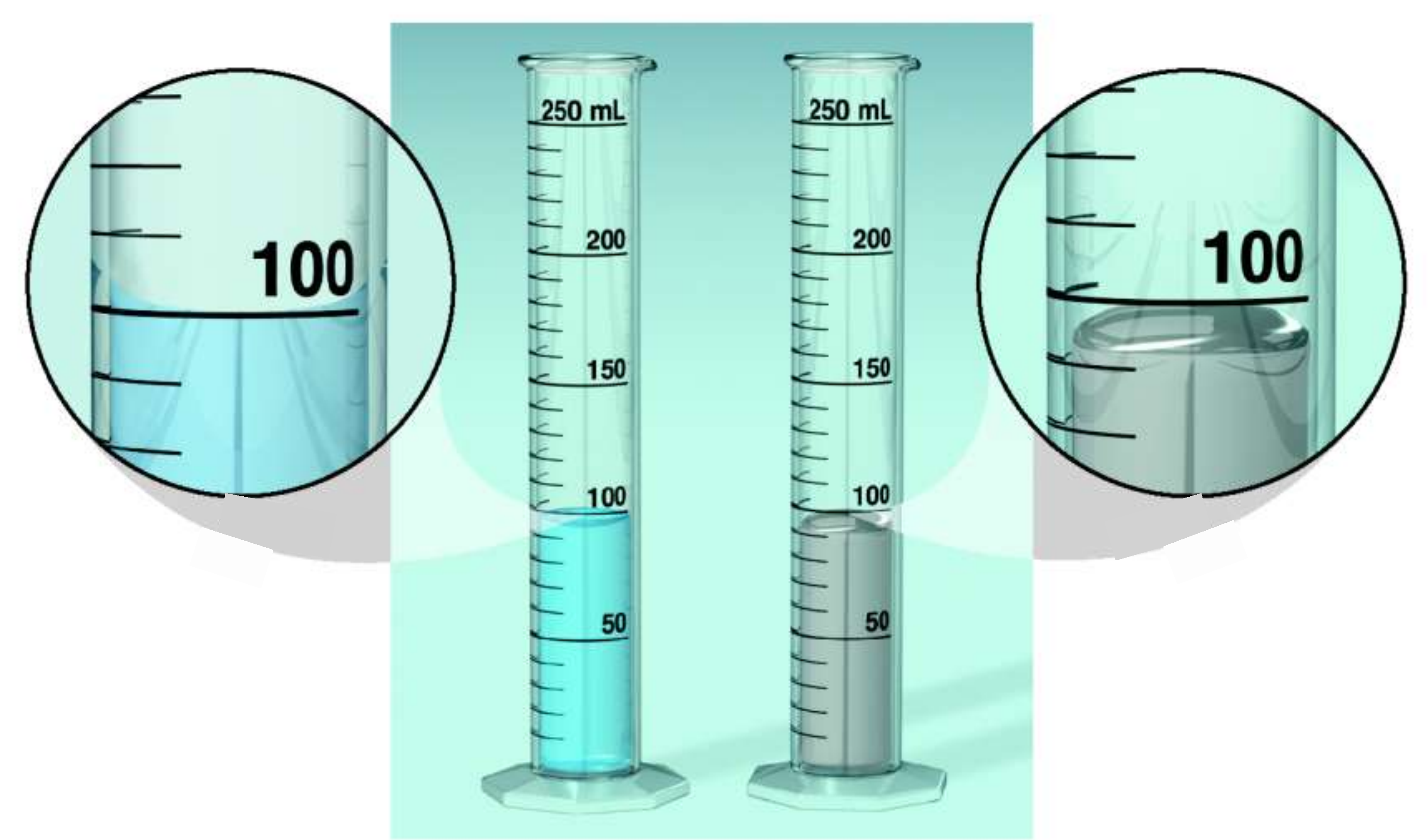
Mercury

convex

Adhesive forces **are intermolecular forces between unlike molecules**

Cohesive forces **are intermolecular forces between like molecules**

Meniscus formation

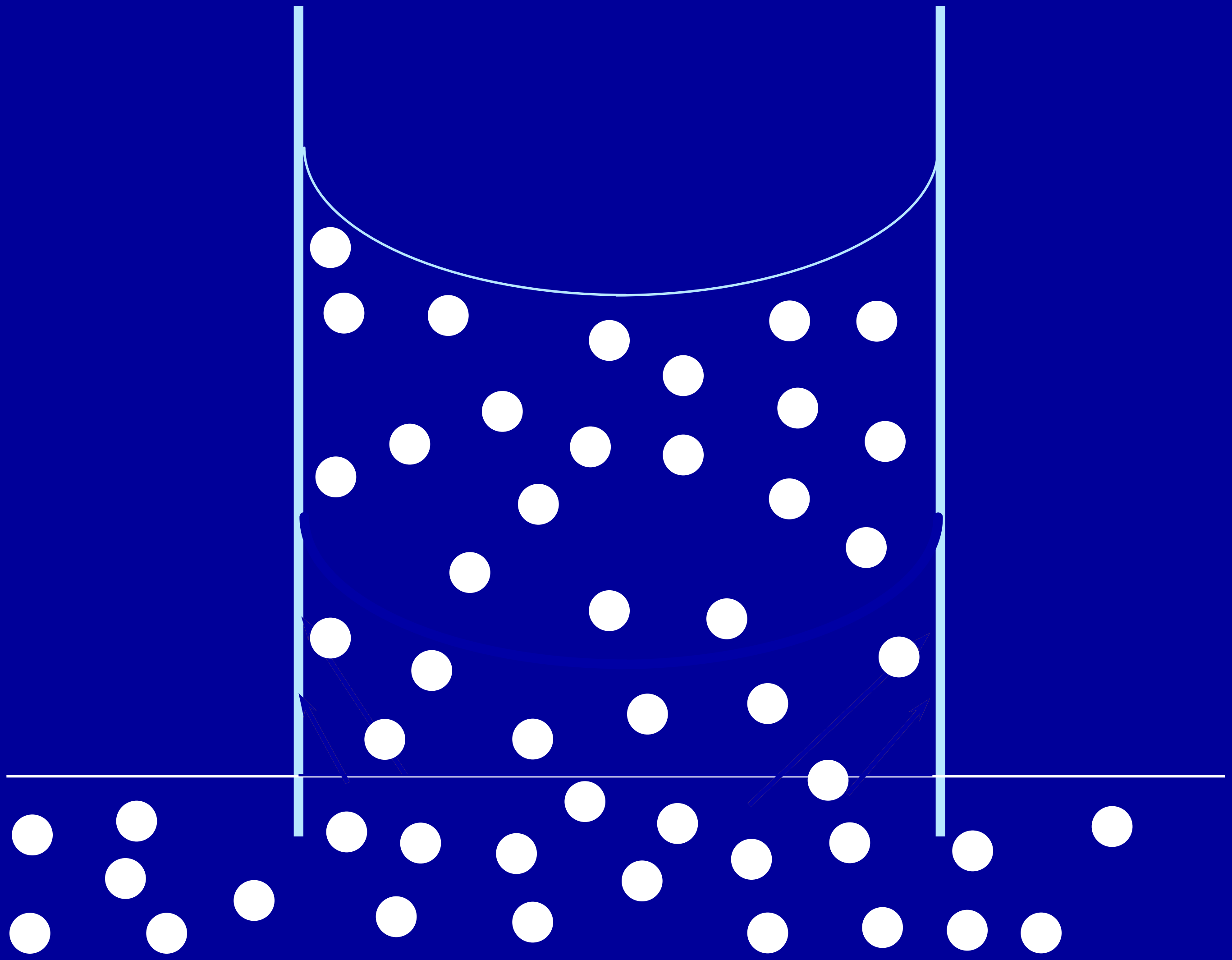


Adhesion > Cohesion

Cohesion > Adhesion

Capillary Action

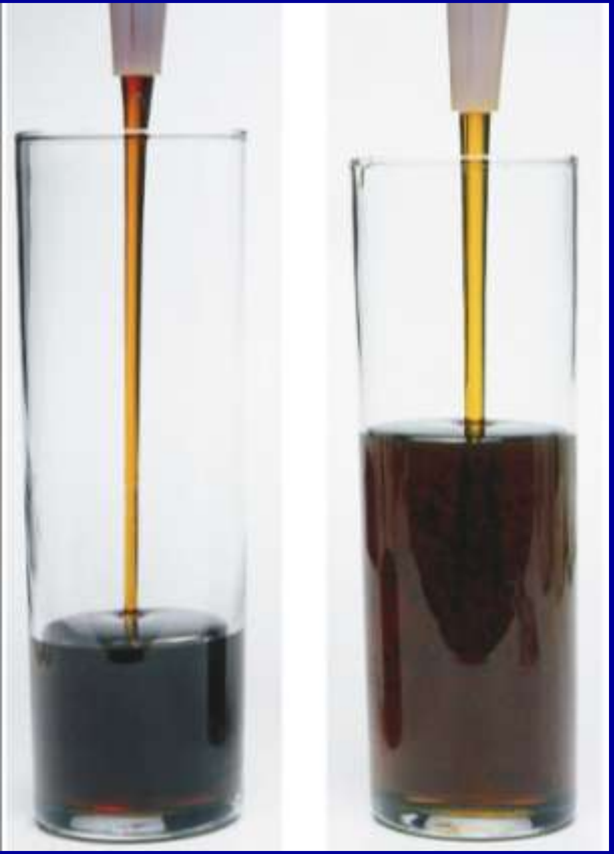
- Capillary action results from intermolecular interactions
- Liquids spontaneously rise in a narrow tube.
- Glass is polar.
- It attracts water molecules (adhesive forces)



Viscosity

- *Viscosity* is a measure of a fluid’s resistance to flow
  - Units: N·s/m^2
  - The higher the viscosity the greater the resistance to flow
  - It varies inversely with temperature

Viscosity



– strong inter molecular forces → highly viscous
– large, complex molecules → highly viscous
– Cyclohexane has a lower viscosity than hexane.
– Because it is a circle- more compact.

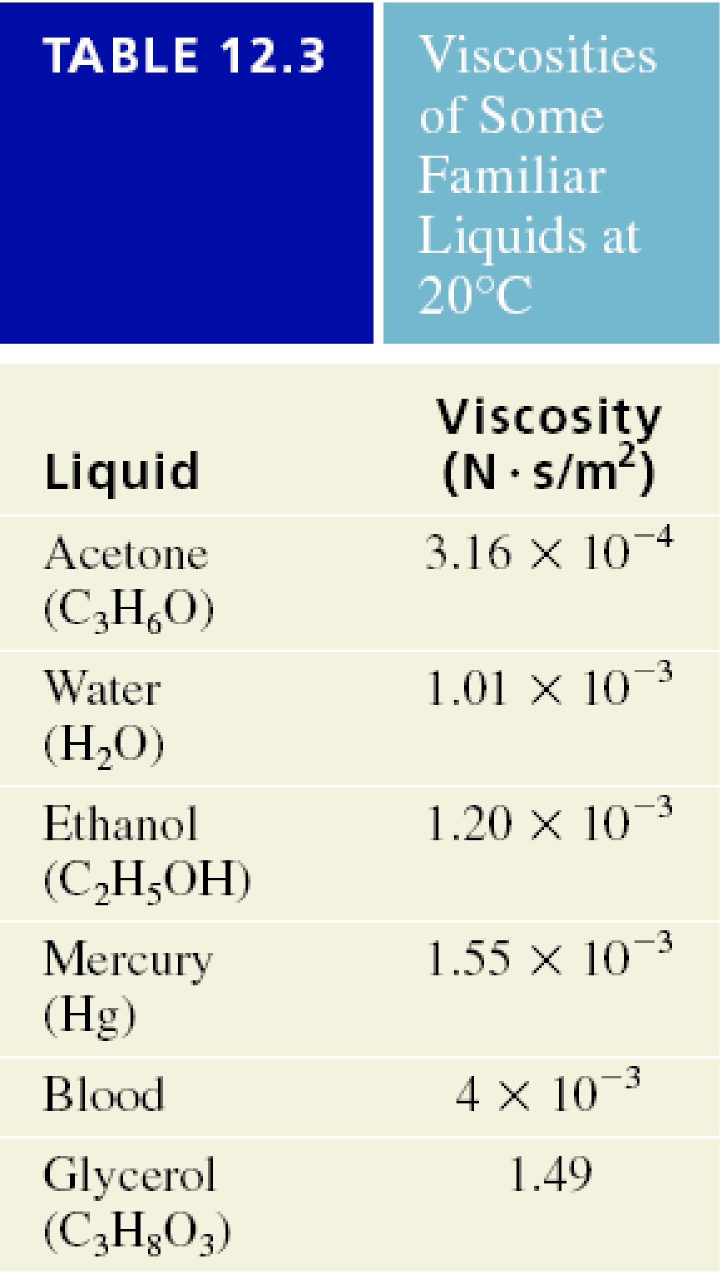
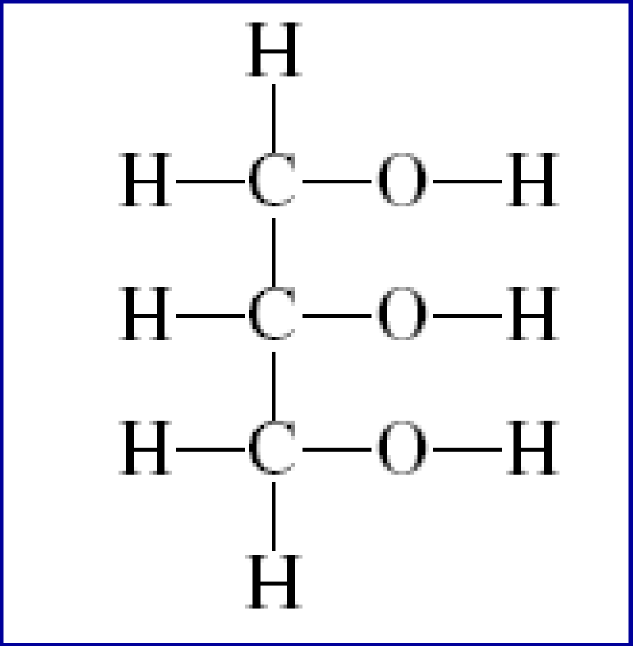


TABLE 12.3 Viscosities of Some Familiar Liquids at 20°C

Liquid	Viscosity $(N \cdot s/m^2)$
Acetone (C_3H_6O)	3.16×10^{-4}
Water (H_2O)	1.01×10^{-3}
Ethanol (C_2H_5OH)	1.20×10^{-3}
Mercury (Hg)	1.55×10^{-3}
Blood	4×10^{-3}
Glycerol ($C_3H_8O_3$)	1.49

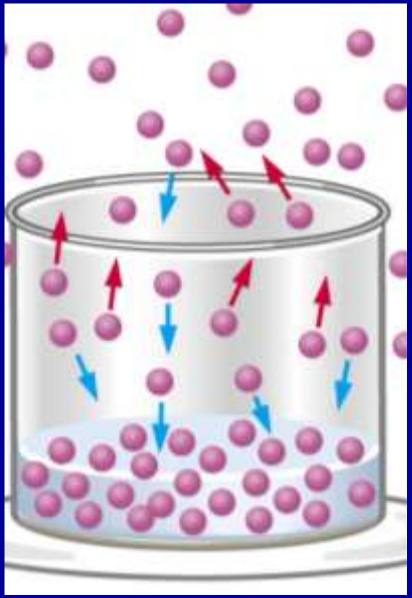


Glycerol – high viscocity due to

- **Three hydrogen bonding sites**
- **Molecular shape**

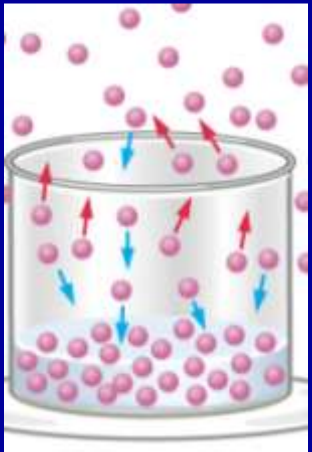
Vapor Pressure

- **vapor-** gas phase above a substance that exists as solid or liquid at 25°C and 1 atm.
- **Vaporization or Evaporation** - change from liquid to gas at or below the boiling point . (Endothermic process)
- **Condensation** is the change of a gas to a liquid (Exothermic process)



Vapor pressure

- **Initially, a liquid in a closed container decreases as molecules enter gaseous phase**
- **When equilibrium is reached, no more net change occurs**
- **Rate of condensation and rate of vaporization become equal**
- Molecules still are changing phase but no net change (Dynamic equilibrium)
  - Gas $\rightleftharpoons$ liquid



Vapor pressure is independent of volume of container as long as some liquid is present (liquid-vapor equilibrium)

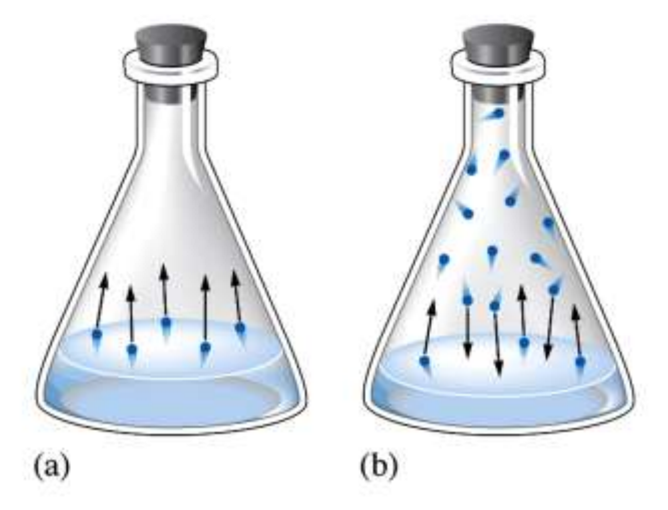
Evaporation and condensation

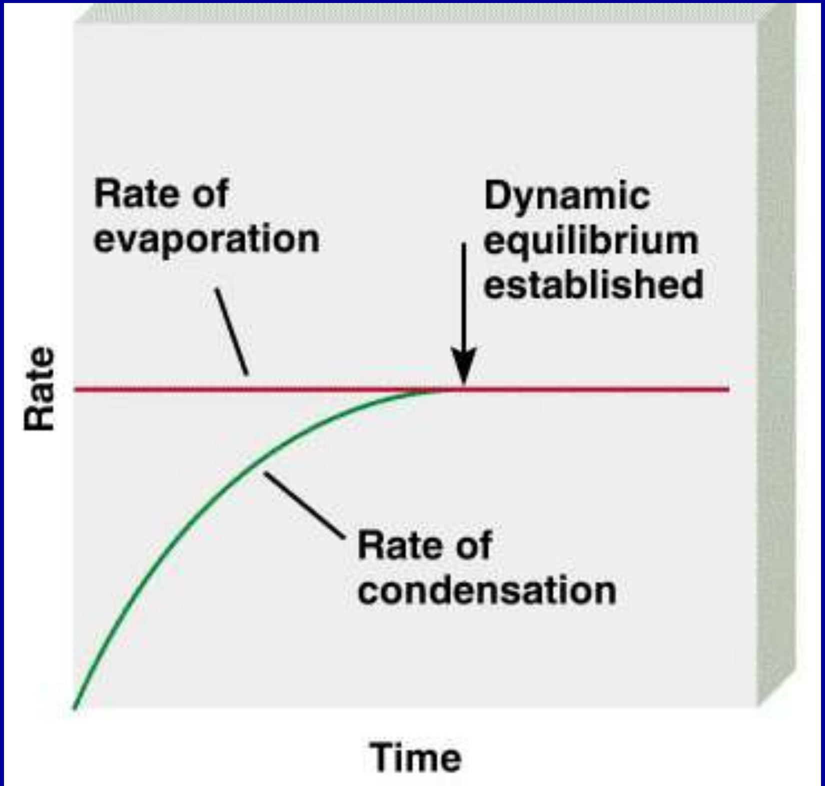
Initially evaporation occurs more rapidly than condensation. Consequently vapor pressure will increase; the rate of condnesationWill increase as well.

$$H_2O\ (l) \rightleftharpoons H_2O\ (g)$$

Dynamic Equilibrium

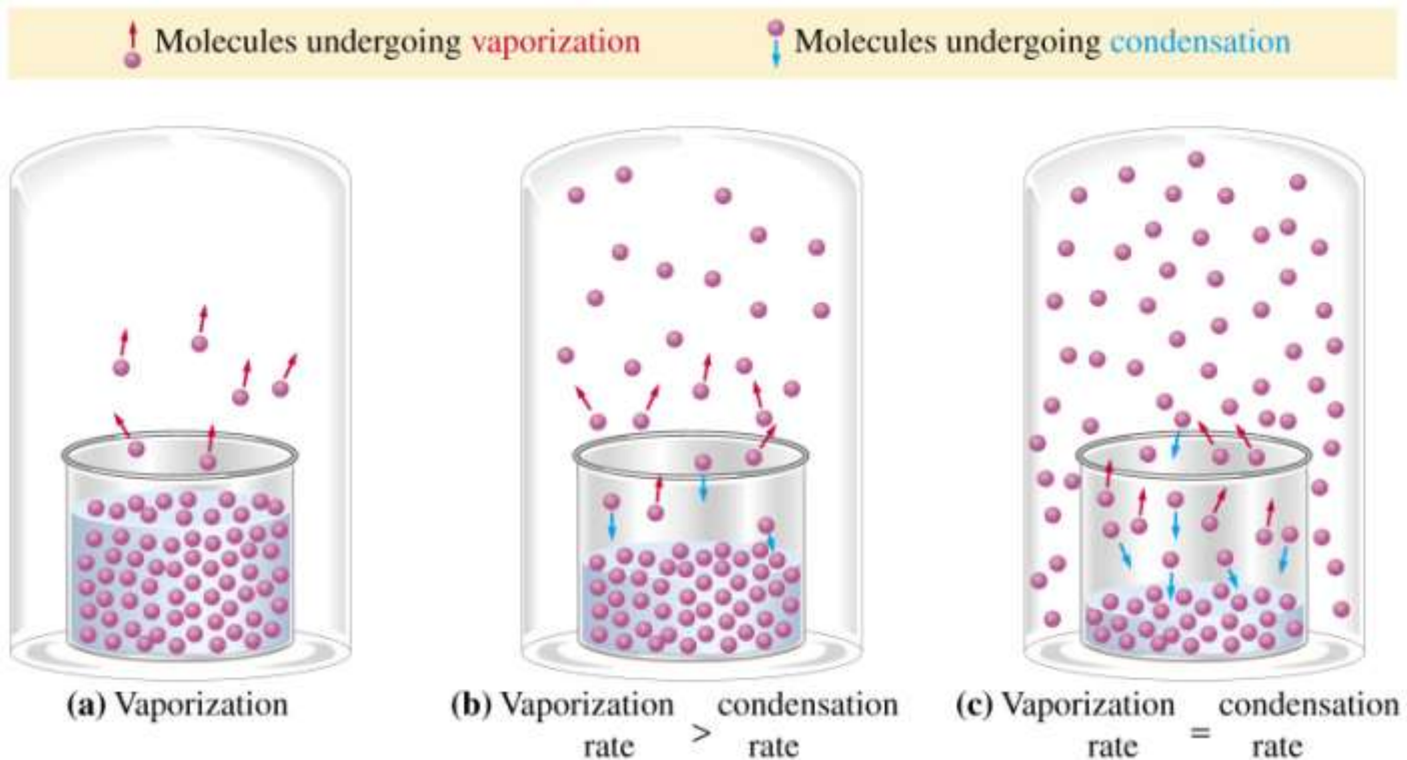
Rate of condensation = Rate of evaporation





Equilibrium vapor pressure or vapor pressure

It is the pressure exerted by the vapor when the vapor is in dynamic equilibrium with the liquid at a constant temperature.



Vapor pressure and nature of liquids

- Vapor pressure depends upon the **nature of the liquid and consequently on the intermolecular forces.**
- Liquids with high vapor P (volatile liquids)
  - – evaporate quickly
  - – weak intermolecular forces
- Liquids with low vapor P
  - – Strong London dispersion forces (large molar masses) or dipole-dipole forces

Vapor pressure and temperature

- Vapor pressure increases with T
- More molecules have enough KE to overcome intermolecular forces

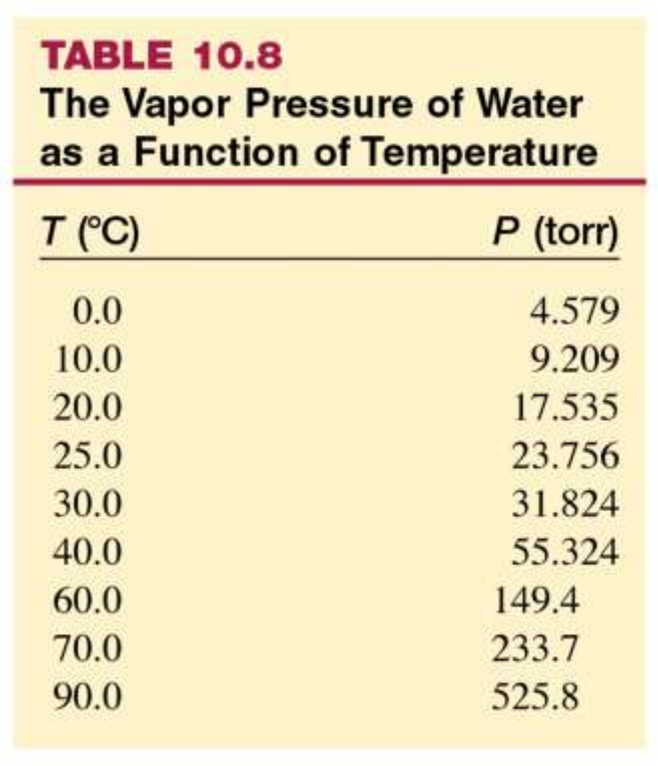
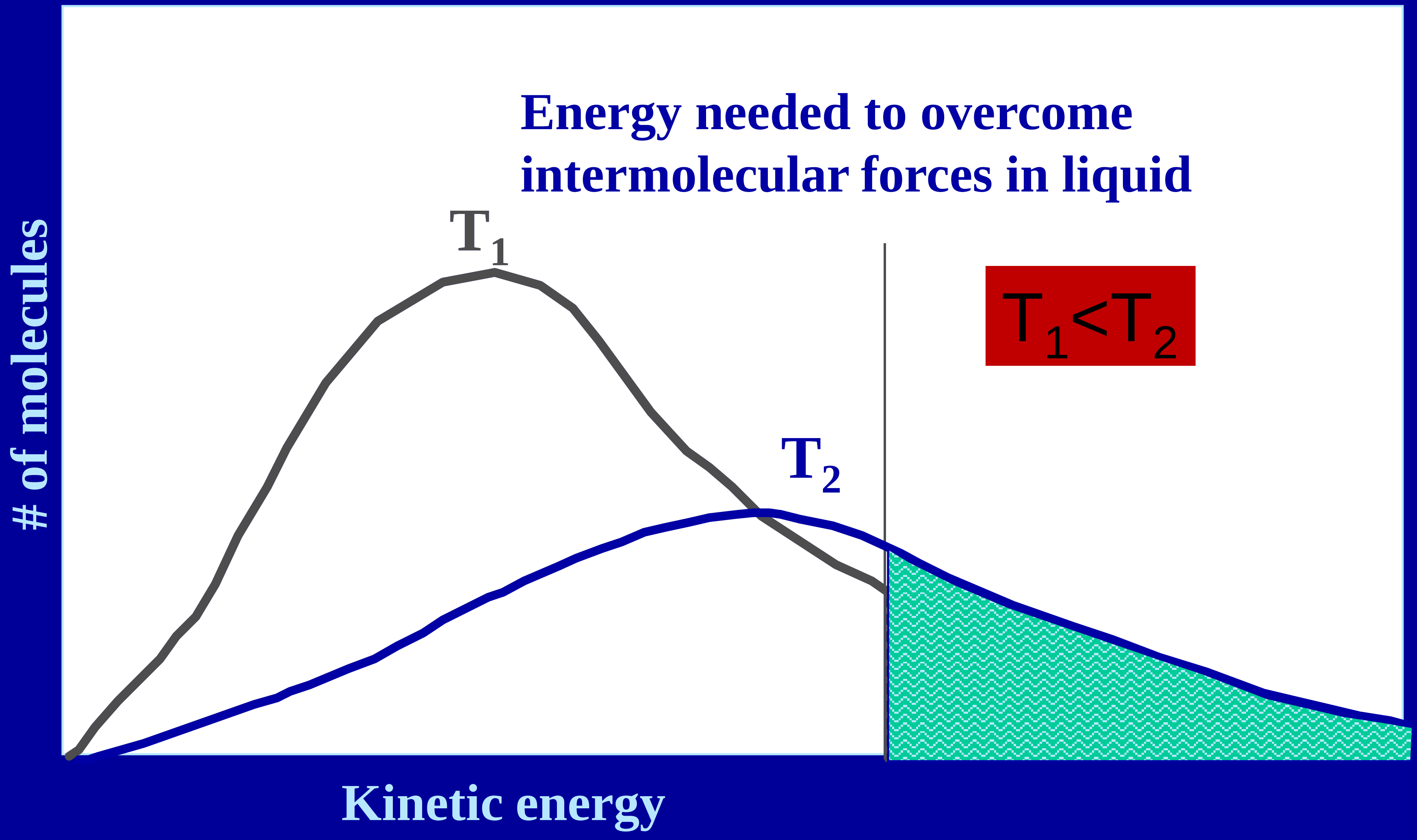


TABLE 10.8

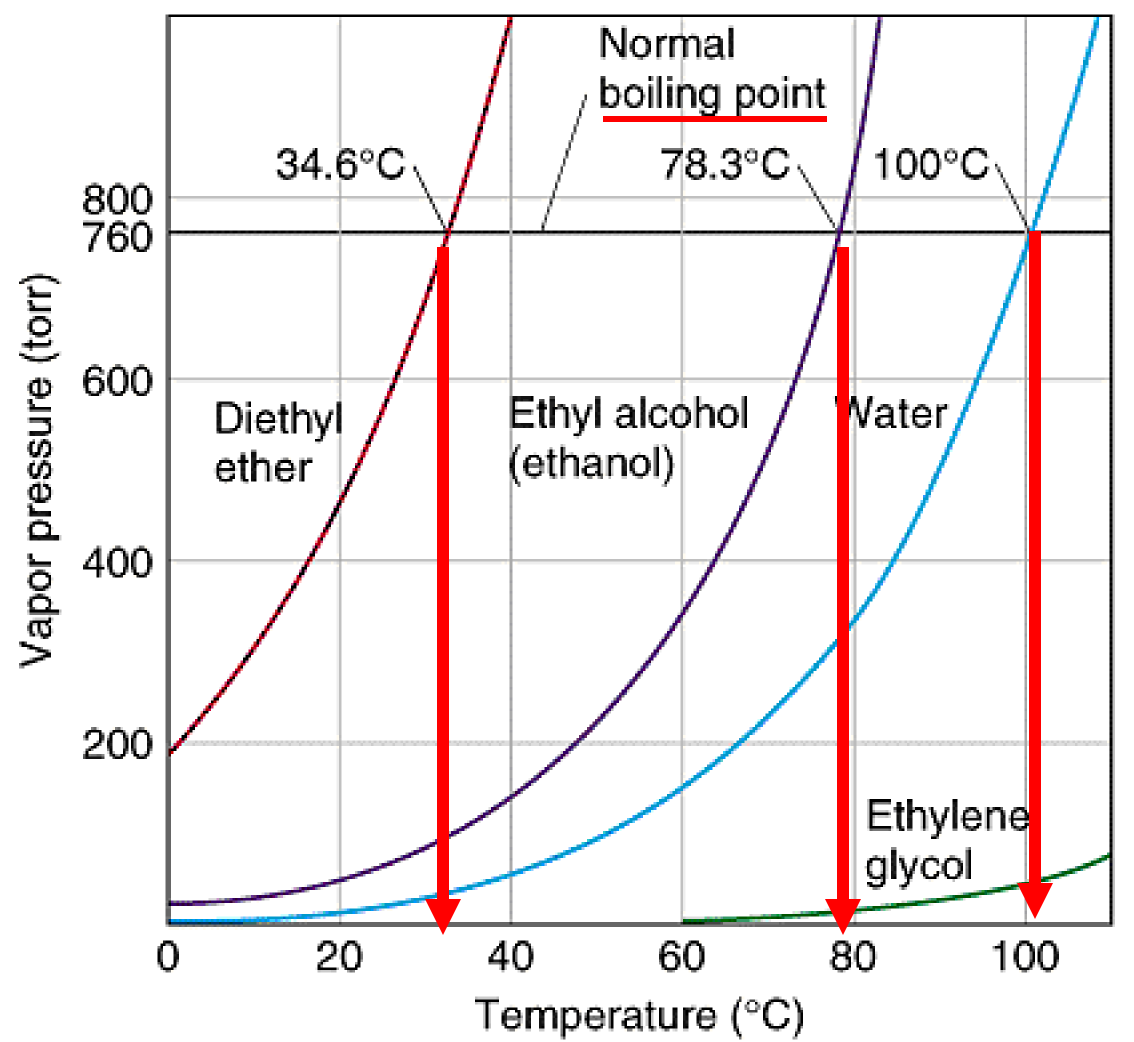
The Vapor Pressure of Water as a Function of Temperature

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

- **At higher temperature more molecules have enough energy - higher vapor pressure.**



VAPOR PRESSURE CURVES



A liquid boils when its vapor pressure = external pressure.

Clausius-Clapeyron Equation

(linear relation between temperature and vapor pressure

$$\ln P = \left(-\frac{\Delta H_{\text{vap}}}{R}\right)\left(\frac{1}{T}\right) + C$$

$$y \quad = \qquad\qquad mx \qquad\qquad + \; b$$

where R = 8.314 J/K · mol

- At two temperatures, T_1 and T_2

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

An unknown compound exhibits a vapor pressure of 255 mmHg at 25.5°C and 434 mmHg at 48.8°C. What is ΔH_{vap} of this substance?

$$T_1 = 25.5^o\,\mathrm{C} + 273.15 = 298.65\ \mathrm{K}$$

$$T_2 = 48.8^o\,\mathrm{C} + 273.15 = 321.95\ \mathrm{K}$$

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

$$\ln\frac{255\ \mathrm{mmHg}}{434\ \mathrm{mmHg}} = \frac{\Delta H_{vap}}{8.314\mathrm{J/K\cdot mol}}\left(\frac{1}{321.95\ \mathrm{K}} - \frac{1}{298.65\ \mathrm{K}}\right)$$

$$-0.53178 = \frac{\Delta H_{vap}}{8.314\mathrm{J/K\cdot mol}}\left(3.1061\mathrm{x}10^{-3} - 3.3484\mathrm{x}10^{-3}\right)$$

$$-0.53178 = \frac{\Delta H_{vap}}{8.314\,\mathrm{J/K \cdot mol}}\left(-2.423\mathrm{x}10^{-4}\ \mathrm{K}^{-1}\right)$$

$$\frac{(-0.53178)(8.314\,\mathrm{J/K \cdot mol})}{-2.423\mathrm{x}10^{-4}\ \mathrm{K}^{-1}} = \Delta H_{vap}$$

$$1.82 \times 10^{4}\ \mathrm{J/mol} = \Delta H_{\mathrm{vap}}$$

$$18.2\ \ \mathrm{kJ/mol} = \Delta H_{\mathrm{vap}}$$

10.3 Crystal Stucture

Types of Solids

- **Crystalline Solids**: highly regular three dimensional arrangement of their components [table salt (NaCl)]
  - Rigid or longrange order; its atoms, molecules or ions occupy specific positions

- **Amorphous solids**: considerable disorder in their structures (glass: components are frozen in place before solidifying and achieving an ordered arrangement)

- The arrangement of particles in a crystalline solid are usually called lattice structure

- The arrangement of particles in a crystalline solid are usually called lattice structure

- Lattice structure depends upon:
  - Nature of particles involved
  - Size of particles involved

- Forces responsible for stability of the crystal are:
  - Ionic forces
  - Covalent bonds
  - Van der Waals forces
  - Hydrogen bonds

Or a combination of some of them

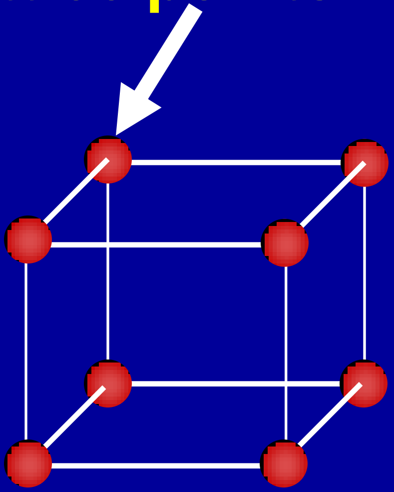
Unit Cells

Representation of Components in a Crystalline Soli

- **Lattice**: A 3-dimensional system that describes the locations of components (atoms, ions, or molecules) that make up the unit cells of a substance.

- **Unit Cell**: The smallest (basic) repeating unit in the lattice.
- Spheres shown on the Unit cell are called lattice points (atoms, ions or molecues)

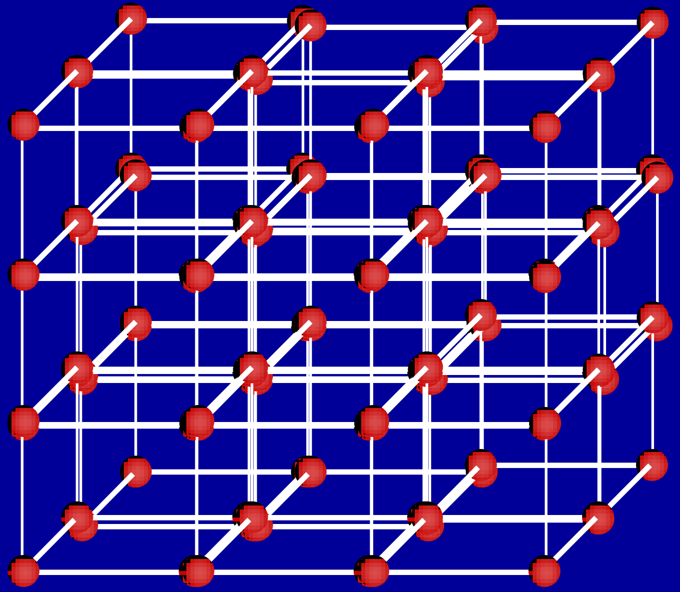
Unit cell



lattice points

At lattice points:

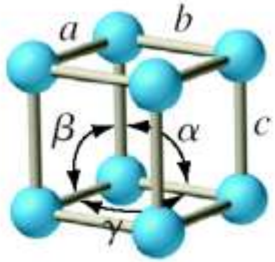
- Atoms
- Molecules
- Ions



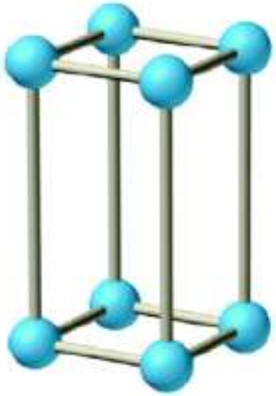
Unit cells in 3 dimensions

The simple cubic cell is the simplest unit cell and has structural particles centered only at its corners

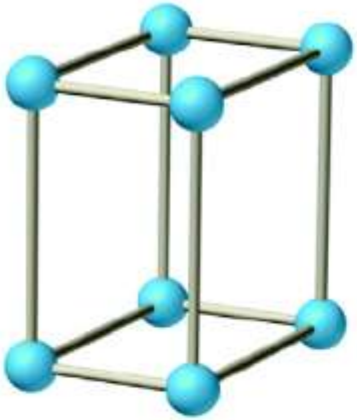
Seven Types of Unit Cells



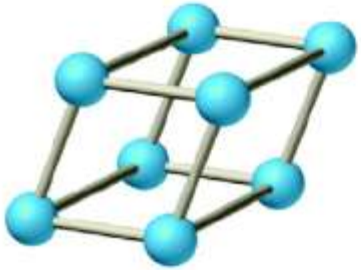
Simple cubic
$a = b = c$
$\alpha = \beta = \gamma = 90^\circ$



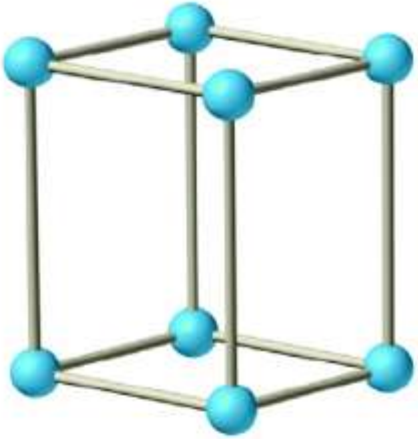
Tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90^\circ$



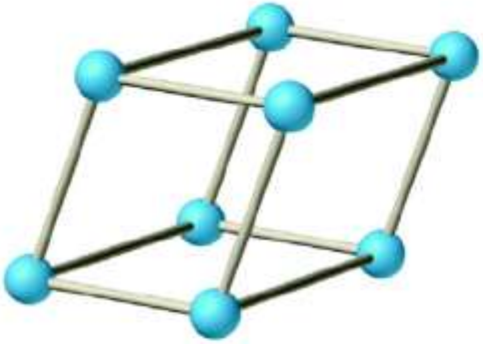
Orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90^\circ$



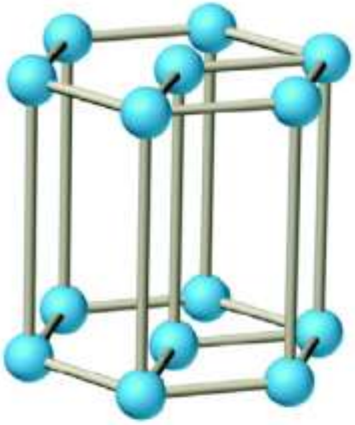
Rhombohedral
$a = b = c$
$\alpha = \beta = \gamma \neq 90^\circ$



Monoclinic
$a \neq b \neq c$
$\gamma \neq \alpha = \beta = 90^\circ$



Triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90^\circ$

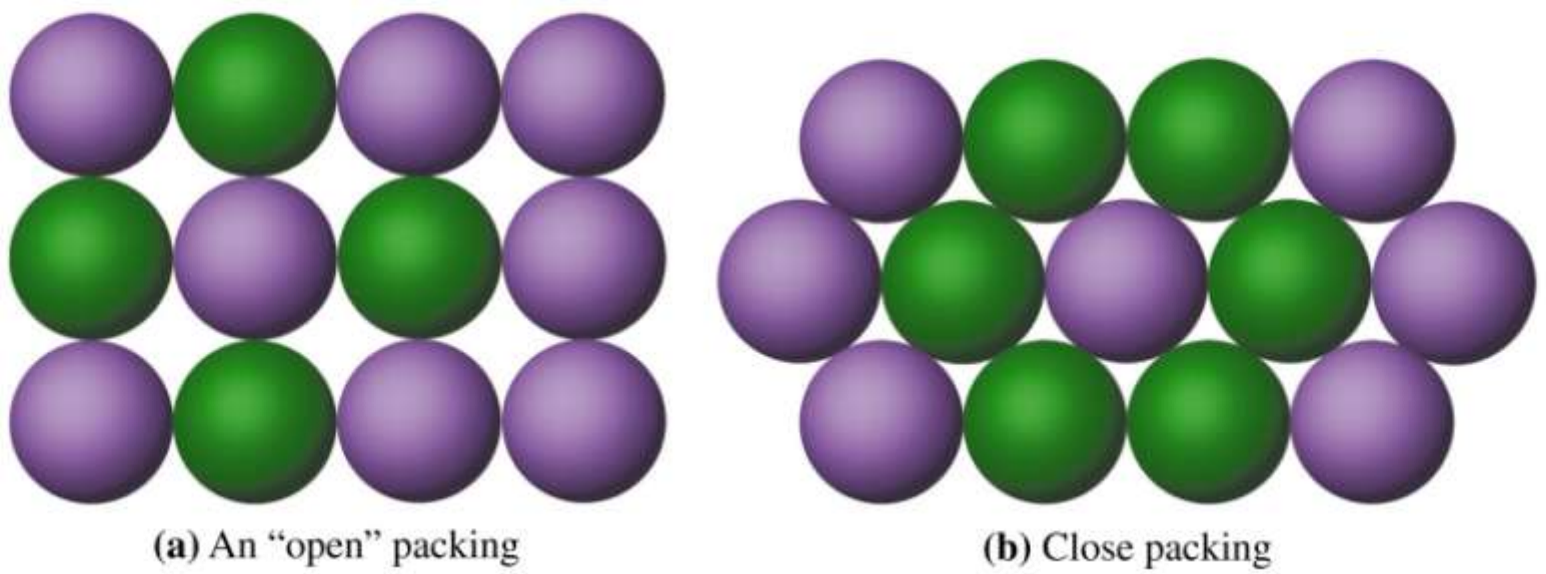


Hexagonal
$a = b \neq c$
$\alpha = \beta = 90^\circ, \gamma = 120^\circ$

Packing spheres

- The way the atoms are arranged to form an ordered three-dimensional structure is called packing
- The type of unit cell is determined by the way the atoms are packed or arranged in layers

Packing in Crystals



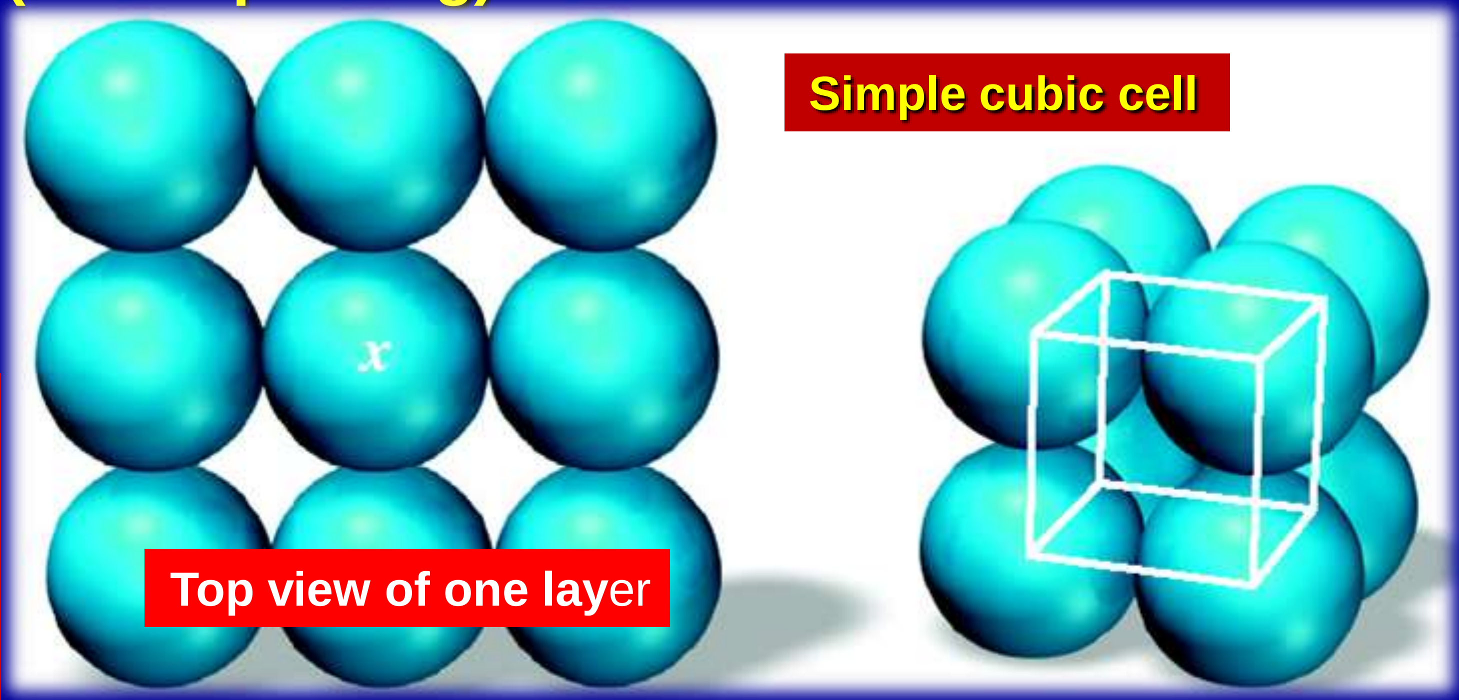
(a) An "open" packing

(b) Close packing

Open" packing has larger voids in between particles compared to close-packed crystals

Coordination number

- Number of atoms (particles) surrounding an atom in a crystal lattice
- coordination number indicates how tightly atoms pack
- Larger coordination numbers indicate tighter packing (closer packing)



Simple cubic cell

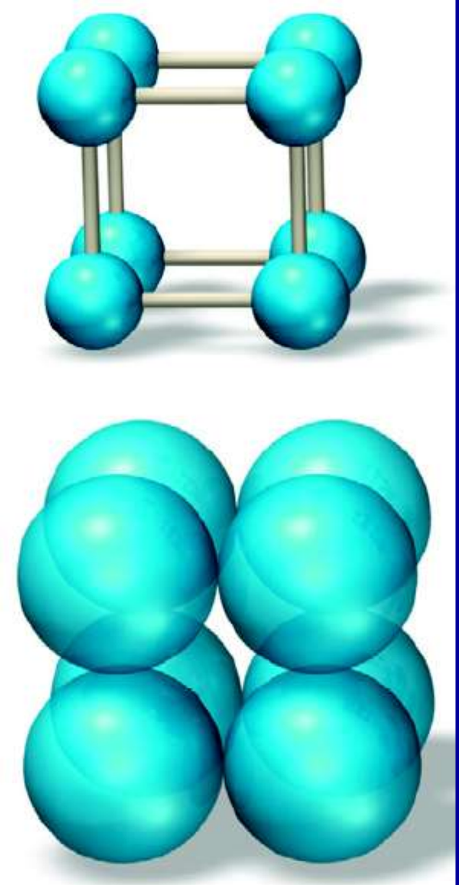
Top view of one layer

coordination number for atom x is 6

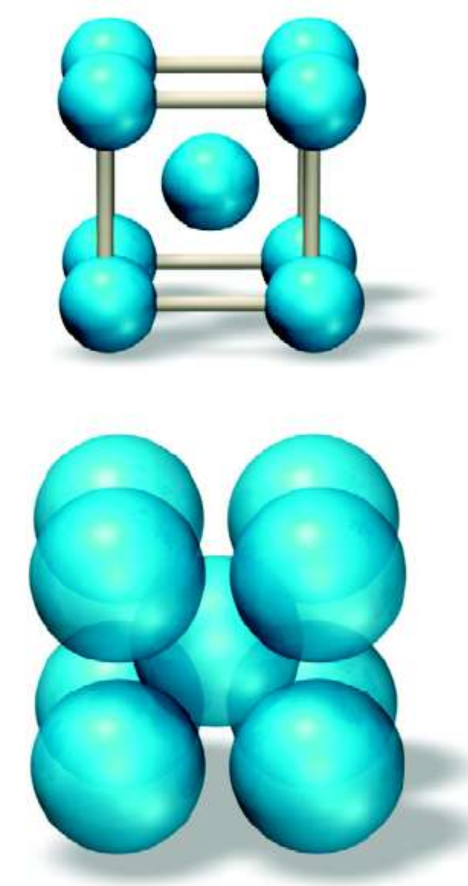
The basic repeating unit in this case is Simple cubic cell

Types of cubic unit cells

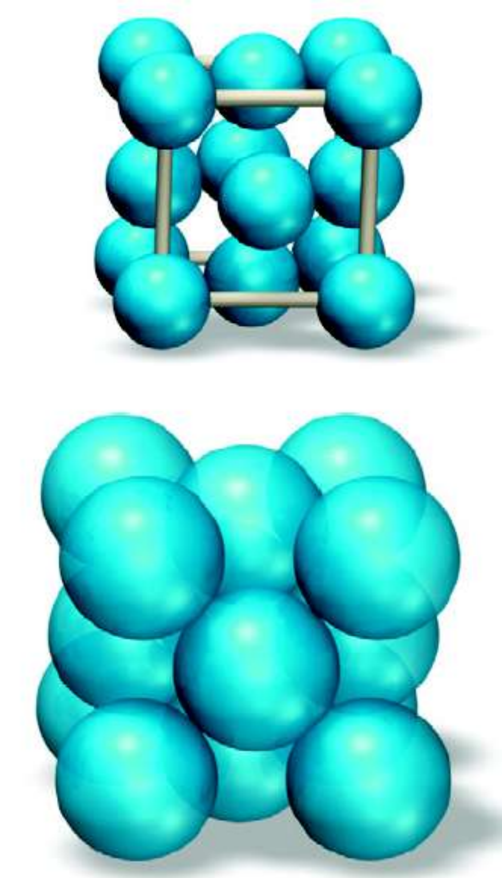
- simple or primitive (scc)
- body-centered (bcc)
- face-centered (fcc)



Primitive cubic

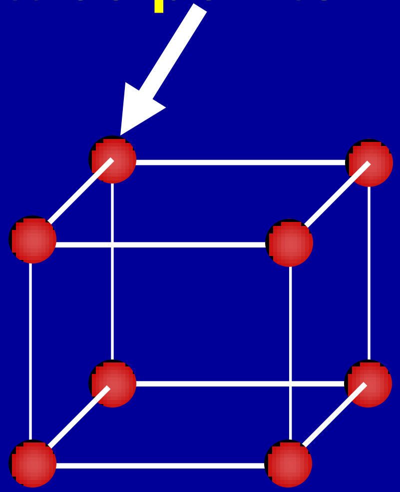


Body-centered cubic



Face-centered cubic

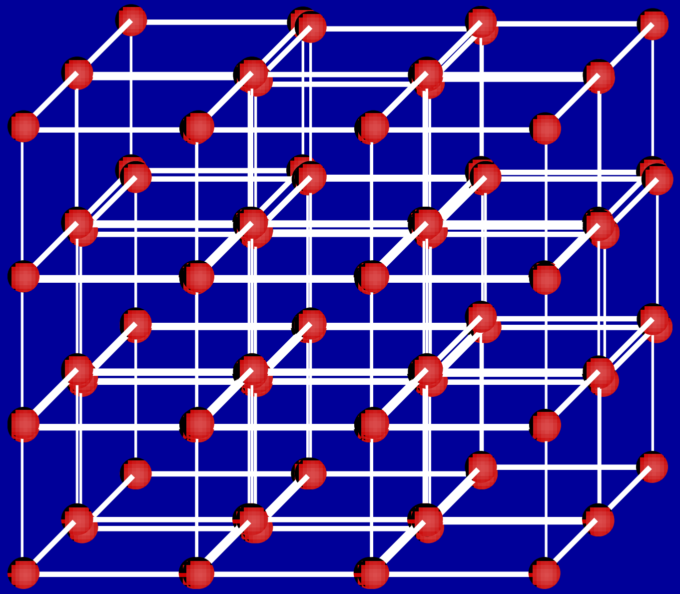
Primitive Cubic



Coordination number is 6

Each atom is attached to 4 atoms in the same layer

One in the layer above and one in the layer below

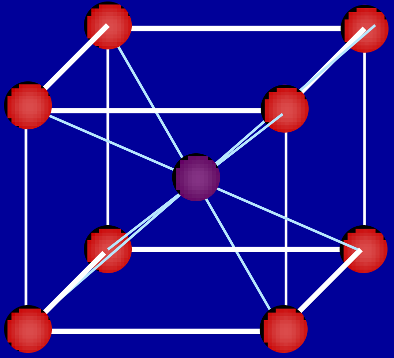


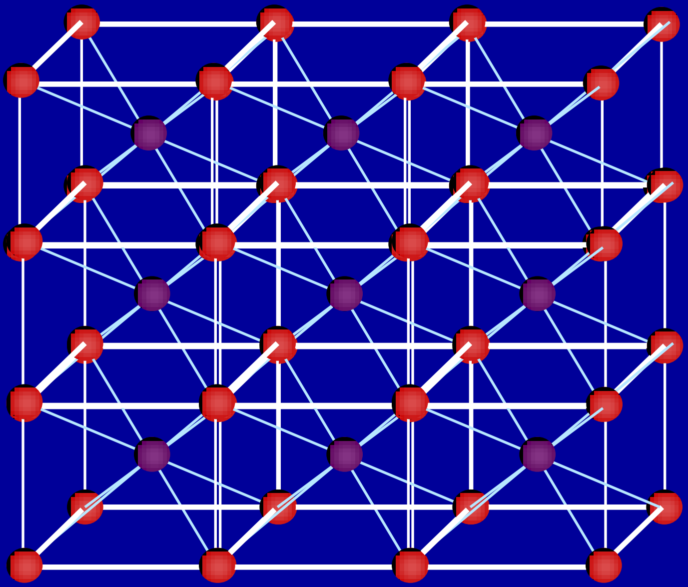
Unit cells in 3 dimensions

The simple cubic cell is the simplest unit cell and has structural particles centered only at its corners

Body-Centered Cubic, bcc

Unit cells in 3 dimensions





The **body-centered cubic**

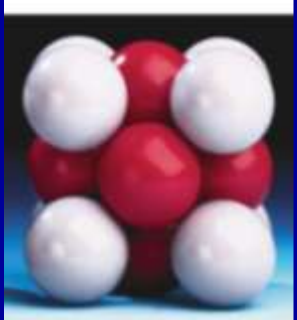
(bcc) structure has an additional structural particle at the **center of the cube**

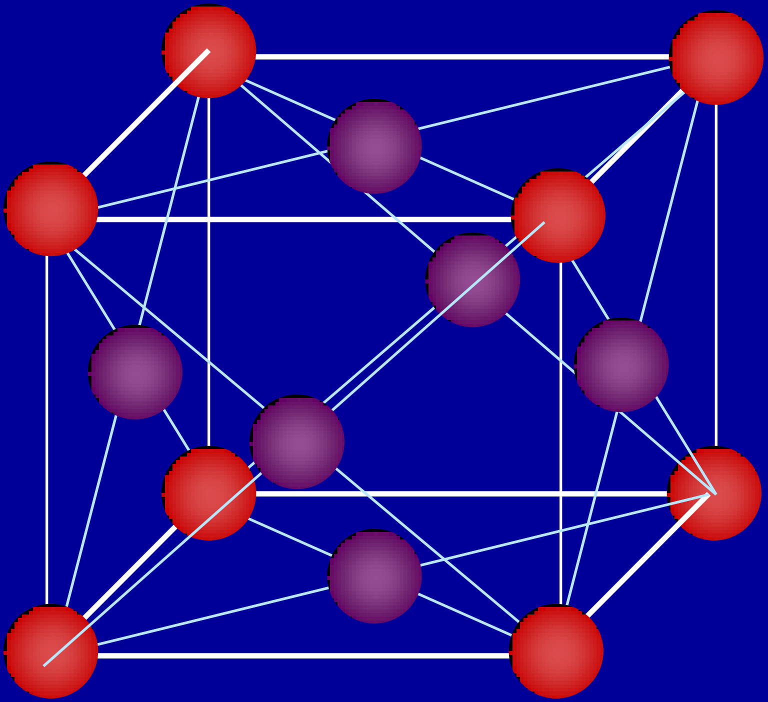
Coordination number is 8

Each atom is in contact of 4 in the layer above and 4 in the layer below

Face-Centered Cubic

The **face-centered cubic (fcc)** structure has an additional structural particle at the **center of each face**





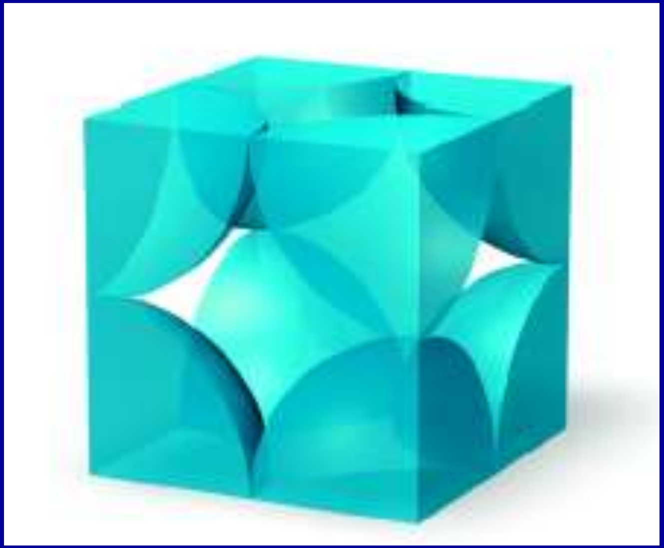
Coordination number is 12

Each atom is in contact of 4 others in its own layer, 4 atoms in the layer above and 4 atoms in the layer below

Allocation of atoms among unit cells

- corner atoms – $^1/_8$ atom within unit cell
- face atoms – $^1/_2$ atom within unit cell
- body atoms – 1 atom within unit cell

- **Number of atoms per unit cell**
  - scc: **1 atom**
  - bcc: **2 atoms**
  - fcc: **4 atoms**



Number of atoms assigned to each type of cell

- **Simple cube**

$$8\ \text{corner atoms}\ \mathrm{X}\ \frac{1}{8} = 1\ \text{atom per cube}$$

- **Body centered cube**

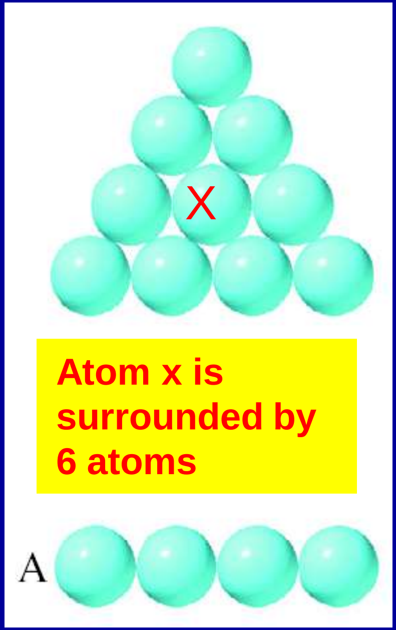
$$8\ \text{corner atoms}\ \mathrm{X}\ \frac{1}{8} + 1\ \text{center atom} = 2\ \text{atoms}$$

- **Face centered cube**

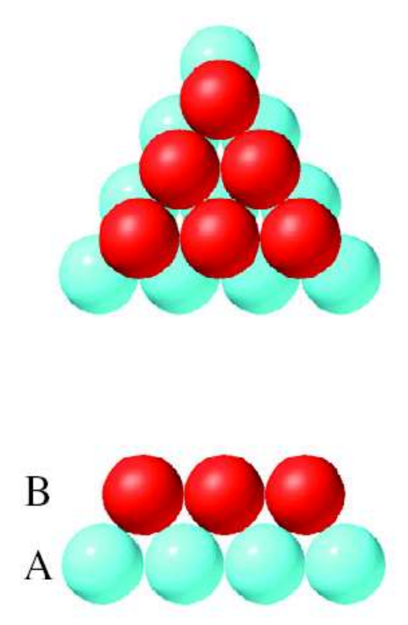
$$8\ \text{corner atoms}\ \mathrm{X}\ \frac{1}{8} + 6\ \text{face atoms}\ \mathrm{X}\ \frac{1}{2} = 4\ \text{atoms}$$

Closest Packing

- most efficient way to arrange atoms in a crystal
  - hexagonal closest packed (ABA)
  - cubic closest packed (ABC)

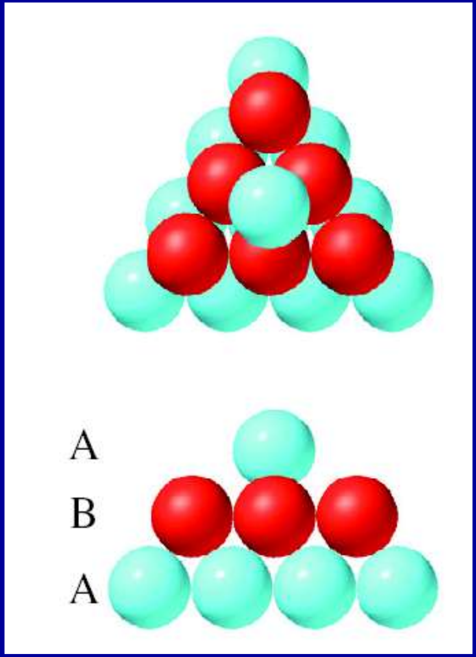


Atom x is surrounded by 6 atoms



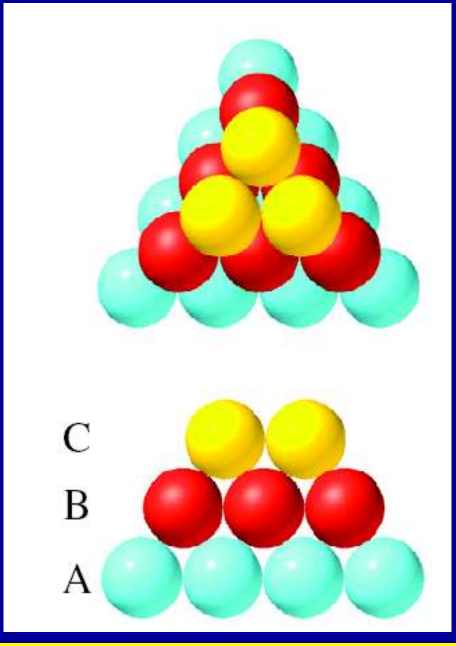
Atoms of the 2nd layer are packed in the depressions of atoms of first layer

All atoms are close together as possible



Atoms of the 3rd layer are packed in the depressions of atoms of 2nd layer

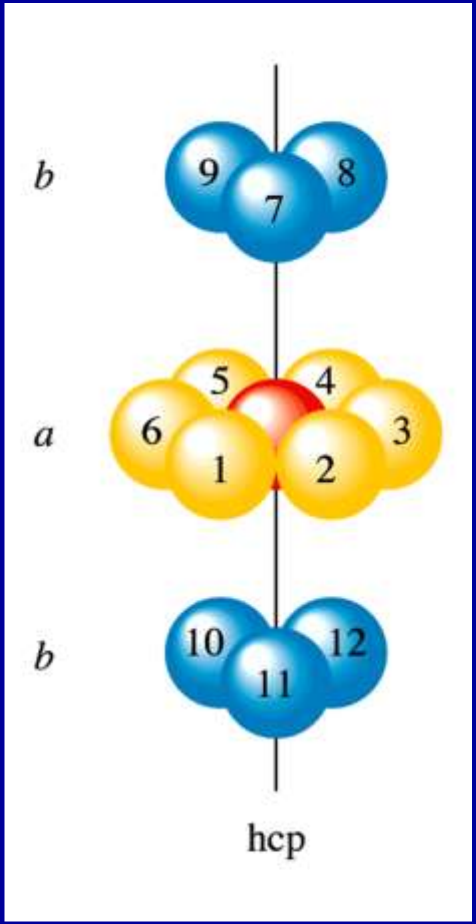
Atoms of 3rd layer set directly above those of the 1st

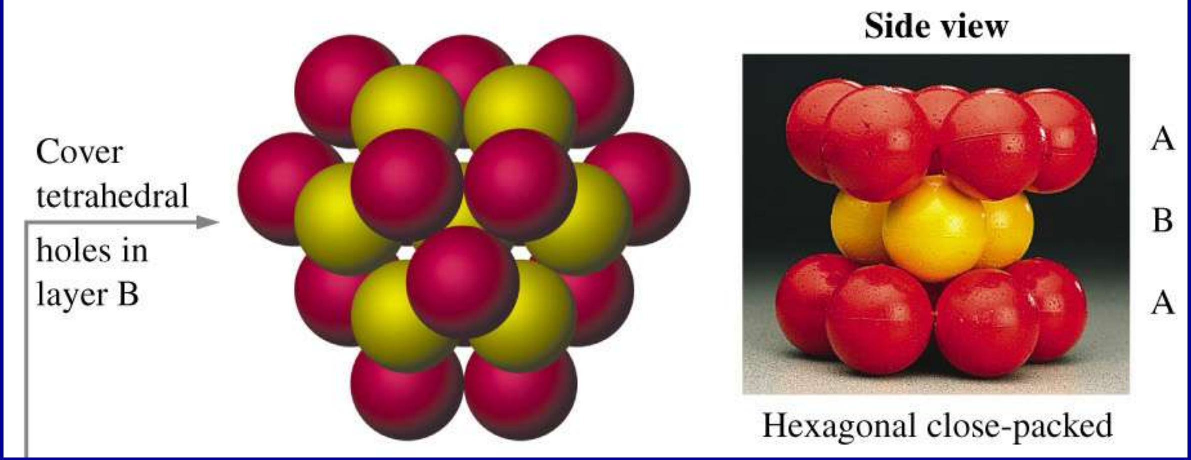


Atoms of the 3rd layer are packed in different set of depressions. They do not lie directly above those of the 1st

Hexagonal close-packed (hcp) structure

It has (aba) arrangements that occur when the spheres of the third layer occupy positions so that each sphere in the third layer lies directly over a sphere in the first layer



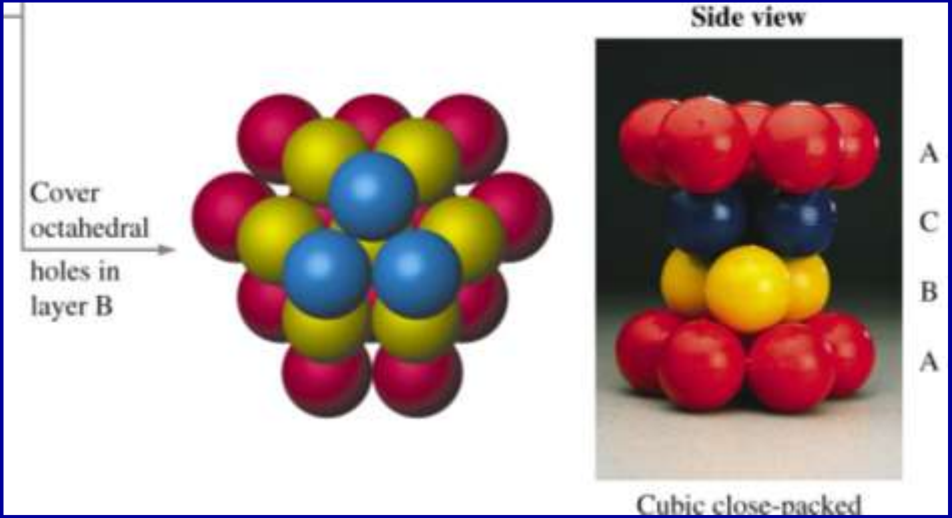


Hexagonal close-packed

Each sphere has a coordination number of 12.
6 in the same layer 3 above and 3 b3low.

Cubic close-packed (ccp) structure

It has (abc) arrangement that occurs when the spheres of the third layer occupy positions that **NO** sphere lies over one in the first layer



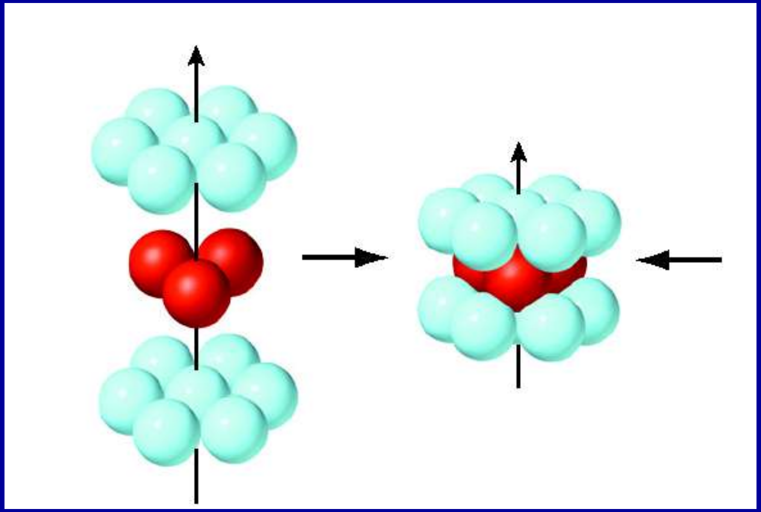
An atom in every fourth layer lies over an atom in the First layer

Each sphere has a coordination number of 12. 6 in the same layer 3 above and 3 b3low.

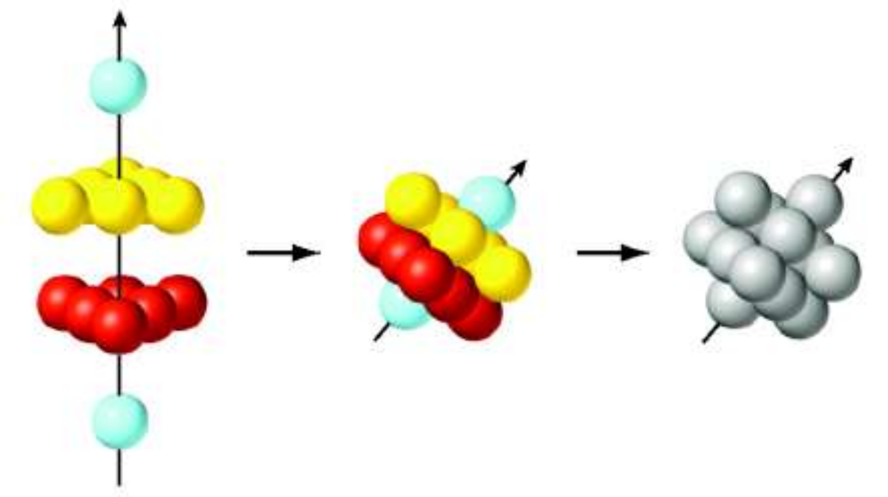
Each substance will crystallize with the arrangement that maximizes its stability

Closest Packing and Cubic Unit Cells

hexagonal



cubic

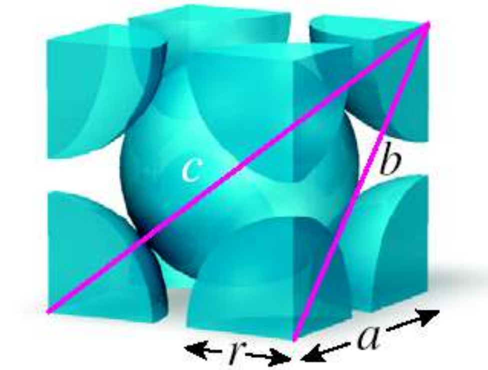


fcc

Geometric Relationships

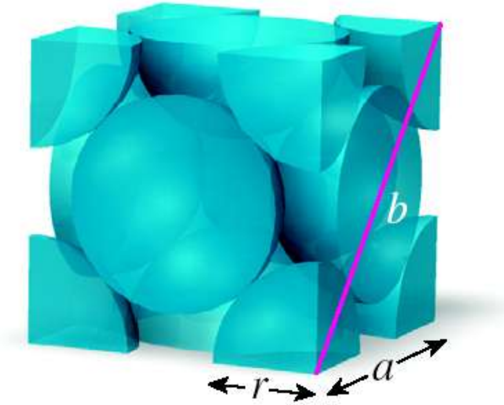
scc

$$a = 2r$$



bcc

$$b^2 = a^2 + a^2$$
$$c^2 = a^2 + b^2$$
$$= 3a^2$$
$$c = \sqrt{3}a = 4r$$
$$a = \frac{4r}{\sqrt{3}}$$



fcc

$$b = 4r$$
$$b^2 = a^2 + a^2$$
$$16r^2 = 2a^2$$
$$a = \sqrt{8}r$$

r = radius of atoms
a = edge length

When silver crystallizes, it forms face-centered cubic cells. The unit cell edge length is 4.087A . Calculate the density of silver.

Mass of unit cell

$$m = \frac{4\ \text{atoms}}{\text{unit cell}} \times \frac{107.9\ \text{amu}}{\text{atom}} \times \frac{1\,\text{g}}{6.022\times10^{23}\ \text{amu}} = 7.167\times10^{-22}\,\text{g}$$

Volume of unit cell

$$a = 4.087\ \overset{\circ}{\text{A}} \times \frac{1\,\text{m}}{1\times10^{10}\ \overset{\circ}{\text{A}}} \times \frac{100\,\text{cm}}{1\,\text{m}} = 4.087\times10^{-8}\,\text{cm}$$

$$V = a^3 = \left(4.087\times10^{-8}\,\text{cm}\right)^3 = 6.827\times10^{-23}\,\text{cm}^3$$

Density of unit cell

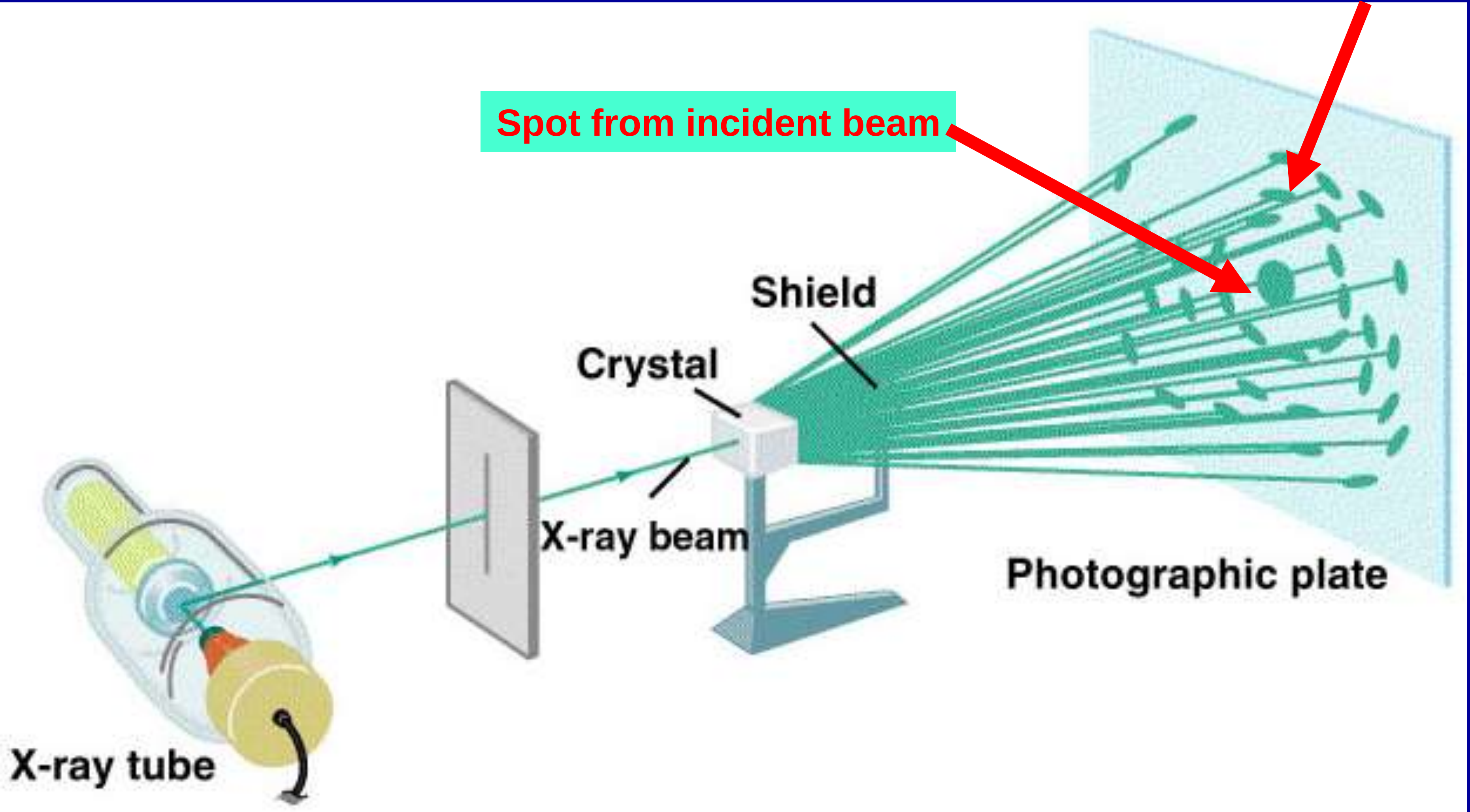
$$d = \frac{m}{V} = \frac{7.167\times10^{-22}\,\text{g/unit cell}}{6.827\times10^{-23}\,\text{cm}^3\text{/unit cell}} = 10.5\,\text{g/cm}^3$$

Structure of crystals using X-Ray analysis of solids

- Sample is powdered
- X-rays of single wavelength is used
- Distance between planes of atoms in the crystal are calculated from the angles at which the rays are diffracted using **Bragg equation**

X-Ray analysis of solids

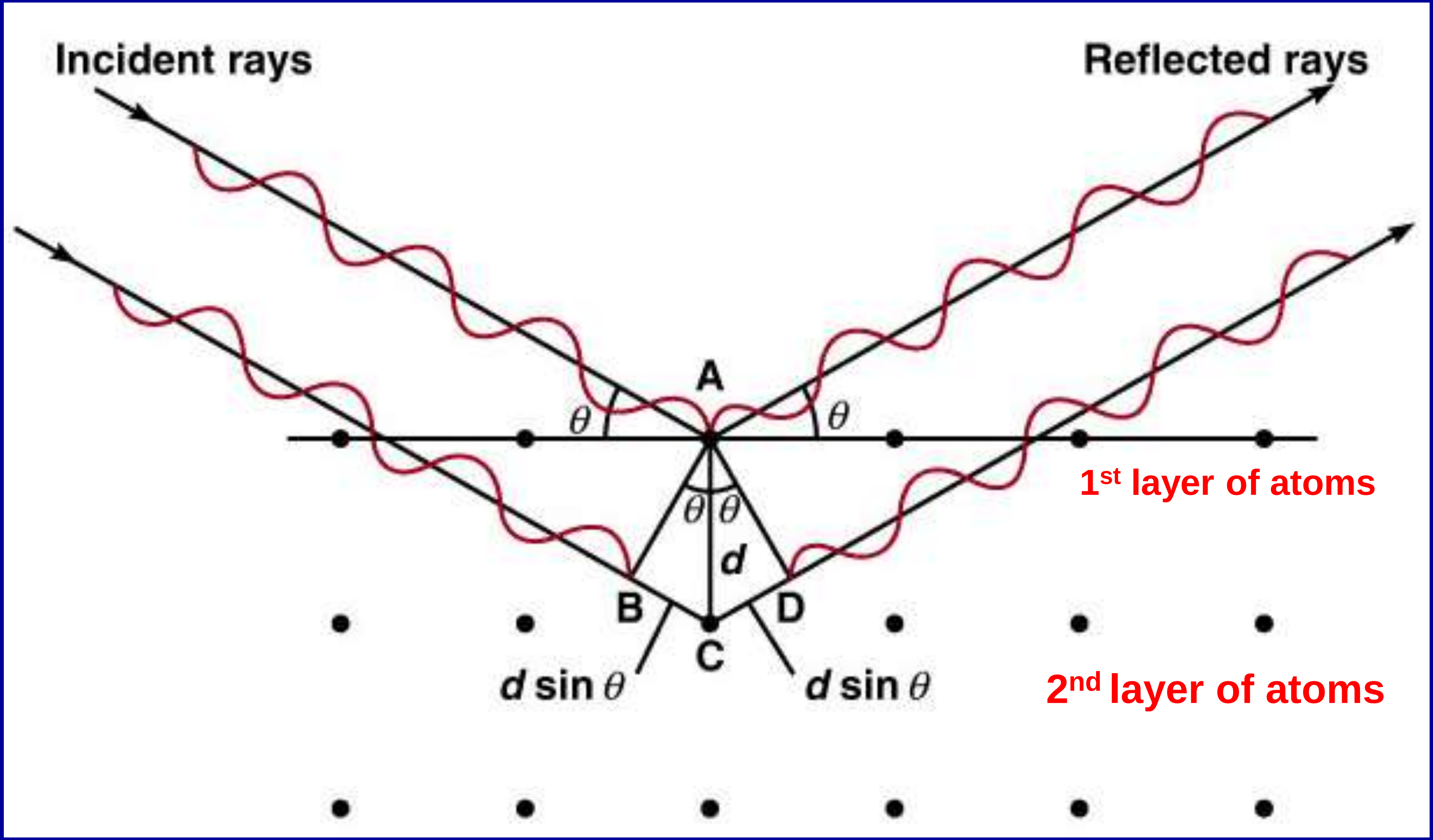
X-Ray diffraction



Spots from diffracted X-rays

Spot from incident beam

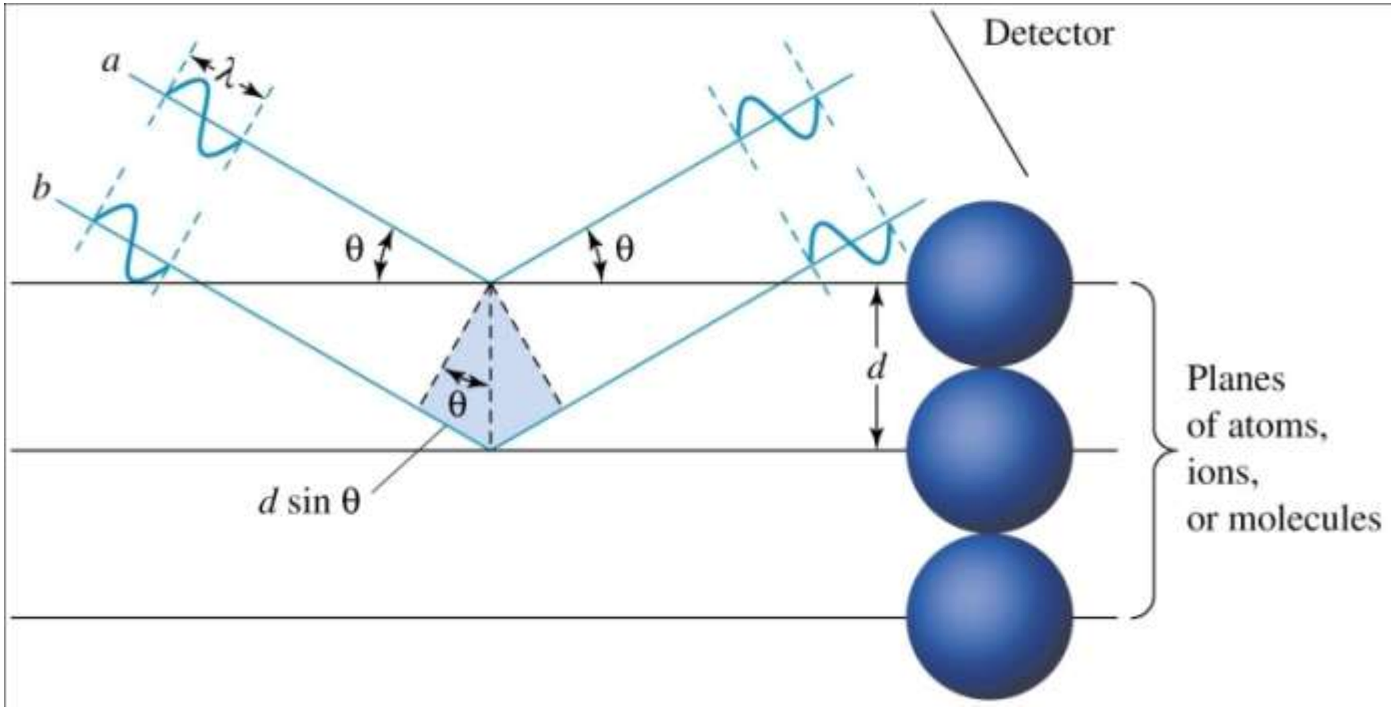
Reflection of X-rays from two layers of atoms



1st layer of atoms

2nd layer of atoms

Extra distance traveled by lower ray = BC + CD = $n\lambda = 2d \sin\theta$



Bragg Equation

$$n\lambda = 2d\sin\theta$$

d = distance between atoms
n = an integer
λ = wavelength of the x-rays

Example

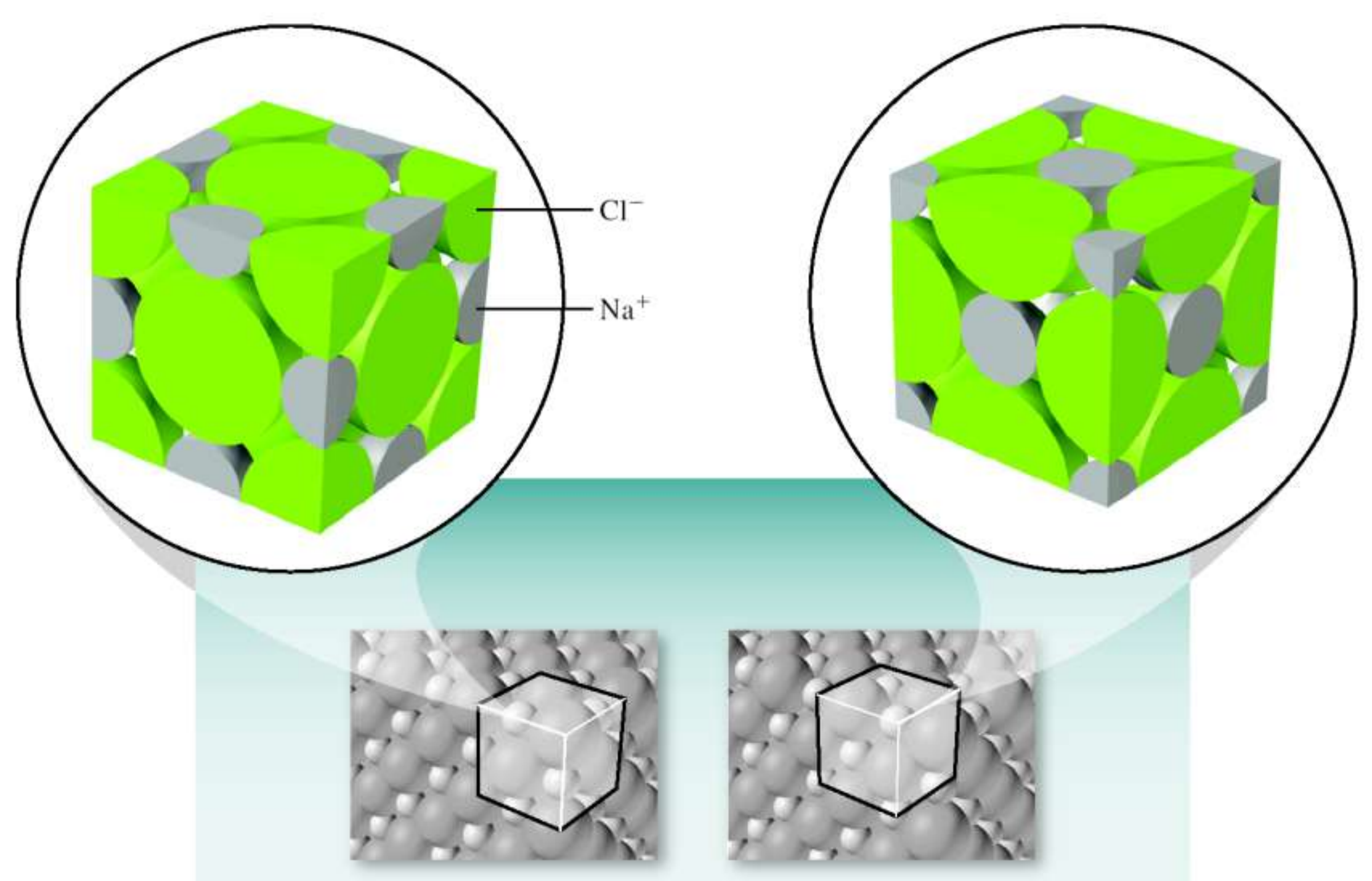
X rays of wavelength of 0.154 nm strikes an aluminum crystal. The crystal rays reflected at an angle of 19.3^{o}. Calculate the spaces between the planes of aluminum atoms that is responsible for this angle of reflection.

12.4 Types of Crystals

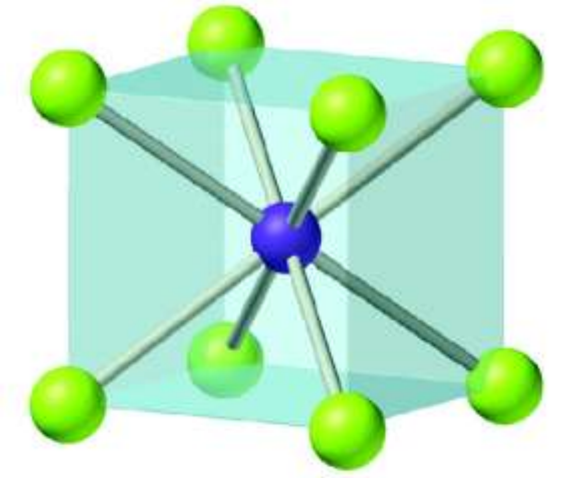
1. Ionic Crystals

- Composed of anions and cations
- Held together by coulombic forces
- Anions generally are bigger than cations
- Size and relative number of each ion determines the crystal structure
- They conduct electric current when dissolved in water
- They possess huge melting and boiling points.
- Atoms are locked in lattice so they are hard and brittle.
- Every electron is accounted for so they are poor conductors-good insulators.

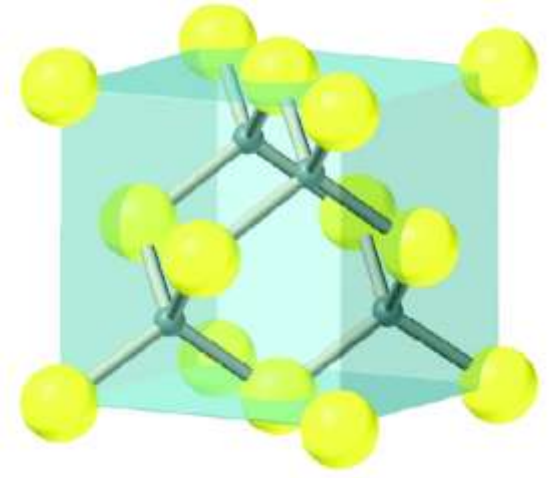
Unit cell of NaCl as defined by Cl^- or Na^+



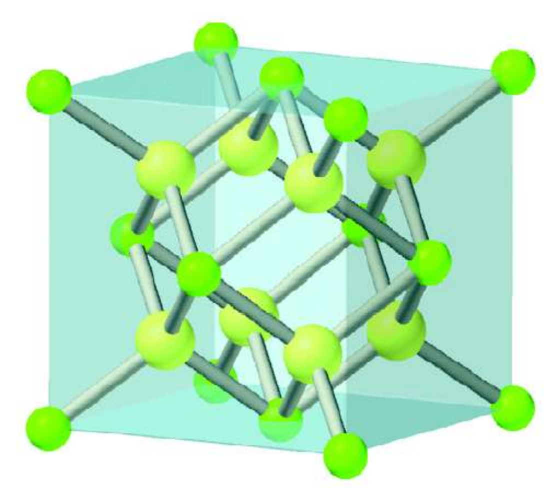
Examples of Ionic Crystal Lattices



CsCl

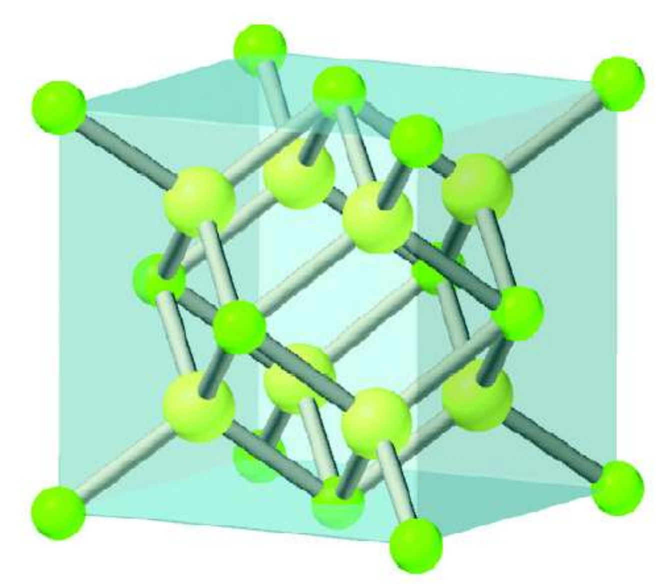


ZnS



CaF_2

How many of each ion are contained within a unit cell of CaF_2?



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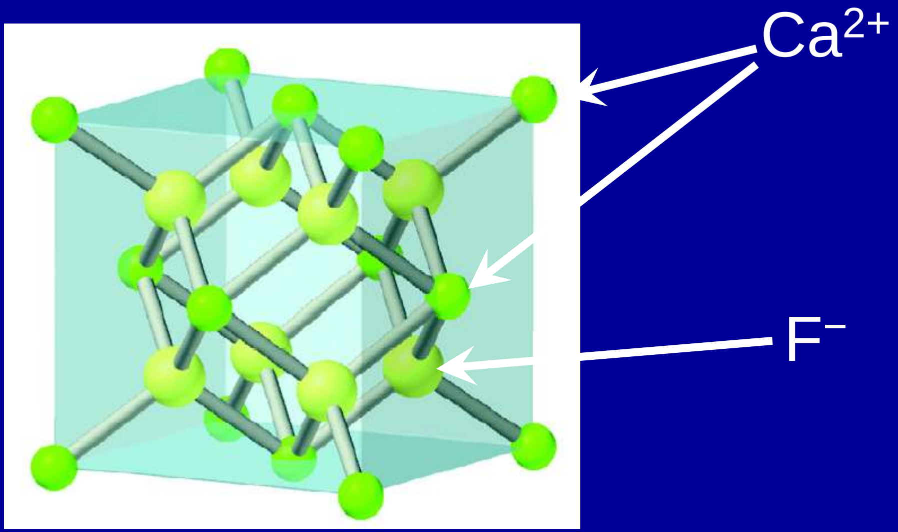


Ca^{2+}

8 corner ions x $^{1}/_{8}$= 1 ion

6 face ions x ½ = 3 ions

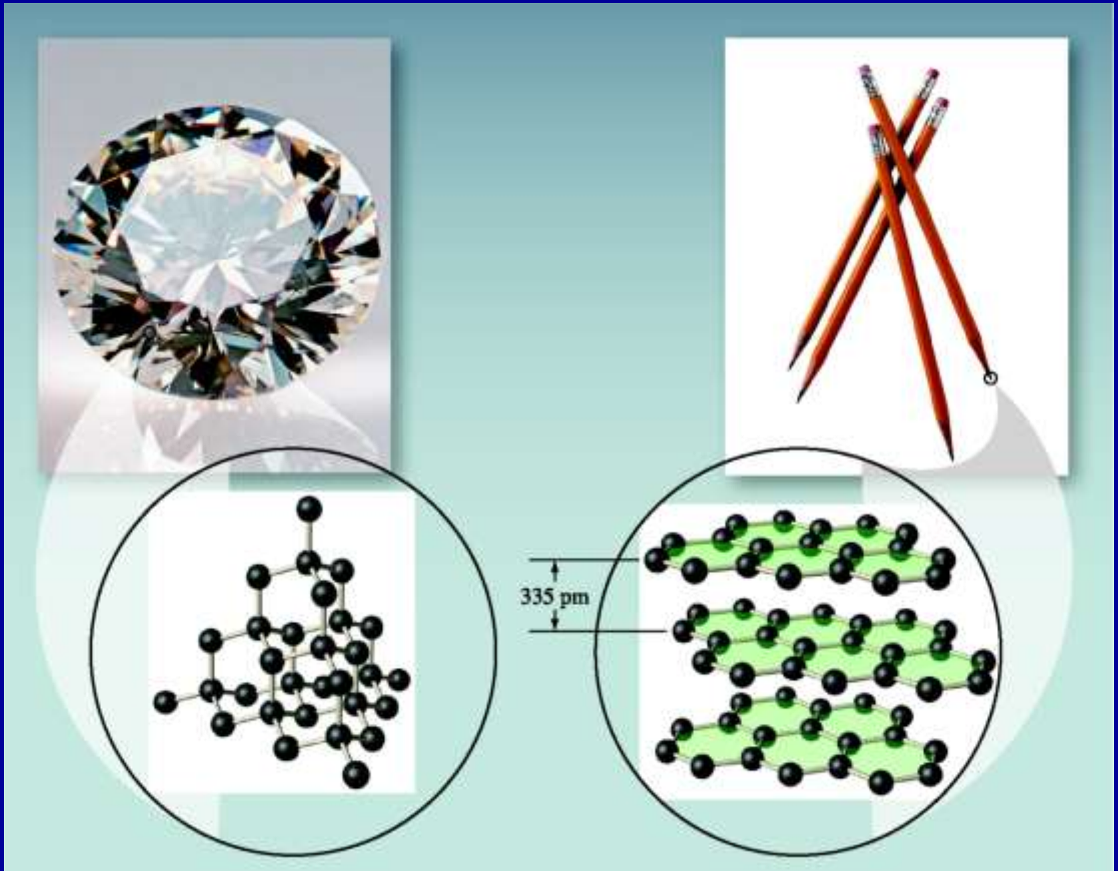
4 ions of Ca^{2+}

F^-

8 body ions x 1 = 8 ions of F^-

2. Covalent crystals

– Held together by covalent bonds

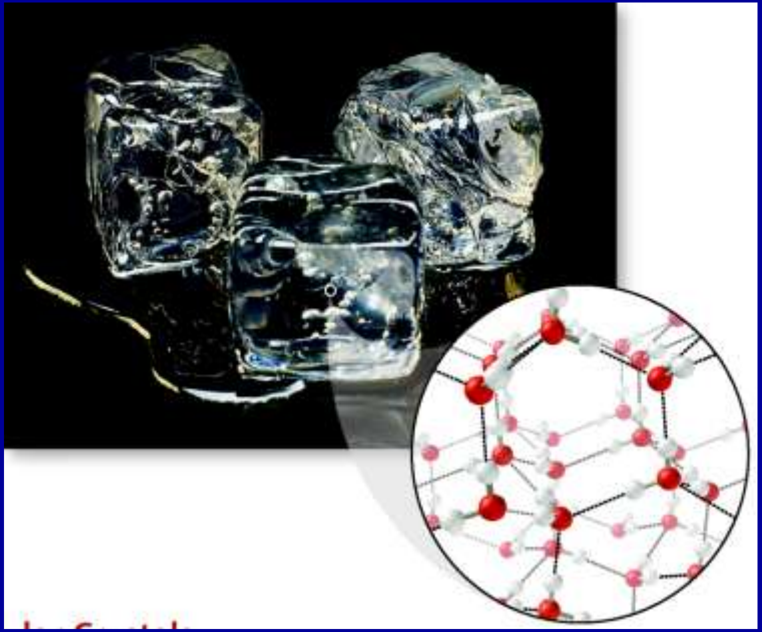


Diamond **Graphite**

3. Molecular crystals

- Lattice points occupied by molecules
- Held together by intermolecular forces (dispersion dipole-dipole forcesand/or hydrogen bonding)

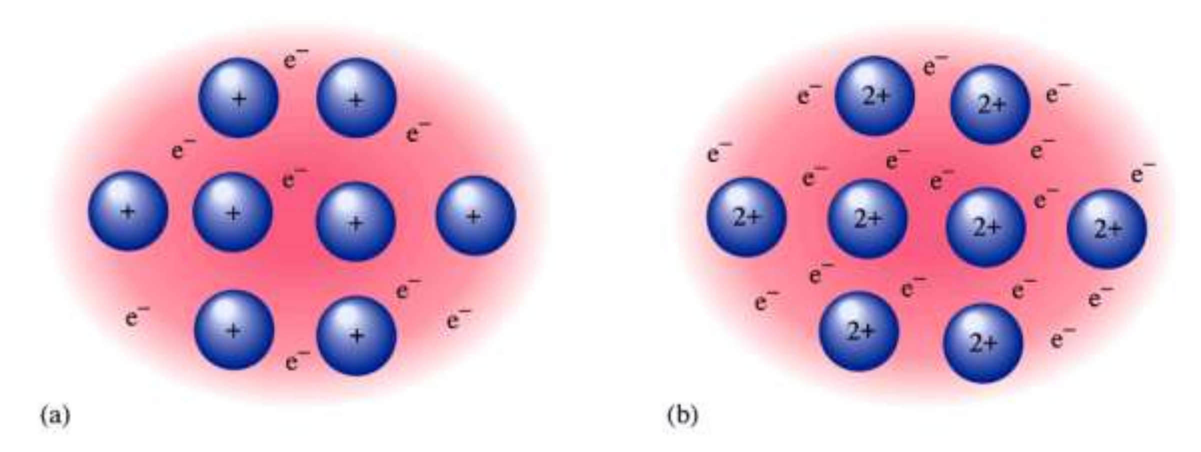
water



Other examples: dry CO_2, S_8, P_4, I_2

4. Metallic crystals

- Lattice points occupied by atoms
- Generally bcc, fcc, hexagonal closest packed
- Very dense
- Bonding arises from delocalized electrons over the entire crystal.
- High electrical conductivity and High thermal conductivity



Metal atoms are imagined as an array of positive ions immersed in a sea of delocalized valence electrons. This is known as the Metallic bond

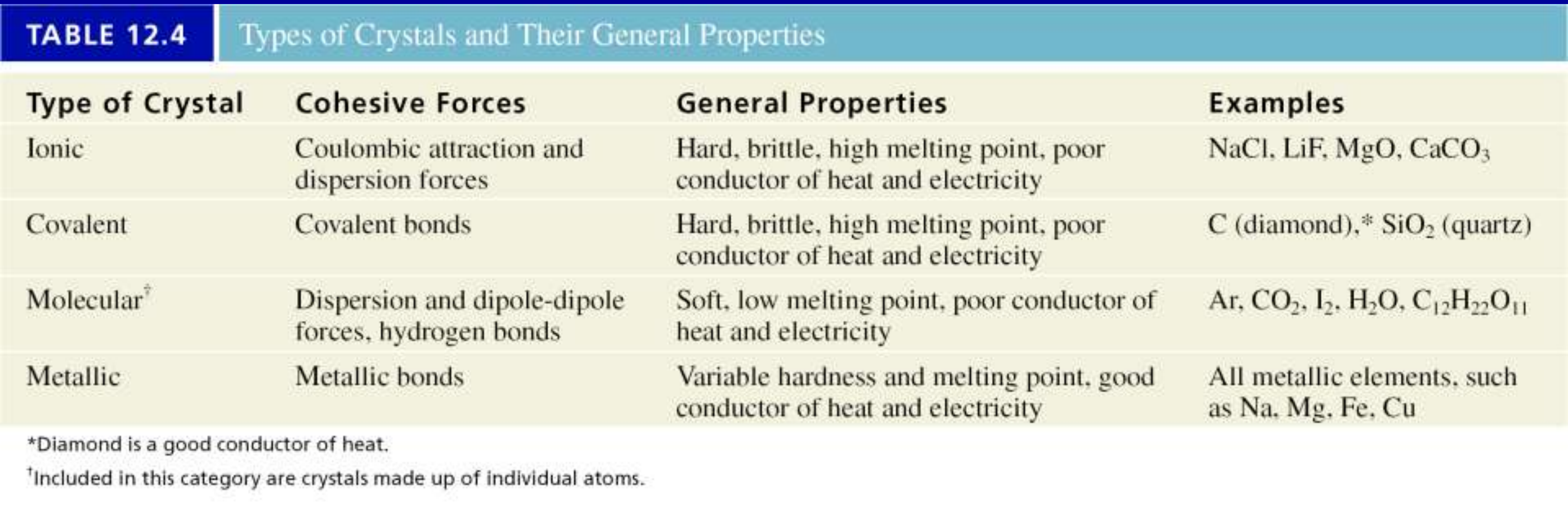


TABLE 12.4 Types of Crystals and Their General Properties

Type of Crystal	Cohesive Forces	General Properties	Examples
Ionic	Coulombic attraction and dispersion forces	Hard, brittle, high melting point, poor conductor of heat and electricity	NaCl, LiF, MgO, $CaCO_3$
Covalent	Covalent bonds	Hard, brittle, high melting point, poor conductor of heat and electricity	C (diamond),[*] SiO_2 (quartz)
Molecular[†]	Dispersion and dipole-dipole forces, hydrogen bonds	Soft, low melting point, poor conductor of heat and electricity	Ar, CO_2, I_2, H_2O, $C_{12}H_{22}O_{11}$
Metallic	Metallic bonds	Variable hardness and melting point, good conductor of heat and electricity	All metallic elements, such as Na, Mg, Fe, Cu

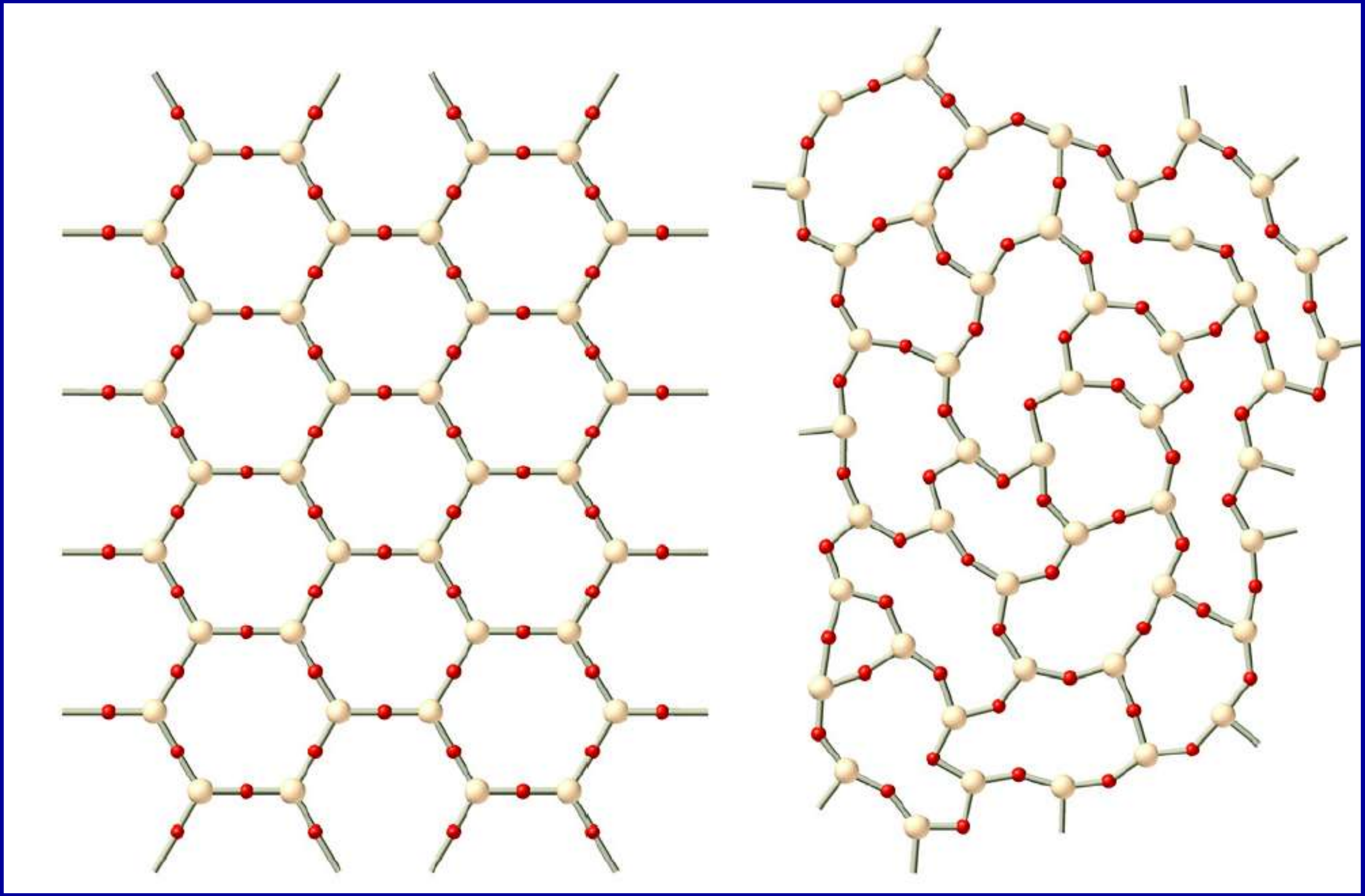
[*] Diamond is a good conductor of heat.

[†] Included in this category are crystals made up of individual atoms.

12.5 Amorphous Solids

- Lack regular arrangement of atoms
- Glass is a familiar and important amorphous solid
  - Optically transparent fusion product of inorganic materials that has cooled to a rigid state without crystallization
  - It is composed mainly by mixing molten SiO_2 with other components such as Na_2O, B_2O_3 and certain transition metal oxides for coloring
  - Behaves more as a liquid than a solid

Comparison of crystalline quartz and amorphous quartz glass



Crystalline Quartz

Amorphous Glass

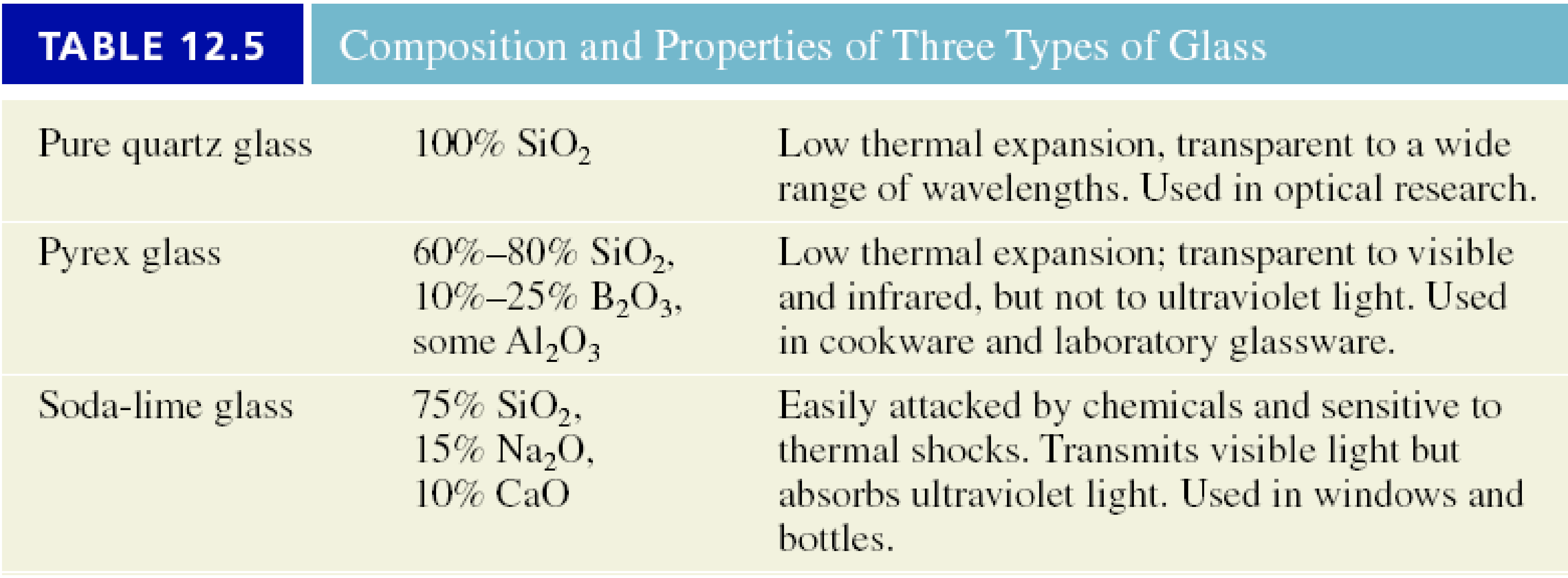


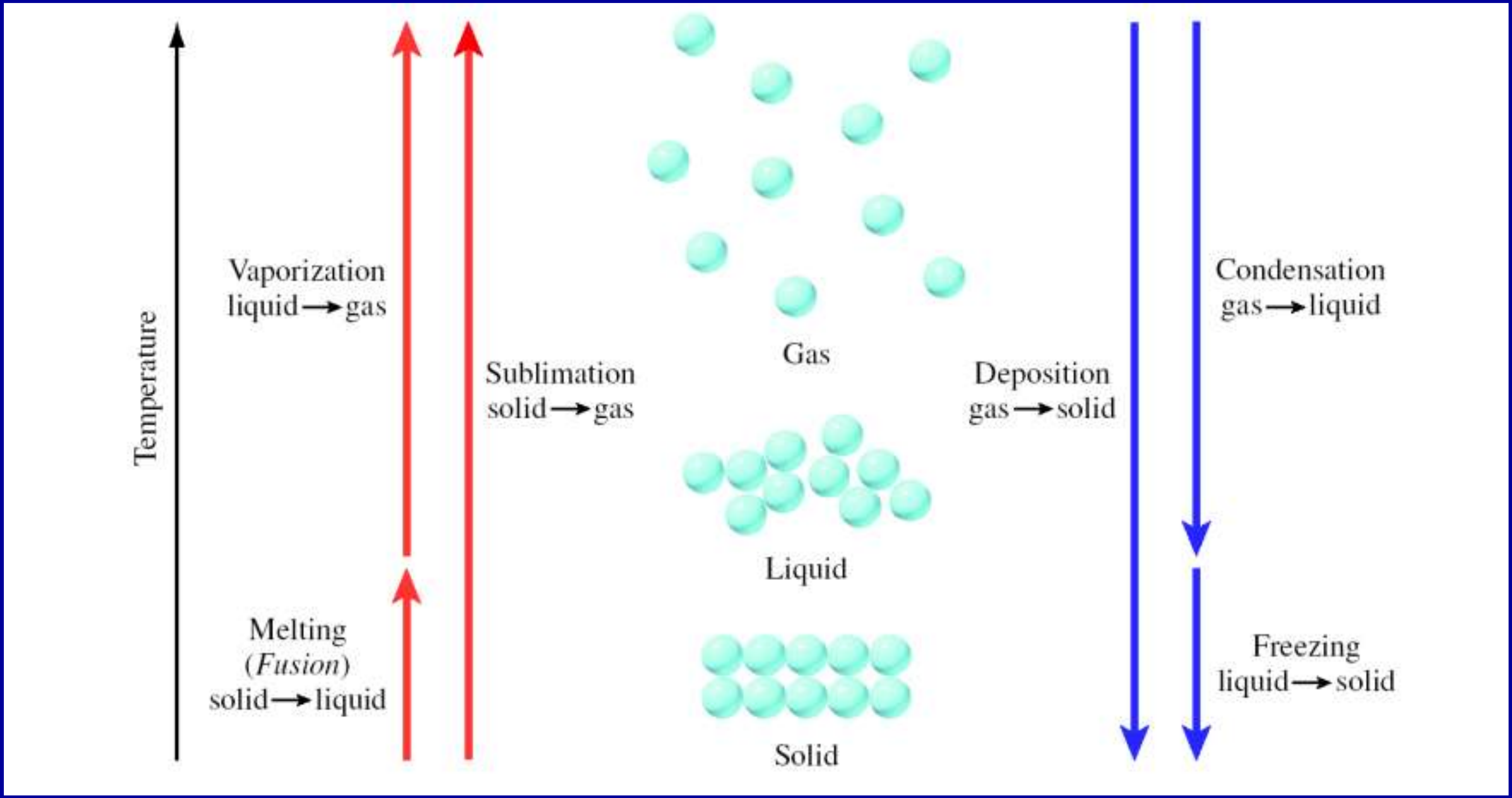
TABLE 12.5 Composition and Properties of Three Types of Glass

Pure quartz glass	100% SiO_2	Low thermal expansion, transparent to a wide range of wavelengths. Used in optical research.
Pyrex glass	60%–80% SiO_2, 10%–25% B_2O_3, some Al_2O_3	Low thermal expansion; transparent to visible and infrared, but not to ultraviolet light. Used in cookware and laboratory glassware.
Soda-lime glass	75% SiO_2, 15% Na_2O, 10% CaO	Easily attacked by chemicals and sensitive to thermal shocks. Transmits visible light but absorbs ultraviolet light. Used in windows and bottles.

12.6 Phase Changes

- ***Phase*** **– homogenous part of a system that is separated from the rest of the system by a well-defined boundary**
- ***Phase change*** **– transition from one phase to another**
  - **Caused by the removal or addition of energy**
  - **Energy involved is usually in the form of heat**

The Six Possible Phase Changes



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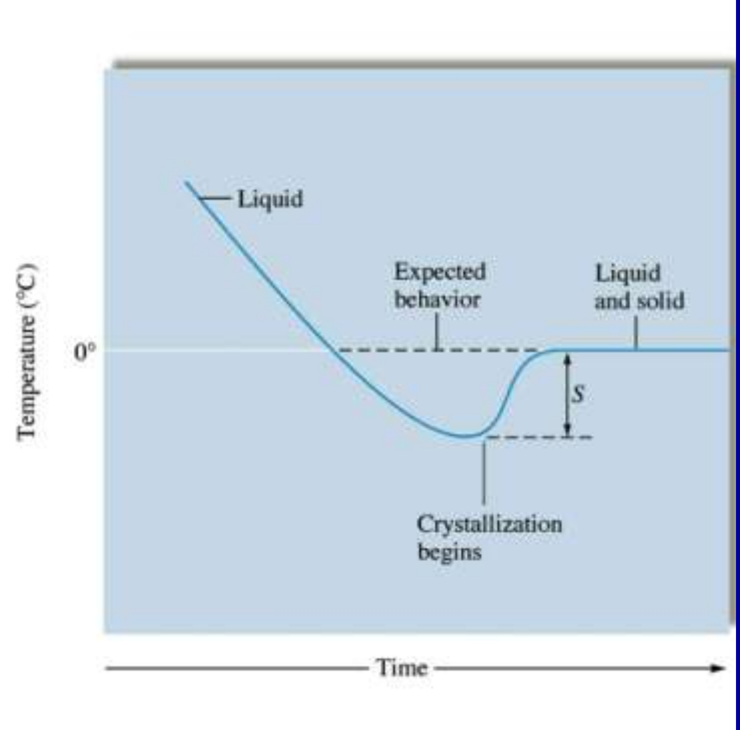
Liquid-Vapor Phase Transition

- Vapor pressure of a liquid increases by increasing the temperature. When the vpor pressure reaches the external pressure, the liquid boils
- Boiling *point (Normal)* – the temperature at which the vapor pressure of liquid equals atmospheric pressure
- ***Molar heat of vaporization*** (ΔH_{vap}) – the amount of heat required to vaporize one mole of a substance at its boiling point usually in kJ/mol
  - Dependent on the strength of intermolecular forces
- ***Condensation*** – opposite of vaporization. A gas can be liquified either by cooling or by applying a pressure

Superheating and supercooling

- Changes of state do not always occur exactly at bp or Fp
  - **supercooling**
    - Material can stay liquid below freezing point because doesn't achieve level of organization needed to make solid
  - **superheating**
    - when heated too quickly, liquid can be raised above boiling point
    - causes "bumping"



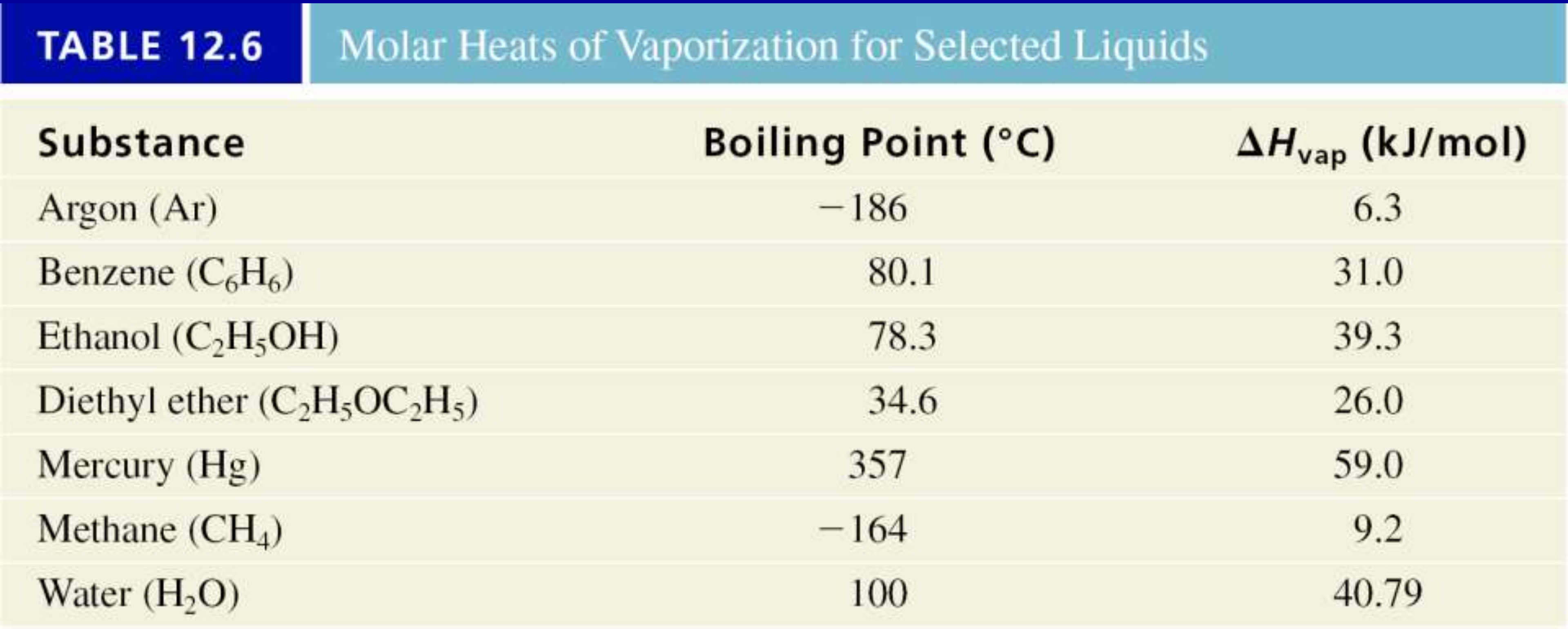


TABLE 12.6 Molar Heats of Vaporization for Selected Liquids

Substance	Boiling Point (°C)	ΔH_{vap} (kJ/mol)
Argon (Ar)	−186	6.3
Benzene (C_6H_6)	80.1	31.0
Ethanol (C_2H_5OH)	78.3	39.3
Diethyl ether ($C_2H_5OC_2H_5$)	34.6	26.0
Mercury (Hg)	357	59.0
Methane (CH_4)	−164	9.2
Water (H_2O)	100	40.79

Critical temperature and Critical pressure

- **Critical temperature (T_c)** – the temperature above which a gas cannot be liquified by application of pressure
- **Critical pressure (P_c)** – the pressure that must be applied to liquefy a gas at T_c.
- **Critical point**

  critical temperature and pressure (for water, T_c = 374°C and 218 atm).
- **Supercritical fluid** – the fluid that exists above T_c and P_c.

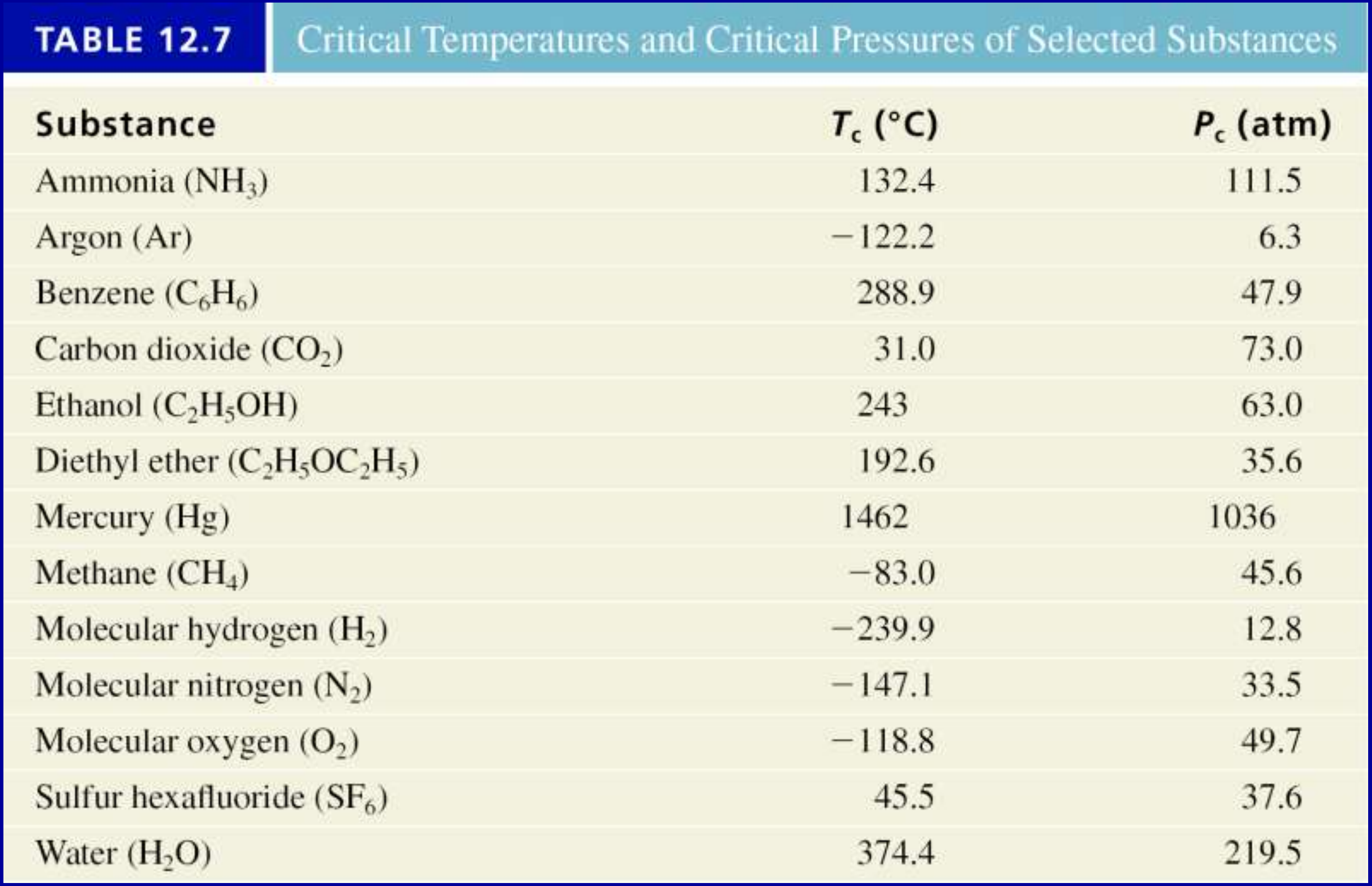


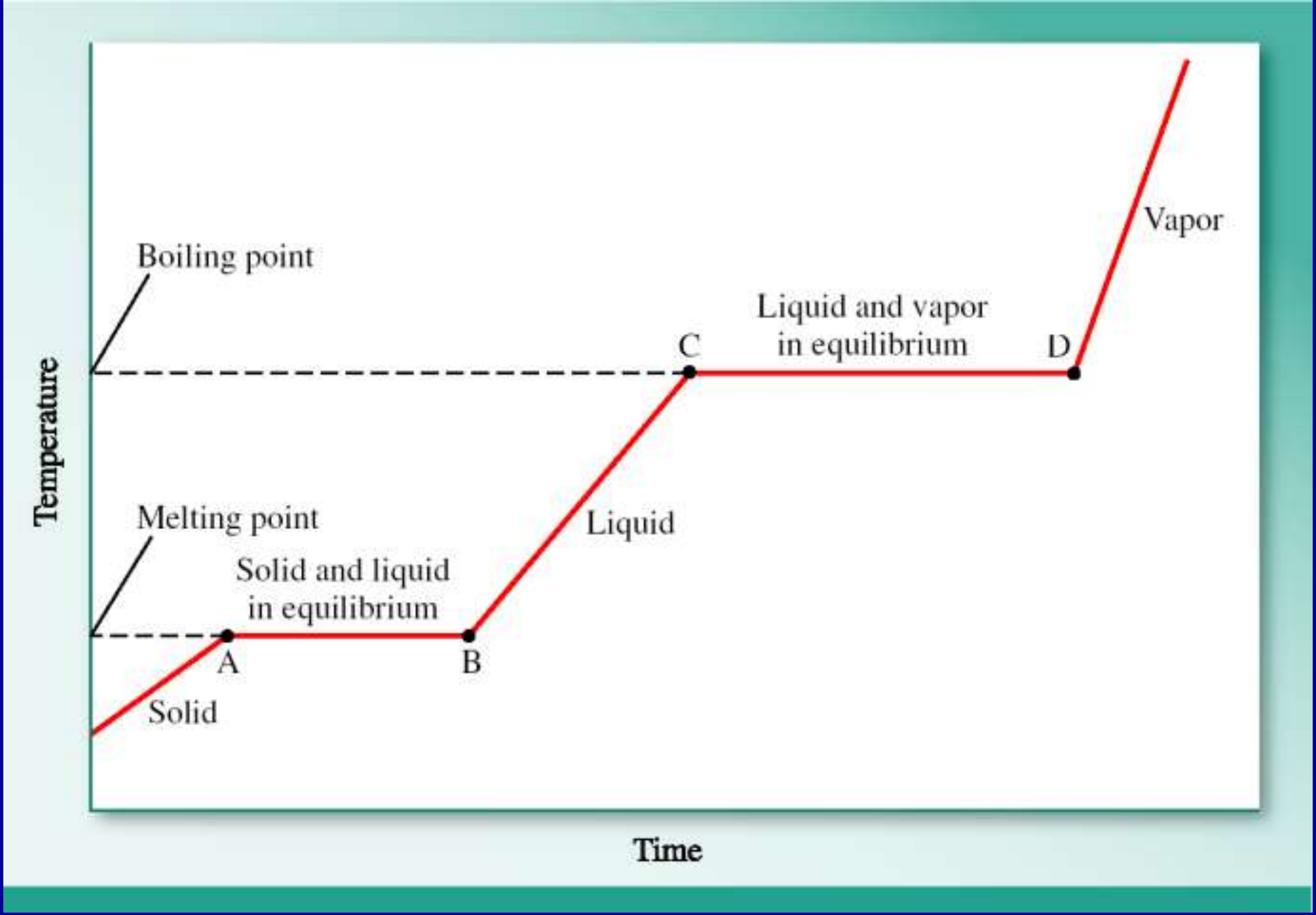
TABLE 12.7 Critical Temperatures and Critical Pressures of Selected Substances

Substance	T_c (°C)	P_c (atm)
Ammonia (NH_3)	132.4	111.5
Argon (Ar)	−122.2	6.3
Benzene (C_6H_6)	288.9	47.9
Carbon dioxide (CO_2)	31.0	73.0
Ethanol (C_2H_5OH)	243	63.0
Diethyl ether ($C_2H_5OC_2H_5$)	192.6	35.6
Mercury (Hg)	1462	1036
Methane (CH_4)	−83.0	45.6
Molecular hydrogen (H_2)	−239.9	12.8
Molecular nitrogen (N_2)	−147.1	33.5
Molecular oxygen (O_2)	−118.8	49.7
Sulfur hexafluoride (SF_6)	45.5	37.6
Water (H_2O)	374.4	219.5

Solid-Liquid Phase Transition

- **Freezing** – transformation of liquid to solid
- **Melting (fusion)** – opposite of freezing
- **Melting point of solid** (**or freezing point of liquid**) – temperature at which the solid and liquid phases coexist in equilibrium
  - Dynamic equilibrium in which the forward and reverse processes are occurring at the same rate
- **Molar heat of fusion (DH_{fus})** – energy to melt one mole of a solid usually in kJ/mol

Typical Heating Curve



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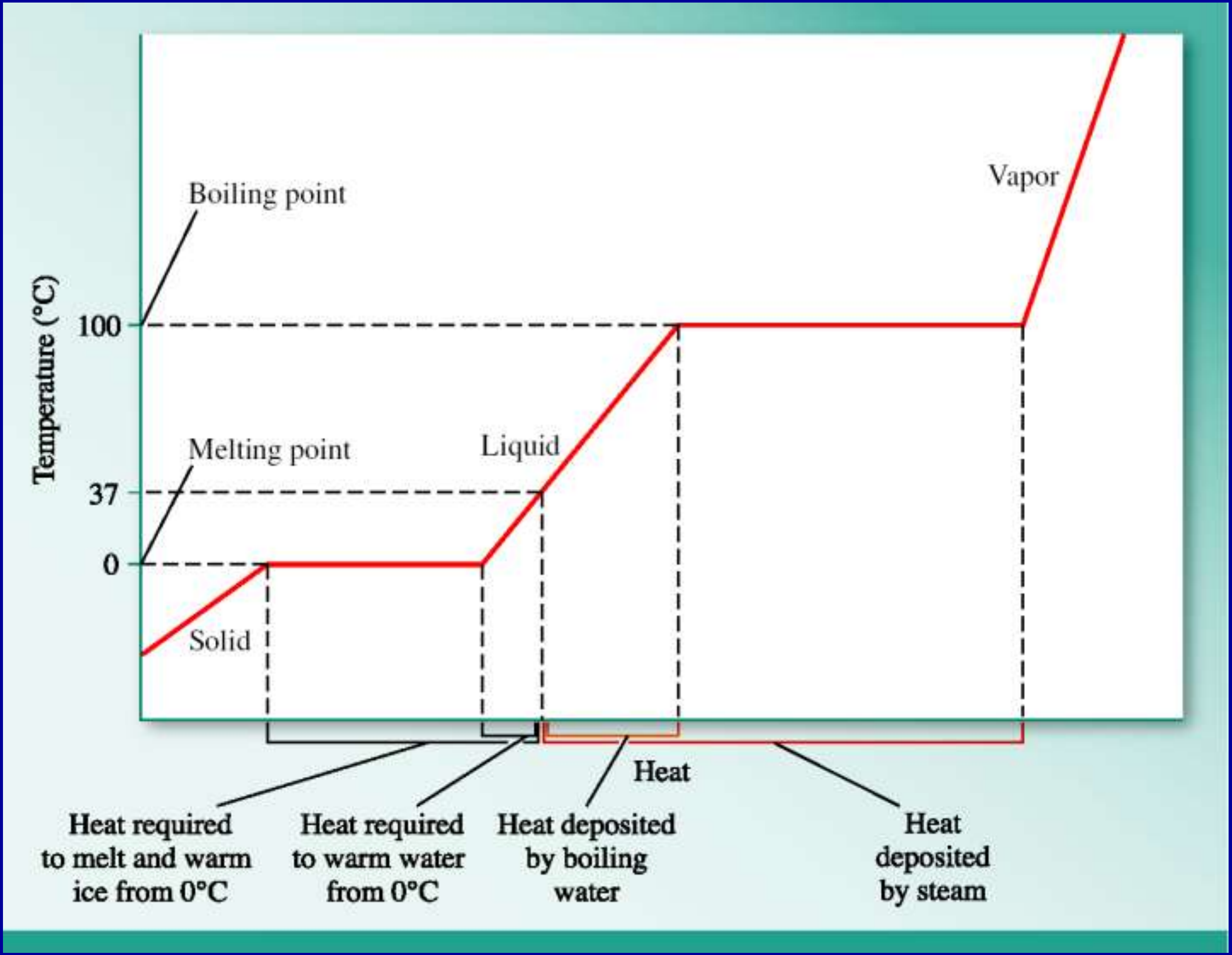
Solid-Vapor Phase Transition

- **Sublimation** – process by which molecules go directly from the solid phase to the vapor phase
- **Deposition** – reverse of sublimation
- **Molar heat of sublimation (ΔH_{sub})** – energy required to sublime one mole of solid usually in kJ/mol

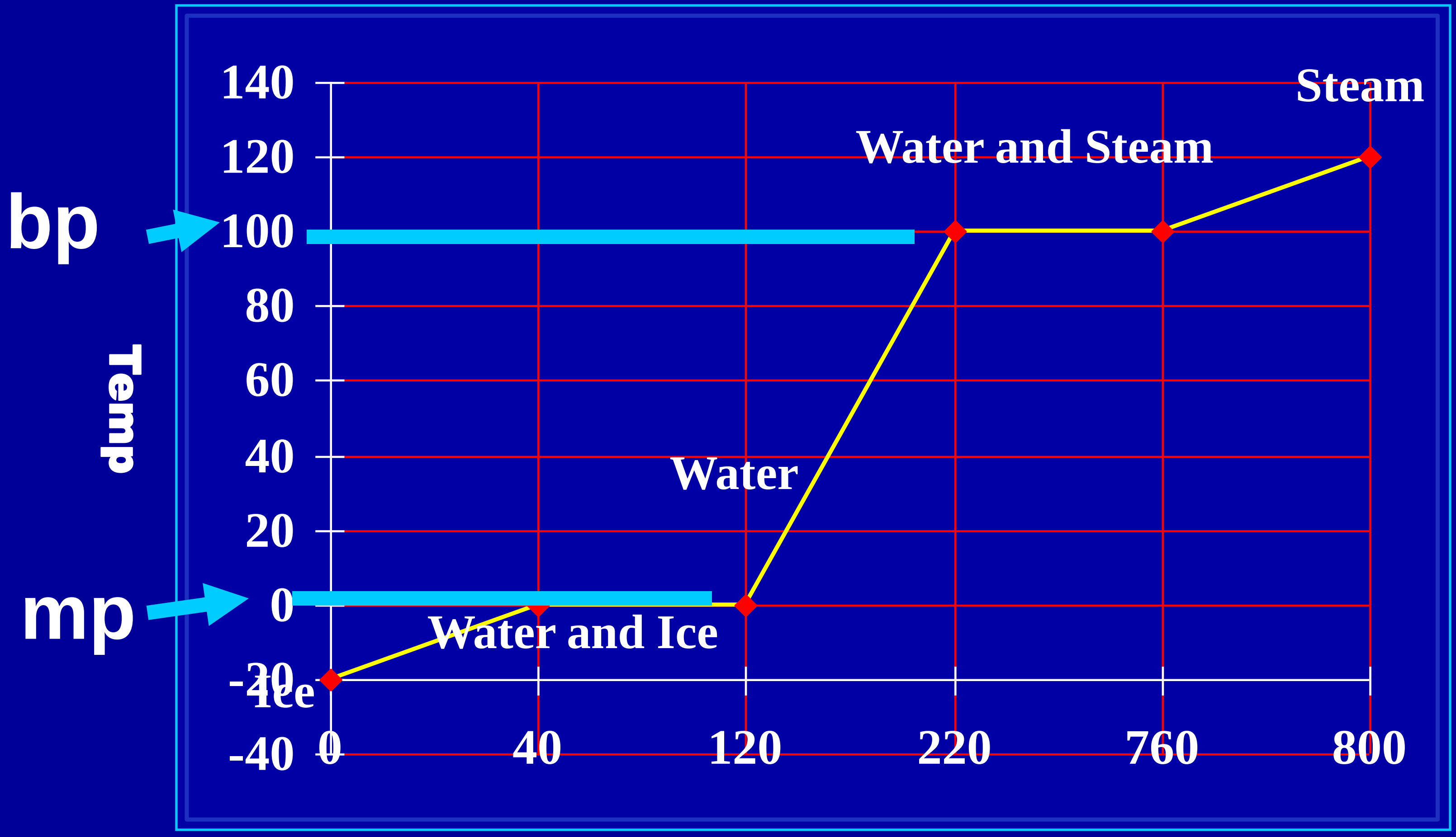
$$\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$$

Iodine

Heating Curve for Water

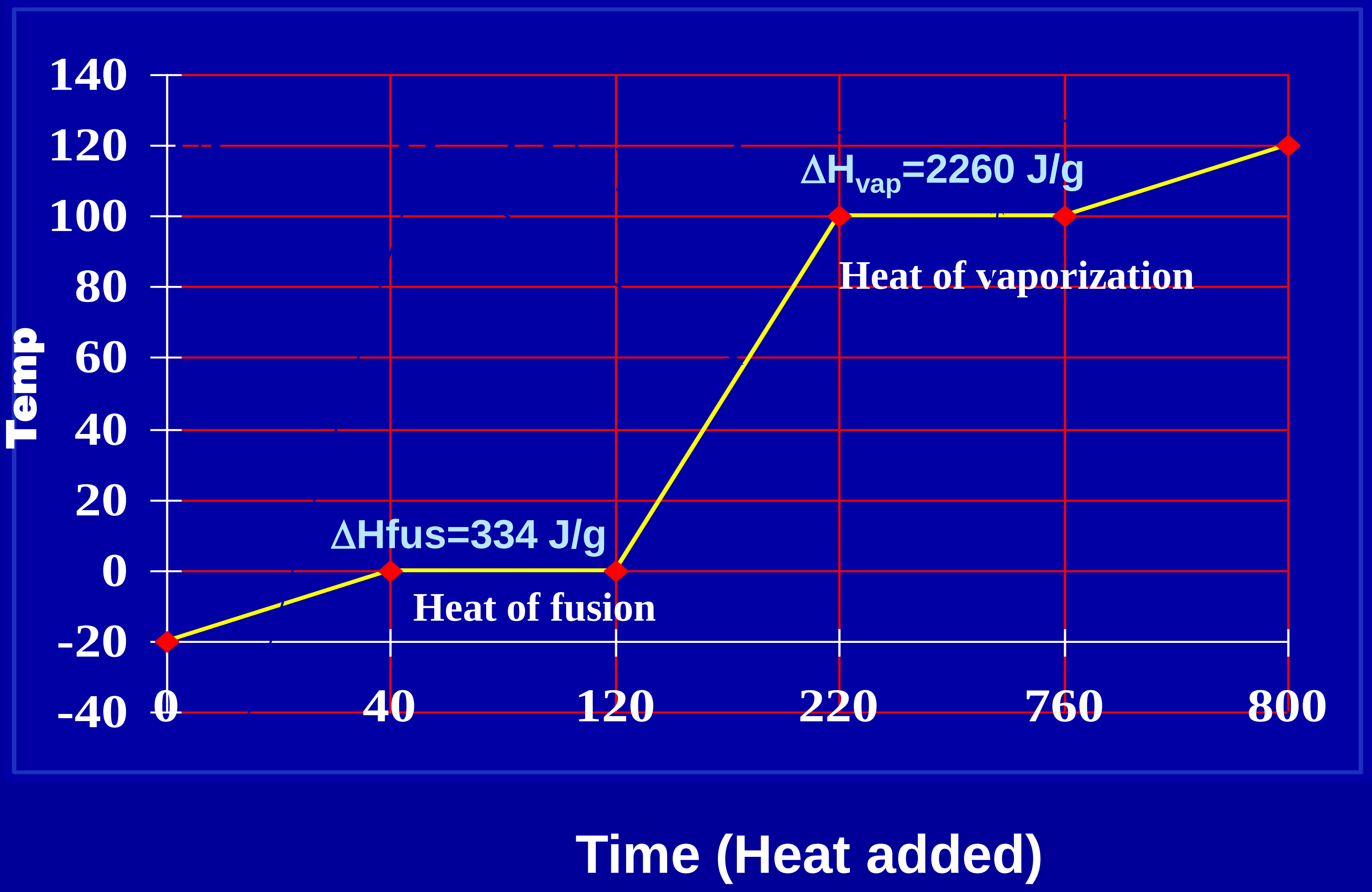


Heating Curve for Water

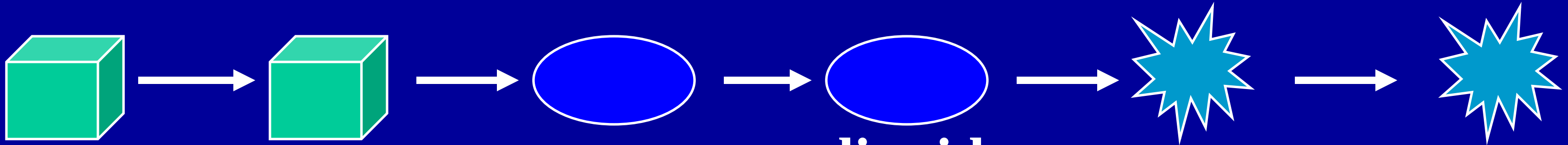


Time (Heat added)

Heating Curve for Water



Calculate the enthalpy change upon converting 1 mole of water from ice at -12°C to steam at 115°C.



solid -12°C → solid 0°C → liquid 0°C → liquid 100°C → gas 100°C → gas 115°C

$$\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 = \Delta H_{total}$$

$$\text{Sp. Ht.} + \Delta H_{fusion} + \text{Sp. Ht.} + \Delta H_{Vaporization} + \text{Sp. Ht.} = \Delta H_{total}$$

Specific Heat of ice = 2.09 J/g•K

ΔH_{fus}=334 J/g

ΔH_{vap}=2260 J/g

Specific Ht. Steam = 1.84 J/g•K

Example

Calculate the amount of energy (in kJ) required to convert 125 g of ice at –10.0ºC to liquid water at the normal boiling point. Assume that the specific heat ice is 2.050 J/gºC. ΔH_{fus} (water) = 6.01 KJ/mol.

Energy to warm ice from –10ºC to 0ºC

$$\Delta T = 0.0^{o}\text{C} - (-10.0^{o}\text{C}) = 10.0^{o}\text{C}$$

$$q = ms\Delta T = 125\ \text{g} \times \frac{2.050\ \text{J}}{\text{g}\cdot{}^{o}\text{C}} \times 10.0^{o}\text{C} = 2.563\times 10^{3}\,\text{kJ}$$

$$2.563\times 10^{3}\,\text{J} \times \frac{\text{kJ}}{1\times 10^{3}\,\text{J}} = 2.563\ \text{kJ}$$

Energy to melt ice at 0ºC

$$125\ \text{g} \times \frac{\text{mol}}{18.02\ \text{g}} = 6.937\ \text{mol}$$

$$q = n\Delta H_{\text{vap}} = 6.937\ \text{mol} \times \frac{6.01\,\text{kJ}}{\text{mol}} = 4.169\times 10^{1}\ \text{kJ}$$

Energy to warm water from 0.0°C to 100.0°C

$$\Delta T = 100.0^{\circ}\mathrm{C} - 0.0^{\circ}\mathrm{C} = 100.0^{\circ}\mathrm{C}$$

$$q = ms\Delta T = 125\ \mathrm{g} \times \frac{4.184\ \mathrm{J}}{\mathrm{g}\cdot^{\circ}\mathrm{C}} \times 100.0^{\circ}\mathrm{C} = 5.230 \times 10^{4}\,\mathrm{J}$$

$$5.230 \times 10^{4}\,\mathrm{J} \times \frac{1\,\mathrm{kJ}}{1 \times 10^{3}\,\mathrm{J}} = 5.230 \times 10^{1}\ \mathrm{kJ}$$

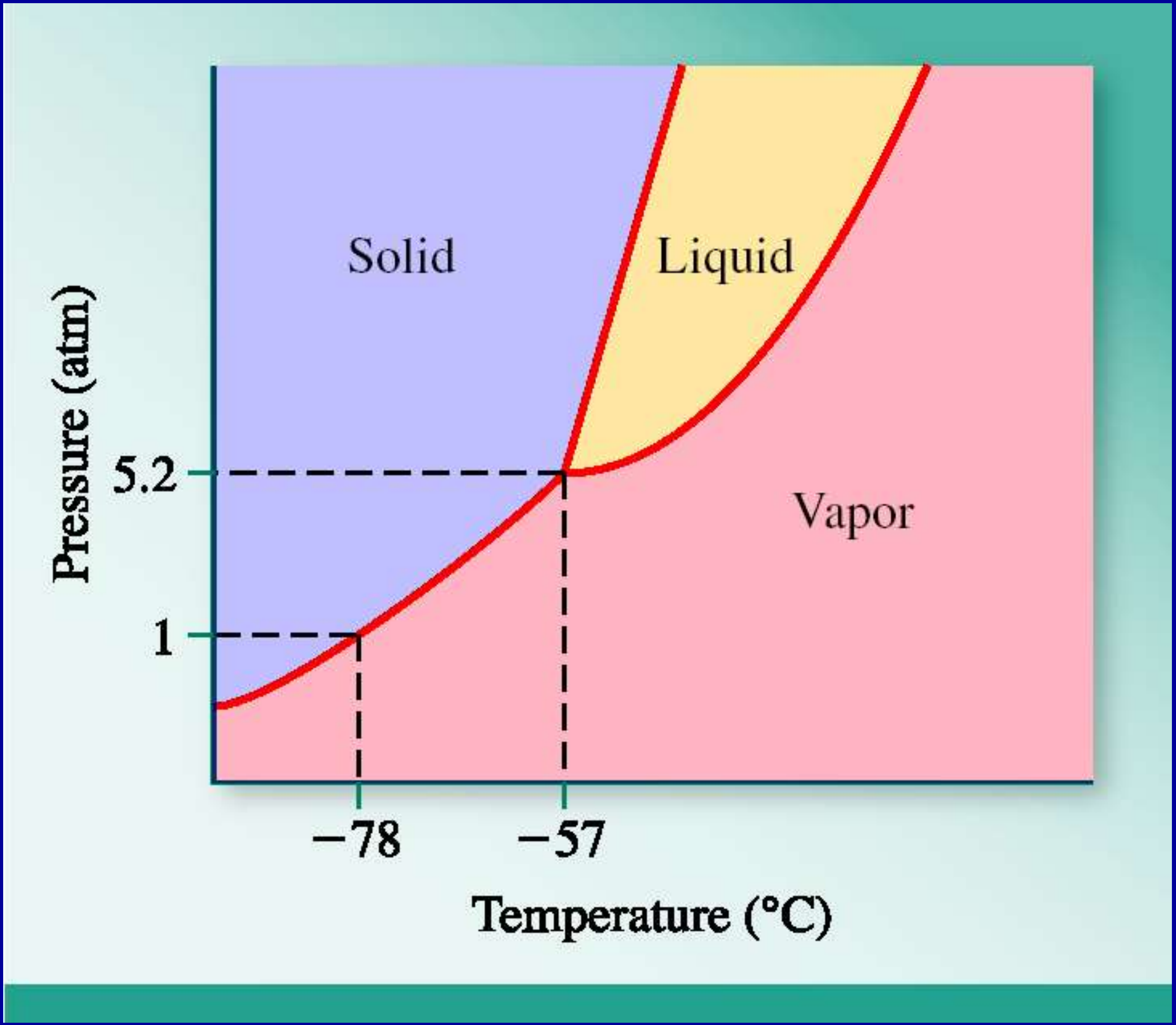
Total energy required

$$2.563\ \mathrm{kJ} + (4.169 \times 10^{1}\,\mathrm{kJ}) + (5.230 \times 10^{1}\,\mathrm{kJ}) = 96.6\mathrm{kJ}$$

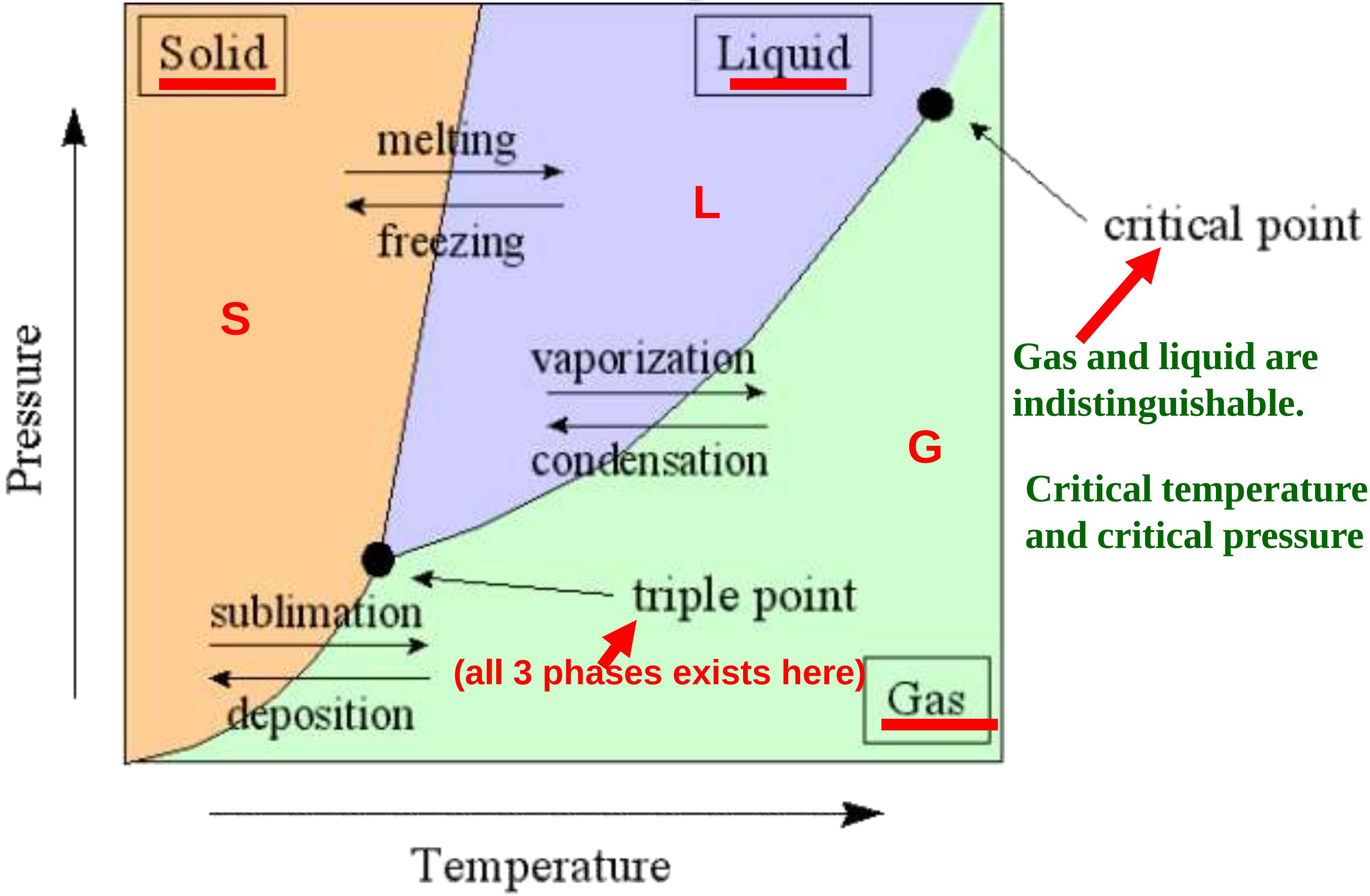
12.7 Phase Diagrams

- **It is a plot summarizing the conditions (temperature and pressure) at which a substance exists as a solid, liquid or gas**
- **A plot representing phases (solid, liquid and gas) of a substance in a closed system (no material escapes into the surroundings and no air is present) as a function of temperature and pressure.**
  - **The plot is divided into three regions (solid, liquid, gas)**
  - ***Phase boundary line* – line separating any two regions**
  - ***Triple point* – the point at which all three phase boundary lines meet**

Phase Diagram of CO_2



Phase changes

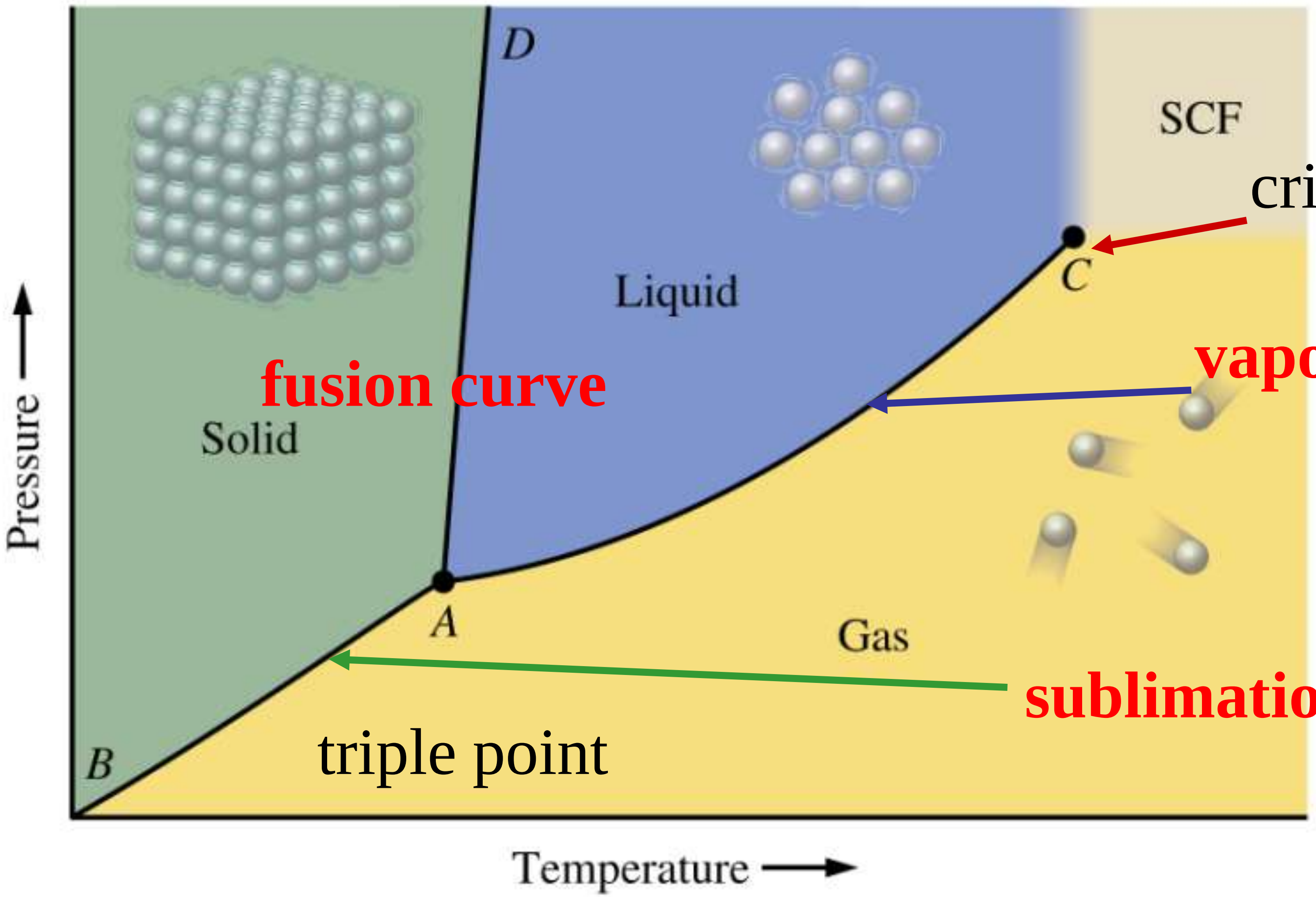


(all 3 phases exists here)

Gas and liquid are indistinguishable.

Critical temperature and critical pressure

Phase Diagrams



critical point

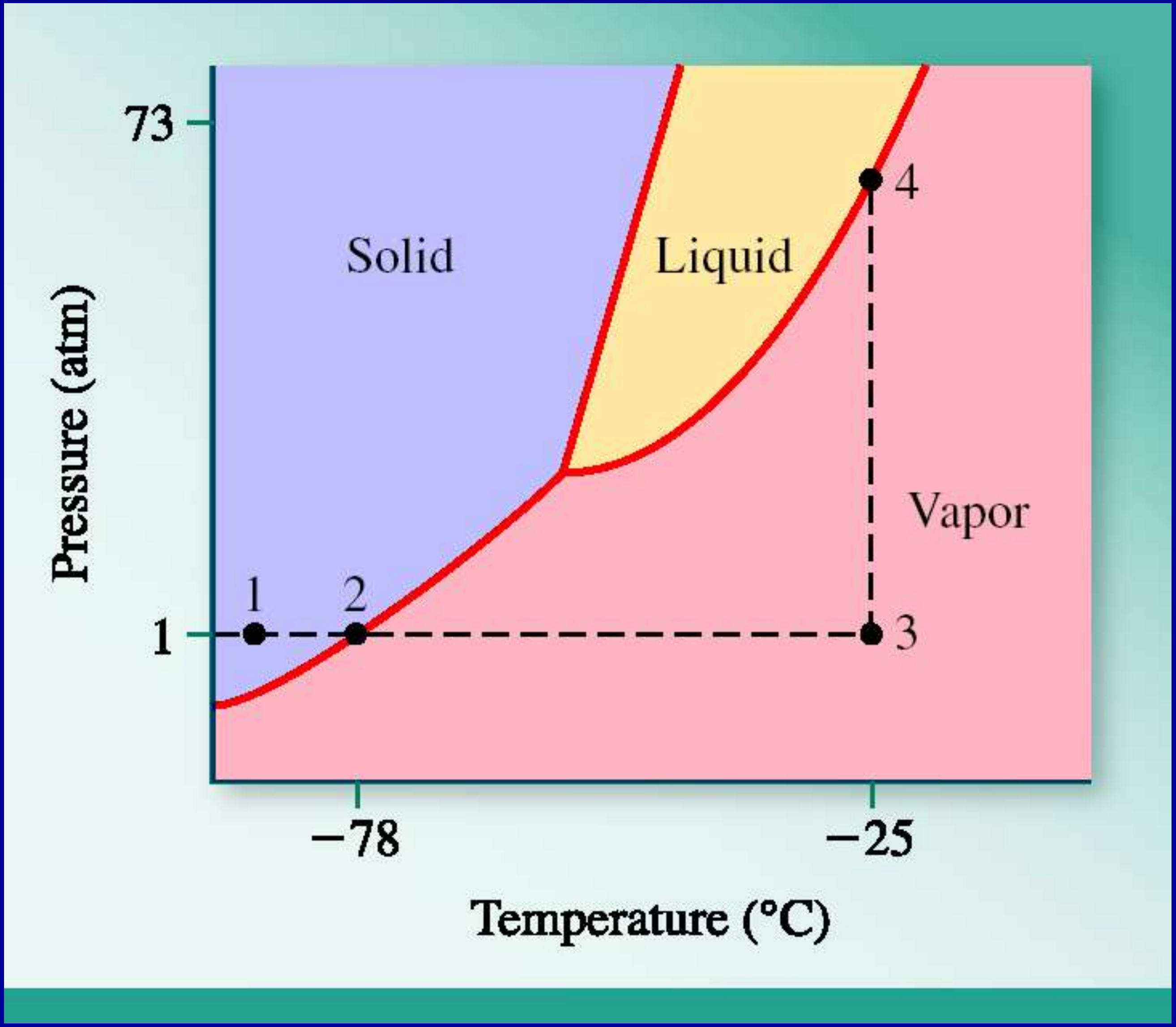
vapor pressure

fusion curve

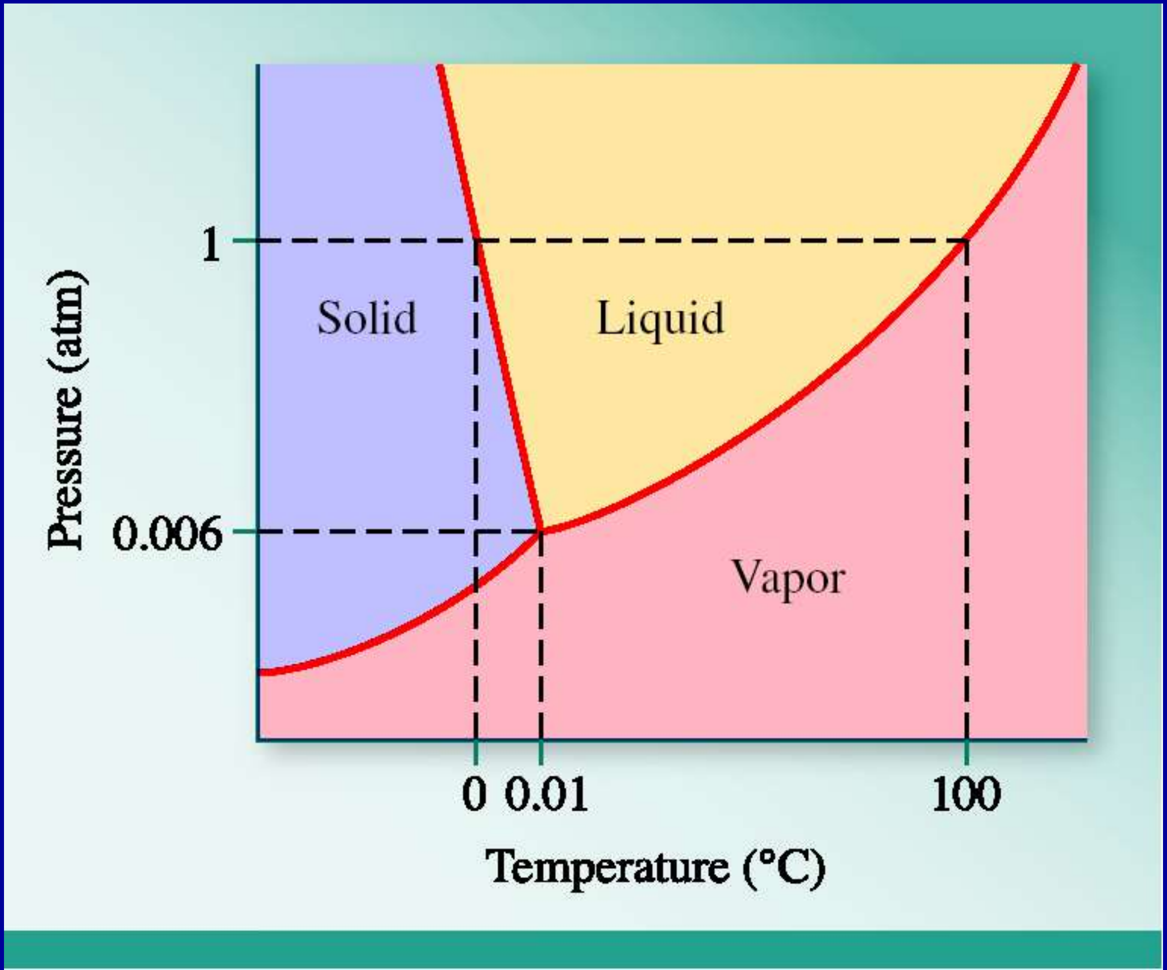
sublimation curve

triple point

Heating CO_2 Starting at –100ºc and 1 atm

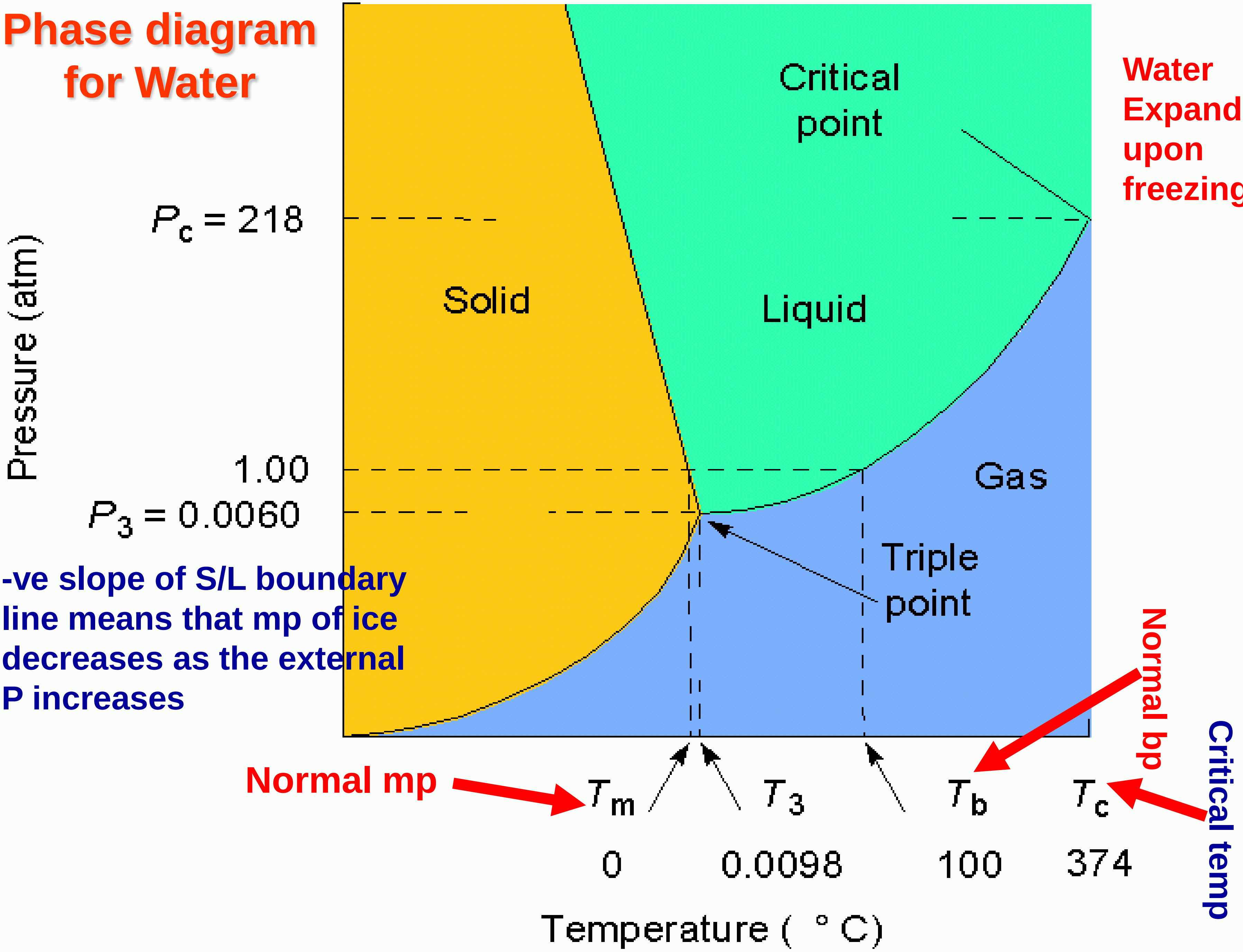


Phase Diagram of H_2O



- Most substances have a positive slope of solid/liquid line
  - because solid is usually more dense than liquid
  - water has a negative slope

Phase diagram for Water



Water Expands upon freezing

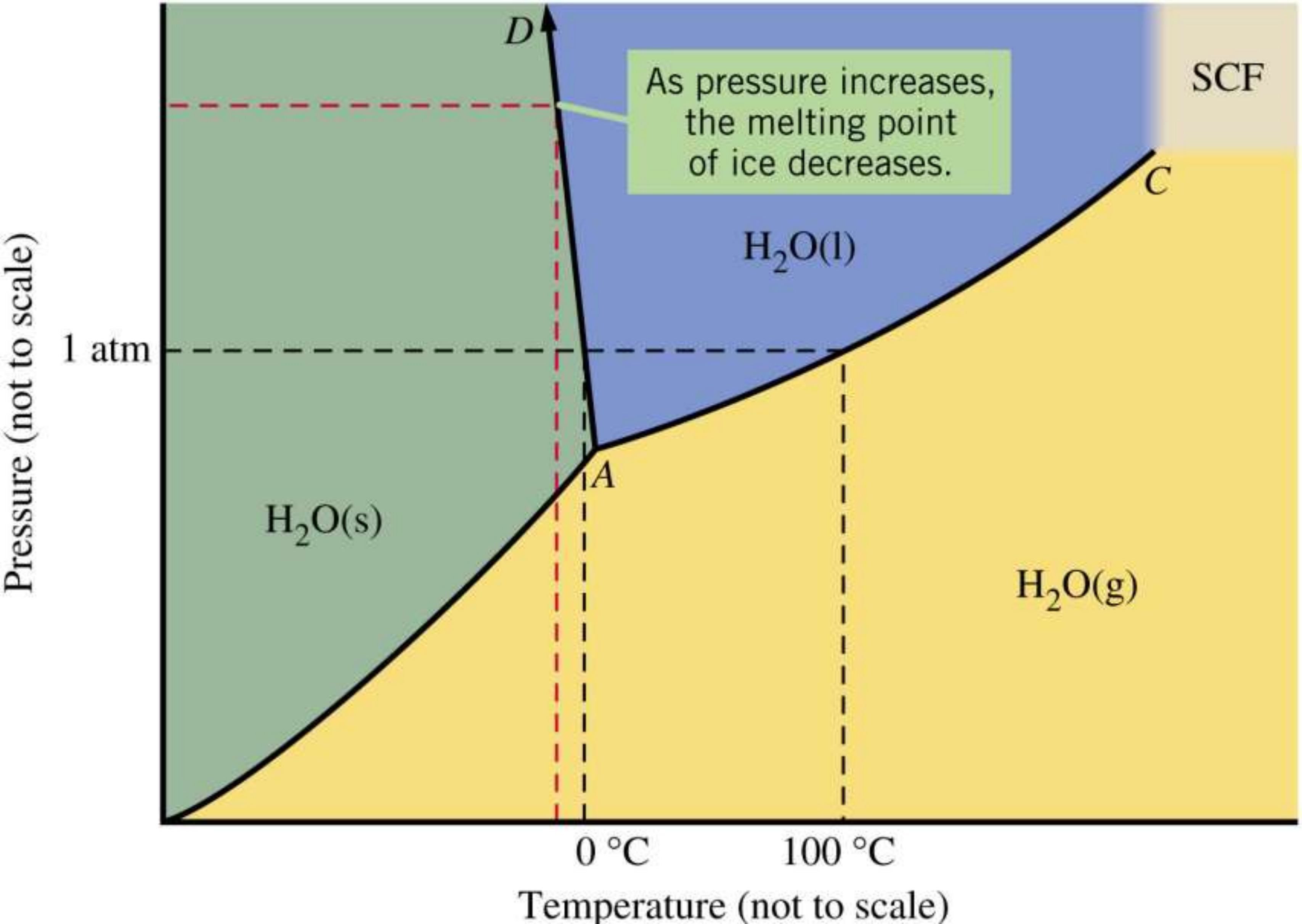
-ve slope of S/L boundary line means that mp of ice decreases as the external P increases

Normal mp

Normal bp

Critical temp

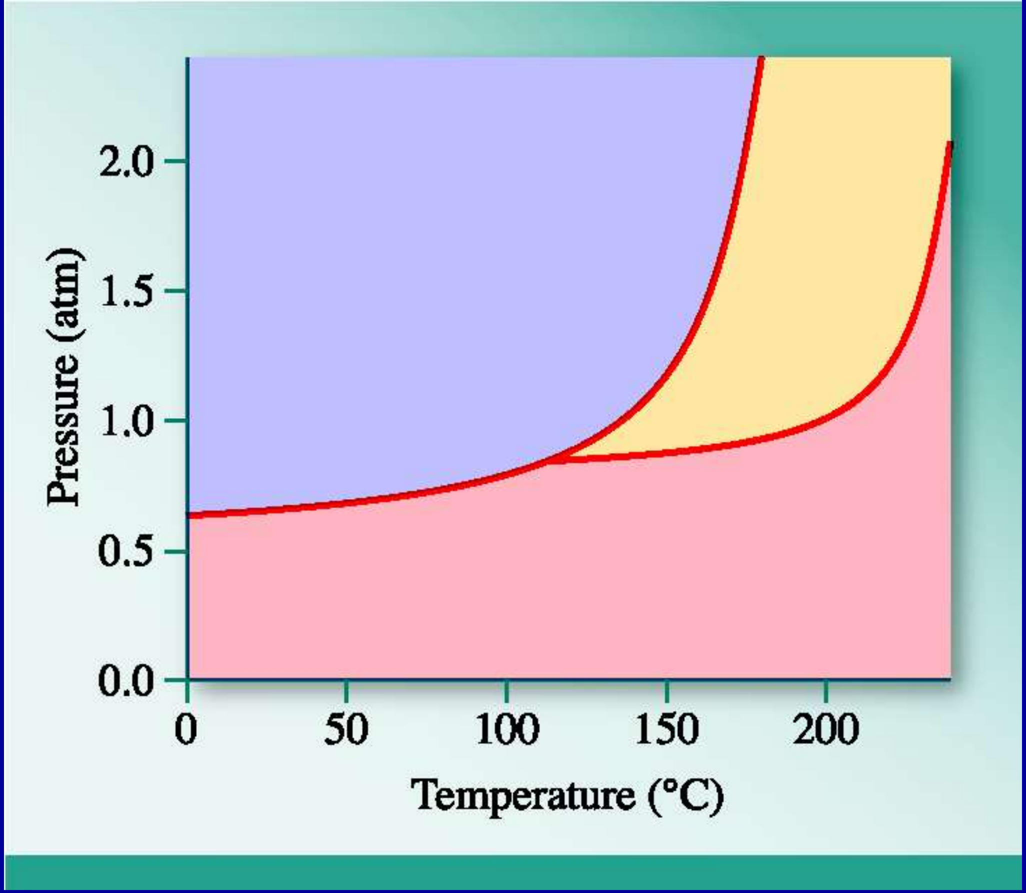
Phase Diagram for H_2O

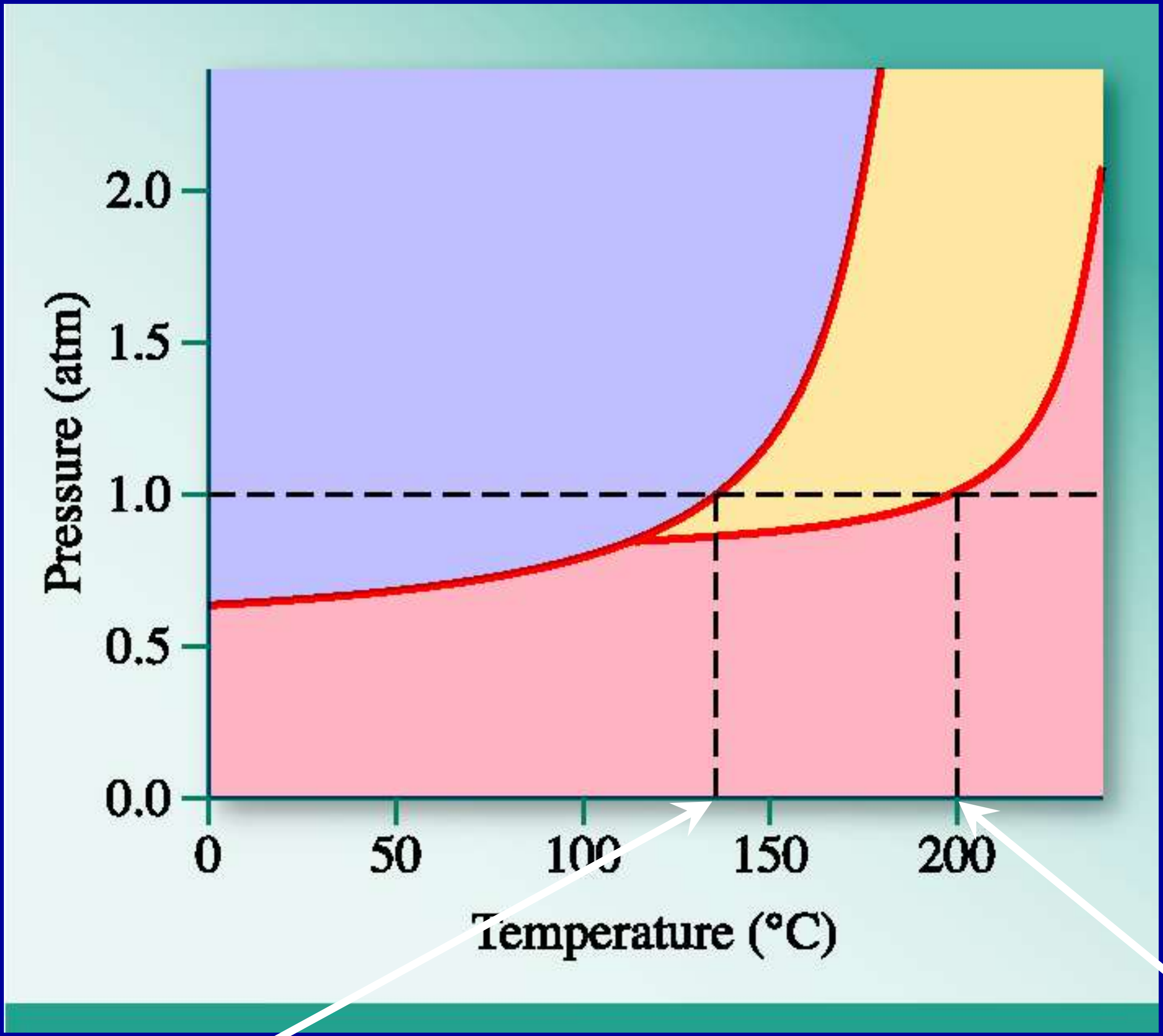


As pressure increases, the melting point of ice decreases.

What is a) the normal* melting point, b) the normal* boiling point and c) the physical state of the substance at 2.0 atm and 110° C?

*normal – measured at 1.00 atm



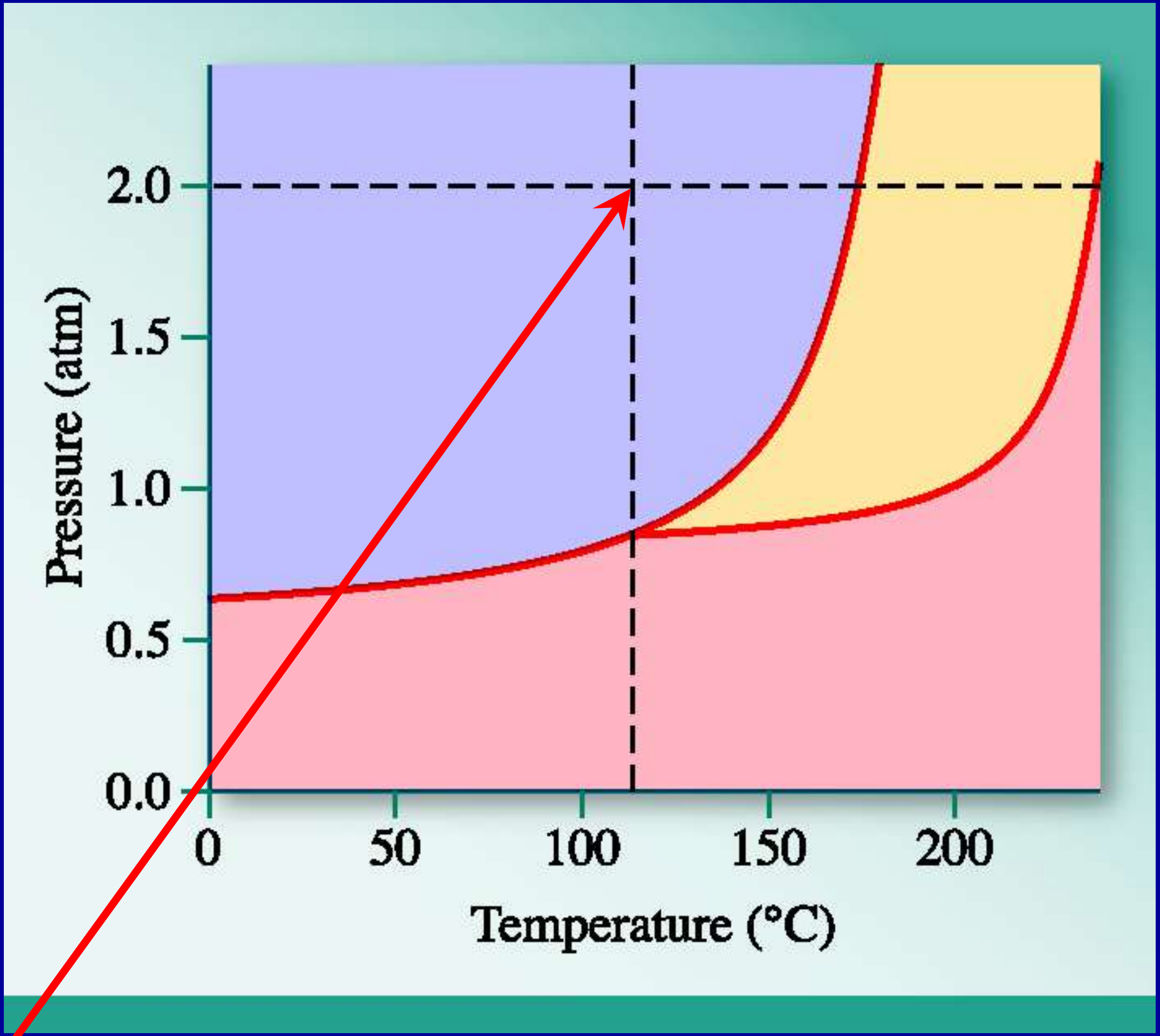


normal melting point

~135^{o}C

normal boiling point

~200^{o}C



solid physical state

Key Points

- Intermolecular forces
  - Dipole-dipole interactions
  - Hydrogen bonding
  - (London) dispersion forces
- Properties of liquids
  - Surface tension
  - Viscosity
  - Vapor pressure
    - Clausius-Clapeyron equation

- Crystal structure
  - Unit cells
    - Lattice point
  - Packing spheres
    - Coordination number
    - Cubic unit cells
  - Closest Packing
- Types of crystals
  - Ionic
  - Covalent
  - Molecular
  - Metallic

- **Amorphous solids**
- **Phase changes**
  - **Liquid-vapor transitions**
    - **Boiling point**
    - **Heat of vaporization**
    - **Critical temperature and pressure**
  - **Solid-liquid transitions**
    - **Melting point**
    - **Heat of fusion**
- **Phase diagrams**