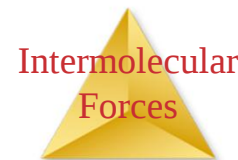


Chemistry, The Central Science, 10th edition
Theodore L. Brown; H. Eugene LeMay, Jr.;
and Bruce E. Bursten

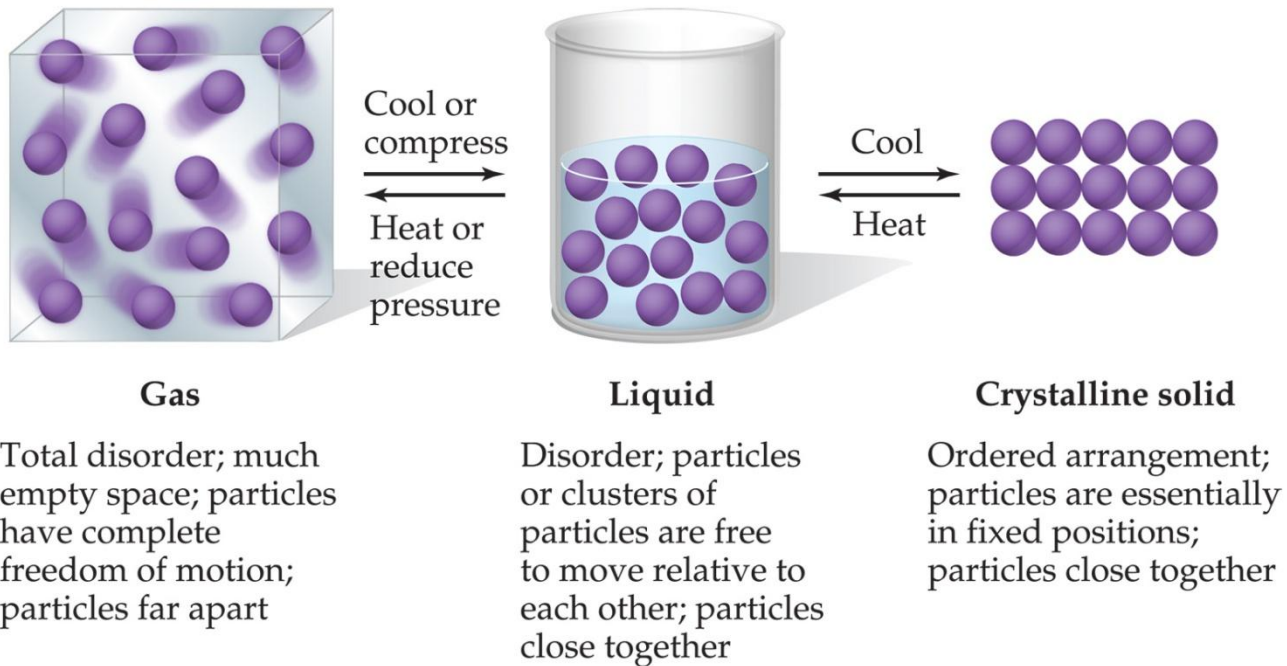
Chapter 11

Intermolecular Forces, Liquids, and Solids



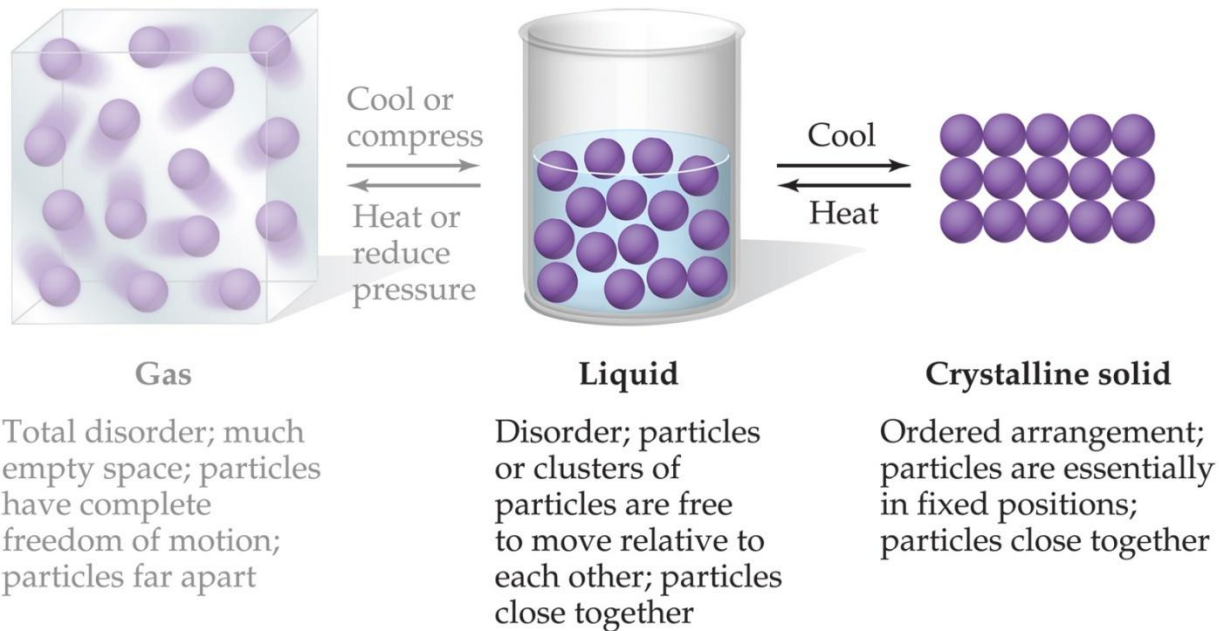
States of Matter

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



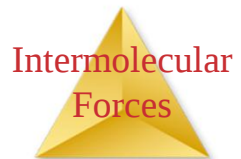
States of Matter

Because in the solid and liquid states particles are closer together, we refer to them as condensed phases.



The States of Matter

- 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



Properties of the Phases

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

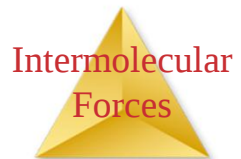
- *Intra* molecular forces

Bonds between atoms

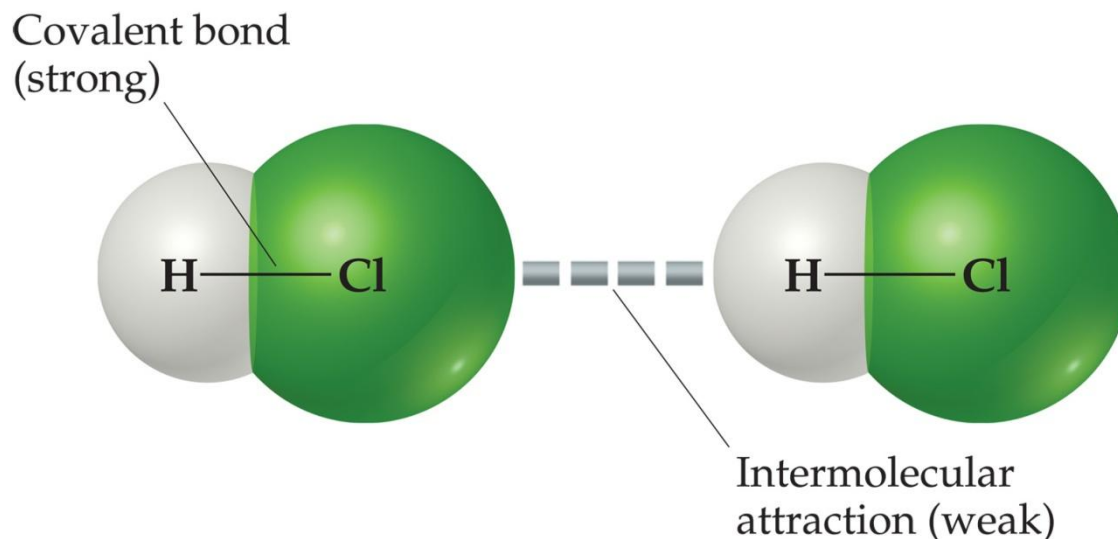
(covered in 115)

- *Inter* molecular forces

Interaction between molecules

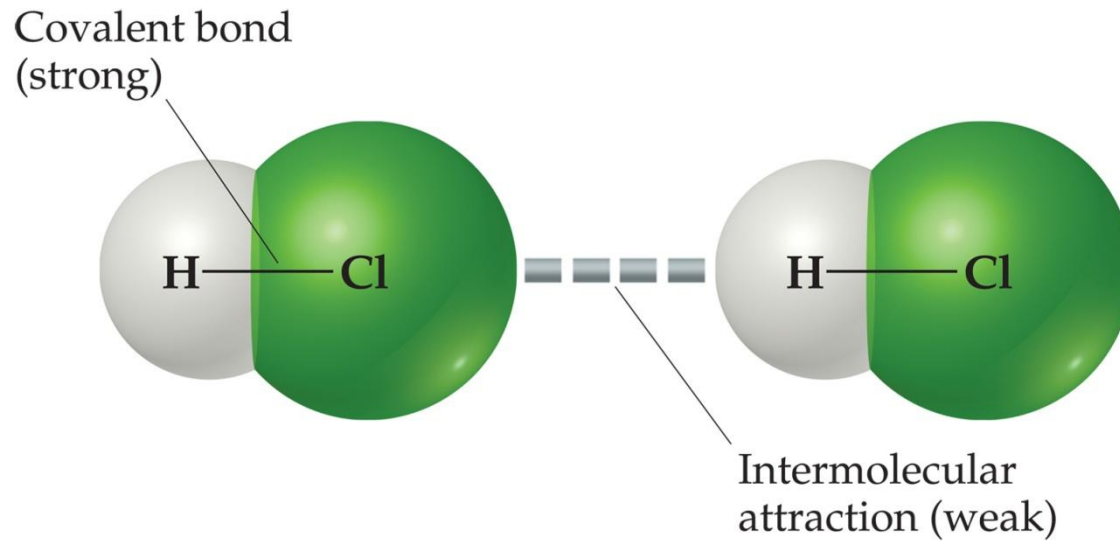


Intermolecular Forces



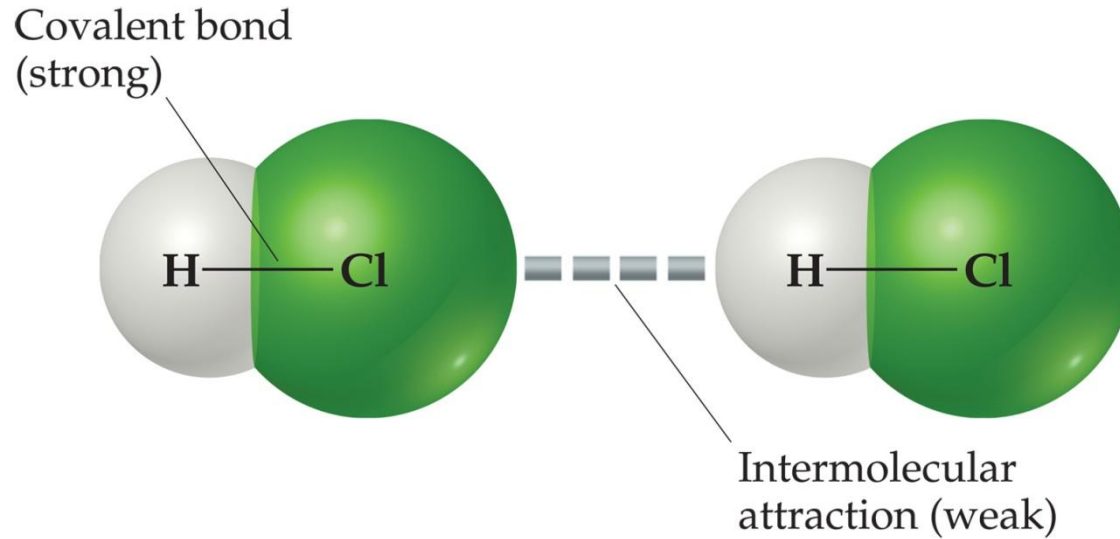
The attractions between molecules are not nearly as strong as the intramolecular attractions that hold compounds together.

Intermolecular Forces



They are, however, strong enough to control physical properties such as boiling and melting points, vapor pressures, and viscosities.

Intermolecular Forces

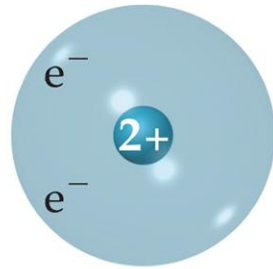


These intermolecular forces as a group are referred to as **van der Waals forces**.

van der Waals Forces

- London dispersion forces
- Dipole-dipole interactions
- Hydrogen bonding

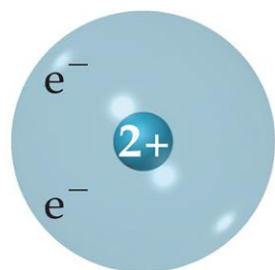
London Dispersion Forces



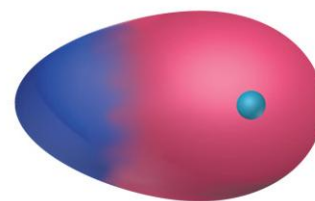
Helium atom 2

While the electrons in the 1s orbital of helium would repel each other (and, therefore, tend to stay far away from each other), it does happen that they occasionally wind up on the same side of the atom.

London Dispersion Forces



Helium atom 2

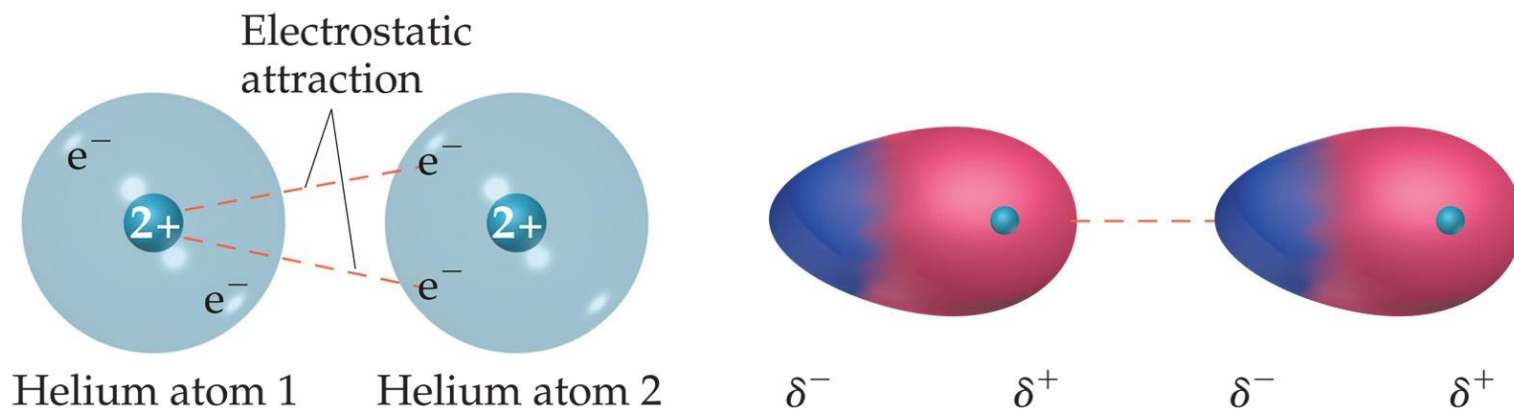


δ^-

δ^+

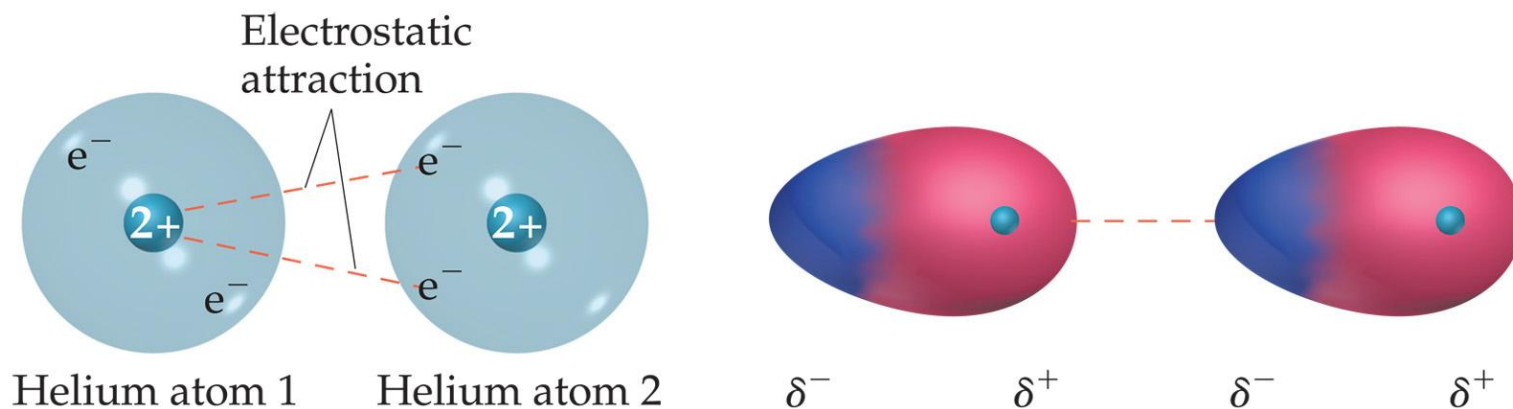
At that instant, then, the helium atom is polar, with an excess of electrons on the left side and a shortage on the right side.

London Dispersion Forces



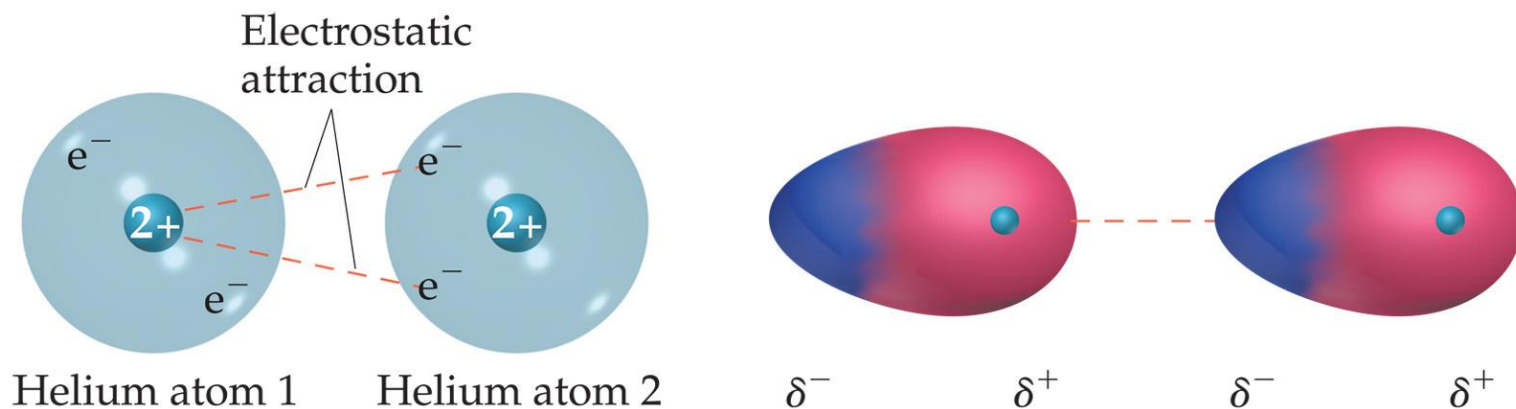
Another helium nearby, then, would have a dipole induced in it, as the electrons on the left side of helium atom 2 repel the electrons in the cloud on helium atom 1.

London Dispersion Forces



London dispersion forces, or dispersion forces, are attractions between an instantaneous dipole and an induced dipole.

London Dispersion Forces

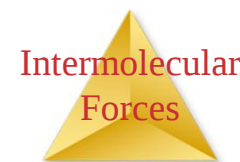


- These forces are present in *all* molecules, whether they are polar or nonpolar.
- The tendency of an electron cloud to distort in this way is called polarizability (to give physical polarity to).

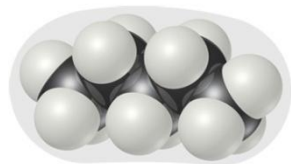
Factors Affecting London Forces

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

- The strength of dispersion forces tends to increase with increased molecular weight.
- Larger atoms have larger electron clouds, which are easier to polarize.



Factors Affecting London Forces



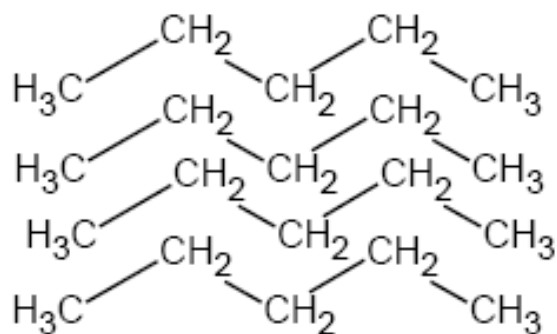
n-Pentane
(bp = 309.4 K)



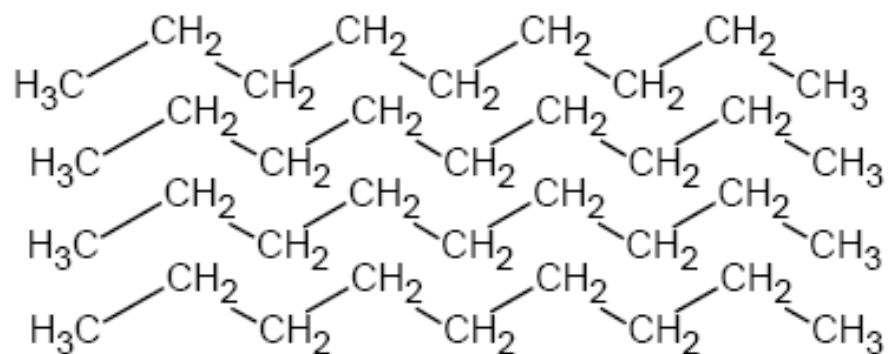
Neopentane
(bp = 282.7 K)

- The shape of the molecule affects the strength of dispersion forces: long, skinny molecules (like *n*-pentane) tend to have stronger dispersion forces than short, fat ones (like neopentane).
- This is due to the increased surface area in *n*-pentane that allows the molecules to make contact over the entire surface area.

Comparing London attractions



four 5-carbon molecules



four 9-carbon molecules

n-pentane, C₅H₁₂

m.p. -130°C

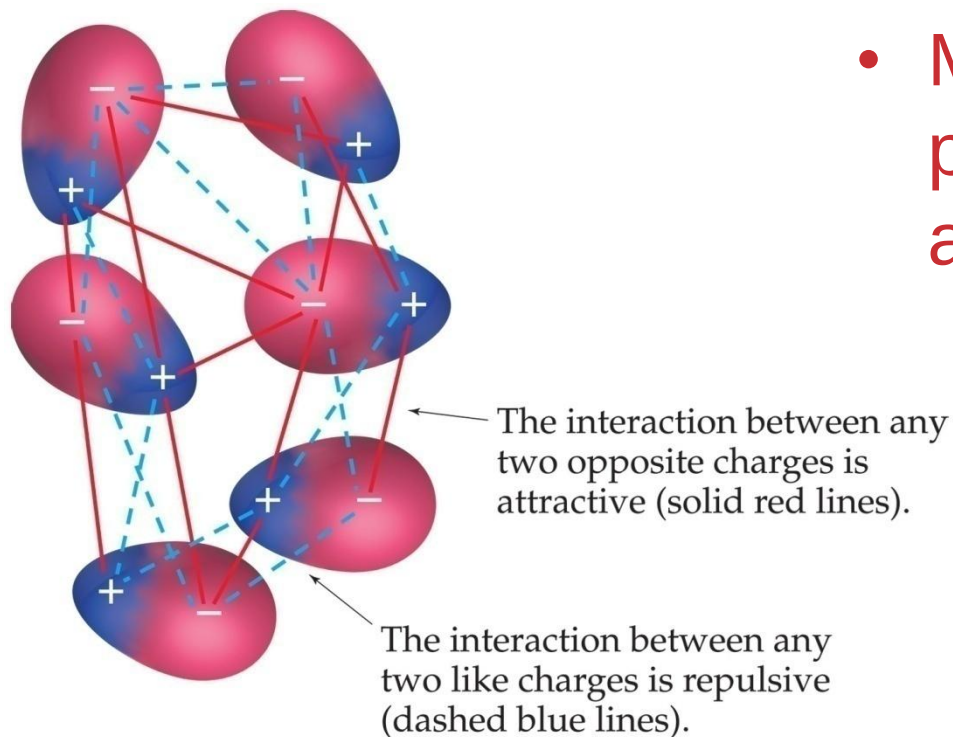
b.p. 36°C

n-nonane, C₉H₂₀

m.p. -54°C

b.p. 151°C

Dipole-Dipole Interactions



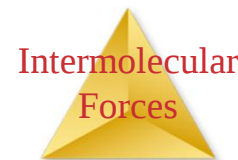
- Molecules that have permanent dipoles are attracted to each other.
 - The positive end of one is attracted to the negative end of the other and vice-versa.
 - These forces are only important when the molecules are close to each other.

Explaining macroscopic behavior by reasoning about intermolecular forces

<u>name</u>	<u>formula</u>	<u>melting point</u>
lauric acid	$\text{C}_{11}\text{H}_{23}\text{COOH}$	44° C
myristic acid	$\text{C}_{13}\text{H}_{27}\text{COOH}$	58° C
palmitic acid	$\text{C}_{15}\text{H}_{31}\text{COOH}$	63° C
stearic acid	$\text{C}_{17}\text{H}_{35}\text{COOH}$	70° C



- As the number of carbons increases in a series of fatty acids...
- the melting point increases.
- This is because...
- as the number of carbons increases, the chains get longer. When the chains are longer, the molecules are bigger.
- The larger the molecule, the greater the dispersion forces.
- When the attractive forces holding particles together is greater, you have to get to a higher temperature to break those forces, so the melting point is higher.



Dipole-Dipole Interactions

Substance	Molecular Weight (amu)	Dipole Moment μ (D)	Boiling Point (K)
Propane, $\text{CH}_3\text{CH}_2\text{CH}_3$	44	0.1	231
Dimethyl ether, CH_3OCH_3	46	1.3	248
Methyl chloride, CH_3Cl	50	1.9	249
Acetaldehyde, CH_3CHO	44	2.7	294
Acetonitrile, CH_3CN	41	3.9	355

For molecules of similar molecular mass the more polar the molecule, the higher is its boiling point.

(Dipole moment is defined as the product magnitude of charge on the atoms and the distance between the two bonded atoms. Its SI unit is coulomb meter).



Which Have a Greater Effect:

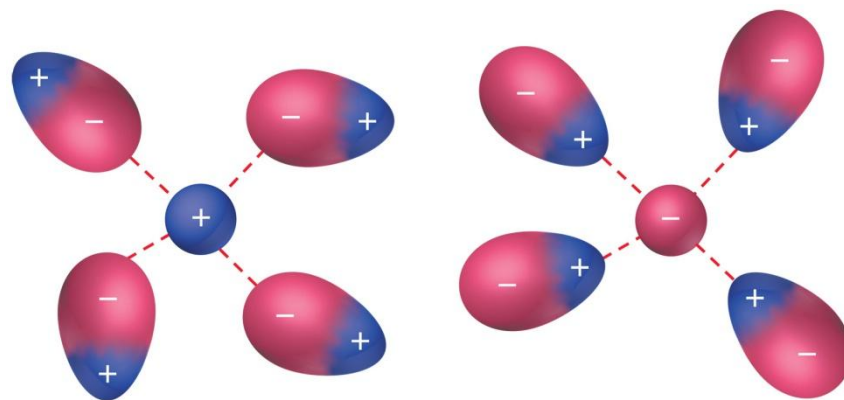
Dipole-Dipole Interactions or Dispersion Forces?

- If two molecules are of comparable size and shape, dipole-dipole interactions will likely be the dominating force.
- If one molecule is much larger than another, dispersion forces will likely determine its physical properties.



Ion-Dipole Interactions

- A fourth type of force, ion-dipole interactions are an important force in solutions of ions.
- The strength of these forces are what make it possible for ionic substances to dissolve in polar solvents.

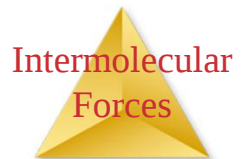


Cation-dipole attractions

Anion-dipole attractions

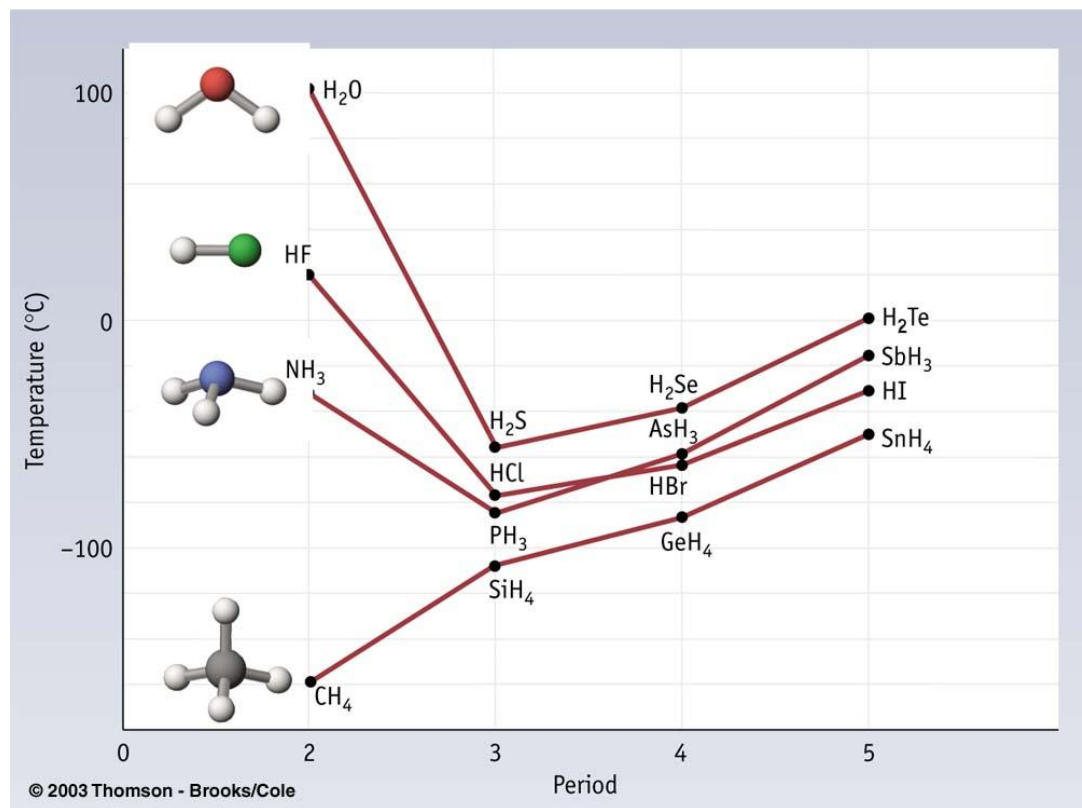
Hydrogen Bonding

- Very Strong intermolecular Bonds between partially positive hydrogen in one molecule and a highly electronegative atom (F, Cl, O, N) in another molecule.



How Do We Explain This?

Boiling
Point



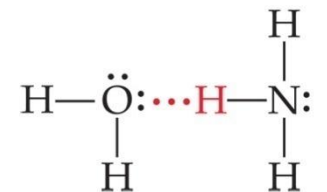
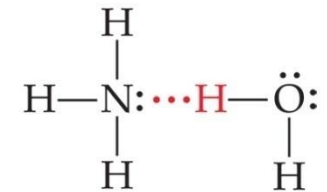
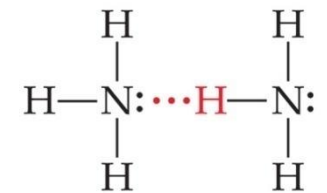
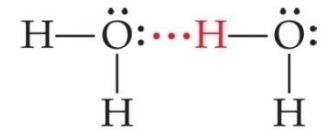
Molecular wt →



- Water has a high boiling point, high specific heat and high heat of vaporization indicating that intermolecular forces between the water molecules are quite strong.
- HF and NH₃ have similar properties

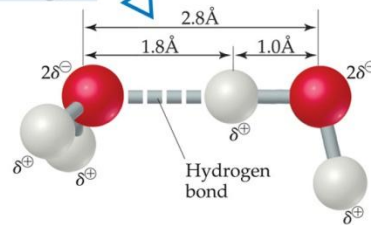
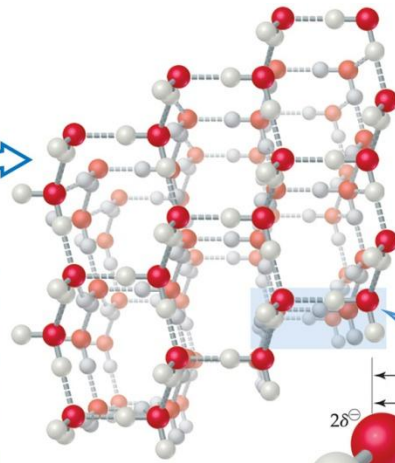
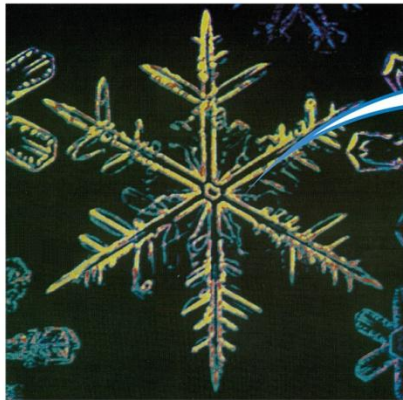
Hydrogen Bonding

- The dipole-dipole interactions experienced when H is bonded to N, O, or F are unusually strong.
- We call these interactions **hydrogen bonds**.



- Hydrogen bonding is a special type of molecular attraction between the hydrogen atom in a polar bond and nonbonding electron pair on a nearby small electronegative ion or atom (usually F, O or N).

Hydrogen Bonding



Hydrogen bonding arises in part from the high electronegativity of nitrogen, oxygen, and fluorine.

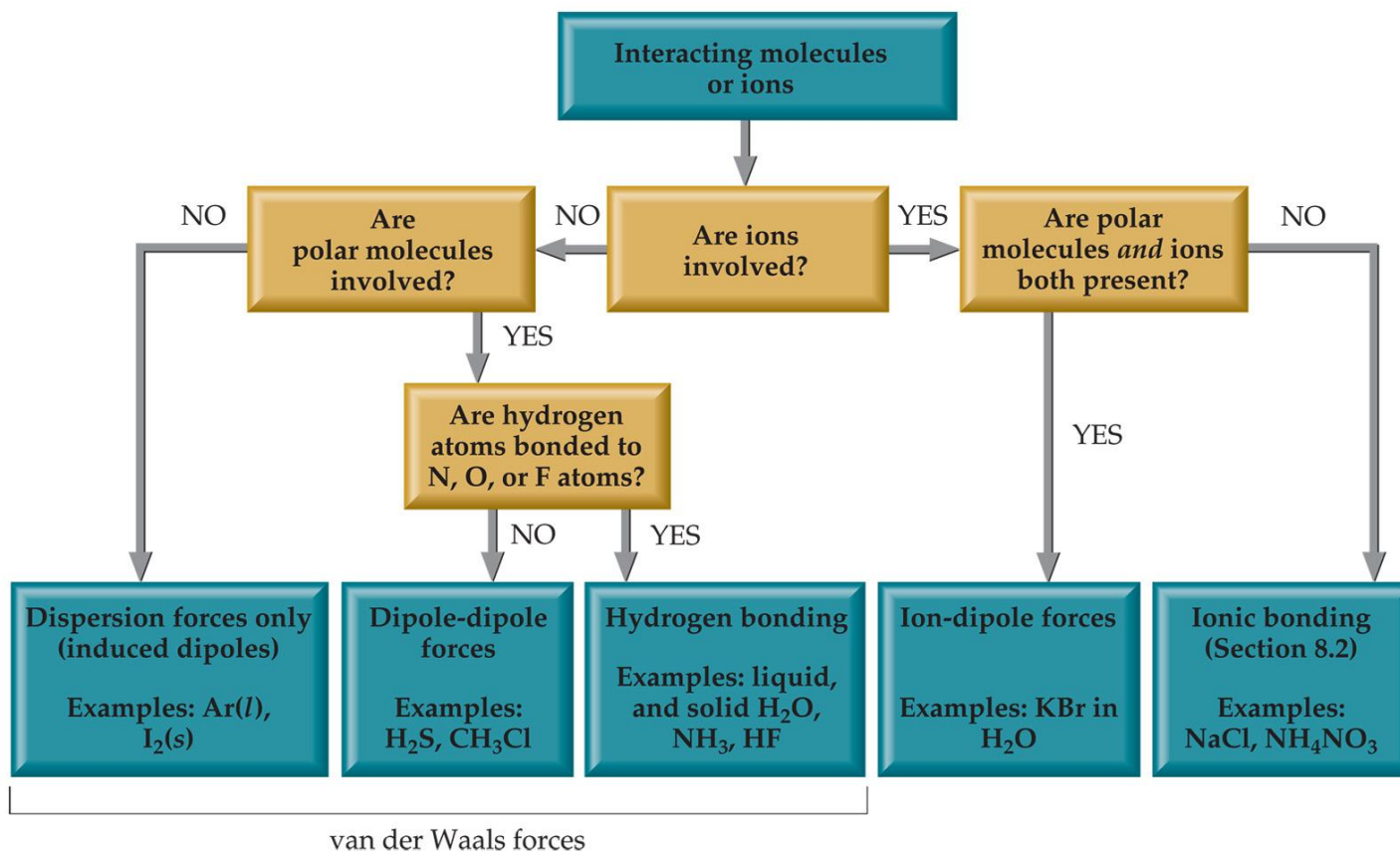
Also, when hydrogen is bonded to one of those very electronegative elements, the hydrogen nucleus is exposed.

In which of the following substances is hydrogen bonding likely to play an important role in determining physical properties: methane (CH_4), hydrazine (H_2NNH_2), methyl fluoride (CH_3F), or hydrogen sulfide (H_2S)?

Draw the Lewis structure for all the above and determine which can support hydrogen bonding.

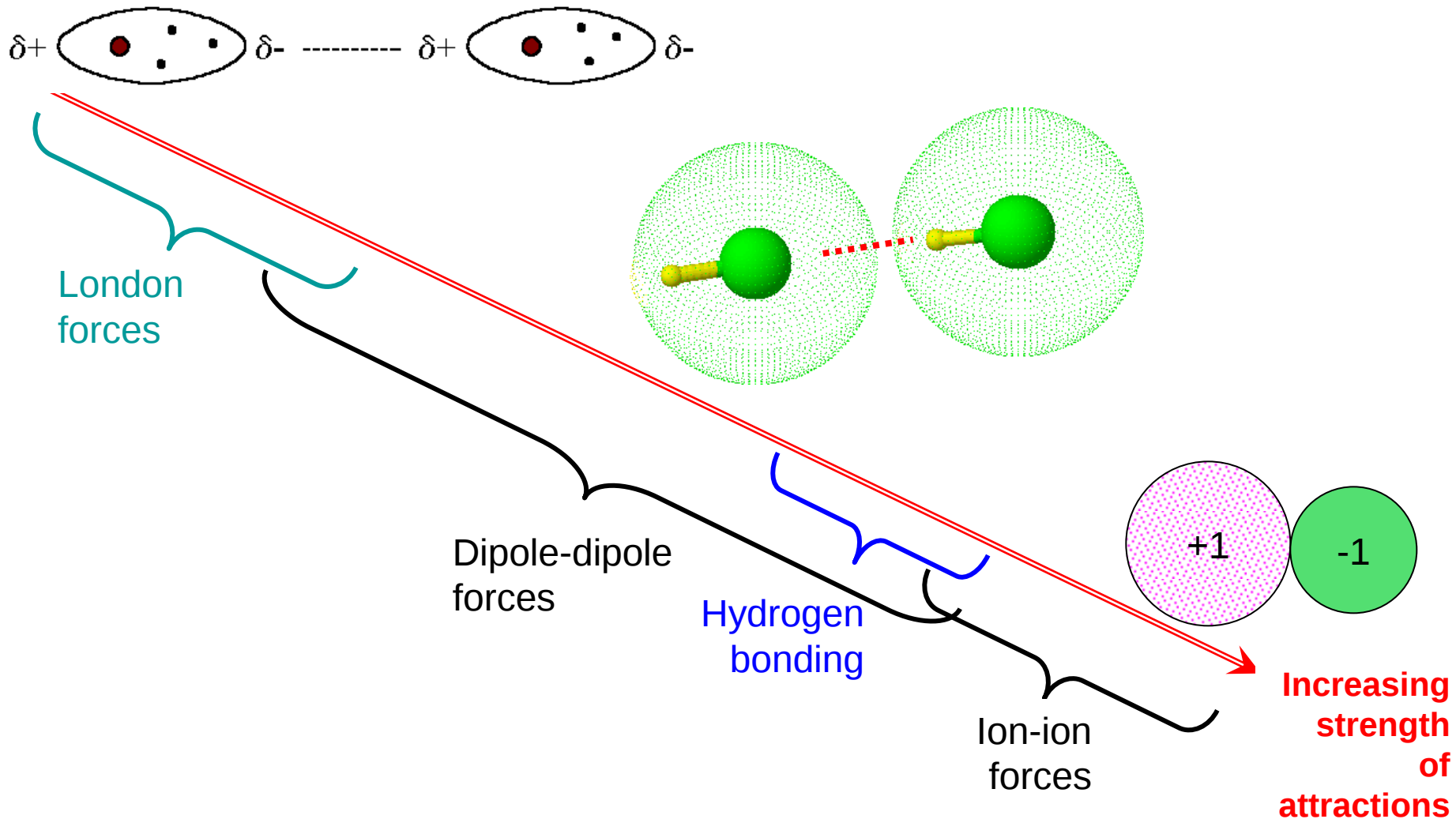
In which of the following substances is significant hydrogen bonding possible: methylene chloride (CH_2Cl_2), phosphine (PH_3), hydrogen peroxide (HOOH), or acetone (CH_3COCH_3)?

Summarizing Intermolecular Forces



Summarizing

From weakest to strongest

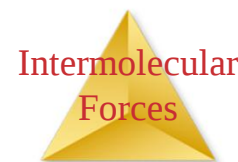


London dispersion forces are always present

- Any molecules that experience one type of attraction, also experience all the weaker types of attractions
- HCl molecules experience:
 - Hydrogen bonding (which is the strongest form of dipole-dipole interactions), and
 - London dispersion forces

List the substances BaCl_2 , H_2 , CO , HF , and Ne in order of increasing boiling points.

- The attractive forces are stronger for ionic substances than for molecular ones
- The intermolecular forces of the remaining substances depend on molecular weight, polarity, and hydrogen bonding. The molecular weights are H_2 (2), CO (28), HF (20), and Ne (20).
- The boiling point of H_2 should be the lowest because it is nonpolar and has the lowest molecular weight.
- The molecular weights of CO , HF , and Ne are roughly the same. Because HF can hydrogen bond, however, it should have the highest boiling point of the three.
- Next is CO , which is slightly polar and has the highest molecular weight. Finally, Ne , which is nonpolar, should have the lowest boiling point of these three.
- The predicted order of boiling points is therefore:



(A)Identify the intermolecular forces present in the following substances, and

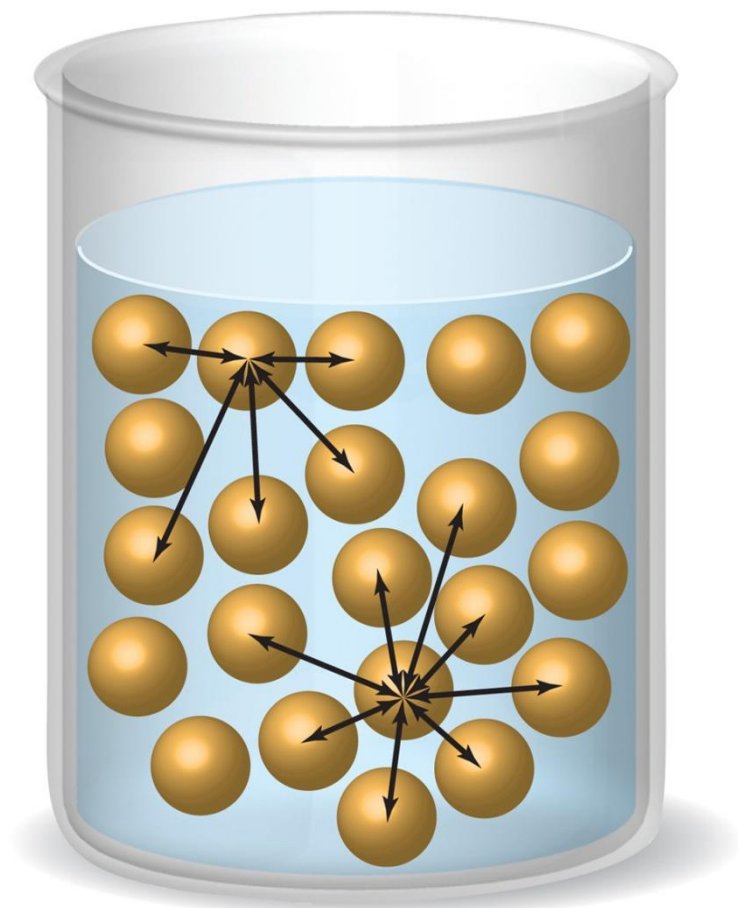
(B) select the substance with the highest boiling point:

CH_3CH_3 , CH_3OH , and $\text{CH}_3\text{CH}_2\text{OH}$

Answers: (a) CH_3CH_3 has only dispersion forces, whereas the other two substances have both dispersion forces and hydrogen bonds; (b) $\text{CH}_3\text{CH}_2\text{OH}$



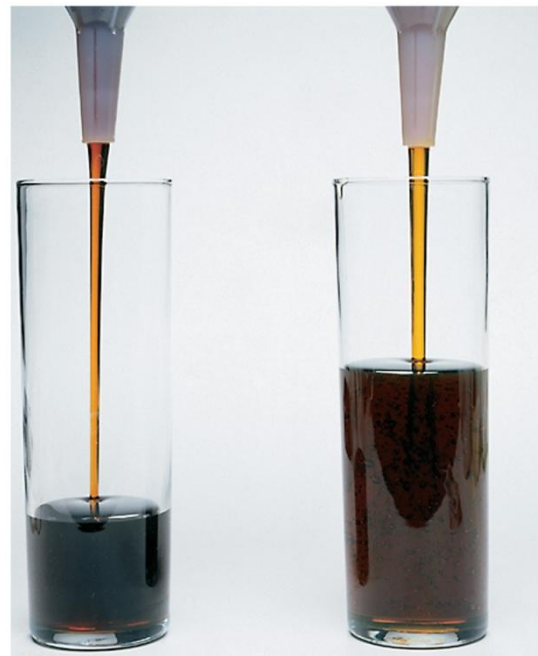
Intermolecular Forces Affect Many Physical Properties



The strength of the attractions between particles can greatly affect the properties of a substance or solution.

Viscosity

- Resistance of a liquid to flow is called **viscosity**.
- It is related to the ease with which molecules can move past each other.
- Viscosity increases with stronger intermolecular forces caused by increase in the molecular weight, and decreases with higher temperature.



Substance	Formula	Viscosity (kg/m-s)
Hexane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	3.26×10^{-4}
Heptane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	4.09×10^{-4}
Octane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	5.42×10^{-4}
Nonane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	7.11×10^{-4}
Decane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	1.42×10^{-3}

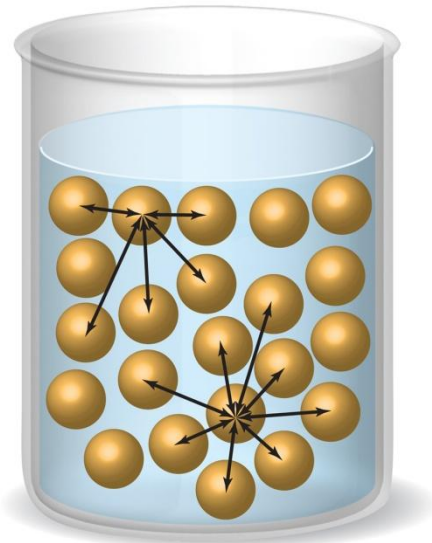
Explaining macroscopic behavior: viscosity

- Viscosity is the resistance to flow in liquids
- Viscosity is dependent on more than just molecule size – it also depends on the kinds of attractive forces between molecules
- Viscosities of various liquids at 20°C (in centipoise)

<u>Liquid</u>	<u>Viscosity (cp)</u>	<u>Type of IM attraction</u>
water	1.002	H-bonding & London
tetrachloromethane (CCl ₄)	0.969	London
olive oil	84	London
oleic acid	25	London
glycerine	1490	H-bonding & London



Surface Tension



Surface tension results from the net inward force experienced by the molecules on the surface of a liquid.

The inward force is driven by maximization of the hydrogen bonding of the water molecules at the surface and results in a tighter packing at the surface.



Water

Hg

What forms the meniscus? Capillary action?

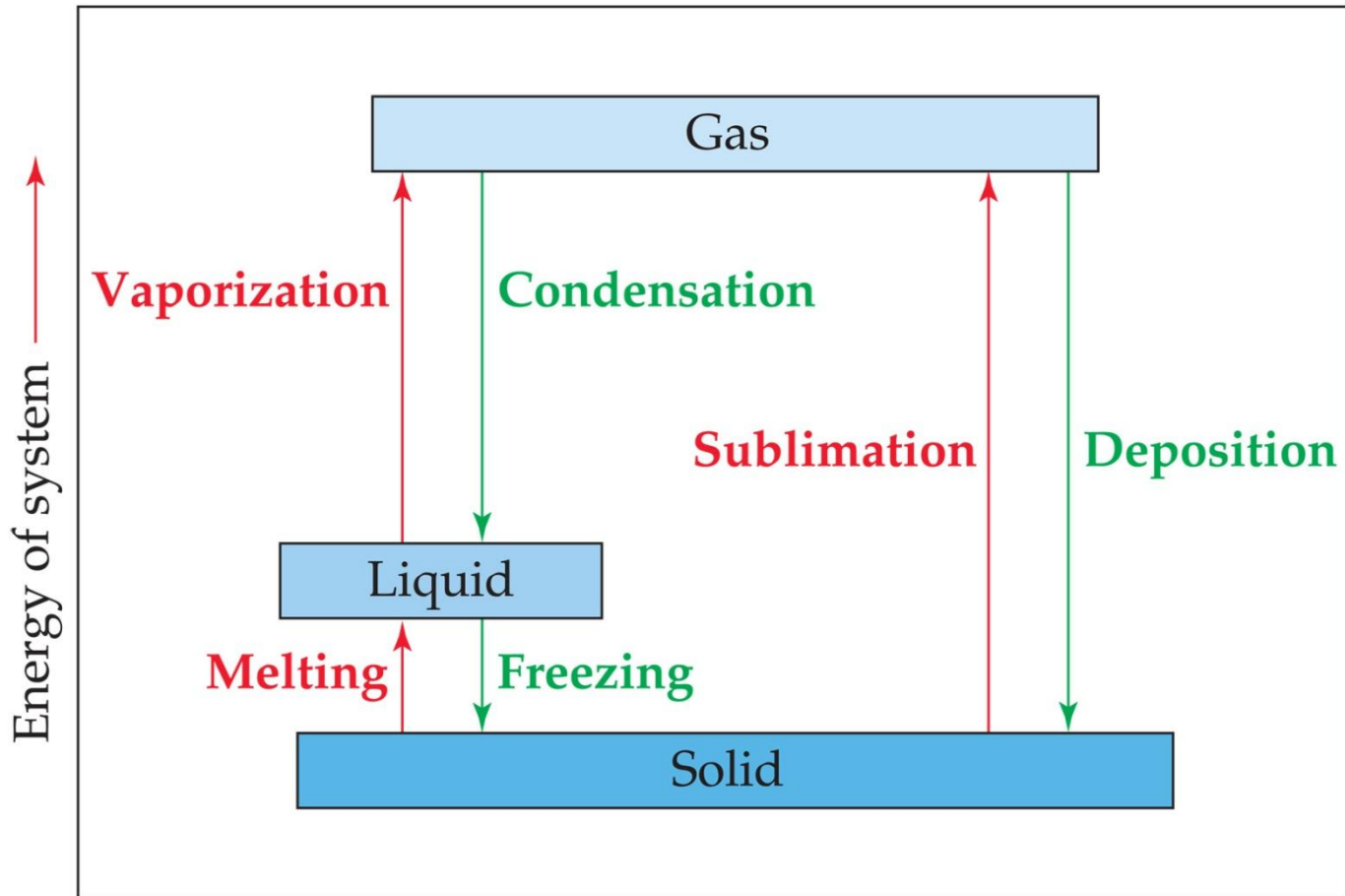
Adhesive (interaction with glass)

VS

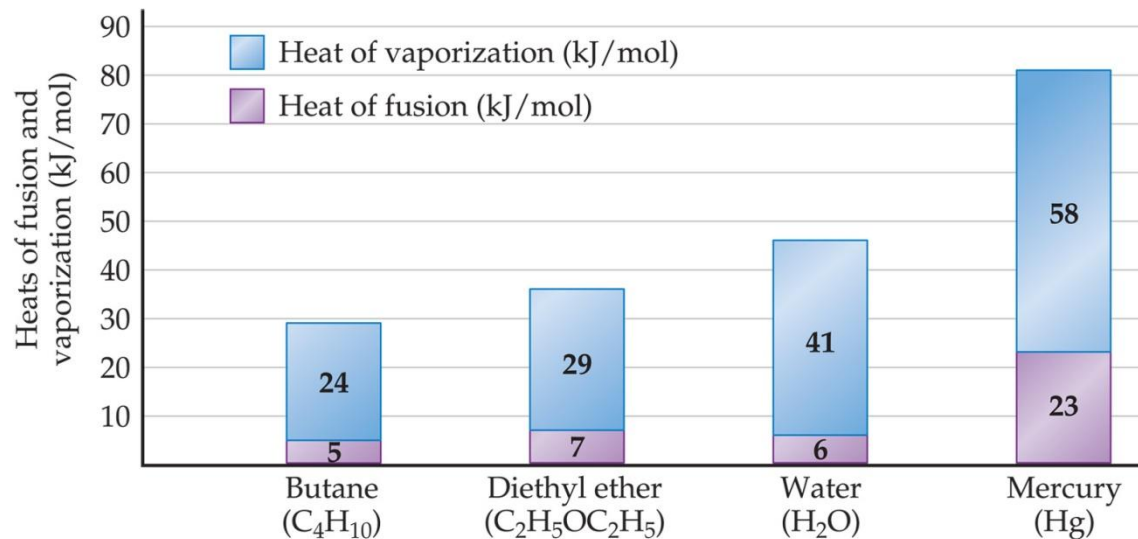
cohesive forces (interaction between molecules)



Phase Changes



Energy Changes Associated with Changes of State

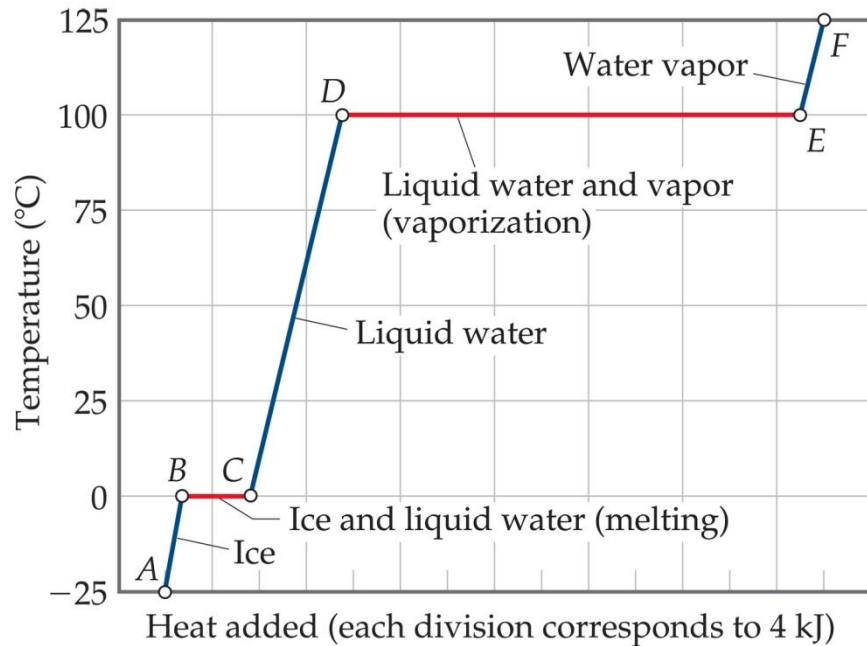


- Heat of Fusion: Energy required to change a solid at its melting point to a liquid.
- Heat of Vaporization: Energy required to change a liquid at its boiling point to a gas.

- Heat of Sublimation: Is the enthalpy change required to transform a solid directly into gaseous state.

- A refrigerator contains an enclosed gas that can be liquefied under pressure. The liquid absorbs heat as it subsequently evaporates and the refrigerator cools in the process. The vapor is then recycled through a compressor.
- The heat absorbed by the liquid during vaporization is released during condensation. This heat is dissipated through cooling coils at the back of the unit.

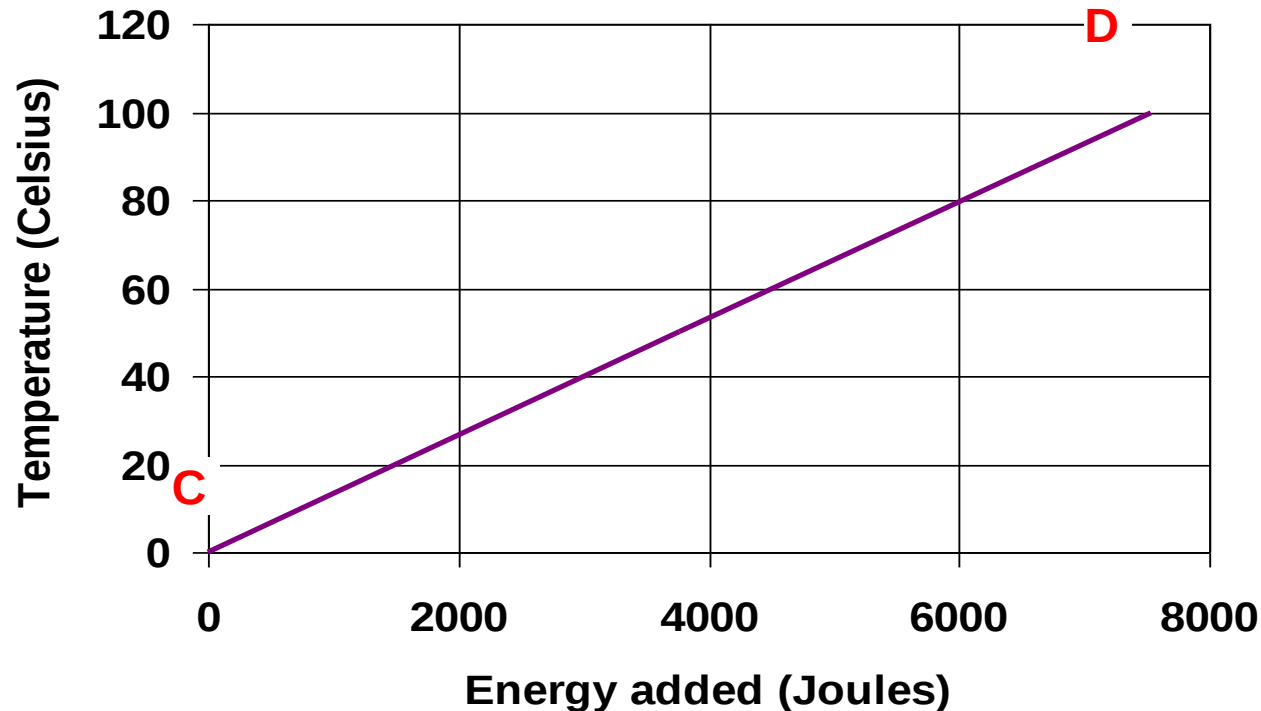
Energy Changes Associated with Changes of State



- The heat added to the system at the melting and boiling points goes into pulling the molecules farther apart from each other.
- The temperature of the substance does not rise during the phase change.

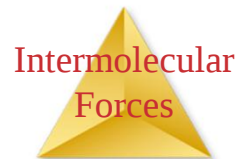
Focus on Liquid to Gas:

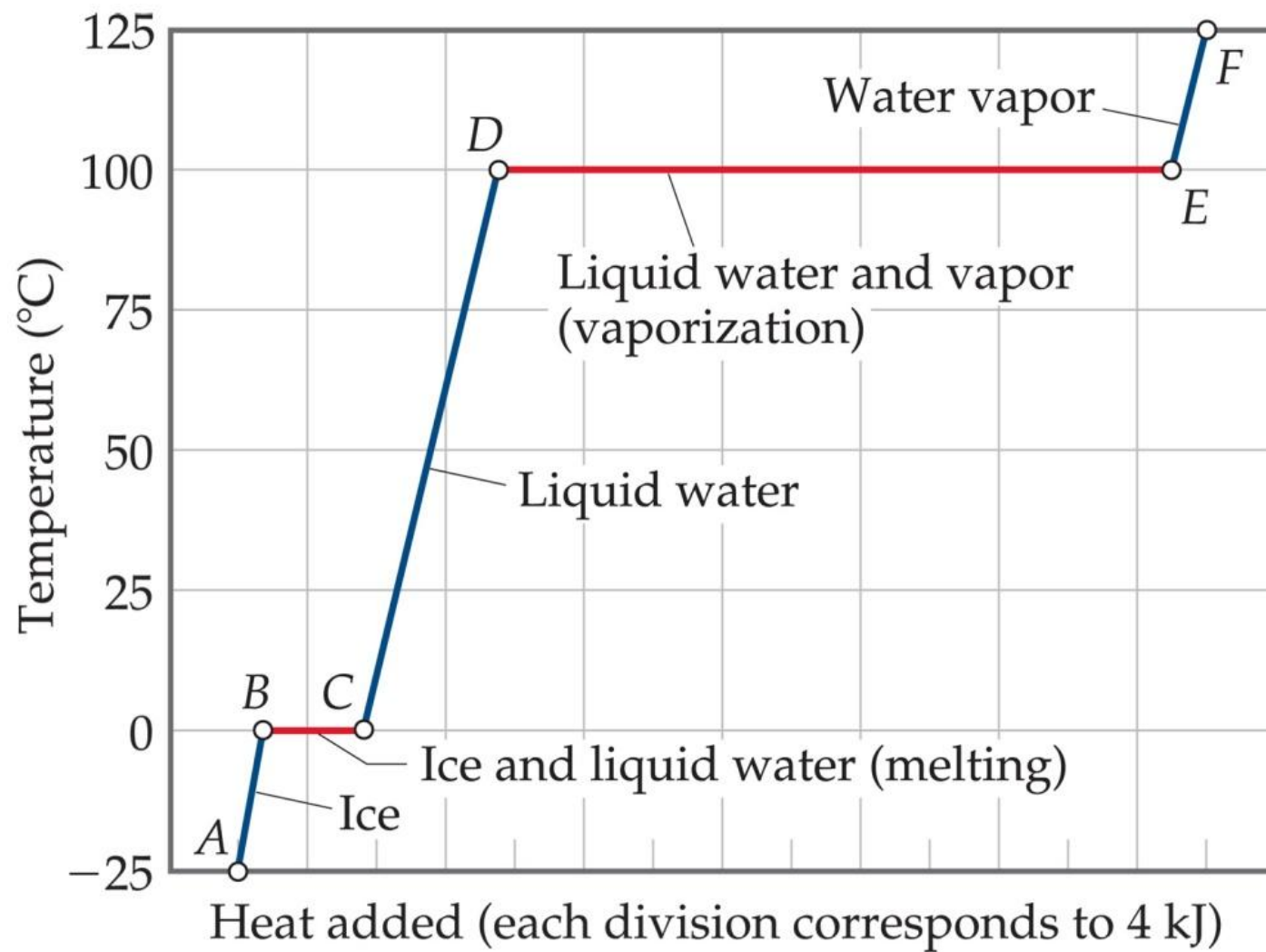
For a 1.00-mol sample of liquid water



What happens if you add more heat energy to liquid water at 100°C?

- It boils
- What is boiling?
 - There is a statistical range of kinetic energies (velocities) of particles in the liquid
 - Some particles will always have enough energy to break away from attractive forces that keep them in liquid → evaporation (**vapor pressure**)
 - As temperature rises, eventually it is high enough that so many particles can break away that their gas pressure (vapor pressure) equals the pressure of the surroundings → boiling
- Boiling continues with no change in temperature until all liquid particles have converted to gas phase
- **Normal boiling point** is temperature at which vapor pressure reaches atmospheric pressure (1 atm, when $p_{atm} = 1\text{atm}$)





$$\Delta H(\text{during warming or cooling}) = mc\Delta T$$

$$\Delta H(\text{phase change}) = n\Delta H_{\text{phase change}}$$

m = mass of sample (g)

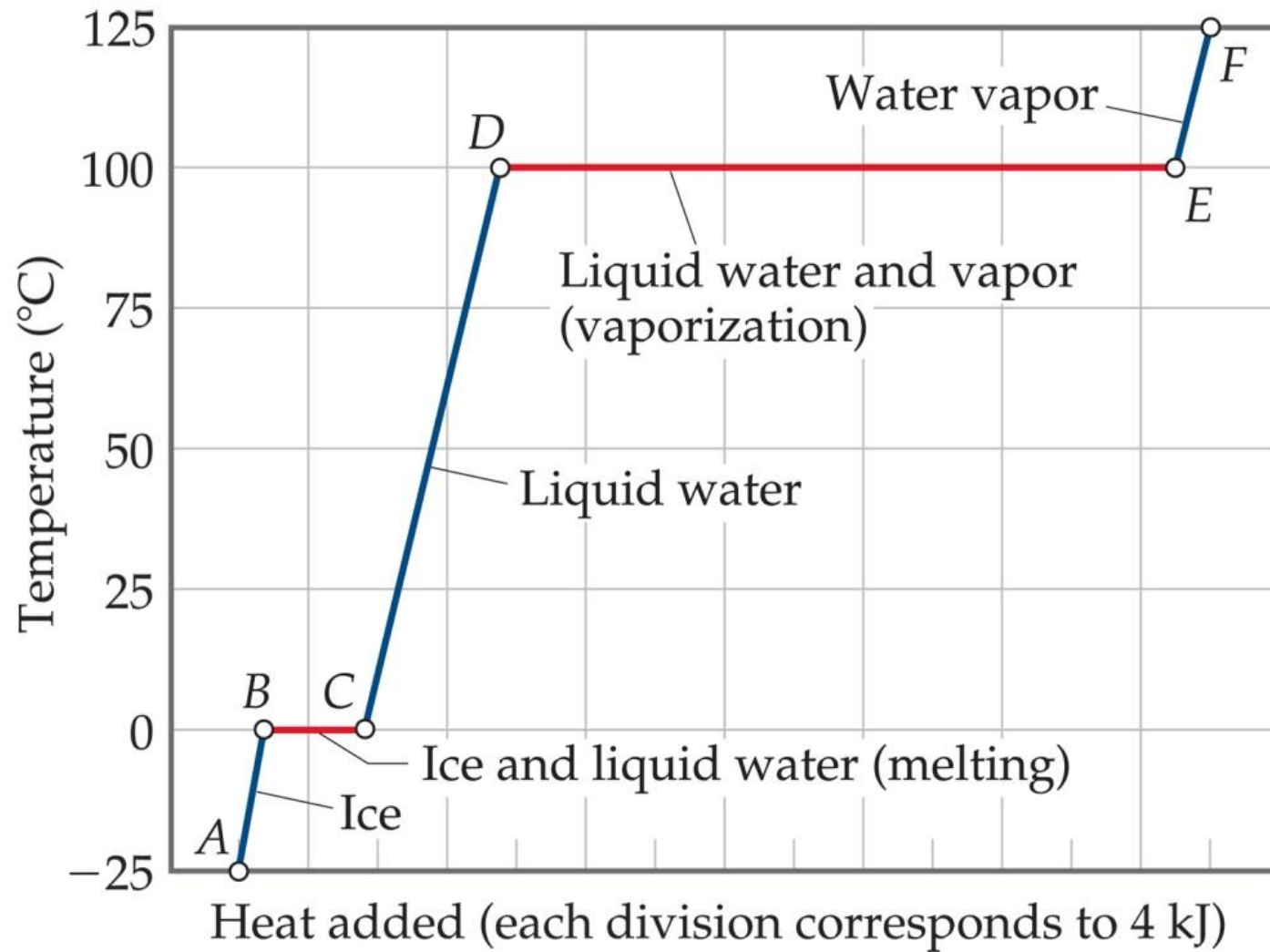
c = specific heat capacity ($\text{J/g}\cdot^{\circ}\text{C}$)

$$\Delta T = T_f - T_i$$

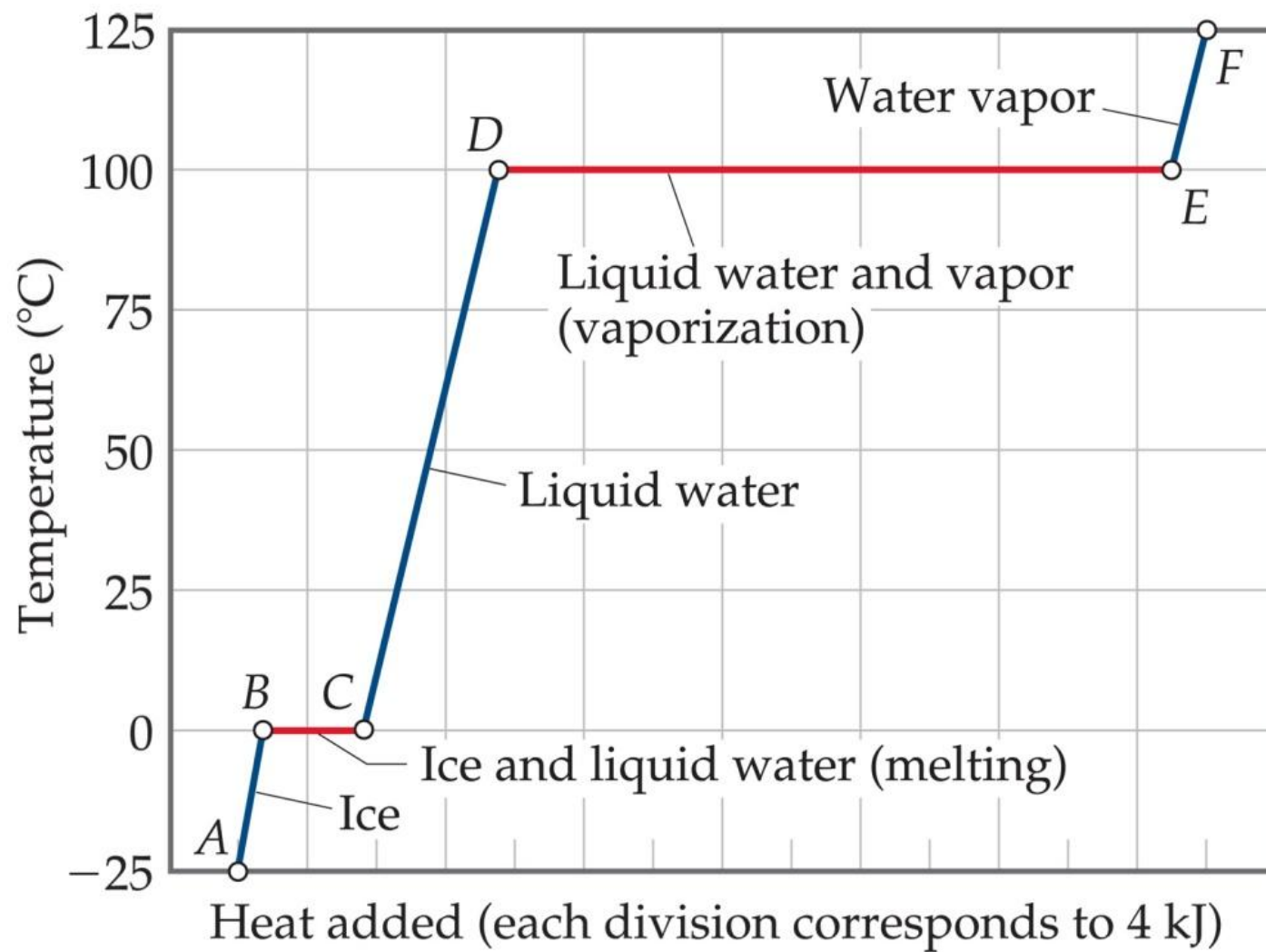
n = moles of substance

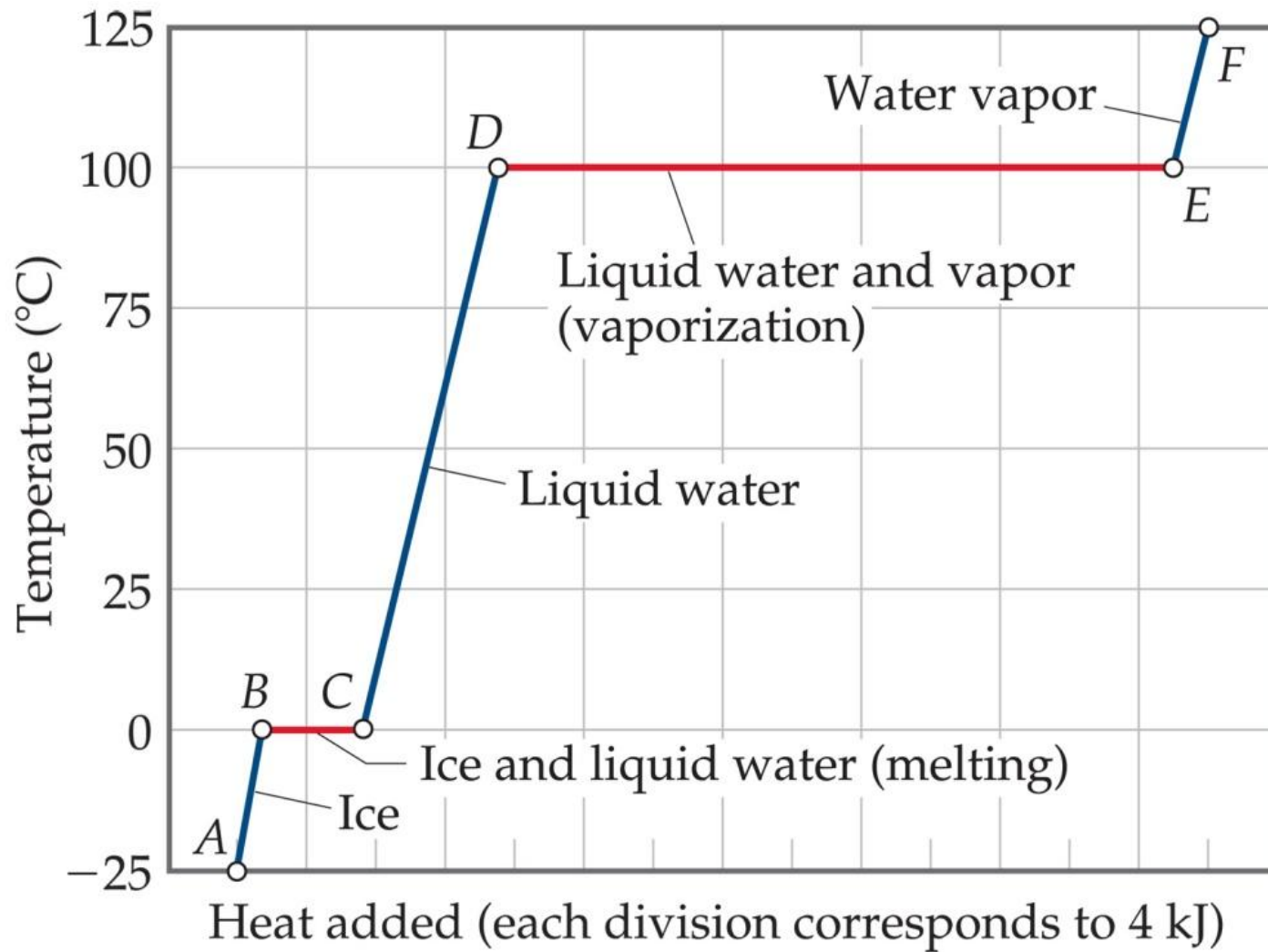
ΔH = molar enthalpy (kJ/mol)



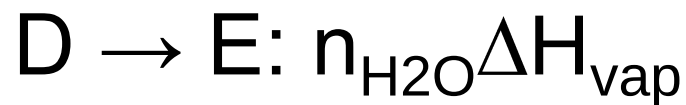
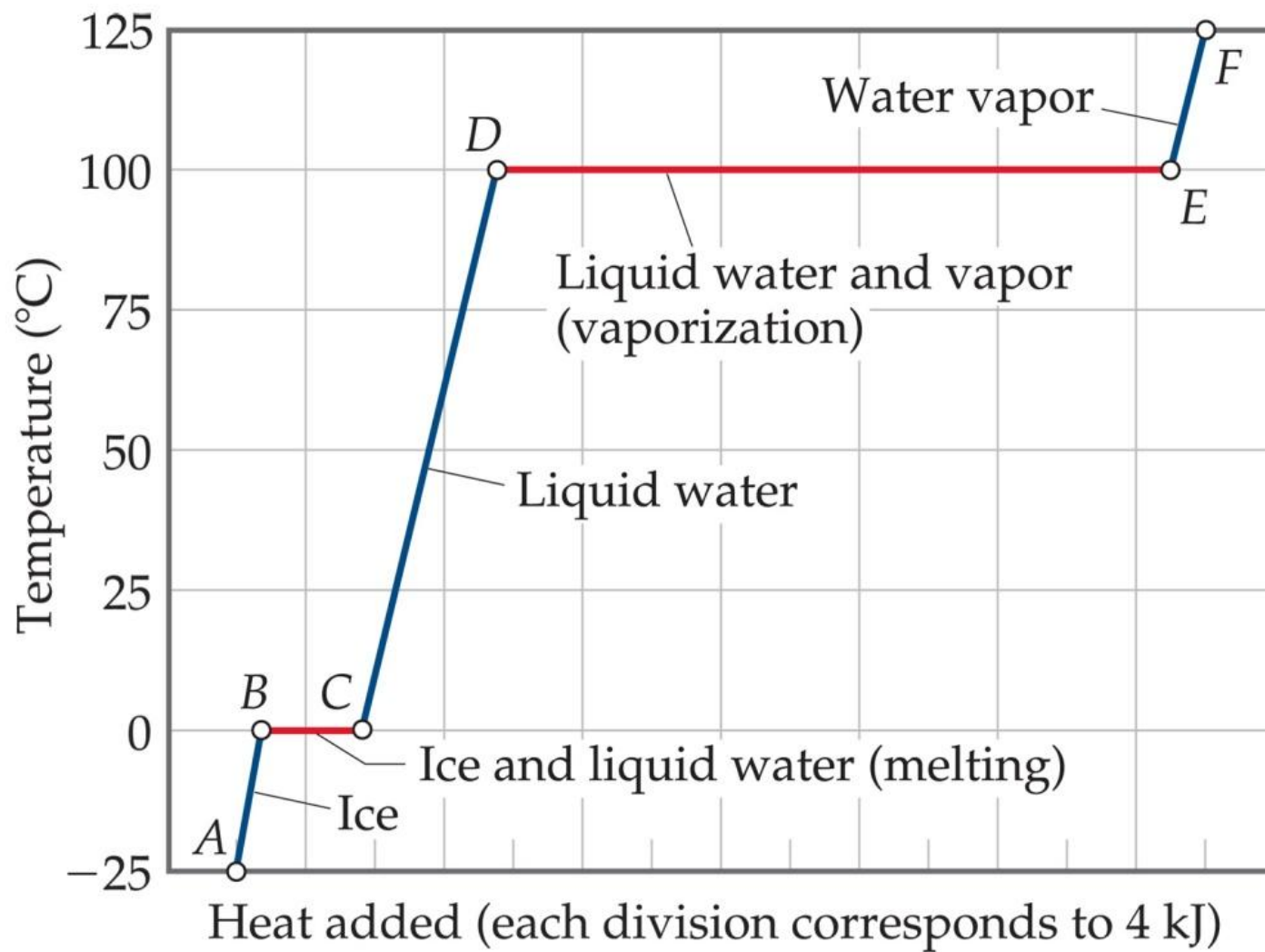


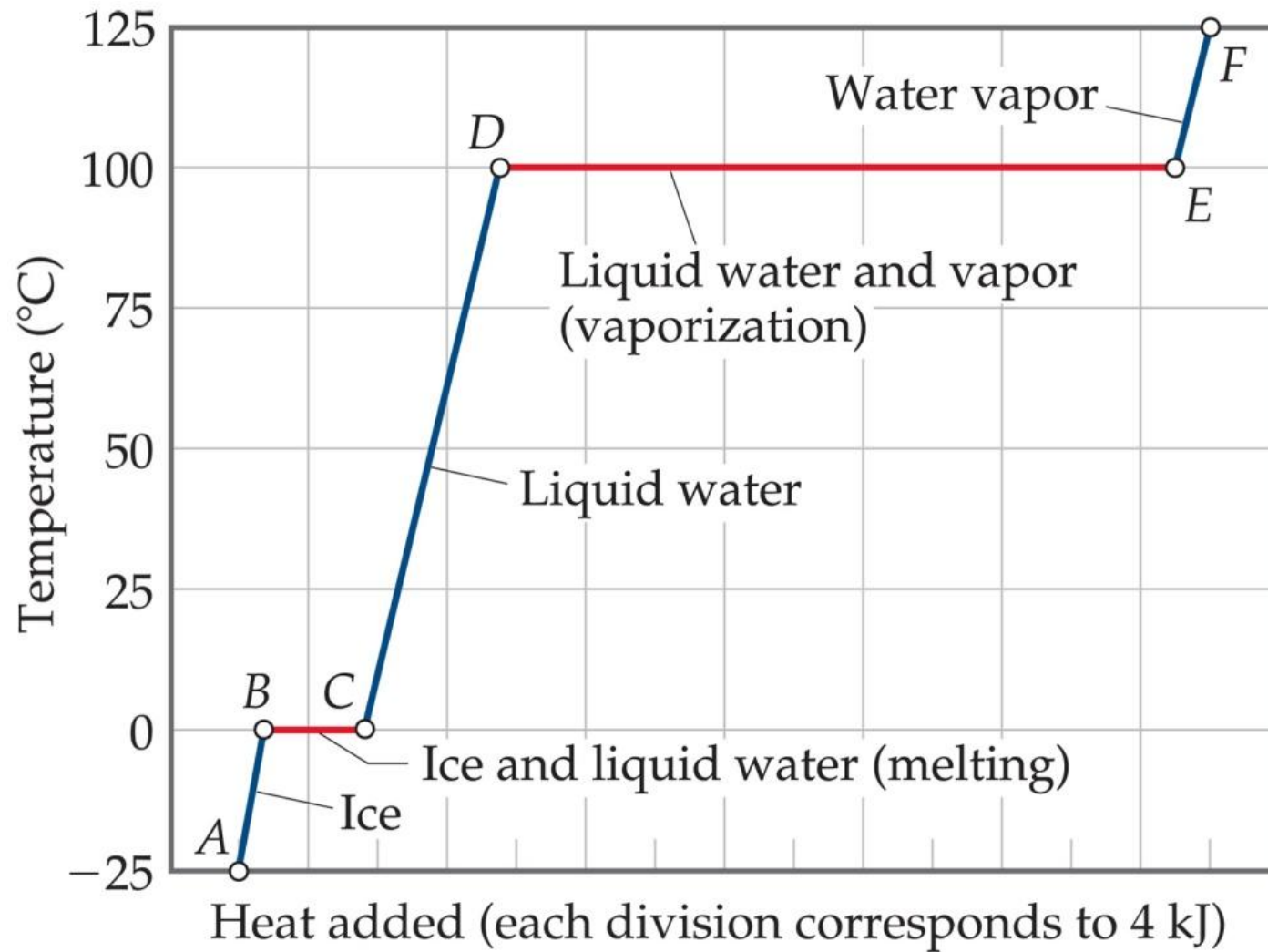
$$A \rightarrow B: c_{\text{ice}} m \Delta T$$



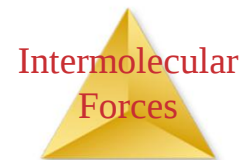


$$C \rightarrow D: c_{\text{water}} m \Delta T$$





$$E \rightarrow F: c_{\text{steam}} m \Delta T$$

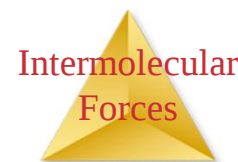


- Calculate the enthalpy change upon converting 1.00 mol of ice at -25°C to water vapor (steam) at 125°C under a constant pressure of 1 atm. The specific heats of ice, water, and steam are 2.09 J/g-K , 4.18 J/g-K and 1.84 J/g-K , respectively.

For H_2O , $\Delta H_{\text{fus}} = 6.01 \text{ kJ/mol}$ and $\Delta H_{\text{vap}} = 40.67 \text{ kJ/mol}$.

$$\Delta H = mc\Delta T$$

At the phase change $\Delta H = n (\Delta H_f)$ or (ΔH_v)



- What is the enthalpy change during the process in which 100.0 g of water at 50.0°C is cooled to ice at –30.0°C? The specific heats of ice, water, and steam are 2.09 J/g-K, 4.18 J/g-K and 1.84 J/g-K, respectively.

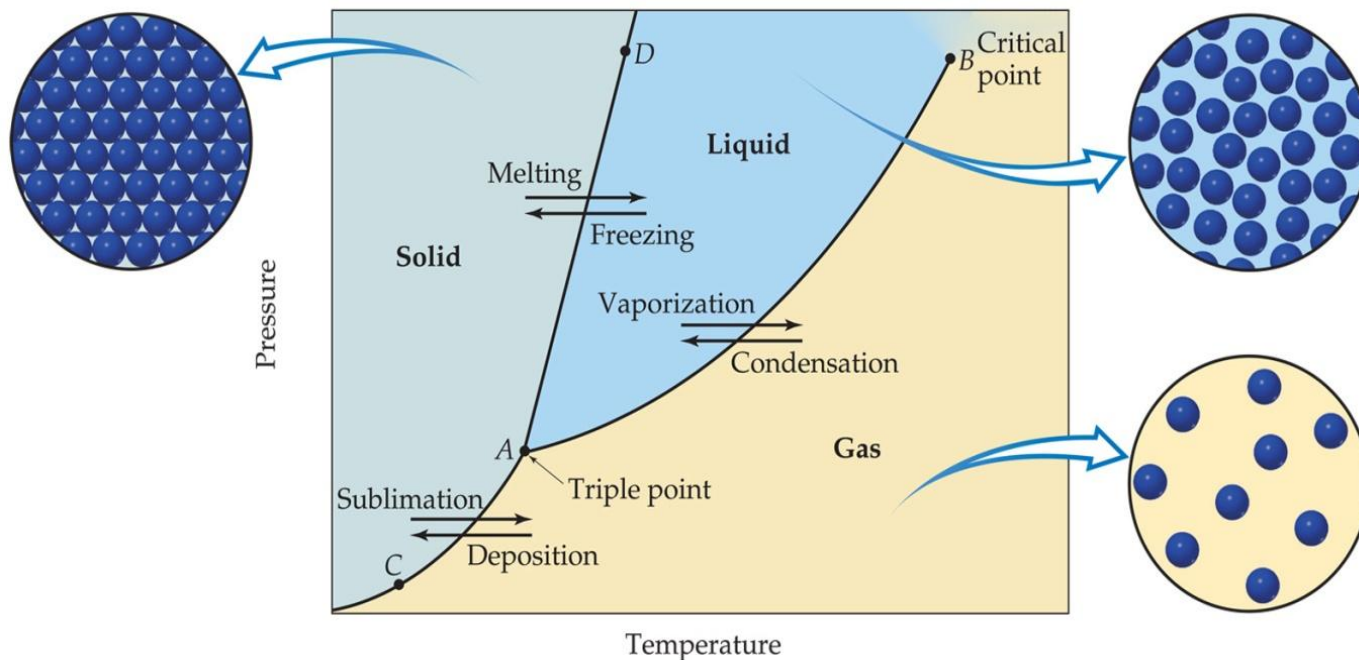
For H₂O, $\Delta H_{\text{fus}} = 6.01 \text{ kJ/mol}$ and $\Delta H_{\text{vap}} = 40.67 \text{ kJ/mol}$.

Phase Diagrams

- Pressure vs Temperature
- Illustrates curves that represent where phase transitions occur at different pressure/temperature points
- Key points
 - Triple point (three phases in equilibrium)
 - Normal boiling and melting points
 - Critical Point (liquid and gas phase has no distinction)

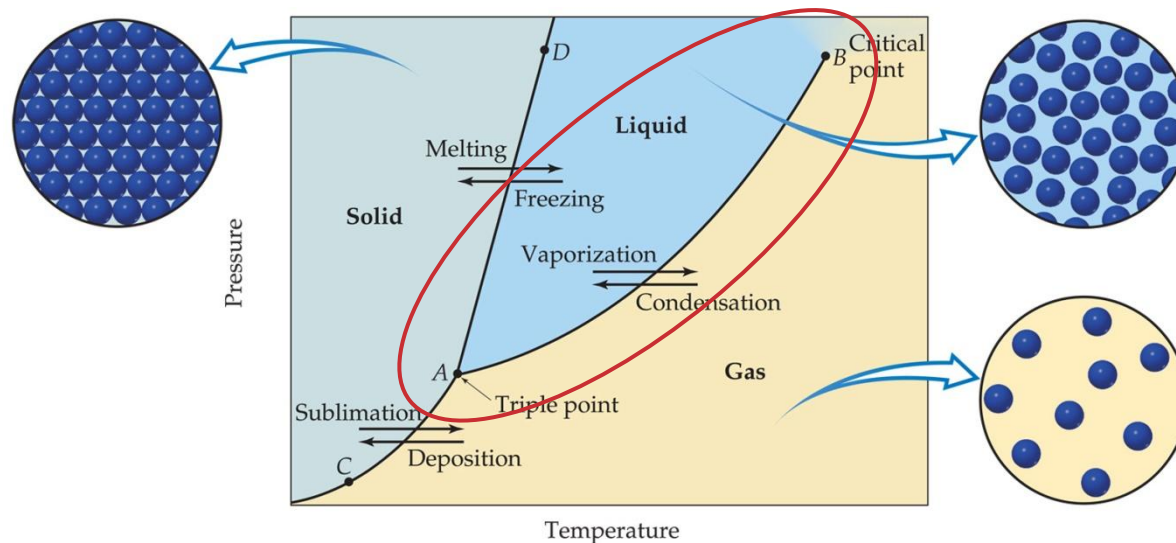
Phase Diagrams

Phase diagrams display the state of a substance at various pressures and temperatures and the places where equilibria exist between phases.



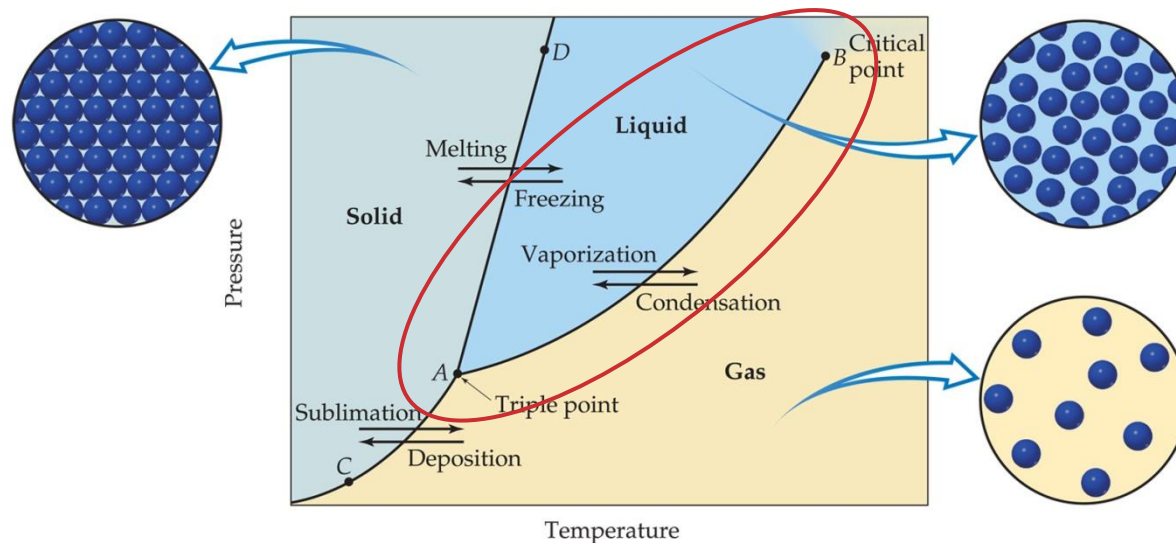
Phase Diagrams

- The *AB* line is the liquid-vapor interface.
- It starts at the triple point (*A*), the point at which all three states are in equilibrium.



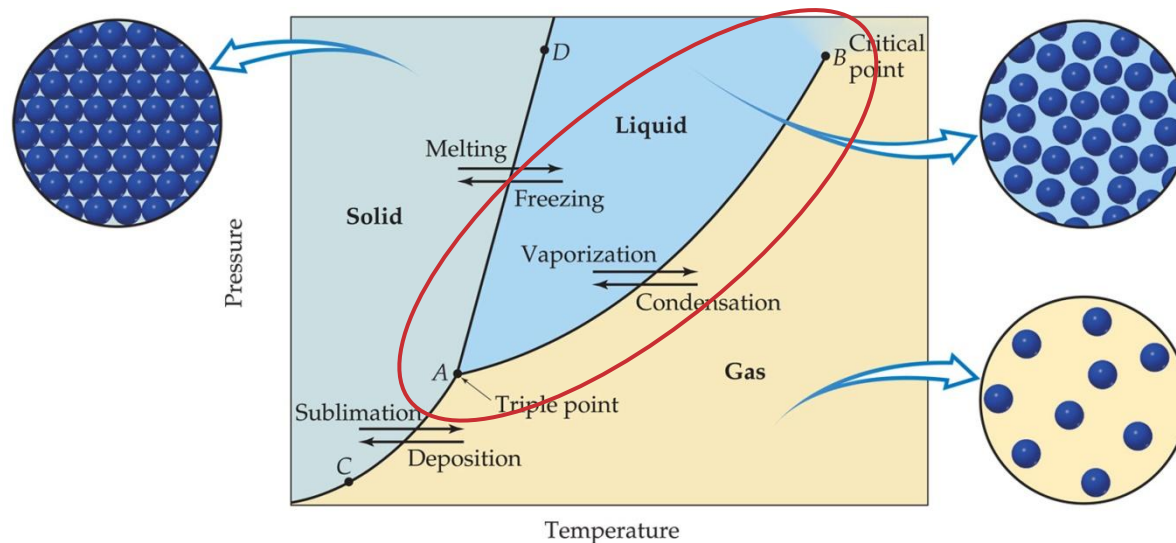
Phase Diagrams

It ends at the critical point (B); which is at the critical temperature and critical pressure, above this critical temperature and critical pressure the liquid and vapor are indistinguishable from each other.



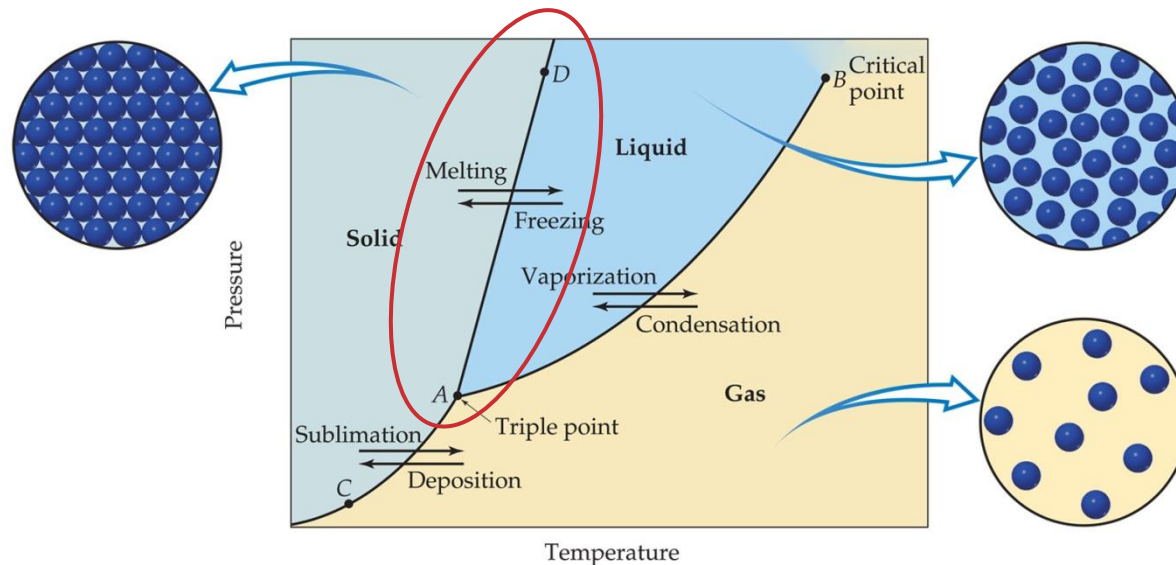
Phase Diagrams

Each point along this line is the boiling point of the substance at that pressure.



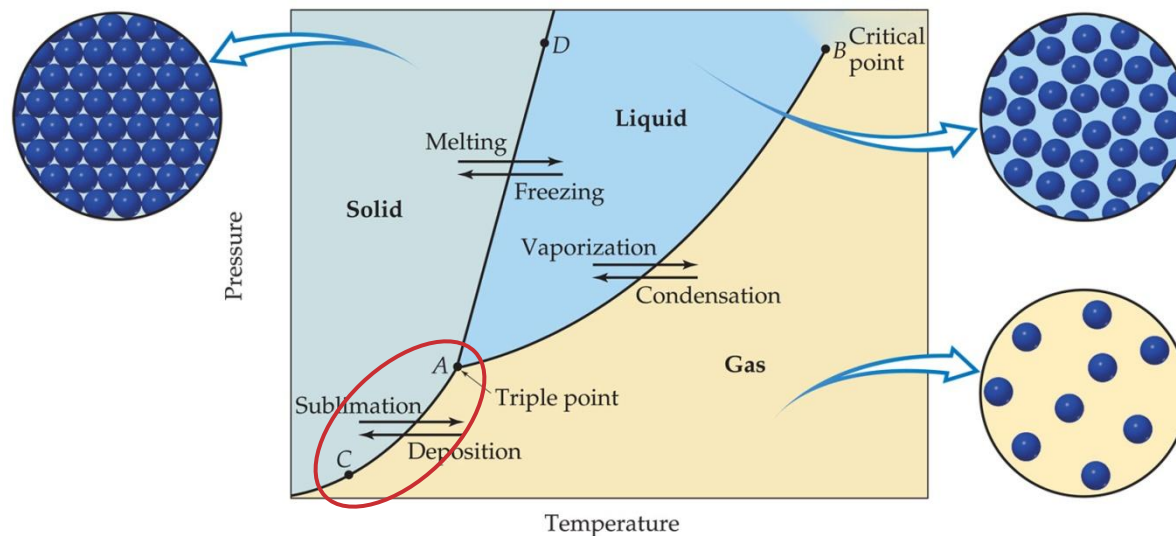
Phase Diagrams

- The *AD* line is the interface between liquid and solid.
- The melting point at each pressure can be found along this line.

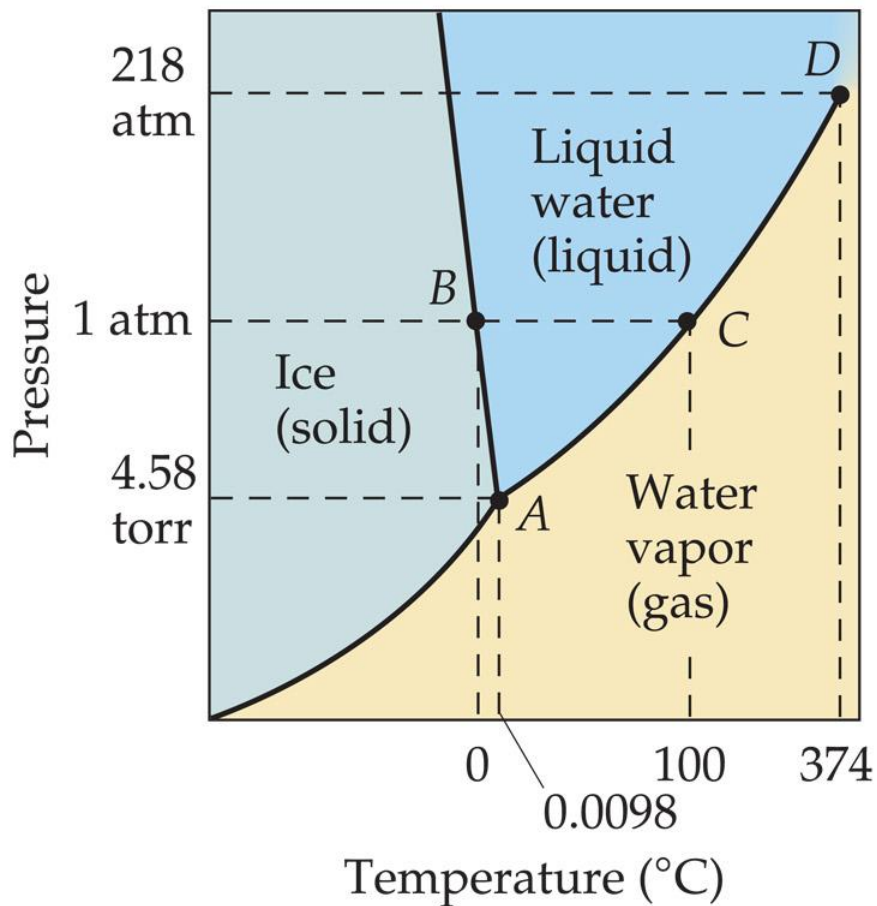


Phase Diagrams

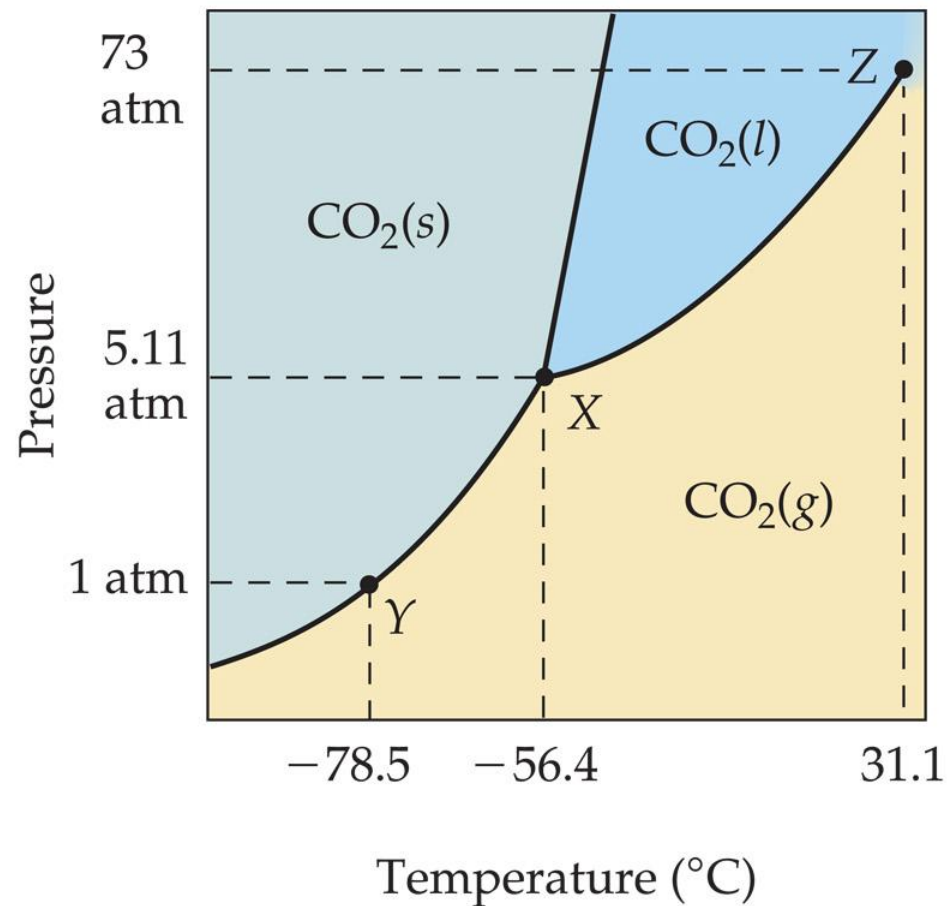
- Below A the substance cannot exist in the liquid state.
- Along the AC line the solid and gas phases are in equilibrium; the sublimation point at each pressure is along this line.



Compare phase diagrams of H_2O and CO_2

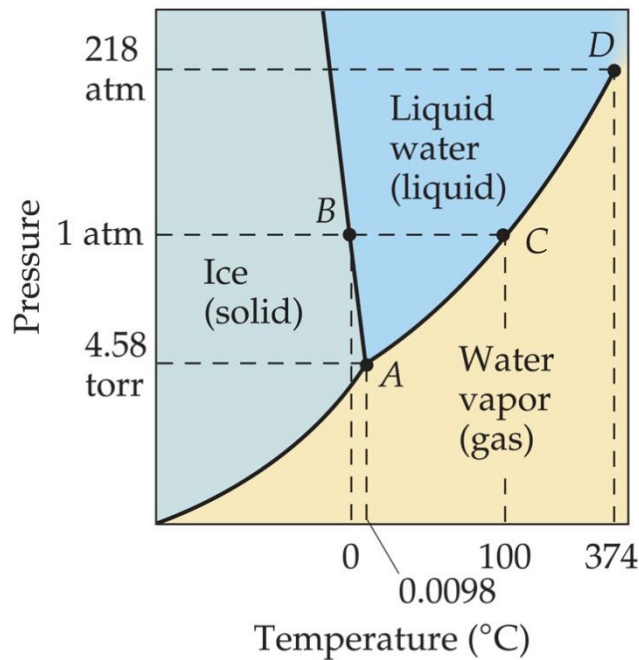


(a)



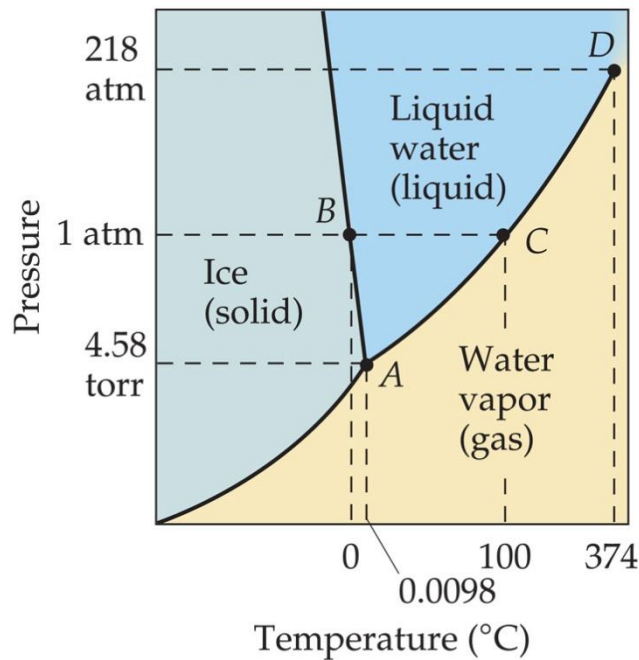
(b)

Phase Diagram of Water



- B is the normal melting point
- C is the normal boiling point
- A is the triple point
- D is the Critical Point
 - Very high for water due to strong H-bonding forces

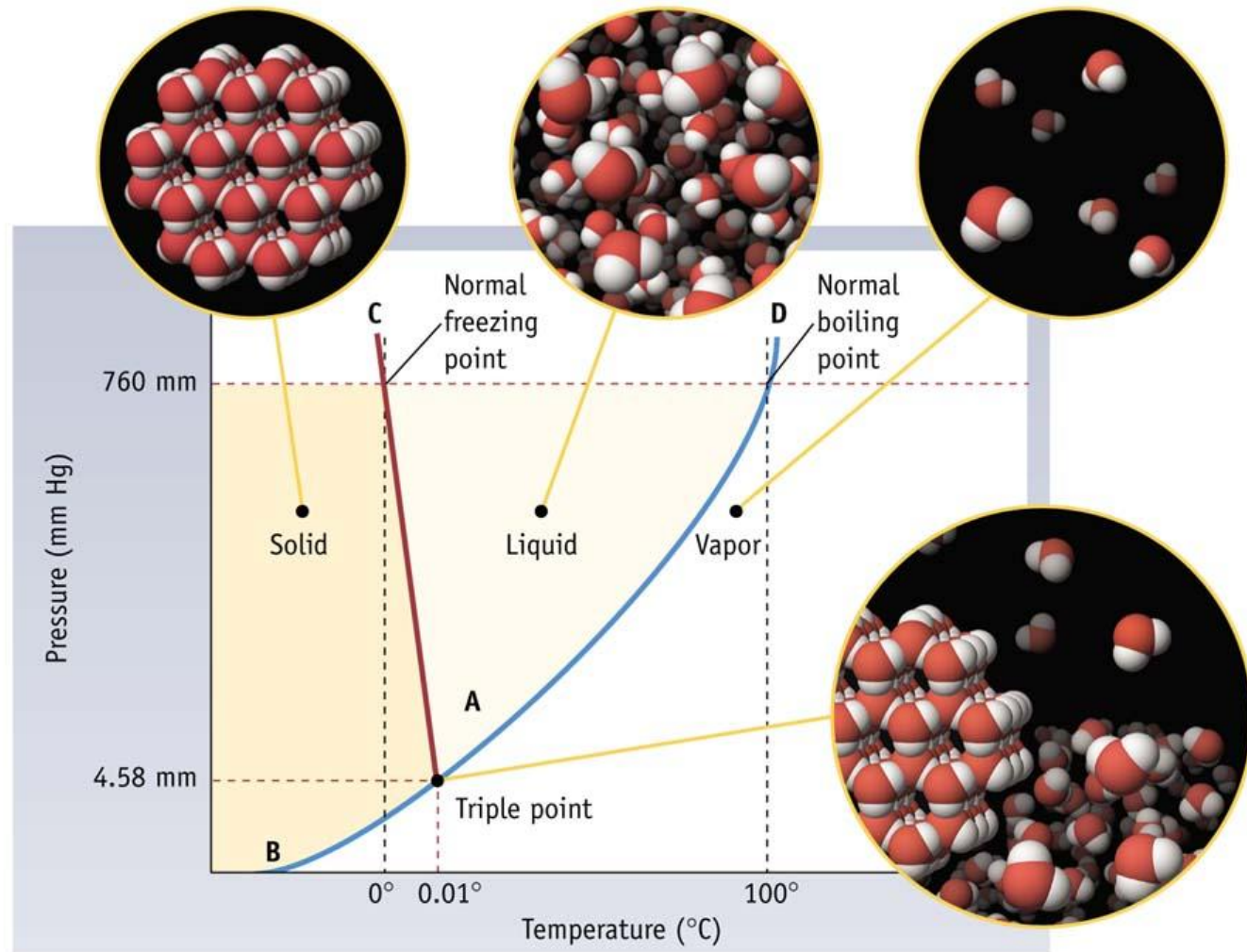
Phase Diagram of Water



- The slope of the solid–liquid line is negative.
 - This means that as the pressure is increased at a temperature just below the melting point, water goes from a solid to a liquid.

H₂O: an unusual phase diagram

- Unusual behavior
- At same T, as you increase p, substance changes from solid to liquid
- Liquid more dense than solid
- Exhibits triple point where all three phases coexist

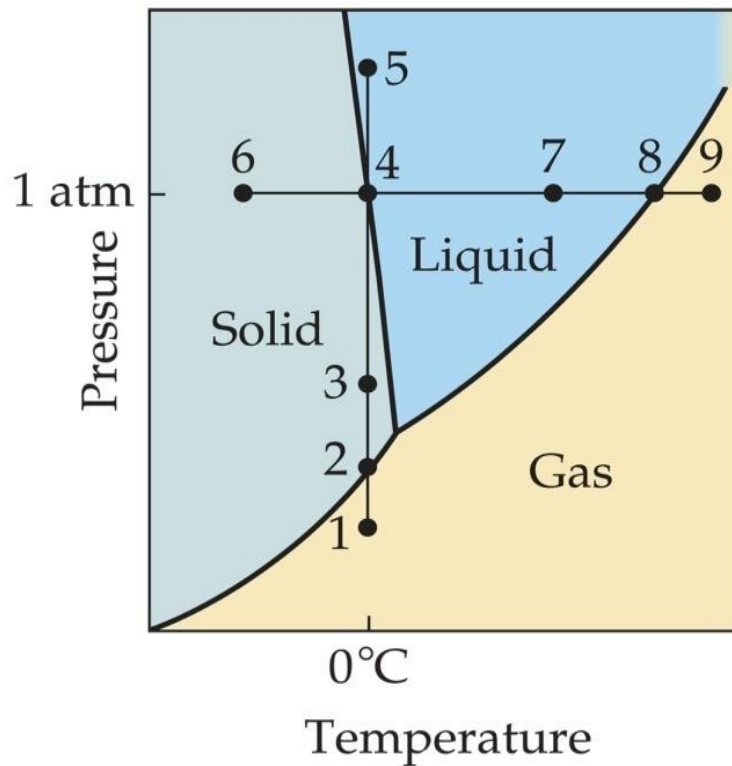


- The negative slope is a consequence of the density of water being less than the density of ice – ice floats

Referring to Figure

describe any changes
in the phases present
when

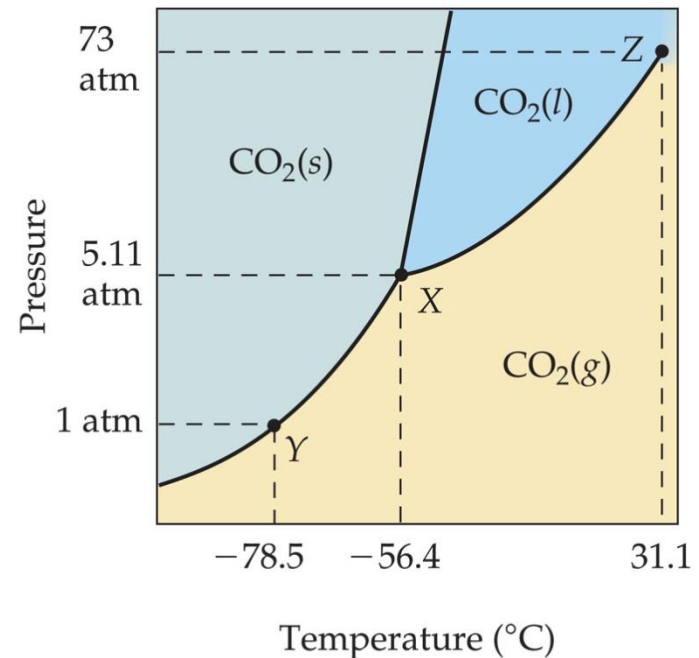
- (a) T is kept at 0°C while the pressure is increased from that at point 1 to that at point 5 (vertical line),
- (b) P is kept at 1.00 atm while the temperature is increased from that at point 6 to that at point 9 (horizontal line).



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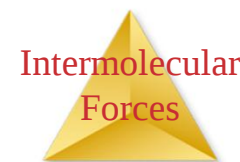
Phase Diagram of Carbon Dioxide

Carbon dioxide cannot exist in the liquid state at pressures below 5.11 atm; CO_2 sublimates at normal pressures.



Critical Temperature and Pressure

- The highest temperature at which a distinct liquid phase can form is called the critical temperature.
- The critical pressure is the pressure required to bring about liquefaction at this critical temperature
- Above the critical temperature the motion energies of the molecules are greater than the attractive forces that lead to the liquid state.
- At critical temperature the properties of the gas and liquid phases become the same resulting in only one phase: the supercritical fluid.



Critical Temperature and Pressure for Water Vapour

Temperature	Pressure
100°C	760 torr
110°C	1075 torr
374°C	1.655×10^5 torr
Higher	No amount of pressure can liquefy the vapor

<u>Substance</u>	<u>Critical temp K</u>	<u>Critical pressure atm</u>
Water	647	217
Ammonia	405	111
H ₂ S	374	89
Propane	370	42
Phosphine	324	64
CO ₂	304	73
O ₂	154	50
Argon	150	48
N ₂	126	33

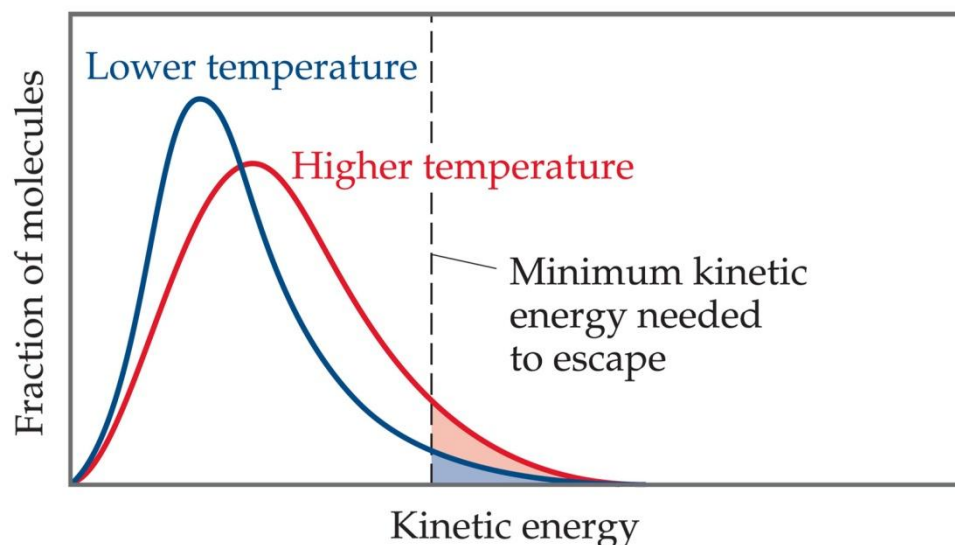
It is impossible to liquefy the gas if it is above its critical temperature, it needs to be cooled to this temperature before it can be liquefied.

The nonpolar low molecular weight substances have lower critical temperatures.

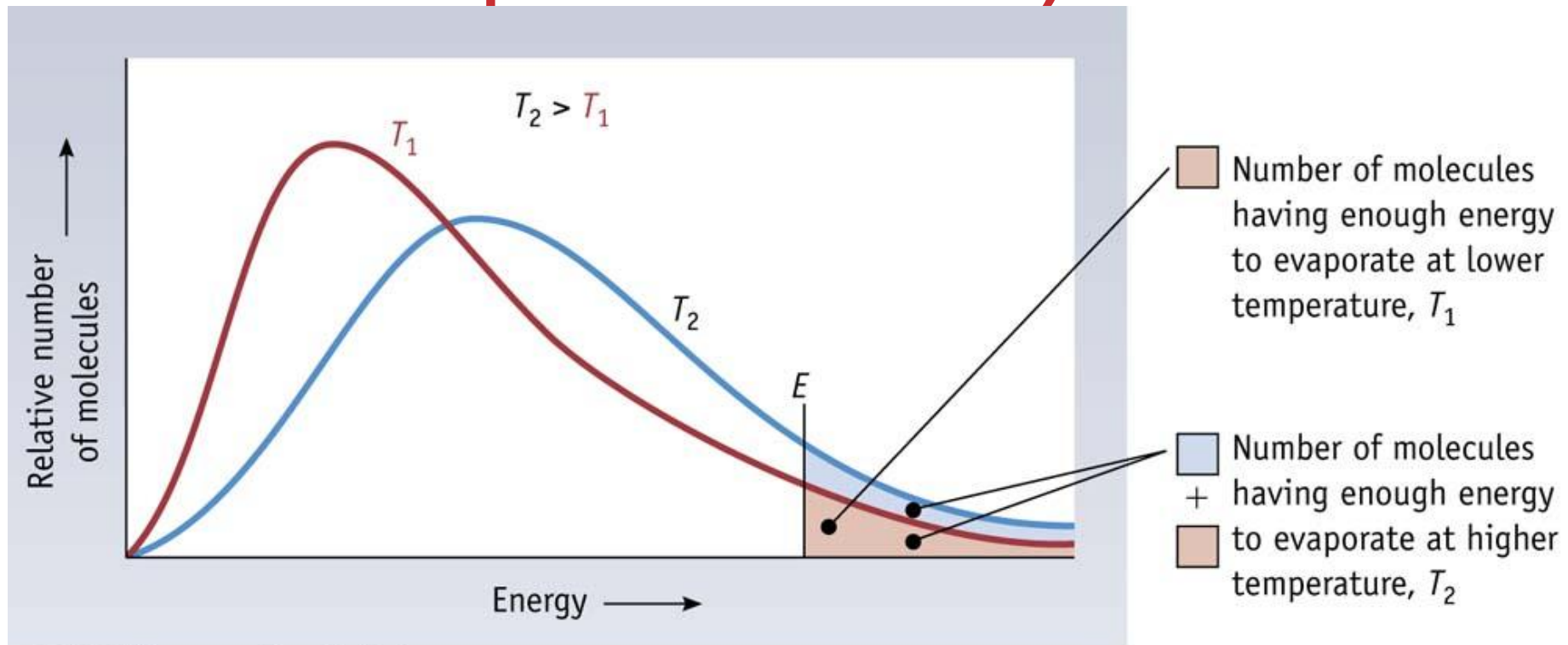


Vapor Pressure

- At any temperature, some molecules in a liquid have enough energy to escape.
- As the temperature rises, the fraction of molecules that have enough energy to escape increases.



Comparing a liquid at two temperatures (at the particle level)



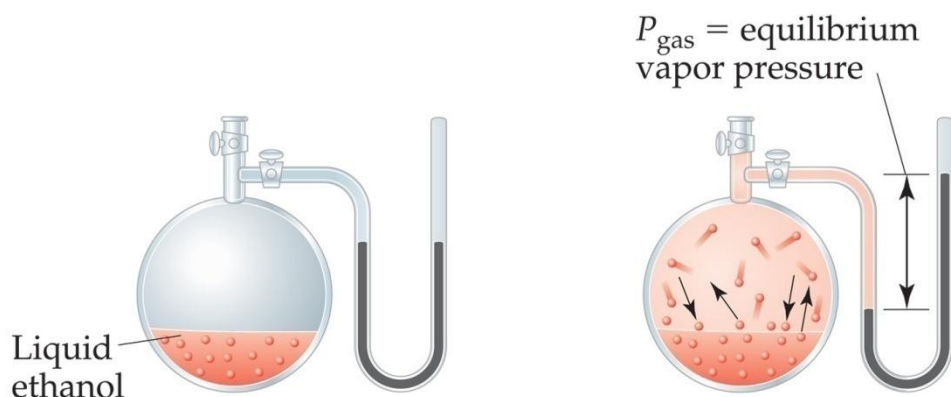
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The effect of temperature on the distribution of kinetic energies in a liquid

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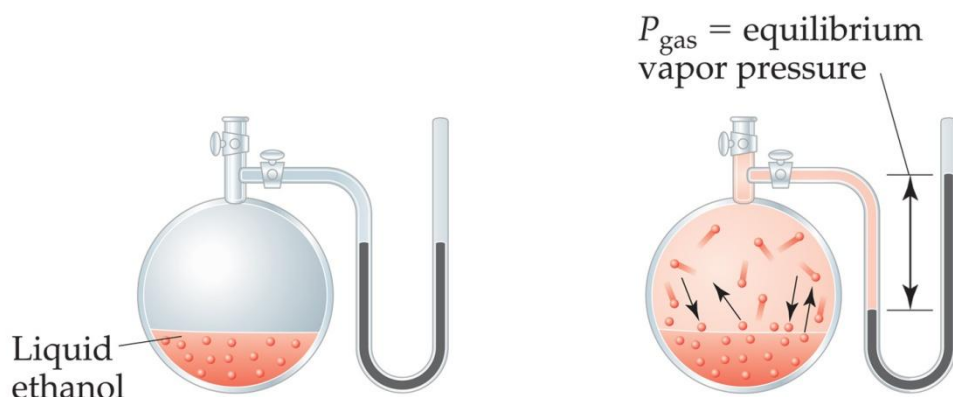
Intermolecular
Forces

Vapor Pressure



As more molecules escape the liquid, the pressure they exert increases.

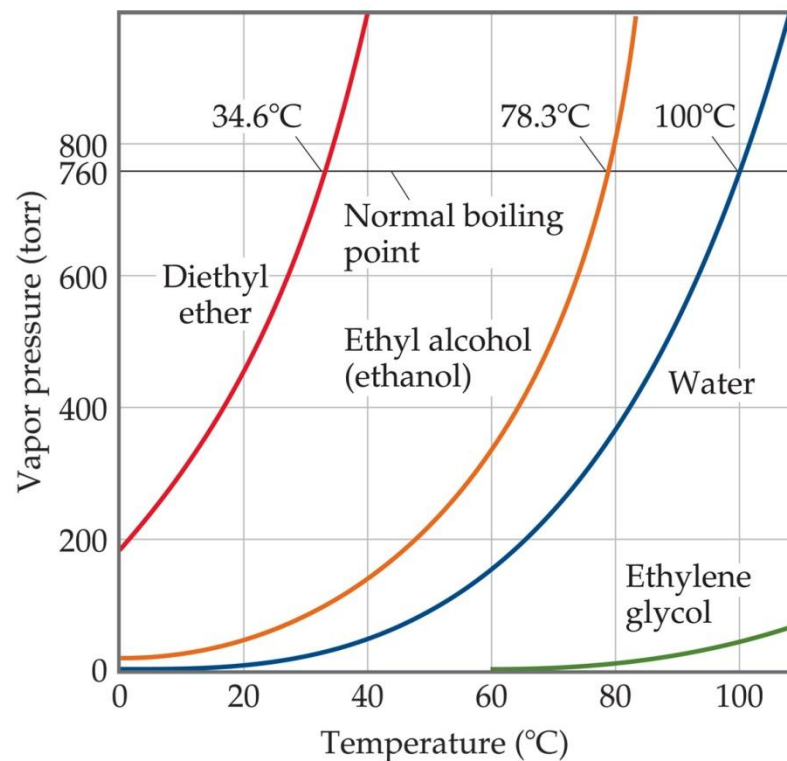
Vapor Pressure



The liquid and vapor reach a state of dynamic equilibrium: liquid molecules evaporate and vapor molecules condense *at the same rate*.

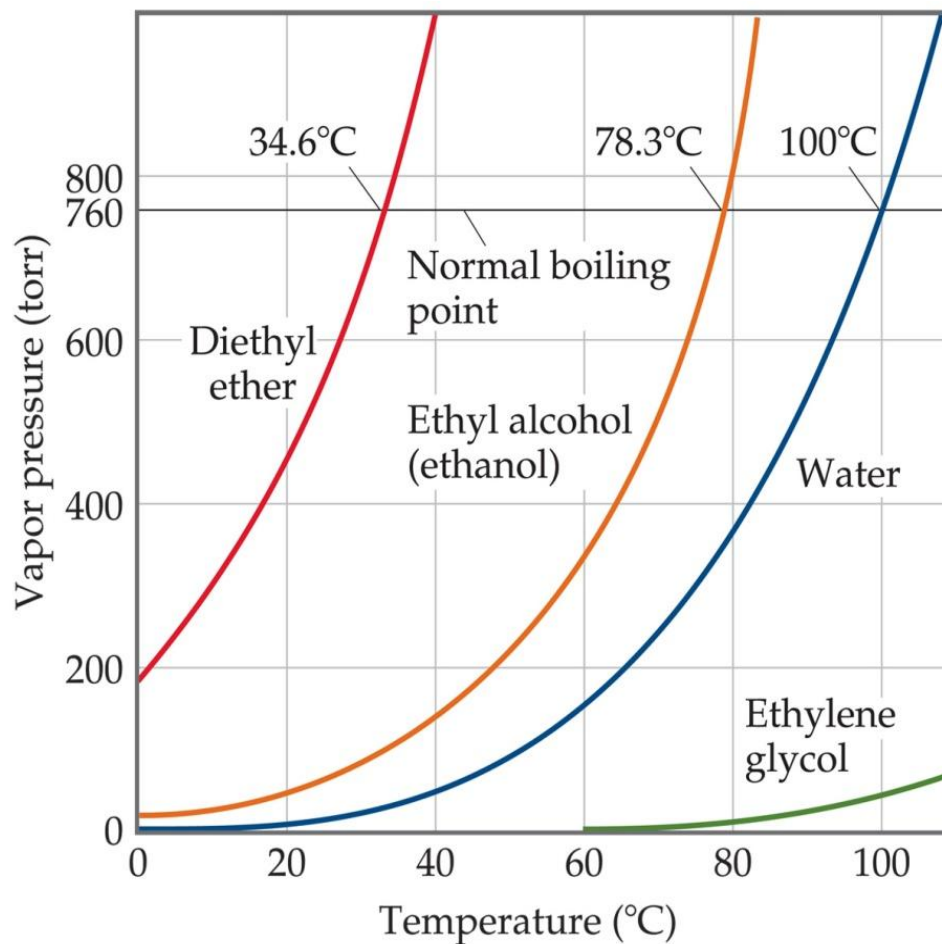
Vapor Pressure

- The boiling point of a liquid is the temperature at which its vapor pressure equals atmospheric pressure.
- The normal boiling point of a liquid is the temperature at which its vapor pressure is 760 torr (1atm).



Understand:

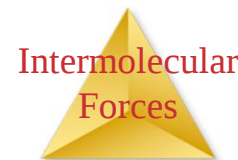
- Pressure cooker
- Boiling water on top of a mountain



Heating curve vs. phase diagram vs. vapor pressure curve

- Heating curve
 - Temperature vs. heat energy added
 - Characteristic up-across-up-across shape
 - Cooling curve is how temperature changes as you remove energy
- Phase diagram
 - Pressure vs. temperature
 - All 3 phases shown with boundaries between them
- Vapor pressure curve
 - The liquid-gas portion of the full phase diagram
 - Vapor pressure line is the boundary between L and G
 - All liquids (and solids too) have vapor pressure

Liquid to gas: As you add energy, the temperature changes. As the temperature changes, the vapor pressure changes.



Types of materials

- **Molecular**
 - Non-polar molecules
 - Octane, C_8H_{18}
 - Fats (e.g., olive oil)
 - Polar molecules
 - Water, H_2O
 - Ammonia, NH_3
 - Acetic acid (vinegar is an aqueous solution of it), CH_3COOH
- **Ionic**
 - Sodium chloride (table salt), $NaCl$
 - Sodium bicarbonate (baking soda), $NaHCO_3$
 - Copper (II) sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$
- **Metallic**
 - Copper metal, Cu
 - Aluminum foil, Al
- **Covalent Interactions**
 - Network
 - Quartz, SiO_2
 - Sand, SiO_2
 - Diamond, C
 - Polymeric
 - Any plastic, such as high density polyethylene (HDPE)
 - Amorphous
 - Glasses
- **Mixtures**

Notice that the names of these categories are based on the type of bonding



Properties that molecular materials exhibit

- Most are liquids or gases at room temperature
- Smallest molecules are gases at room temperature
- Only very large molecules are solids at room temperature
- All have relatively low melting points (near or below room temperature)
- Most feel soft
- Chemical composition is usually carbon, hydrogen, oxygen, nitrogen and a few others (“organic”)
- In liquid state, *usually* do not conduct electricity
- Some can dissolve in water and others cannot



Properties that ionic materials exhibit

- All are solids at room temperature
- Very high melting points
- Do not conduct electricity in solid state
- Conduct electricity in liquid state
- Crystalline
- Brittle, break along flat/planar surfaces
- When they contain transition metals, usually are colored; when they do not contain transition metals, usually are white
- Generally called “salts” because they can be made from mixing together an acid and a base
- Some can dissolve in water and others cannot



Properties that metallic materials exhibit

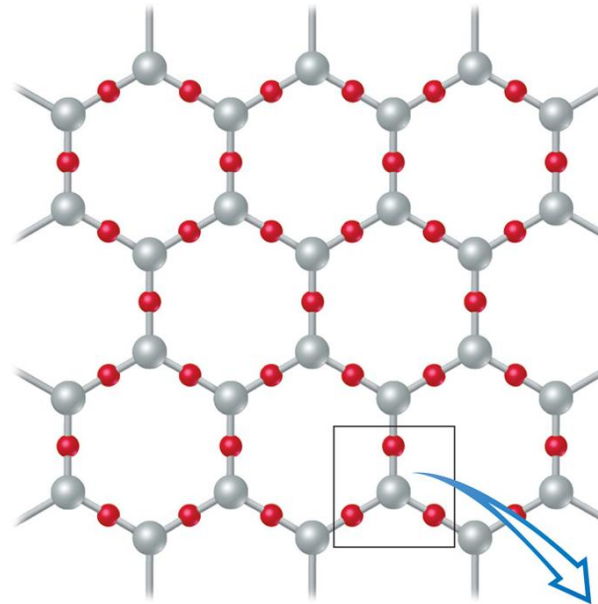
- Lustrous (shiny)
- Malleable (can be pounded into a pancake)
- Ductile (can be bent)
- Conduct electricity
- Sometimes rust (oxidize)
- Never dissolve in water

Solids

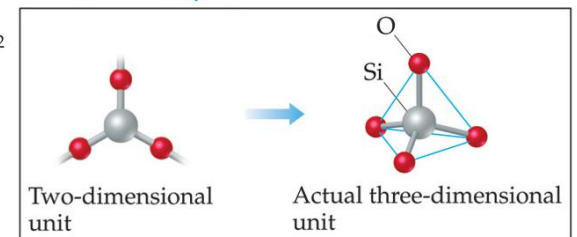
- We can think of solids as falling into two groups:

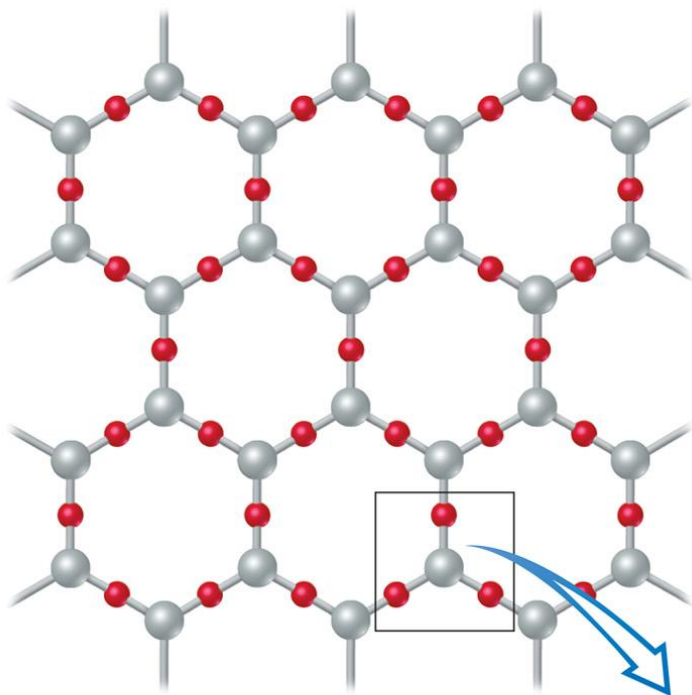
Crystalline—particles are in highly ordered arrangement.

Amorphous—no particular order in the arrangement of particles

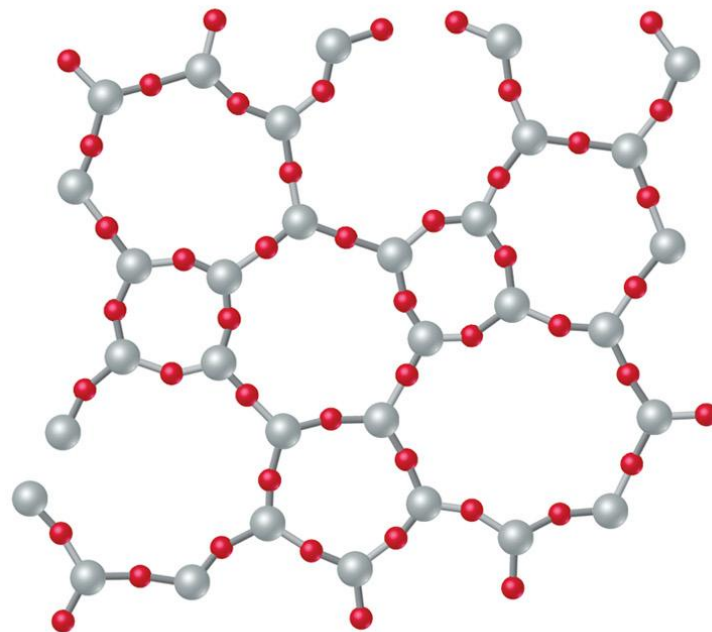


Crystalline SiO₂

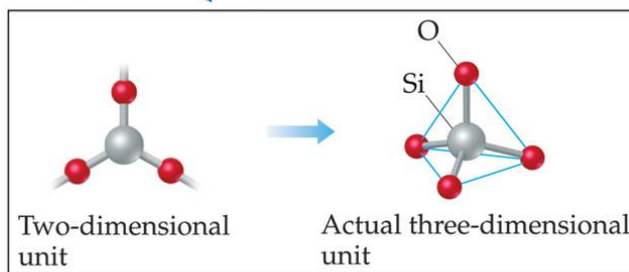




Crystalline SiO_2



Amorphous SiO_2



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(a)



(b)



(c)

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Unit Cells

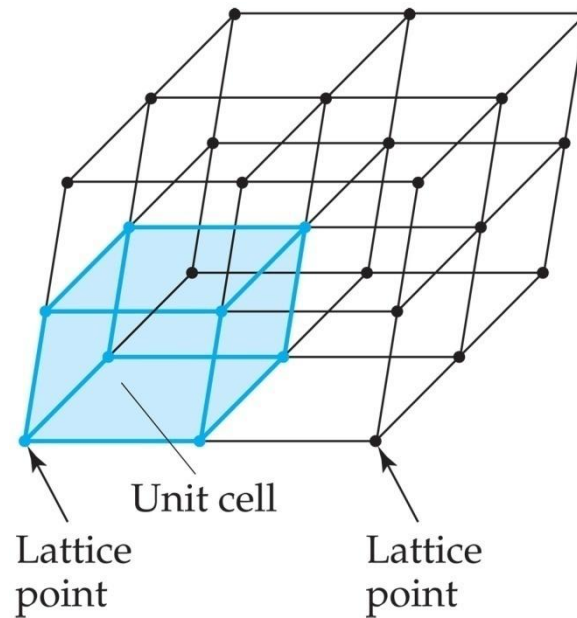
- We can think of a crystalline solid as being built of bricks.
- Each brick is a unit cell.
- Each crystalline solid is represented by a crystal lattice.

The crystal lattice is like a scaffolding for the solid.

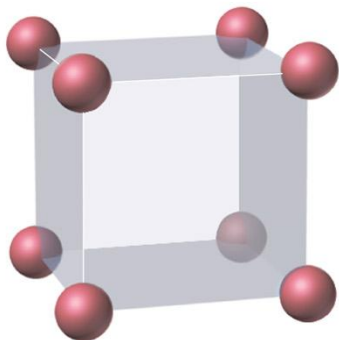
A Unit Cell

- The unit cell is the fundamental concept in solid state chemistry
- It is the smallest representation of structure which carries all the information necessary to construct unambiguously an infinite lattice.

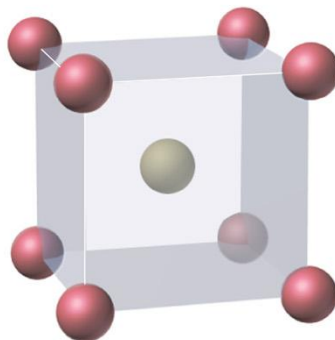
Crystalline Solids



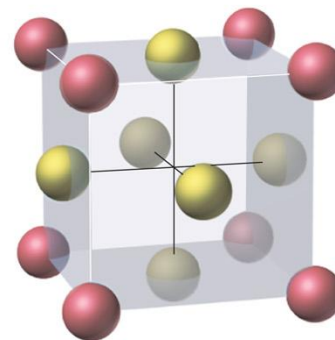
- There are three kinds of unit cells
- Primitive cubic
- Body - centered cubic
- Face - centered cubic



Primitive cubic



Body-centered cubic

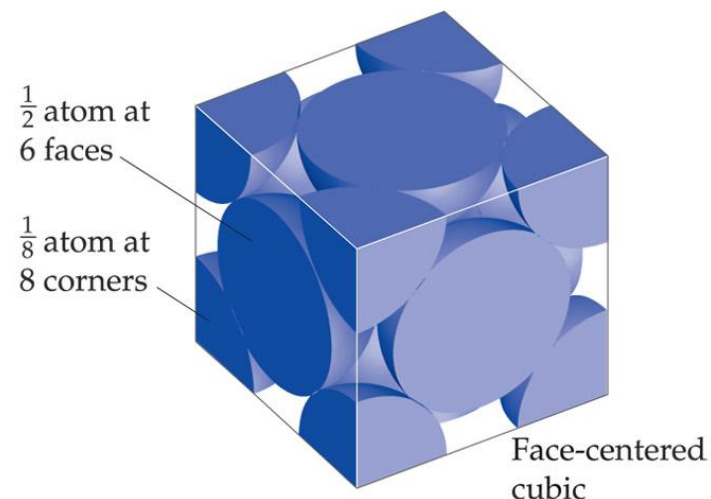
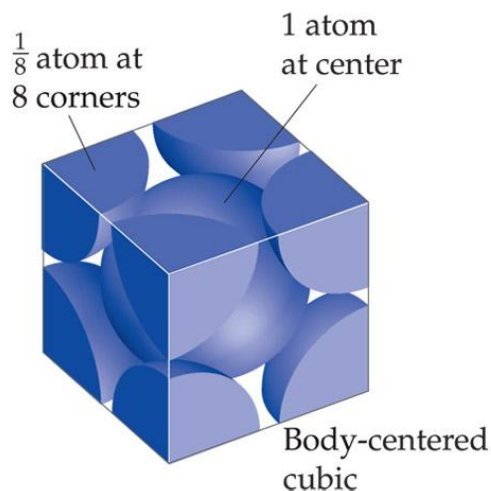
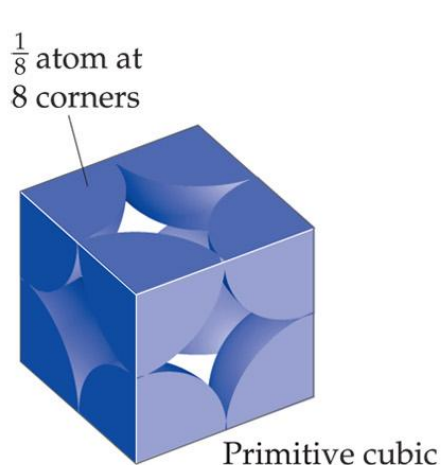


Face-centered cubic

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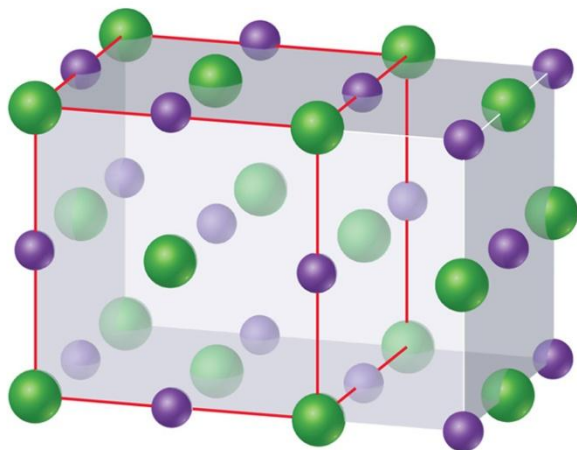
- Primitive cubic : When lattice points are at the corners only
- Body centered cubic: When the lattice point also occurs at the center of the unit cell
- Face centered cubic: When the cell has lattice points at the center of each face as well as at each corner.

Crystalline Solids

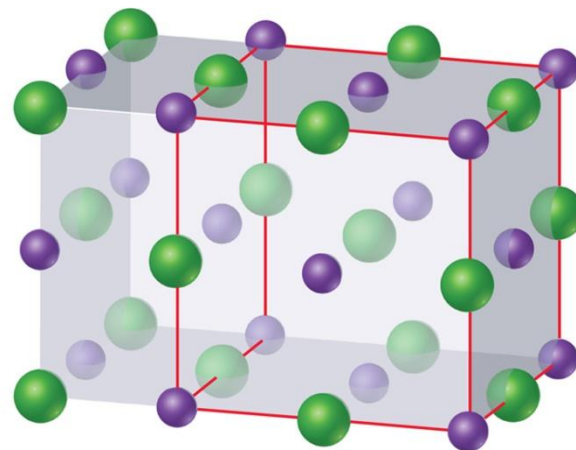


There are several types of basic arrangements in crystals, such as the ones shown above.

Crystal Structure of Sodium Chloride



(a)



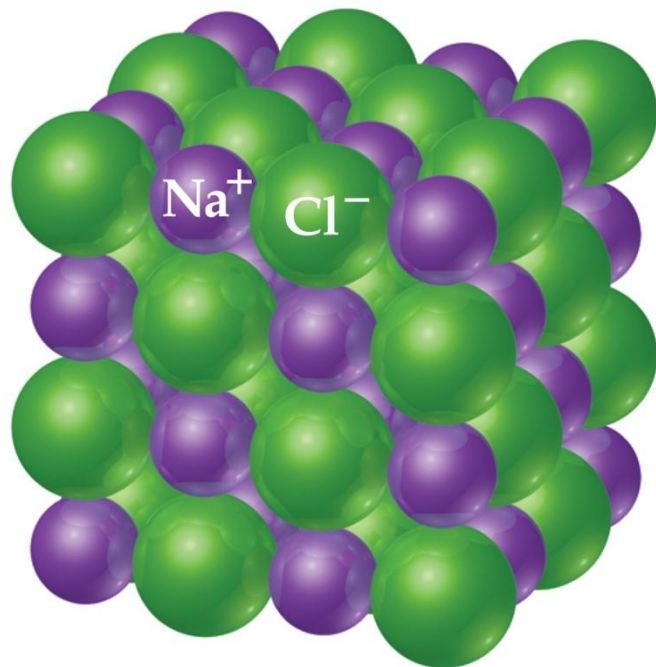
(b)

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- NaCl is a face centered cubic as we can center either the Na^+ ion or the Cl^- ion on the lattice point of a face centered cubic unit cell

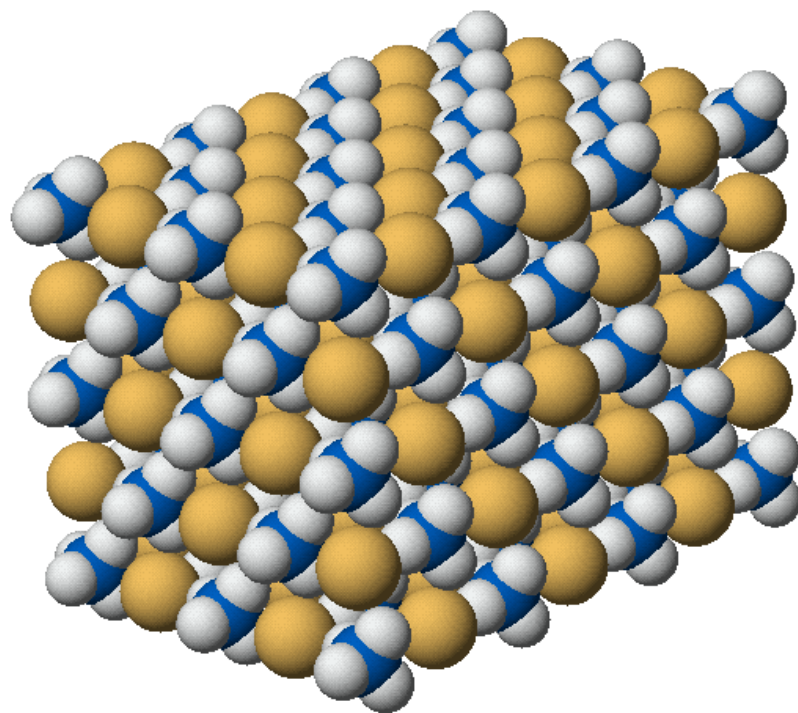
Some examples of ionic solids (particle level illustrations)

Sodium chloride
(NaCl)



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Ammonium chloride
(NH₄Cl)



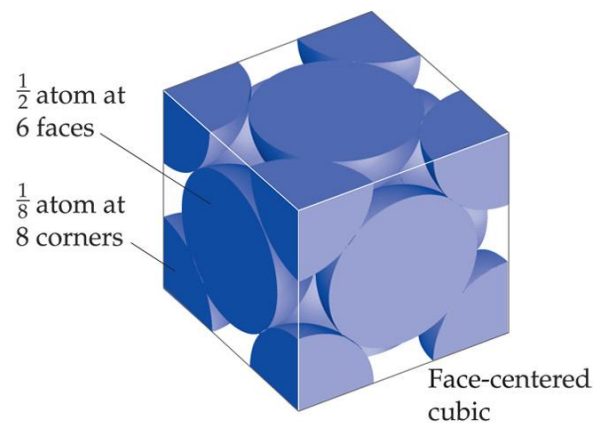
Attractions in Ionic Crystals

In ionic crystals, ions pack themselves so as to maximize the attractions and minimize repulsions between the ions.

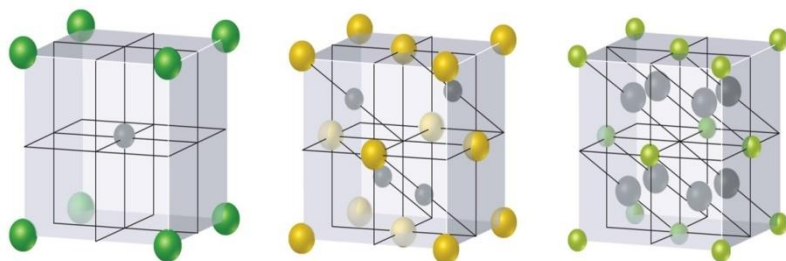
Crystalline Solids

We can determine the empirical formula of an ionic solid by determining how many ions of each element fall within the unit cell.

Position in Unit Cell	Fraction in Unit Cell
Center	1
Face	$\frac{1}{2}$
Edge	$\frac{1}{4}$
Corner	$\frac{1}{8}$



Ionic Solids



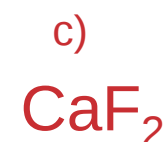
Position in Unit Cell	Fraction in Unit Cell
Center	1
Face	$\frac{1}{2}$
Edge	$\frac{1}{4}$
Corner	$\frac{1}{8}$

What are the empirical formulas for these compounds?

(a) Green: chlorine; Gray: cesium

(b) Yellow: sulfur; Gray: zinc

(c) Green: calcium; Gray: fluorine

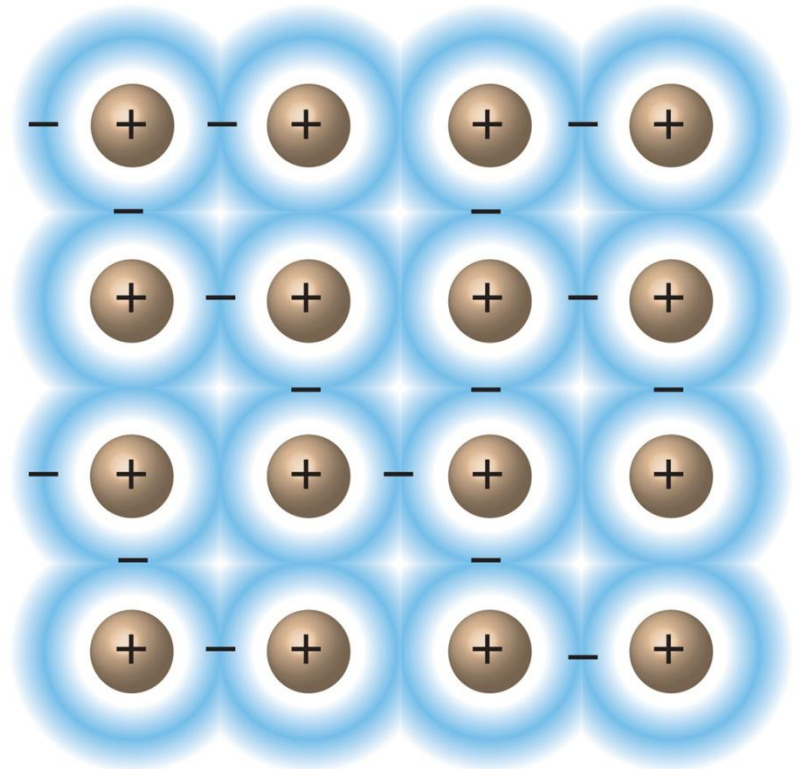


Types of Bonding in Crystalline Solids

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, often poor 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

Metallic Solids

- Metals are not covalently bonded, but the attractions between atoms are too strong to be van der Waals forces.
- In metals, valence electrons are delocalized throughout the solid.

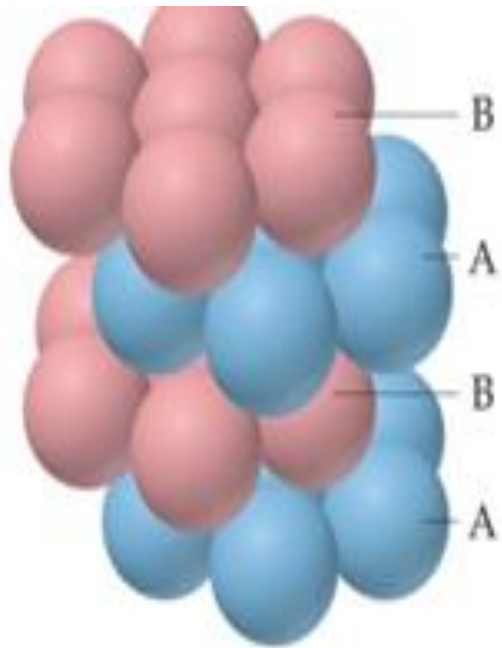


Metallic bonding

- Delocalized valence electrons
- Equal sized spheres can be arranged like this (such as bonding in metals)
- Maximize attractive forces



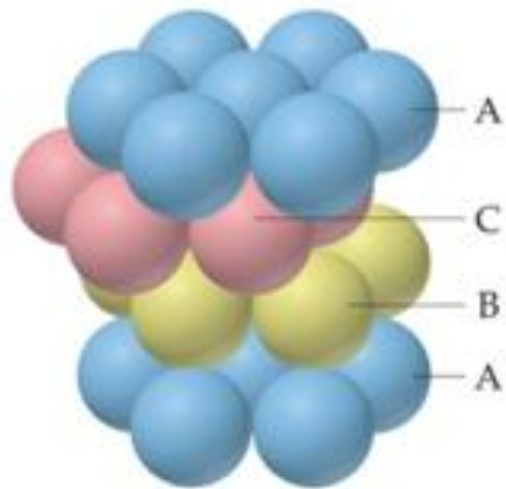
Close-packed
layer of spheres



(b)

- Hexagonal close packing

Cubic close packing



(c)

nc.

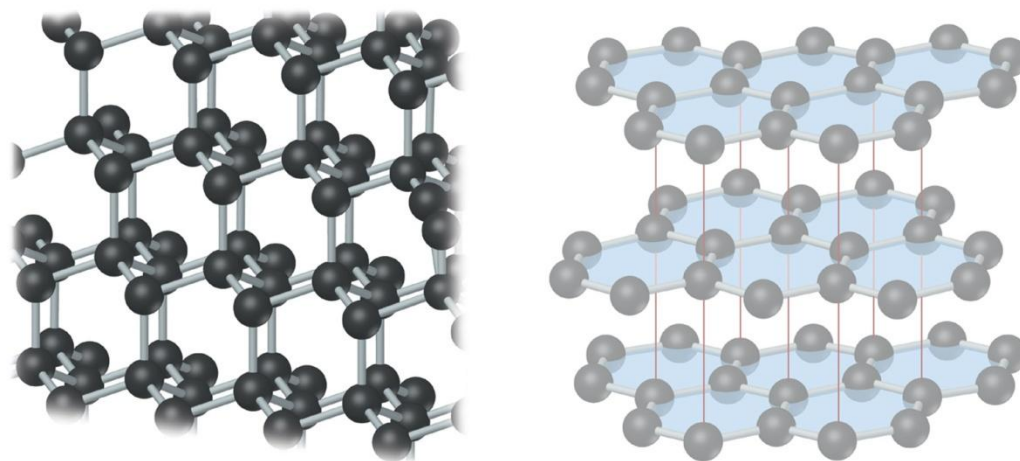
- In each of these structures there are 12 equidistant neighbors.
- Thus the particles are thought to have a coordination number of 12.
- The coordination number is the number of particles immediately surrounding a particle in the crystal.

- In both types of close packing 74% of the total volume of the structure is occupied by the spheres and 26% is empty space.

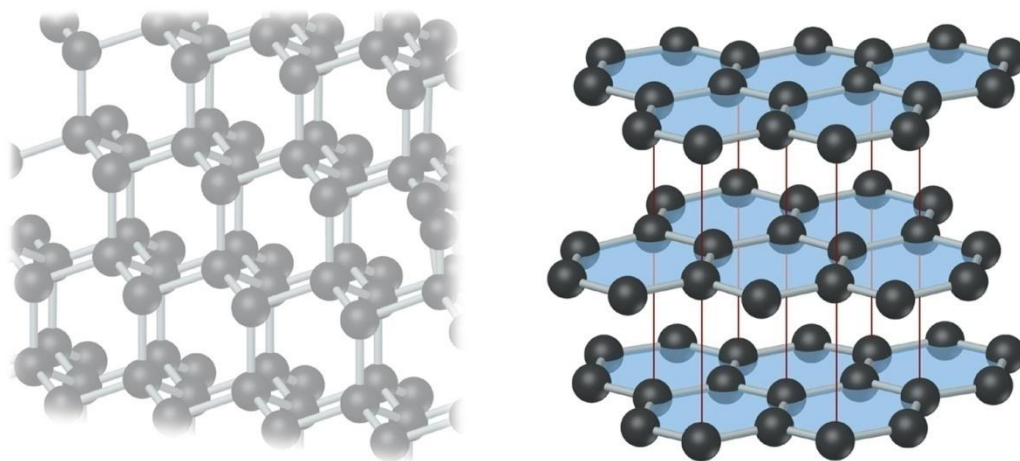
- In comparison each sphere in the body centered cubic structure has a coordination number of 8 and only 68% of the space is occupied. In the primary cubic structure the coordination number is 6 and only 52 % of the space is occupied.

- The higher the coordination number the greater the packing efficiency

Covalent Networks



- Diamonds are an example of a covalent-network solid in which atoms are covalently bonded to each other.
- sp^3 hybridized
 - They tend to be hard and have high melting points.



- Graphite exists as layers of sp^2 hybridized carbons
- Electrons are delocalized in the plane of the layers
- The layers are held together by van der Waals forces.
 - They tend to be softer and have lower melting points.