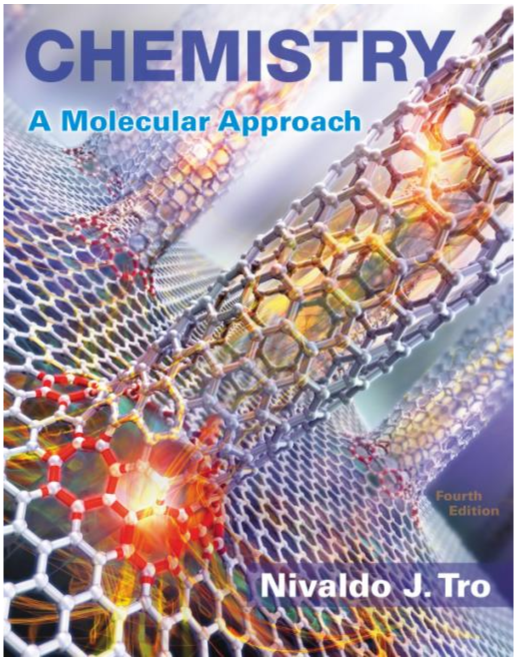


Lecture Presentation

Chapter 11

Liquids, Solids, and Intermolecular Forces

Water, No Gravity

- In the space station there are no spills. Rather, the water molecules stick together to form a floating, oscillating blob.
- The blob stops oscillating and forms a near perfect sphere due to **intermolecular forces**.
- Intermolecular attractive forces exist among all particles that make up matter.
- The very existence of condensed states—solid, liquid, or gas—depends on the magnitude of intermolecular forces among the constituent particles relative to the amount of thermal energy in the sample.

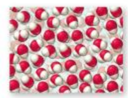
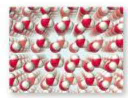
Three States of Water

Notice that the densities of ice and liquid water are much larger than the density of steam.

Notice that the densities and molar volumes of ice and liquid water are much closer to each other than to steam.

Notice that the density of ice is larger than the density of liquid water. This is not the norm but is vital to the development of life as we know it.

TABLE 11.1 The Three States of Water

Phase	Temperature (°C)	Density (g/cm^3, at 1 atm)	Molar Volume	Molecular View
Gas (steam)	100	5.90×10^{-4}	30.5 L	
Liquid (water)	20	0.998	18.0 mL	
Solid (ice)	0	0.917	19.6 mL	

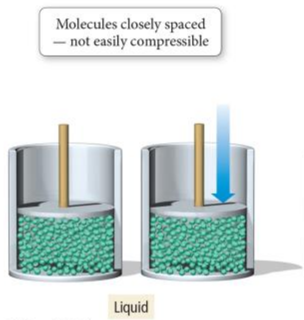
Properties of the Three States of Matter

TABLE 11.2 Properties of the States of Matter

State	Density	Shape	Volume	Strength of Intermolecular Forces (Relative to Thermal Energy)
Gas	Low	Indefinite	Indefinite	Weak
Liquid	High	Indefinite	Definite	Moderate
Solid	High	Definite	Definite	Strong

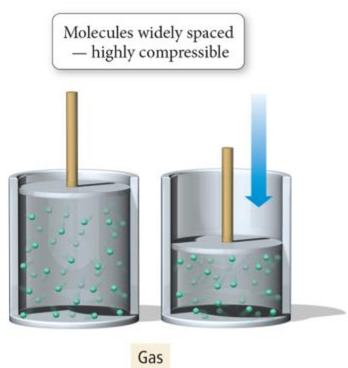
Liquids

- The particles in a liquid are closely packed, but they have some ability to move around.
- The close packing results in liquids being incompressible.
- But the ability of the particles to move allows liquids to take the shape of their container and to flow. However, they don't have enough freedom to escape or expand to fill the container.



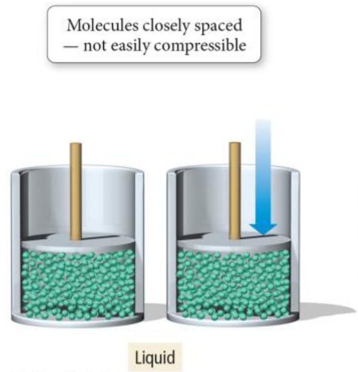
Gases

- In the gas state, the particles have complete freedom of motion and are not held together.
- The particles are constantly flying around, bumping into each other and the container.
- There is a large amount of space between the particles compared to the size of the particles.
  - Therefore, the molar volume of the gas state of a material is much larger than the molar volume of the solid or liquid states.

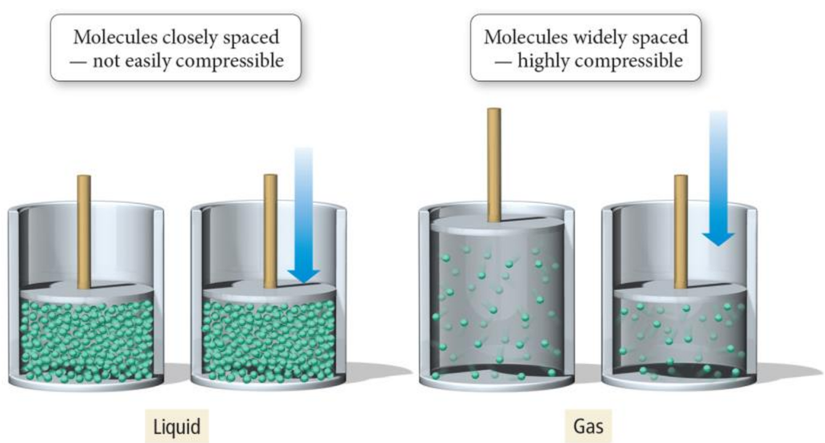


Gases

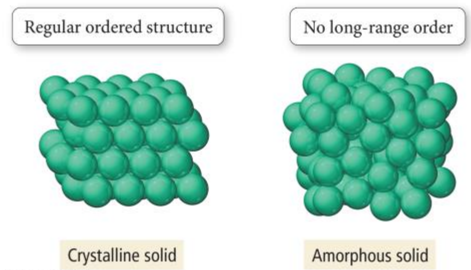
- Gases are compressible because there is a lot of empty space, so the particles can be squeezed closer together.
- Because the particles are not held in close contact and are moving freely, gases expand to fill and take the shape of their container.



Compressibility



Solids



- The particles in a solid are packed close together and are fixed in position, though they may vibrate.
- The close packing of the particles results in solids being incompressible.
- The inability of the particles to move around results in solids retaining their shape and volume when placed in a new container and prevents the solid from flowing.

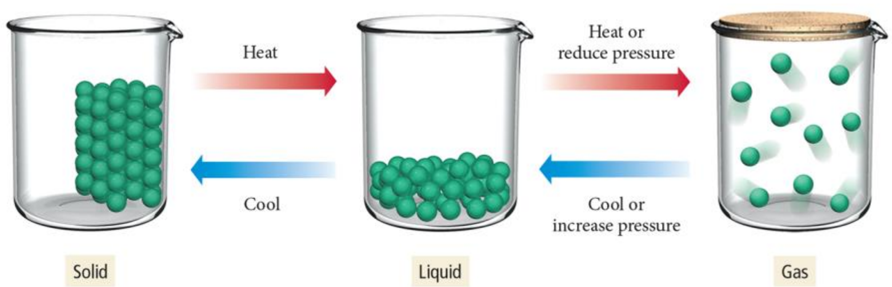
Solids

- Some solids have their particles arranged in an orderly geometric pattern; we call these **crystalline solids**.
  - Salt and diamonds
- Other solids have particles that do not show a regular geometric pattern over a long range; we call these **amorphous solids**.
  - Plastic and glass

Phase Changes

- Changing the material's state requires changing the amount of kinetic energy the particles have or limiting their freedom.
- Solids melt and liquids boil when heated.
- Transition between liquid and solid can also be induced by changing pressure.
- Gases can be condensed by decreasing the temperature and/or increasing the pressure.
  - Pressure can be increased by decreasing the gas volume.
  - Reducing the volume reduces the amount of translational freedom the particles have.

Phase Changes



Gas Structure

When a liquefied propane tank is opened, some of the propane escapes as gas, lowering the pressure in the tank.

Intermolecular Forces

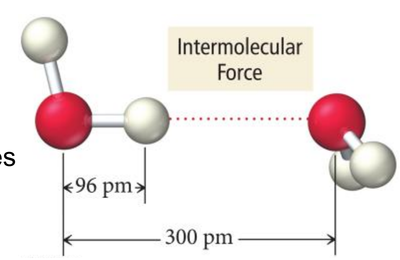
- The structure of particles determines the strength of the intermolecular forces that hold the substance together.
- The particles are attracted to each other by electrostatic forces.
- The intermolecular forces determine the state of the substance.
- The strength of the attractive forces varies depending on the kind(s) of particles.
- The stronger the attractive forces among the particles, the more they resist moving.
  - However, no material completely lacks particle motion.

Intermolecular Attractions

- The strength of the attractions among the particles of a substance determines its state.
- At room temperature, moderate to strong attractive forces result in materials being solids or liquids.
- The stronger the attractive forces are, the higher will be the boiling point of the liquid and the melting point of the solid.
  – Other factors also influence the melting point.

Why Are Molecules Attracted to Each Other?

- Intermolecular attractions are due to attractive forces between opposite charges.
  – + ion to − ion
  – + end of polar molecule to − end of polar molecule
    - H-bonding especially strong
  – Even nonpolar molecules will have temporary charges.
- **Larger charge = stronger attraction**
- **Longer distance = weaker attraction**
- However, these attractive forces are small relative to the bonding forces among atoms.
  – Generally smaller charges
  – Generally over much larger distances



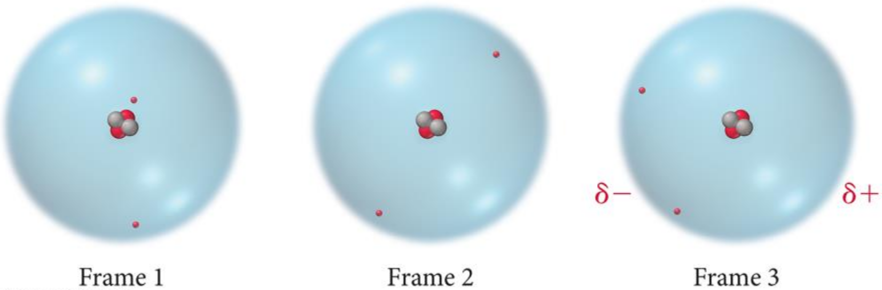
Kinds of Attractive Forces

- Temporary polarity in the molecules due to unequal electron distribution leads to attractions called **dispersion forces**.
- Permanent polarity in the molecules due to their structure leads to attractive forces called **dipole–dipole attractions**.
- An especially strong dipole–dipole attraction results when H is attached to an extremely electronegative atom. These are called **hydrogen bonds**.

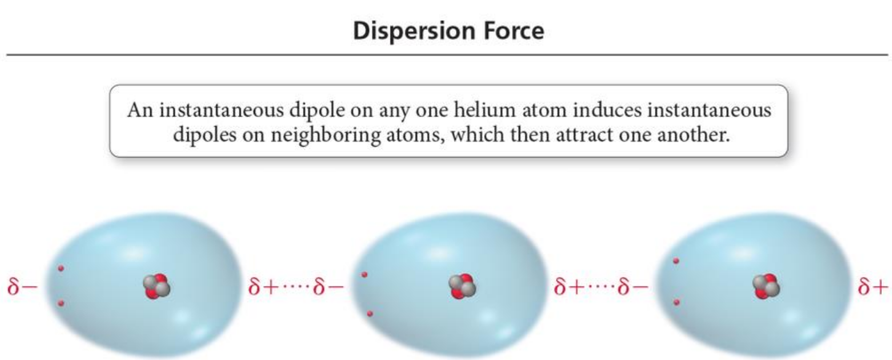
Dispersion Forces

- Fluctuations in the electron distribution in atoms and molecules result in a temporary dipole.
  - Region with excess electron density has partial (–) charge.
  - Region with depleted electron density has partial (+) charge.
- The attractive forces caused by these temporary dipoles are called **dispersion forces**.
  - AKA London forces
- All molecules and atoms will have them.
- As a temporary dipole is established in one molecule, it induces a dipole in all the surrounding molecules.

Dispersion Force



Dispersion Force



Size of the Instantaneous Dipole

- The magnitude of the instantaneous dipole depends on several factors.
- Polarizability of the electrons
  - Volume of the electron cloud
  - **Larger molar mass = more electrons = larger electron cloud = increased polarizability = stronger attractions**
- Shape of the molecule
  - **More surface-to-surface contact = larger induced dipole = stronger attraction**

Effect of Molecular Size on Size of Dispersion Force

The noble gases are all nonpolar atomic elements.

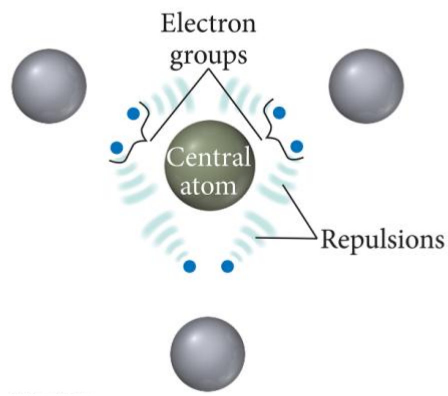
The stronger the attractive forces among the molecules, the higher the boiling point will be.

TABLE 11.3 Boiling Points of the Noble Gases

Noble Gas	Molar Mass (g/mol)	Boiling Point (K)
He	4.00	4.2
Ne	20.18	27
Ar	39.95	87
Kr	83.80	120
Xe	131.30	165

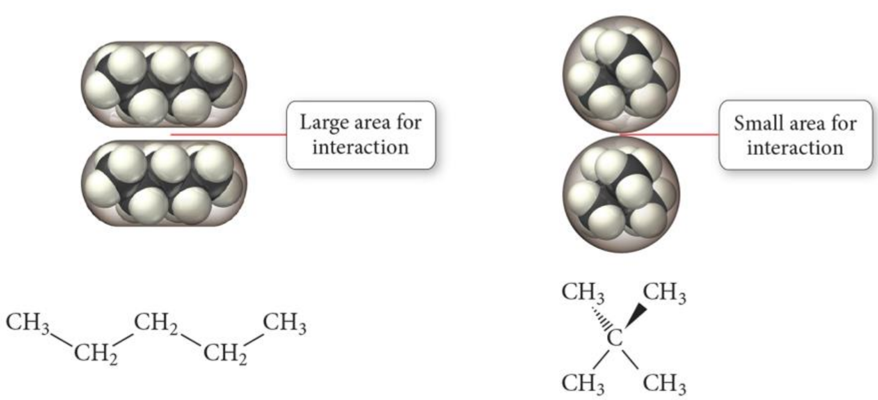
Effect of Molecular Size on Size of Dispersion Force

As the molar mass increases, the number of electrons increases. Therefore, the strength of the dispersion forces increases.



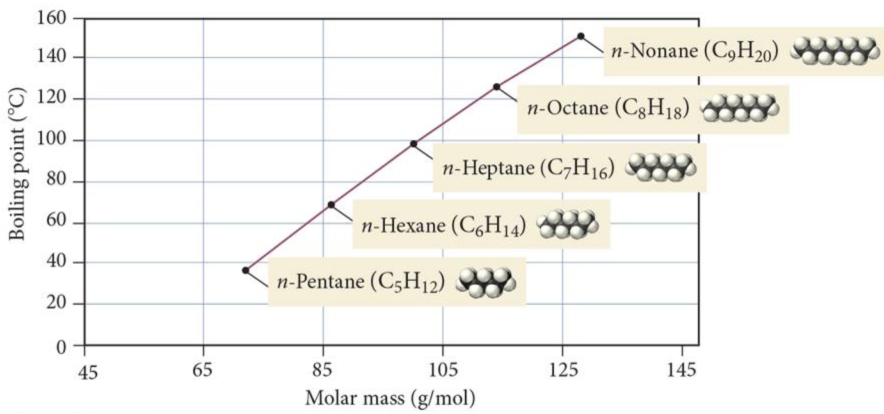
The stronger the attractive forces among the molecules, the higher the boiling point will be.

Effect of Molecular Shape on Size of Dispersion Force



(a) *n*-Pentane (b) Neopentane

Boiling Points of *n*-Alkanes



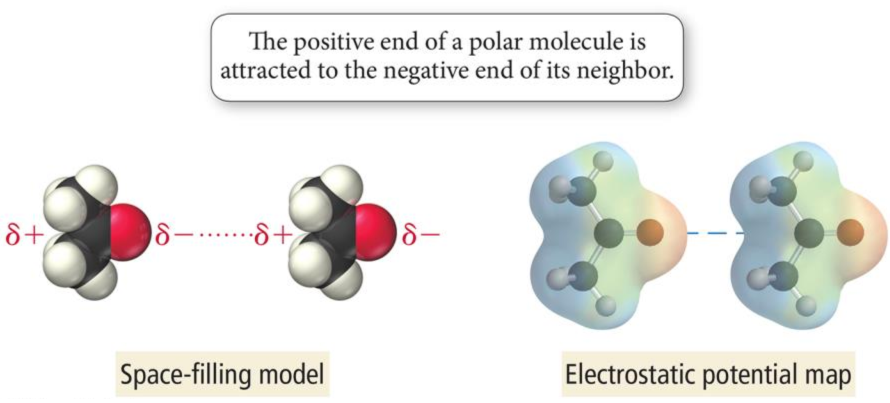
Alkane Boiling Points

- Branched chains have lower boiling points than straight chains.
- The straight-chain isomers have more surface-to-surface contact.

Dipole–Dipole Forces

- Polar molecules have a permanent dipole.
  - Bond polarity and shape
  - Dipole moment
  - The always-present induced dipole
- The permanent dipole adds to the attractive forces among the molecules, raising the boiling and melting points relative to nonpolar molecules of similar size and shape.

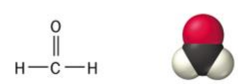
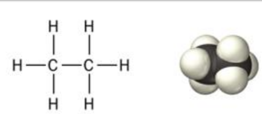
Dipole–Dipole Interaction



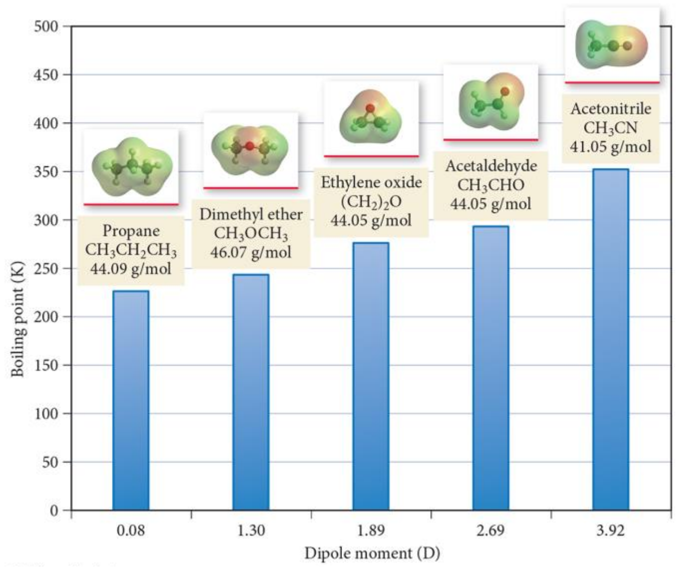
Trends in the Strength of Intermolecular Attraction

- The stronger the attractions among the atoms or molecules, the more energy it will take to separate them.
- Boiling a liquid requires that we add enough energy to overcome all the attractions among the particles.
  - However, not breaking the covalent bonds
- *The higher the normal boiling point of the liquid, the stronger the intermolecular attractive forces.*

Effect of Dipole–Dipole Attraction on Boiling and Melting Points

Name	Formula	Molar Mass (g/mol)	Structure	bp (°C)	mp (°C)
Formaldehyde	CH_2O	30.03		−19.5	−92
Ethane	C_2H_6	30.07		−88	−172

Dipole Movement and Boiling Point



Attractive Forces and Solubility

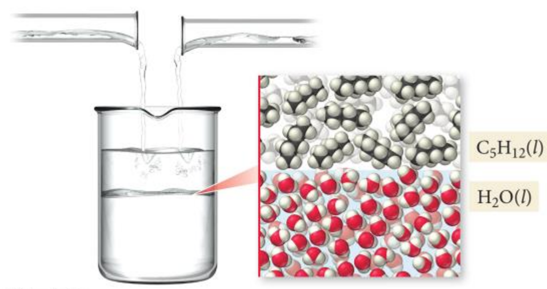
- Solubility depends, in part, on the attractive forces of the solute and solvent molecules.
  - *Like dissolves like.*
  - *Miscible liquids will always dissolve in each other.*
- Polar substances dissolve in polar solvents.
  - **Hydrophilic groups = OH, CHO, C═O, COOH, NH_2, Cl**
- Nonpolar molecules dissolve in nonpolar solvents.
  - **Hydrophobic groups = C—H, C—C**
- Many molecules have both hydrophilic and hydrophobic parts; solubility in water becomes a competition between the attraction of the polar groups for the water and the attraction of the nonpolar groups for their own kind.

Immiscible Liquids

Pentane, C_5H_{12}, is a nonpolar molecule.

Water is a polar molecule.

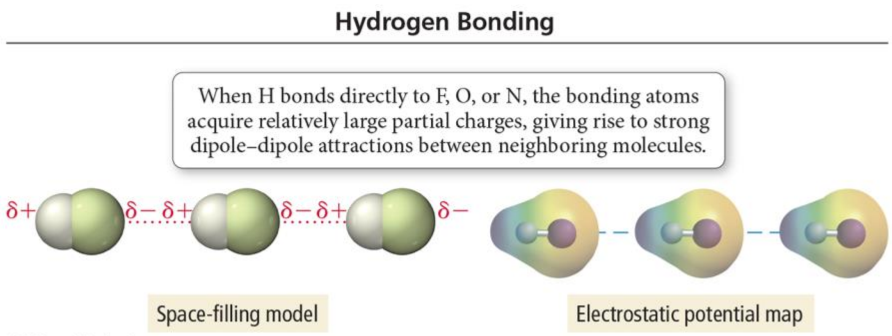
The attractive forces among the water molecules are much stronger than their attractions for the pentane molecules. The result is that the liquids are immiscible.



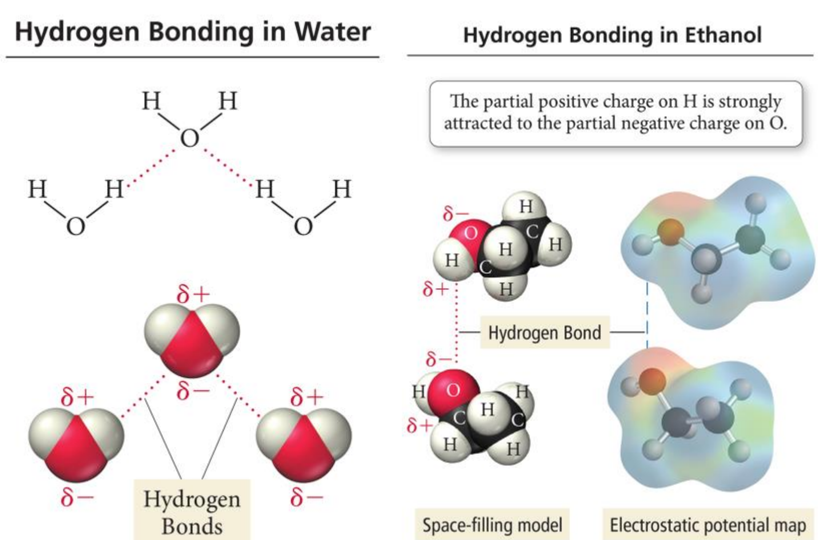
Hydrogen Bonding

- When a small, very electronegative atom is bonded to hydrogen, it strongly pulls the bonding electrons toward it.
  - O–H, N–H, or F–H
- Because hydrogen has no other electrons, when its electron is pulled away, the nucleus becomes de-shielded, exposing the H proton.
- The exposed proton acts as a very strong center of positive charge, attracting all the electron clouds from neighboring molecules.

Hydrogen Bonding



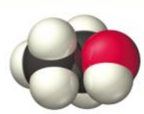
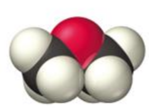
Hydrogen Bonding in Water and Ethanol



Hydrogen Bonds

- Hydrogen bonds are very strong intermolecular attractive forces.
  - Stronger than dipole–dipole or dispersion forces
- Substances that can hydrogen bond will have higher boiling points and melting points than similar substances that cannot.
- But, hydrogen bonds are not nearly as strong as chemical bonds.
  - 2–5% the strength of covalent bonds

Effect of Hydrogen Bonding on Boiling Point

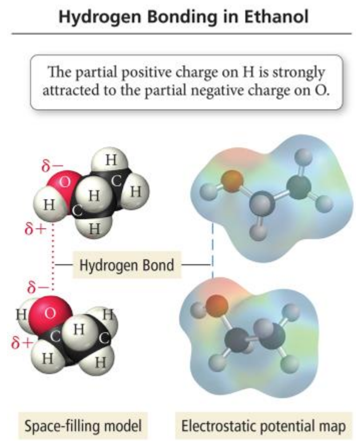
Name	Formula		Molar Mass (g/mol)	Structure	bp (°C)	mp (°C)
Ethanol	C_2H_6O		46.07	CH_3CH_2OH	78.3	−114.1
Dimethyl ether	C_2H_6O		46.07	CH_3OCH_3	−22.0	−138.5

Boiling Points of Group 4A and 6A Compounds

HF, H_2O, and NH_3 have hydrogen bonds. Therefore, they have higher boiling points than would be expected from the general trends.

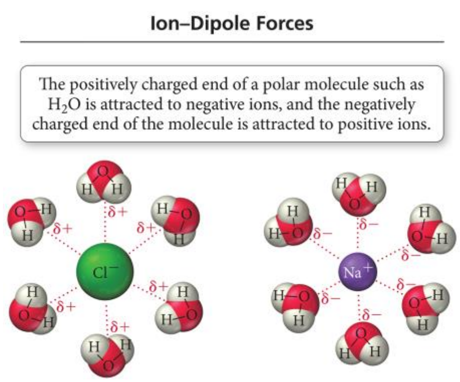
For nonpolar molecules, such as the hydrides of group 4, the intermolecular attractions are due to dispersion forces. Therefore, they increase down the column, causing the boiling point to increase.

Polar molecules, such as the hydrides of groups 5–7, have both dispersion forces and dipole–dipole attractions. Therefore, they have higher boiling points than the corresponding group 4 molecules.



Ion–Dipole Forces

- In a mixture, ions from an ionic compound are attracted to the dipole of polar molecules.
- The strength of the ion–dipole attraction is one of the main factors that determines the solubility of ionic compounds in water.



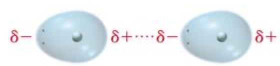
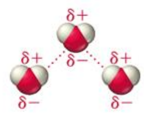
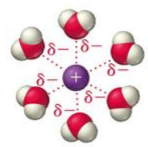
Summary

- Dispersion forces are the weakest of the intermolecular forces.
- Dispersion forces are present in all molecules and atoms.
- The magnitude of the dispersion forces increases with molar mass.
- Polar molecules also have dipole–dipole attractive forces.

Summary (cont.)

- Hydrogen bonds are the strongest of the intermolecular attractive forces a pure substance can have.
- Hydrogen bonds will be present when a molecule has H directly bonded to either O, N, or F atoms.
  - The only example of H bonded to F is HF.
- Ion–dipole attractions are present in mixtures of ionic compounds with polar molecules.
- Ion–dipole attractions are the strongest intermolecular attraction.
- Ion–dipole attractions are especially important in aqueous solutions of ionic compounds.

TABLE 11.4 Types of Intermolecular Forces

Type	Present In	Molecular Perspective	Strength
Dispersion*	All molecules and atoms		0.05–20+ kJ/mol
Dipole–dipole	Polar molecules		3–20+ kJ/mol
Hydrogen bonding	Molecules containing H bonded to F, O, or N		10–40 kJ/mol
Ion–dipole	Mixtures of ionic compounds and polar compounds		30–100+ kJ/mol

*The dispersion force can become very strong (as strong and even stronger than the others) for molecules of high molar mass.

Surface Tension

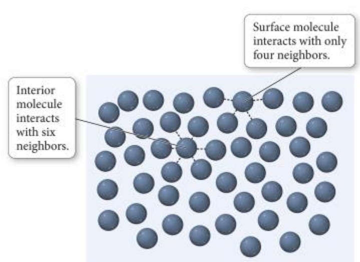
- Surface tension is a property of liquids that results from the tendency of liquids to minimize their surface area.
- To minimize their surface area, liquids form drops that are spherical.
  – As long as there is no gravity

Surface Tension

- The layer of molecules on the surface behaves differently than the interior because the cohesive forces on the surface molecules have a net pull into the liquid interior.
- The surface layer acts like an elastic skin, allowing you to “float” a paper clip even though steel is denser than water.

Surface Tension

- Because they have fewer neighbors to attract them, the surface molecules are less stable than those in the interior.
  - Have a higher potential energy
- The surface tension of a liquid is the energy required to increase the surface area a given amount.
  - Surface tension of H_2O = 72.8 mJ/m^2
    - At room temperature
  - Surface tension of C_6H_6 = 28 mJ/m^2



Factors Affecting Surface Tension

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

Viscosity

- **Viscosity** is the resistance of a liquid to flow.
  - 1 poise = 1 P = 1 g/cm · s
  - Often given in centipoise, cP
    - H_2O = 1 cP at room temperature
- Larger intermolecular attractions = higher viscosity

TABLE 11.5 Viscosity of Several Hydrocarbons at 20 °C

Hydrocarbon	Molar Mass (g/mol)	Formula	Viscosity (cP)
n-Pentane	72.15	$CH_3CH_2CH_2CH_2CH_3$	0.240
n-Hexane	86.17	$CH_3CH_2CH_2CH_2CH_2CH_3$	0.326
n-Heptane	100.2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	0.409
n-Octane	114.2	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	0.542
n-Nonane	128.3	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	0.711

Factors Affecting Viscosity

- The stronger the intermolecular attractive forces, the higher the liquid's viscosity will be.
- The more spherical the molecular shape, the lower the viscosity will be.
  - Molecules roll more easily.
  - Less surface-to-surface contact lowers attractions.

Factors Affecting Viscosity

- Raising the temperature of a liquid reduces its viscosity.
  - Raising the temperature of the liquid increases the average kinetic energy of the molecules.
  - The increased molecular motion makes it easier to overcome the intermolecular attractions and flow.

TABLE 11.6 Viscosity of Liquid Water at Several Temperatures

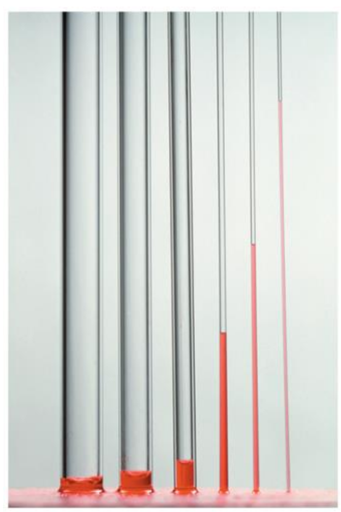
Temperature (°C)	Viscosity (cP)
20	1.002
40	0.653
60	0.467
80	0.355
100	0.282

Capillary Action

- **Capillary action** is the ability of a liquid to flow up a thin tube against the influence of gravity.
  - The narrower the tube, the higher the liquid rises.
- Capillary action is the result of two forces working in conjunction, the cohesive and adhesive forces.
  - Cohesive forces hold the liquid molecules together.
  - Adhesive forces attract the outer liquid molecules to the tube's surface.

Capillary Action

- The adhesive forces pull the surface liquid up the side of the tube, and the cohesive forces pull the interior liquid with it.
- The liquid rises up the tube until the force of gravity counteracts the capillary action forces.
- The narrower the tube diameter, the higher the liquid will rise up the tube.



Meniscus

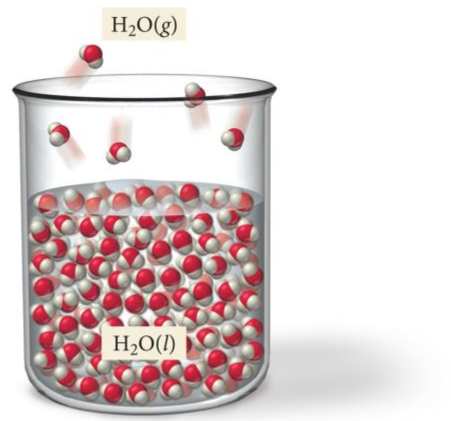
- The curving of the liquid surface in a thin tube is due to the competition between adhesive and cohesive forces.
- The meniscus of water is concave in a glass tube because its adhesion to the glass is stronger than its cohesion for itself.
- The meniscus of mercury is convex in a glass tube because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

The Molecular Dance

- Molecules in a liquid are constantly in motion.
  - Vibrational and limited rotational and translational
- The *average* kinetic energy is proportional to the temperature.
- However, some molecules have more kinetic energy than the average, and others have less.

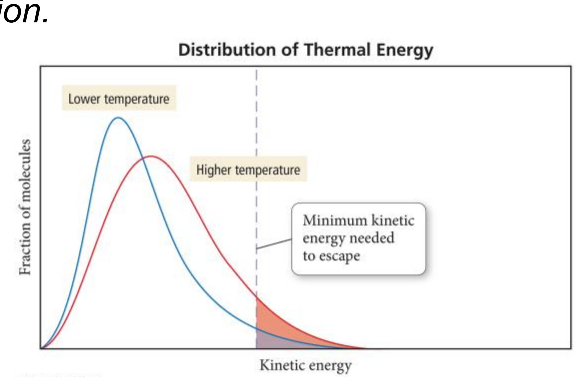
Vaporization

- If these high-energy molecules are at the surface, they may have enough energy to overcome the attractive forces.
  - Therefore, *the larger the surface area, the faster the rate of evaporation*.
- This will allow them to escape the liquid and become a **vapor**.



Distribution of Thermal Energy

- Only a small fraction of the molecules in a liquid have enough energy to escape.
- But, as the temperature increases, the fraction of the molecules with "escape energy" increases.
- *The higher the temperature, the faster the rate of evaporation.*



Condensation

- Some molecules of the vapor will lose energy through molecular collisions.
- The result will be that some of the molecules will get captured back into the liquid when they collide with it.
- Also, some may stick and gather together to form droplets of liquid, particularly on surrounding surfaces.
- We call this process **condensation**.

Evaporation versus Condensation

- Vaporization and condensation are opposite processes.
- In an open container, the vapor molecules generally spread out faster than they can condense.
- The net result is that the rate of vaporization is greater than the rate of condensation, and there is a net loss of liquid.
- However, in a closed container, the vapor is not allowed to spread out indefinitely.
- The net result in a closed container is that at some time the rates of vaporization and condensation will be equal.

Effect of Intermolecular Forces on Evaporation and Condensation

- The weaker the attractive forces among molecules, the less energy they will need to vaporize.
- Also, weaker attractive forces means that more energy will need to be removed from the vapor molecules before they can condense.
- The net result will be more molecules in the vapor phase and a liquid that evaporates faster; *the weaker the attractive forces, the faster the rate of evaporation.*
- Liquids that evaporate easily are said to be **volatile**.
  – For example, gasoline, fingernail polish remover
- Liquids that do not evaporate easily are called **nonvolatile**.
  – For example, motor oil

Energetics of Vaporization

- When the high-energy molecules are lost from the liquid, it lowers the average kinetic energy.
- If energy is not drawn back into the liquid, its temperature will decrease; therefore, *vaporization is an endothermic process*.
  – Condensation is an exothermic process.
- Vaporization requires input of energy to overcome the attractions among molecules.

Heat of Vaporization

- The amount of heat energy required to vaporize one mole of the liquid is called the **heat of vaporization, ΔH_{vap}.**
  - Sometimes called the enthalpy of vaporization
- It is always endothermic; therefore, ΔH_{vap} is +.
- It is somewhat temperature dependent.
- $\Delta H_{condensation} = -\Delta H_{vaporization}$

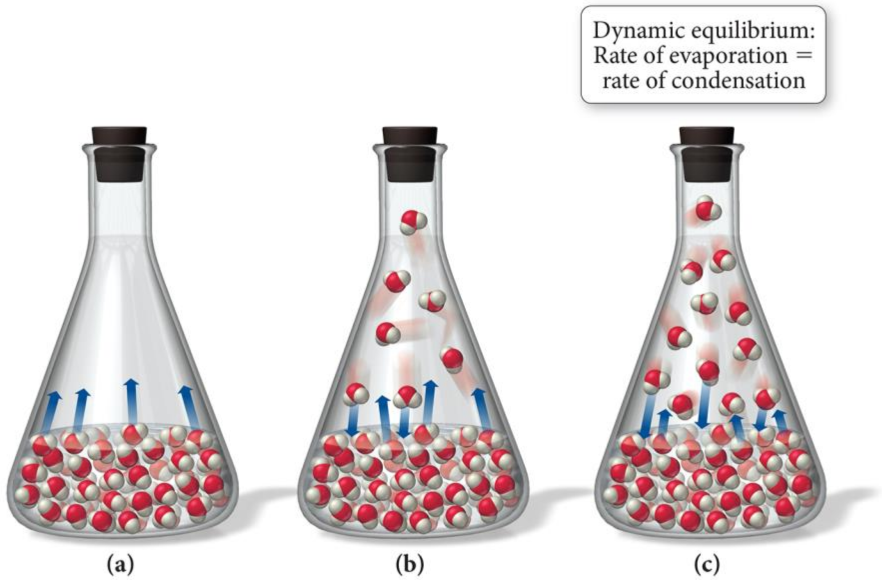
TABLE 11.7 Heats of Vaporization of Several Liquids at Their Boiling Points and at 25 °C

Liquid	Chemical Formula	Normal Boiling Point (°C)	ΔH_{vap}(kJ/mol) at Boiling Point	ΔH_{vap}(kJ/mol) at 25 °C
Water	H_2O	100	40.7	44.0
Rubbing alcohol (isopropyl alcohol)	C_3H_8O	82.3	39.9	45.4
Acetone	C_3H_6O	56.1	29.1	31.0
Diethyl ether	$C_4H_{10}O$	34.6	26.5	27.1

Dynamic Equilibrium

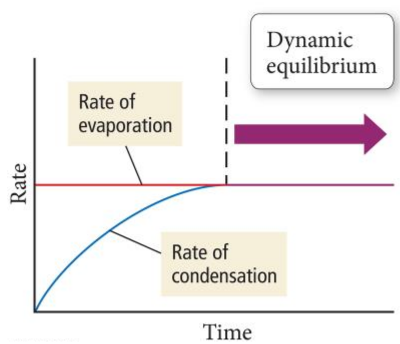
- In a closed container, once the rates of vaporization and condensation are equal, the total amount of vapor and liquid will not change.
- Evaporation and condensation are still occurring, but because they are opposite processes, there is no net gain or loss of either vapor or liquid.

Dynamic Equilibrium



Dynamic Equilibrium

- When two opposite processes reach the same rate so that there is no gain or loss of material, we call it a **dynamic equilibrium**.
  - This does *not* mean there are equal amounts of vapor and liquid; it means that they are *changing* by equal amounts.



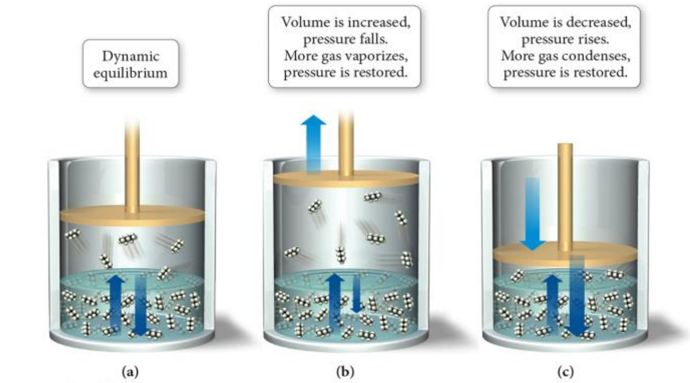
Vapor Pressure

- The pressure exerted by a vapor when it is in dynamic equilibrium with its liquid is called the **vapor pressure**.
  - Remember using Dalton's law of partial pressures to account for the pressure of the water vapor when collecting gases by water displacement?
- The weaker the attractive forces among the molecules, the more molecules will be in the vapor.
- Therefore, *the weaker the attractive forces, the higher the vapor pressure*.
  - The higher the vapor pressure, the more volatile the liquid.

Vapor–Liquid Dynamic Equilibrium

- If the volume of the chamber is increased, it will decrease the pressure of the vapor inside the chamber.
  - At that point, there are fewer vapor molecules in a given volume, causing the rate of condensation to slow.
- Therefore, for a period of time, the rate of vaporization will be faster than the rate of condensation, and the amount of vapor will increase.
- Eventually, enough vapor accumulates so that the rate of the condensation increases to the point where it is once again as fast as evaporation.
  - Equilibrium is reestablished.
- At this point, the vapor pressure will be the same as it was before.

Changing the Container's Volume Disturbs the Equilibrium



Initially, the rate of vaporization and condensation are equal and the system is in dynamic equilibrium.

When the volume is increased, the rate of vaporization becomes faster than the rate of condensation.

When the volume is decreased, the rate of vaporization becomes slower than the rate of condensation.

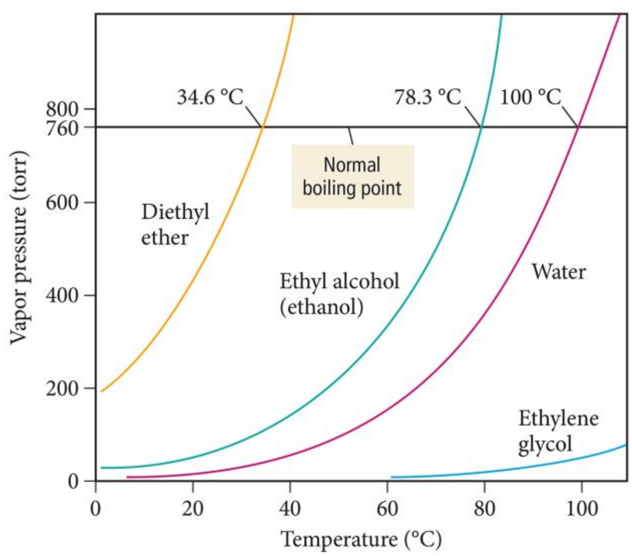
Dynamic Equilibrium

- A system in dynamic equilibrium can respond to changes in the conditions.
- *When conditions change, the system shifts its position to relieve or reduce the effects of the change*.

Temperature Dependence of Vapor Pressure

- Increasing the temperature increases the number of molecules able to escape the liquid.
- The net result is that *as the temperature increases, the vapor pressure increases*.
- Small changes in temperature can make big changes in vapor pressure.
  - The rate of growth depends on the strength of the intermolecular forces.

Vapor Pressure Curves



Boiling Point

- When the temperature of a liquid reaches a point where its vapor pressure is the same as the external pressure, vapor bubbles can form anywhere in the liquid, not just on the surface.
- This phenomenon is what is called **boiling**, and the temperature at which the vapor pressure equals external pressure is the **boiling point**.

Boiling Point

- *The normal boiling point is the temperature at which the vapor pressure of the liquid = 1 atm*.
- The lower the external pressure, the lower the boiling point of the liquid.

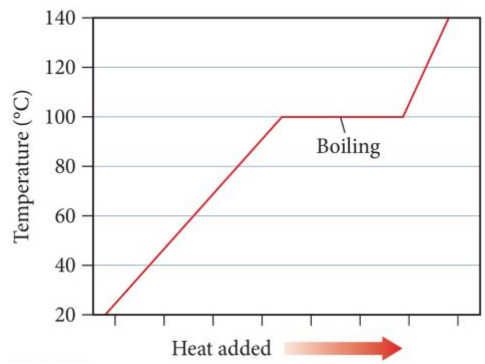
TABLE 11.8 Boiling Points of Water at Several Locations of Varied Altitudes

Location	Elevation (ft)	Approximate Pressure (atm)*	Approximate Boiling Point of Water (°C)
Mount Everest, Tibet (highest mountain peak on Earth)	29,035	0.32	78
Mount McKinley (Denali), Alaska (highest mountain peak in North America)	20,320	0.46	83
Mount Whitney, California (highest mountain peak in 48 contiguous U.S. states)	14,495	0.60	87
Denver, Colorado (mile high city)	5,280	0.83	94
Boston, Massachusetts (sea level)	20	1.0	100

*The atmospheric pressure in each of these locations is subject to weather conditions and can vary significantly from these values.

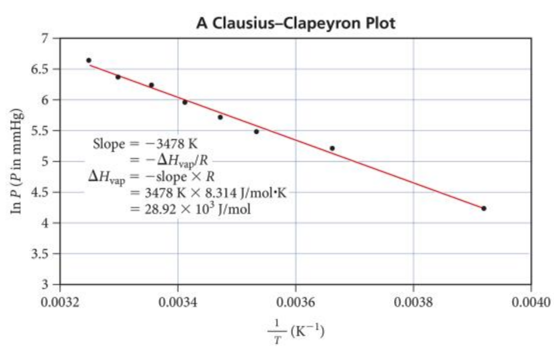
Heating Curve of a Liquid

- As you heat a liquid, its temperature increases linearly until it reaches the boiling point.
  - $q = \text{mass} \times C_s \times \Delta T$
- Once the temperature reaches the boiling point, all the added heat goes into boiling the liquid; the temperature stays constant.
- Once all the liquid has been turned into gas, the temperature can again start to rise.



Clausius–Clapeyron Equation

- The logarithm of the vapor pressure versus inverse absolute temperature is a linear function.
- A graph of $\ln(P_{vap})$ versus $1/T$ is a straight line.
- The slope of the line is ΔH_{vap}/8.314 J/mol·K.
  - Units for ΔH_{vap} are J/mol.



Clausius–Clapeyron Equation: Two-Point Form

- The equation below can be used with just two measurements of vapor pressure and temperature.
  - However, it generally gives less precise results.
    - Fewer data points will not give as precise an average because there is less averaging out of the errors, as with any other sets of measurements.
- It can also be used to predict the vapor pressure if you know the heat of vaporization and the normal boiling point.
  - Remember, the vapor pressure at the normal boiling point is 760 torr.

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

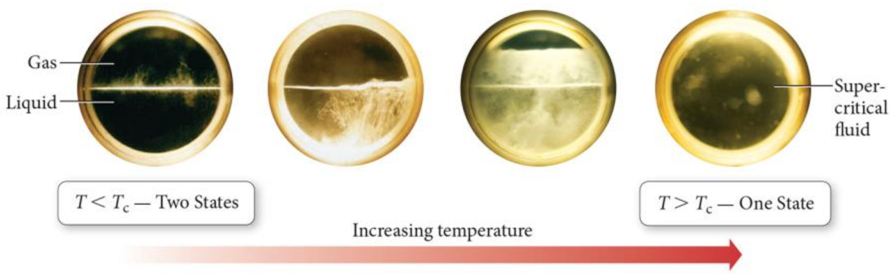
Clausius–Clapeyron equation (two-point form)

The Critical Point

- The temperature required to produce a supercritical fluid is called the **critical temperature**.
- The pressure at the critical temperature is called the **critical pressure**.
- At the critical temperature or higher temperatures, the gas cannot be condensed to a liquid, no matter how high the pressure gets.

Supercritical Fluid

- As a liquid is heated in a sealed container, more vapor collects, causing the pressure inside the container to rise, the density of the vapor to increase, and the density of the liquid to decrease.
- At some temperature, the meniscus between the liquid and vapor disappears, and the states commingle to form a **supercritical fluid**.
- Supercritical fluids have properties of both gas and liquid states.

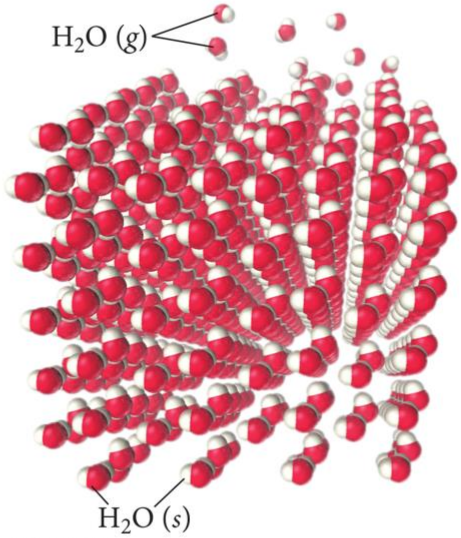


Sublimation and Deposition

- Molecules in a solid have thermal energy that allows them to vibrate.
- Surface molecules with sufficient energy may break free from the surface and become a gas; this process is called **sublimation**.
- The capturing of vapor molecules into a solid is called **deposition**.
- The solid and vapor phases exist in dynamic equilibrium in a closed container at temperatures below the melting point.
  - Therefore, *molecular solids have a vapor pressure*.

solid gas $\xrightleftharpoons[\text{deposition}]{\text{sublimation}}$

Sublimation

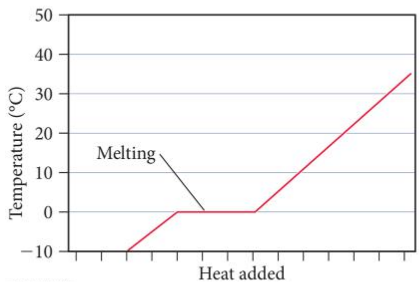


Melting = Fusion

- As a solid is heated, its temperature rises, and the molecules vibrate more vigorously.
- Once the temperature reaches the melting point, the molecules have sufficient energy to overcome some of the attractions that hold them in position, and the solid melts (or fuses).
- The opposite of melting is freezing.

Heating Curve of a Solid

- As you heat a solid, its temperature increases linearly until it reaches the melting point.
  - q = mass × C_s × ΔT
- Once the temperature reaches the melting point, all the added heat goes into melting the solid.
  - The temperature stays constant.
- Once all the solid has been turned into liquid, the temperature can again start to rise.
  - Ice/water will always have a temperature of 0 °C at 1 atm.



Energetics of Melting

- When the high-energy molecules are lost from the solid, it lowers the average kinetic energy.
- If energy is not drawn back into the solid, its temperature will decrease; therefore, *melting is an endothermic process*, and freezing is an exothermic process.
- Melting requires input of energy to overcome the attractions among molecules.

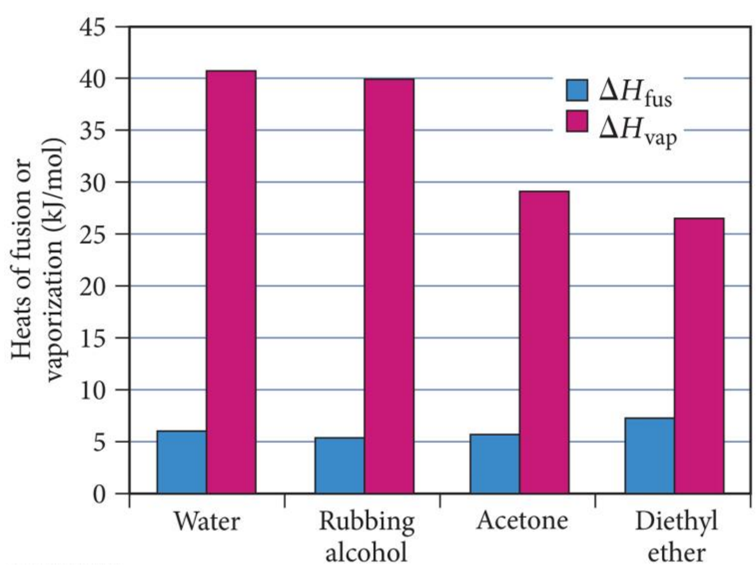
Heat of Fusion

- The amount of heat energy required to melt one mole of the solid is called the **heat of fusion, ΔH_{fus}**.
  - Sometimes called the enthalpy of fusion
- It is always endothermic; therefore, ΔH_{fus} is +.
- It is somewhat temperature dependent.
- $\Delta H_{crystallization} = -\Delta H_{fusion}$
- Generally much less than ΔH_{vap} .
- $\Delta H_{sublimation} = \Delta H_{fusion} + \Delta H_{vaporization}$

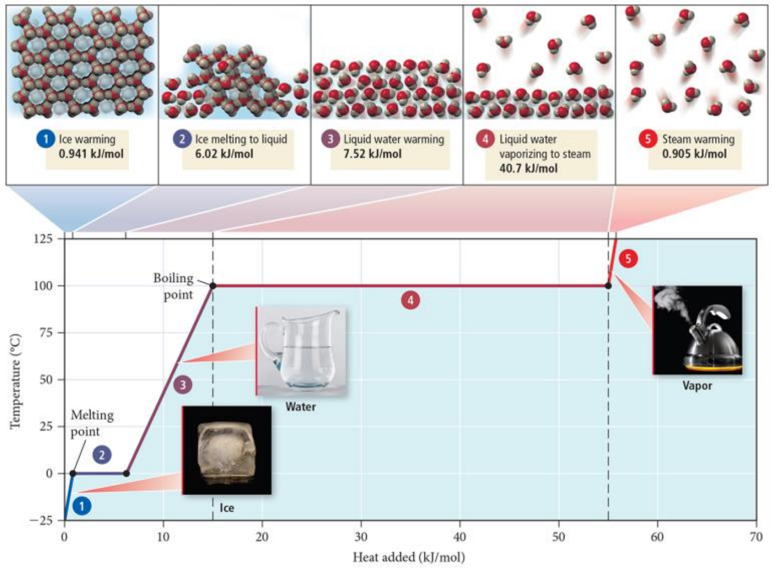
TABLE 11.9 Heats of Fusion of Several Substances

Liquid	Chemical Formula	Melting Point (°C)	ΔH_{fus}(kJ/mol)
Water	H_2O	0.00	6.02
Rubbing alcohol (isopropyl alcohol)	C_3H_8O	−89.5	5.37
Acetone	C_3H_6O	−94.8	5.69
Diethyl ether	$C_4H_{10}O$	−116.3	7.27

Heats of Fusion and Vaporization



Heating Curve of Water



Segment 1

- Heating 1.00 mole of ice at −25.0 °C up to the melting point, 0.0 °C
- q = mass × C_s × ΔT
  - Mass of 1.00 mole of ice = 18.0 g
  - C_s = 2.09 J/mol · °C

$$q = (18.0\ \text{g}) \times \left(2.09\ \frac{\text{J}}{\text{g} \cdot {}^\circ\text{C}}\right) \times (0.0^\circ\text{C} - (-25.0^\circ\text{C}))$$

$$q = 941\ \text{J} = 0.941\ \text{kJ}$$

Segment 2

- Melting 1.00 mole of ice at the melting point, 0.0 °C
- $q = n \cdot \Delta H_{fus}$
  - n = 1.00 mole of ice
  - ΔH_{fus} = 6.02 kJ/mol

$$q = (1.00\ \text{mol}) \times \left(6.02\ \tfrac{\text{kJ}}{\text{mol}}\right)$$
$$q = 6.02\ \text{kJ}$$

Segment 3

- Heating 1.00 mole of water at 0.0 °C up to the boiling point, 100.0 °C
- q = mass × C_s × ΔT
  - Mass of 1.00 mole of water = 18.0 g
  - C_s = 2.09 J/mol · °C

$$q = (18.0\ \text{g}) \times \left(4.18\ \tfrac{\text{J}}{\text{g} \cdot {}^\circ\text{C}}\right) \times (100.0^\circ\text{C} - (0.0^\circ\text{C}))$$
$$q = 7.52 \times 10^3\ \text{J} = 7.52\ \text{kJ}$$

Segment 4

- Boiling 1.00 mole of water at the boiling point, 100.0 °C
- $q = n \cdot \Delta H_{vap}$
  - n = 1.00 mole of ice
  - ΔH_{fus} = 40.7 kJ/mol

$$q = (1.00\ \text{mol}) \times \left(40.7\ \tfrac{\text{kJ}}{\text{mol}}\right)$$
$$q = 40.7\ \text{kJ}$$

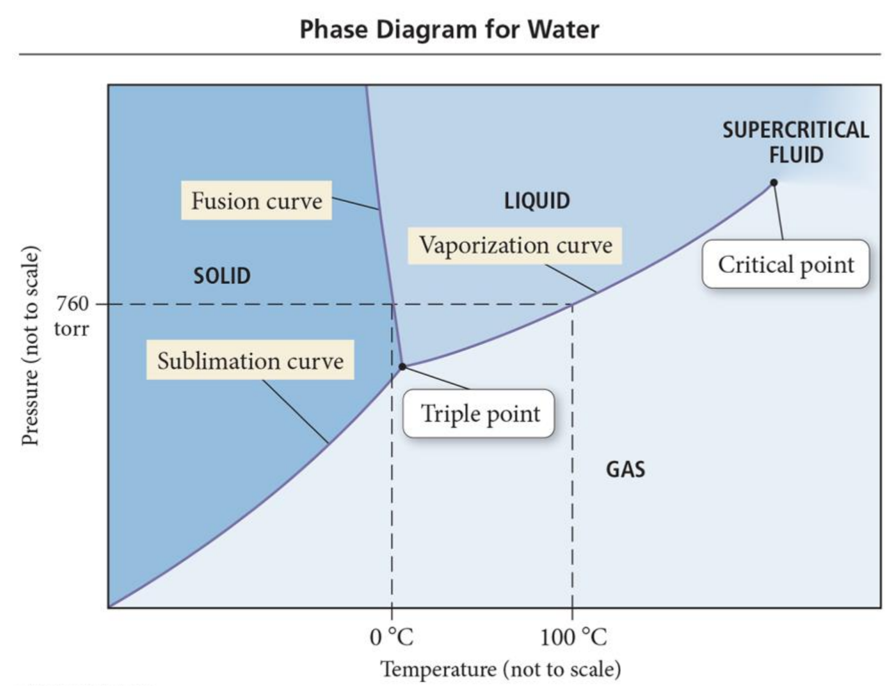
Segment 5

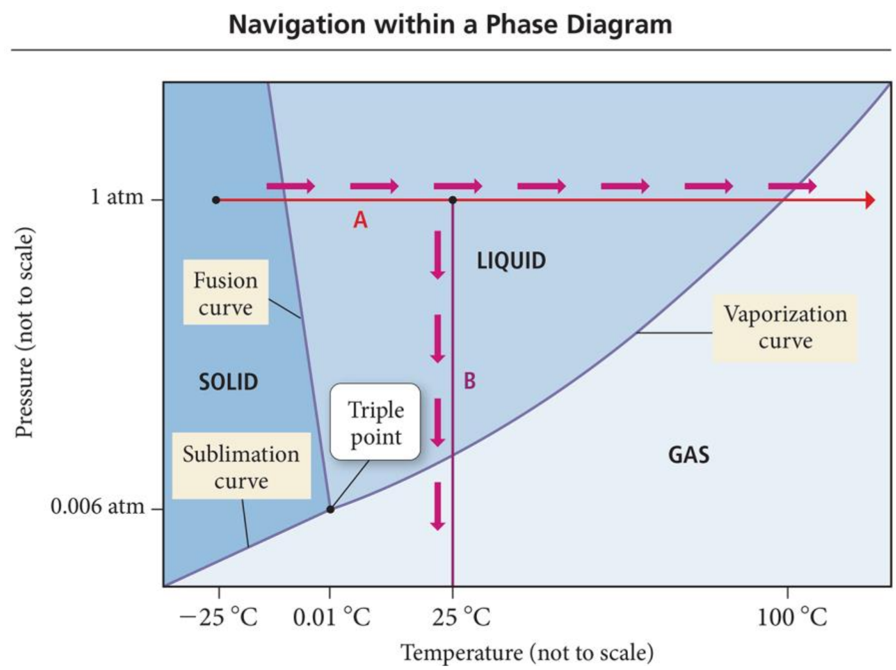
- Heating 1.00 mole of steam at 100.0 °C up to 125.0 °C
- $q = \text{mass} \times C_s \times \Delta T$
  - Mass of 1.00 mole of water = 18.0 g
  - C_s = 2.01 J/mol · °C

$$q = (18.0\ \text{g}) \times \left(2.01\ \tfrac{\text{J}}{\text{g}\cdot{}^\circ\text{C}}\right) \times (125.0^\circ\text{C} - (100.0^\circ\text{C}))$$
$$q = 904\ \text{J} = 0.904\ \text{kJ}$$

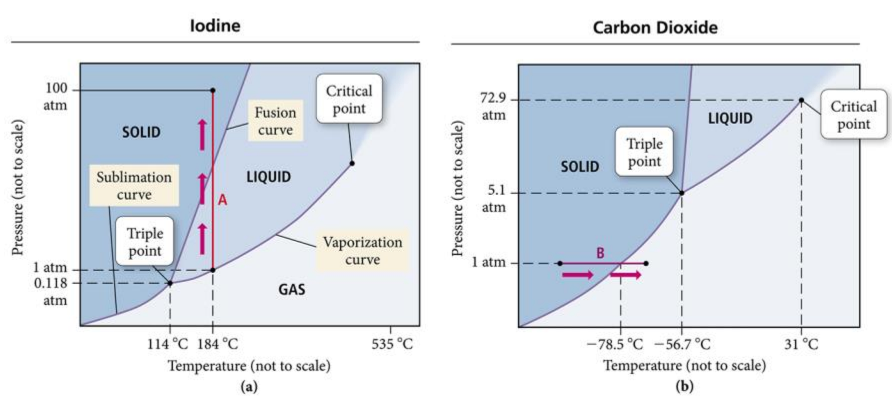
Phase Diagrams

- Phase diagrams describe the different states and state changes that occur at various temperature/pressure conditions.
- Regions represent states.
- Lines represent state changes.
  - The liquid/gas line is the vapor pressure curve.
  - Both states exist simultaneously.
  - The critical point is the farthest point on the vapor pressure curve.
- Triple point is the temperature/pressure condition where all three states exist simultaneously.
- For most substances, the freezing point increases as pressure increases.





Phase Diagrams for Other Substances



Water: An Extraordinary Substance

- Water is a liquid at room temperature.
  - Most molecular substances with similar molar masses are gases at room temperature.
    - For example, NH_3, CH_4
  - This is due to H bonding among molecules.
- Water is an excellent solvent, dissolving many ionic and polar molecular substances.
  - It has a large dipole moment.
  - Even many small nonpolar molecules have some solubility in water.
    - For example, O_2, CO_2

Water: An Extraordinary Substance

- Water has a very high specific heat for a molecular substance.
  - Moderating effect on coastal climates
- Water expands when it freezes at a pressure of 1 atm.
  - About 9%
  - Making ice less dense than liquid water

Boiling Points of Main-Group Hydrides

- The hydrogen bonds present in water result in a relatively high boiling point.