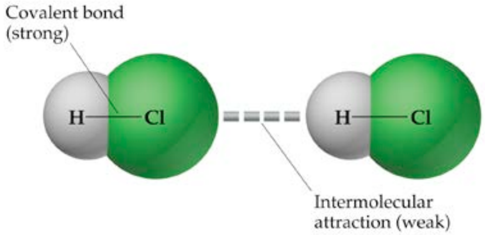
Chapter 11. Intermolecular Forces, Liquids, and Solids

11.2 Intermolecular Forces

- Intermolecular forces are much weaker than ionic or covalent bonds (e.g., 16 kJ/mol versus 431 kJ/mol for HCl).



- Melting or boiling = broken intermolecular forces

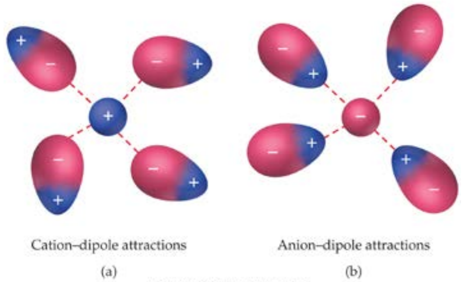
- Intermolecular forces are formed when a substance condenses.
  - Boiling points reflect IMF strength → high b.p. = strong attractive forces.

  - Melting points also reflect the strength of attractive forces.
    → high m.p. = strong attractive forces.

- *van der Waals* forces = IMFs between neutral molecules. <15% as strong as a covalent or ionic bond
  - London-dispersion forces
  - dipole-dipole forces
  - hydrogen-bonding

Ion-Dipole Forces (important in solutions – ionic compound interacts with molecule)

- **Ion-dipole** forces (interaction between an ion, e.g. Na^+ and the partial charge on the end of a polar molecule/dipole, such as water) are important in solutions, esp. those that are polar.



- especially important for solutions of ionic substances in polar liquids, e.g. NaCl (*aq*)

Dipole-Dipole Forces

- **Dipole-dipole forces** exist between neutral polar molecules.

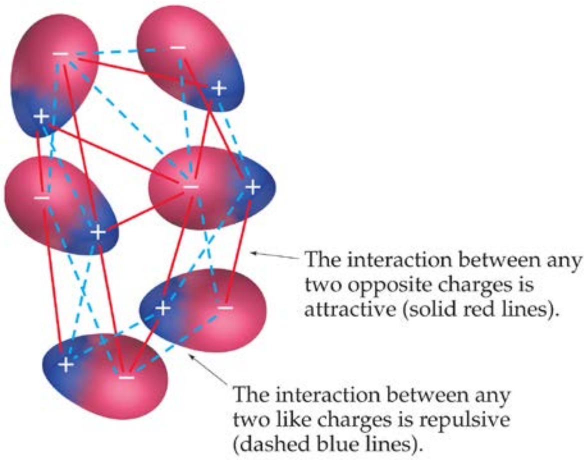
- Dipole-dipole forces are weaker than ion-dipole forces.

- Polar molecules attract each other.
  - The partially positive end of one molecule attracts the partially negative end of another.

- Polar molecules need to be close together to form strong dipole-dipole interactions.

- If two molecules have about the same mass and size, then dipole-dipole forces increase with increasing polarity.

- For molecules of similar polarity, those with smaller volumes often have greater dipole–dipole attractions.



The interaction between any two opposite charges is attractive (solid red lines).

The interaction between any two like charges is repulsive (dashed blue lines).

TABLE 11.2 Molecular Weights, Dipole Moments, and Boiling Points of Several Simple Organic Substances

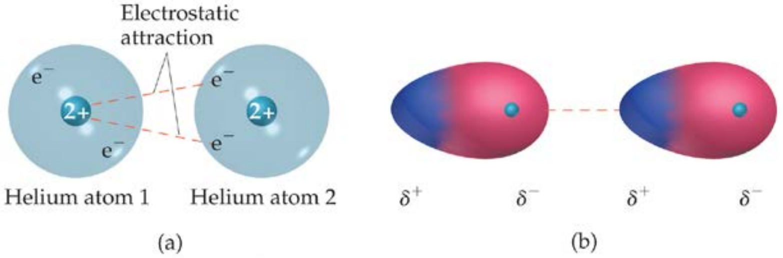
Substance	Molecular Weight (amu)	Dipole Moment μ (D)	Boiling Point (K)
Propane, $CH_3CH_2CH_3$	44	0.1	231
Dimethyl ether, CH_3OCH_3	46	1.3	248
Methyl chloride, CH_3Cl	50	1.9	249
Acetaldehyde, CH_3CHO	44	2.7	294
Acetonitrile, CH_3CN	41	3.9	355

London Dispersion Forces

- weakest of all intermolecular forces
- exist between all molecules
- Adjacent neutral molecules can affect each other:

  The nucleus of one molecule (or atom) attracts the electrons of the adjacent molecule (or atom)
  → distortion of the electron clouds for a moment
  → formation of an *instantaneous* dipole
  → induction of another instantaneous dipole in an adjacent molecule (or atom)

- These two temporary dipoles attract each other
- attractive force = **London dispersion force**



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Dispersion forces.

On the average, the charge distribution in the helium atoms is spherical, as represented by the spheres in (a).
At a particular instant, however, there can be a nonspherical arrangement of the electrons, as indicated by the location of the electrons (e–) in (a) and by the nonspherical shape of the electron cloud in (b).
The nonspherical electron distributions produce momentary dipoles and allow momentary electrostatic attractions between atoms that are called London dispersion forces or merely dispersion forces.

- What affects the strength of a dispersion force?
  - Molecules must be very close together for these attractive forces to occur.
  - **Polarizability** = the ease with which an electron cloud can be deformed.

- larger (greater the number of electrons) → more polarizable
  - London dispersion forces ↑ as molecular weight ↑

- shape of the molecule
  - ↑ SA available for contact → the greater the dispersion forces.
    - London dispersion forces between spherical molecules are smaller than those between more cylindrically shaped molecules.
      - e.g. *n*-pentane vs. neopentane.

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Molecular shape affects intermolecular attraction.

The *n*-pentane molecules make more contact with each other than do the neopentane molecules.
Thus, *n*-pentane has the greater intermolecular attractive forces and therefore has the higher boiling point (bp).

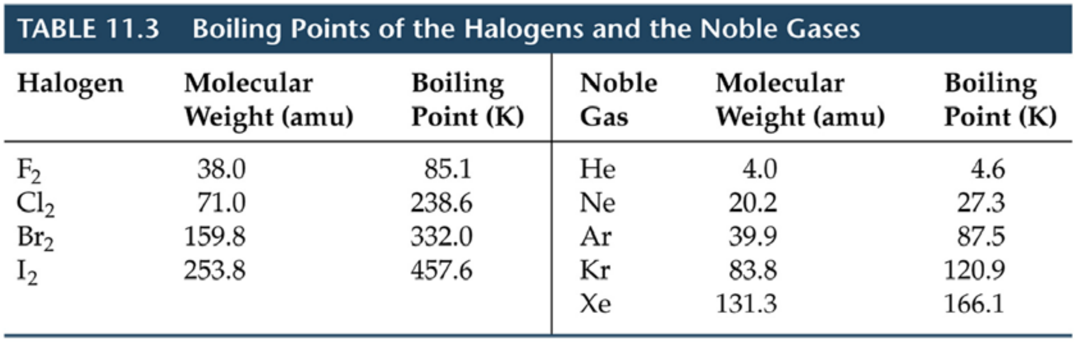


TABLE 11.3 Boiling Points of the Halogens and the Noble Gases

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

Sample Exercise 11.1 (p. 443)

The dipole moments of acetonitrile, CH_3CN, and methyl iodide, CH_3I, are 3.9 D and 1.62 D, respectively.

a) Which of these substances will have the greater dipole-dipole attractions among its molecules?

b) Which of these substances will have the greater London dispersion attractions?

c) The boiling points of CH_3CN and CH_3I are 354.8 K and 315.6 K, respectively. Which substance has the greatest overall attractive forces?

Practice Exercise 11.1

Of Br_2, Ne, HCl, HBr, and N_2, which is likely to have

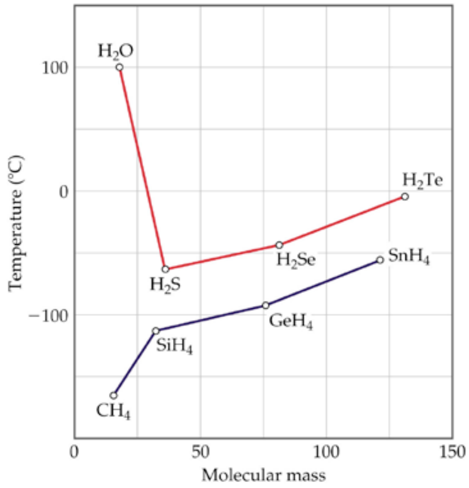
a) the largest intermolecular dispersion forces?

b) the largest dipole-dipole attractive forces?

Hydrogen Bonding

- b.p.'s of compounds with H-F, H-O, and H-N bonds are abnormally high.
  → their IMFs are abnormally strong.

- Hydrogen bonding = special case of dipole-dipole interactions
  - H-bonding requires:
    - H bonded to a small electronegative element (most important for compounds of F, O, and N).
    - An unshared electron pair on a nearby small electronegative ion or atom (usually F, O, or N on another molecule).
  - Electrons in the H-X bond (X is the more electronegative element) lie much closer to X than H.
  - H has only one electron, so in the H-X bond, the $H^{\delta+}$ presents an almost bare proton to the $X^{\delta-}$.
    → H-bonds are strong (vary from about 4 kJ/mol to 25 kJ/mol).
    - They are much weaker than ordinary chemical bonds.
- Intermolecular and intramolecular hydrogen bonds have exceedingly important biological significance – stabilizing protein structure, in DNA structure and function, etc.

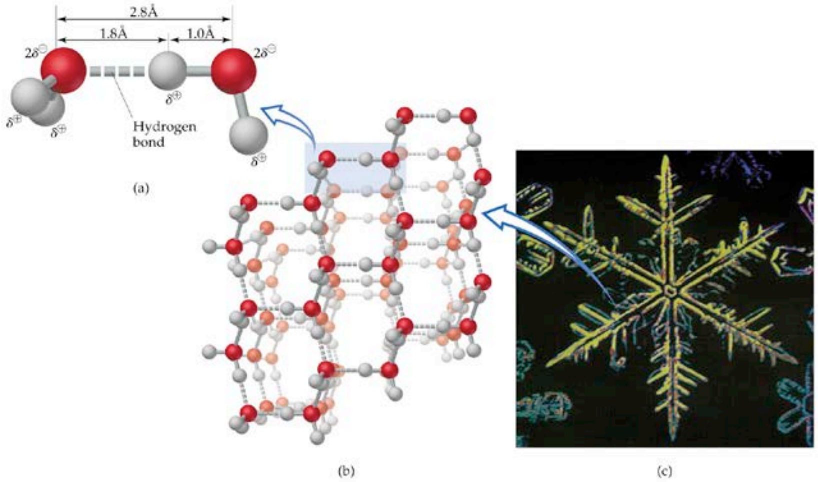


Boiling point as a function of molecular weight.

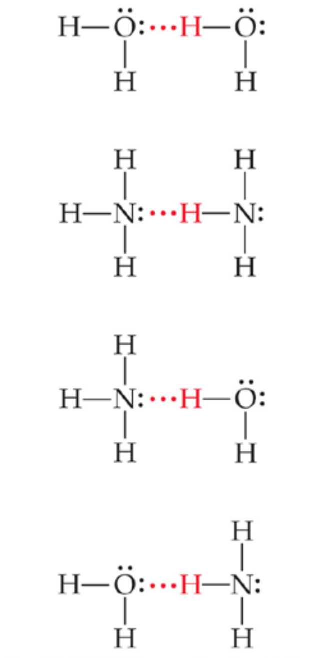
The boiling points of the group 4A (bottom) and 6A (top) hydrides are shown as a function of molecular weight. In general, the boiling points increase with increasing molecular weight, because of the increasing strength of dispersion forces. The very strong hydrogen-bonding forces between H_2O molecules, however, cause water to have an unusually high boiling point.

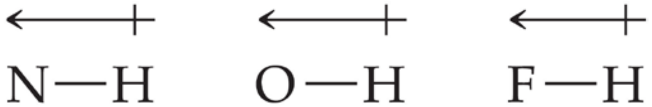
Floating Ice

- An interesting consequence of H-bonding is that ice floats
  - The molecules in solids are usually more closely packed than those in liquids.
    - Therefore, solids are usually more dense than liquids.
  - Ice is ordered with an open structure to optimize H-bonding.
    - In water the H–O bond length is 1.0 Å.
      - The O…H hydrogen bond length is 1.8 Å.
    - Water molecules in ice are arranged in an open, regular hexagon.
      - Each δ+ H points towards a lone pair on O.
    - Therefore, ice is less dense than water.
  - Ice floats, so it forms an insulating layer on top of lakes, rivers, etc. Therefore, aquatic life can survive in winter.
  - Water expands on freezing.
    - Frozen water in pipes may cause them to break in cold weather.



Examples of Hydrogen Bonding





Hydrogen bonds.

Hydrogen bonds can be considered unique dipole–dipole attractions. Because F, N, and O are so electronegative, a bond between hydrogen and any of these three elements is quite polar, with hydrogen at the positive end as shown in the figure. The hydrogen atom has no inner core of electrons. Thus, the positive side of the bond dipole has the concentrated charge of the partially exposed, nearly bare proton of the hydrogen nucleus. This positive charge is attracted to the negative charge of an electronegative atom in a nearby molecule. Because the electron-poor hydrogen is so small, it can approach an electronegative atom very closely and thus interact strongly with it.

Sample Exercise 11.2 (p. 444)

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)?

Practice Exercise 11.2

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)?

Comparing Intermolecular Forces

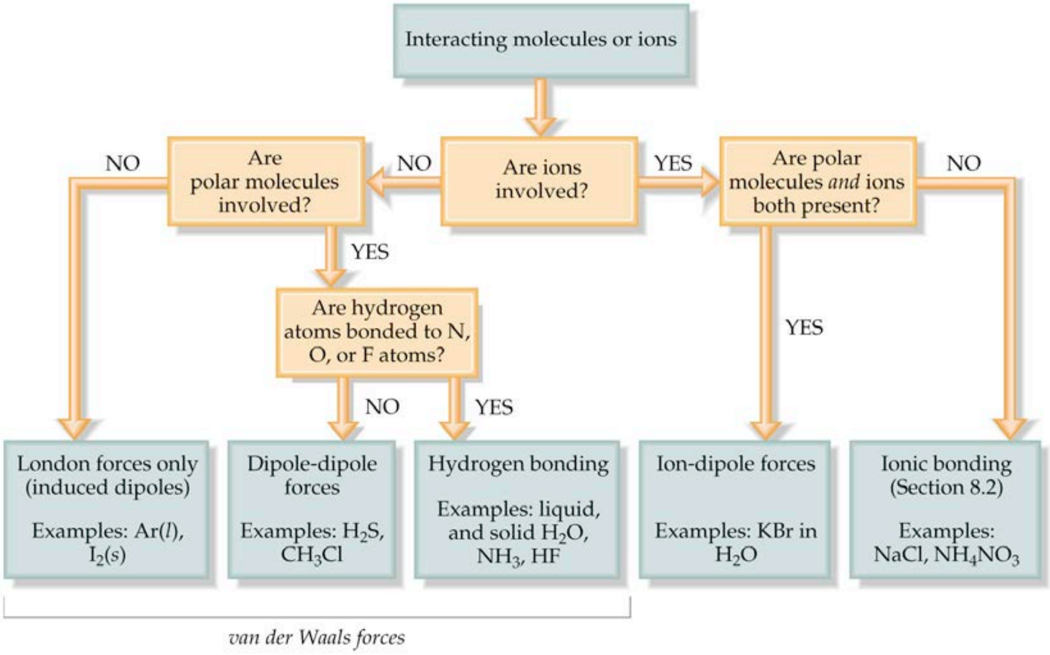
- Dispersion forces - found in all substances, strength dep. on molecular shapes and molecular weights.

- Dipole-dipole forces – only found in polar molecules - add to the effect of dispersion forces.

- H-bonding = special case of dipole-dipole interactions.
  - strongest of the intermolecular forces involving neutral species.
  - most important for H compounds of N, O and F.

- Ion-dipole interactions are stronger than H-bonds..

- Remember: ordinary ionic or covalent bonds are much stronger than these interactions!



Sample Exercise 11.3 (p. 447)

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

Practice Exercise 11.3

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, CH_3CH_2OH.

11.3 Some Properties of Liquids

Viscosity

- **Viscosity** = resistance of a liquid to flow.

- A liquid flows by sliding molecules over one another.

- Viscosity depends on:
  - IMFs: stronger IMFs → ↑ viscosity.
  - The tendency of molecules to become entangled:
    - Viscosity ↑ as molecules become entangled with one another.
  - Temperature: Viscosity usually ↓ with an ↑ in temperature.

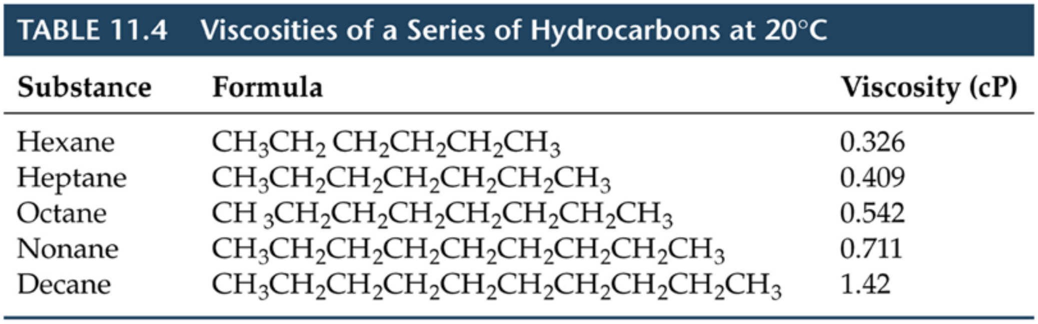


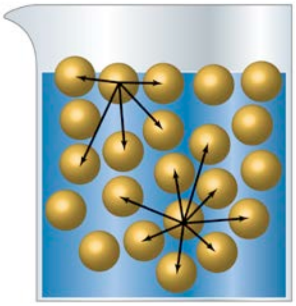
TABLE 11.4 Viscosities of a Series of Hydrocarbons at 20°C

Substance	Formula	Viscosity (cP)
Hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	0.326
Heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	0.409
Octane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	0.542
Nonane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	0.711
Decane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	1.42

Surface Tension

- Bulk molecules (those in the liquid) are equally attracted to their neighbors

- Surface molecules are only attracted inward towards the bulk molecules
  → surface molecules are packed more closely than bulk molecules
  → causes the liquid to behave as if it had a "skin"



Surface tension = amount of E required to ↑ the SA of a liquid by a unit amount

- ↑ IMFs → ↑ surface tension.
  - Water has a high surface tension (H-bonding)
  - Hg(l) has an even higher surface tension (v. strong metallic bonds between Hg atoms).

Effects of Cohesive and adhesive forces:

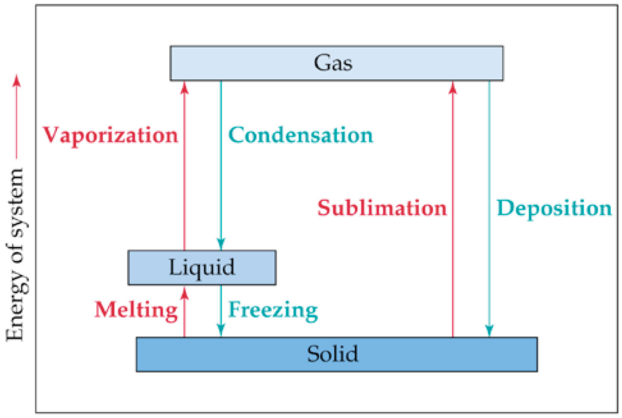
- ***Cohesive forces*** = IMFs that bind molecules **to one another**
- ***Adhesive forces*** = IMFs that bind molecules **to a surface**

- e.g. meniscus in a tube filled with liquid
  - If **adhesive forces** are > cohesive forces
    → the liquid surface is attracted to its container more than the bulk molecules
    → meniscus is U-shaped (e.g., water in glass)
  - If **cohesive forces** are > adhesive forces → meniscus curves downwards (e.g., $Hg_{(l)}$ in glass)

- **Capillary action** = the rise of liquids up very narrow tubes.
  - The liquid climbs until ***adhesive*** and ***cohesive*** forces are balanced by gravity.

11.4 Phase Changes

- **Phase changes** are changes of state.
  - *Sublimation*: solid → gas.
  - *Melting* or *fusion*: solid → liquid.
  - *Vaporization*: liquid → gas.
  - *Deposition*: gas → solid.
  - *Condensation*: gas → liquid.
  - *Freezing*: liquid → solid.



Energy Changes Accompanying Phase Changes

Melting or *fusion*: $\Delta H_{fus} > 0$ (endothermic).

- The enthalpy of fusion is known as the **heat of fusion**.

Vaporization: $\Delta H_{vap} > 0$ (endothermic).

- The enthalpy of vaporization = **heat of vaporization**.

Sublimation: $\Delta H_{sub} > 0$ (endothermic).

- The enthalpy of sublimation is called the **heat of sublimation.**

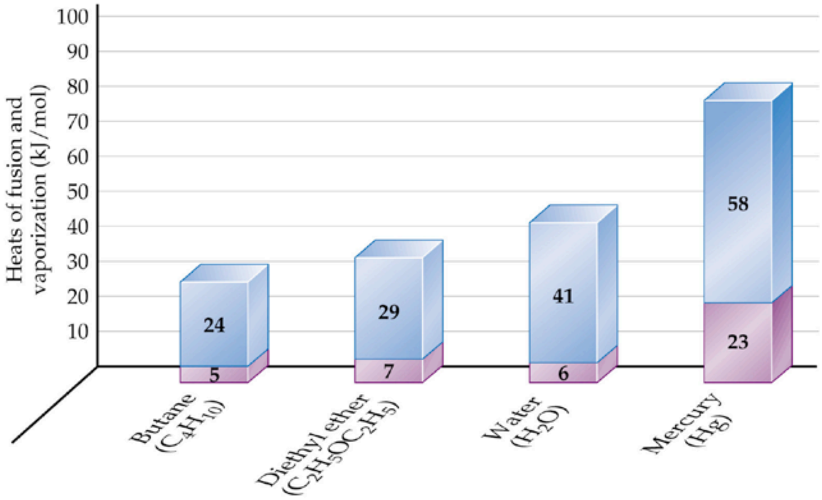
Deposition: $\Delta H_{dep} < 0$ (exothermic).

Condensation: $\Delta H_{con} < 0$ (exothermic).

Freezing: $\Delta H_{fre} < 0$ (exothermic).

Note:

- Generally $\Delta H_{fus} < \Delta H_{vap}$:
  - takes more E to completely separate molecules than to partially separate them.



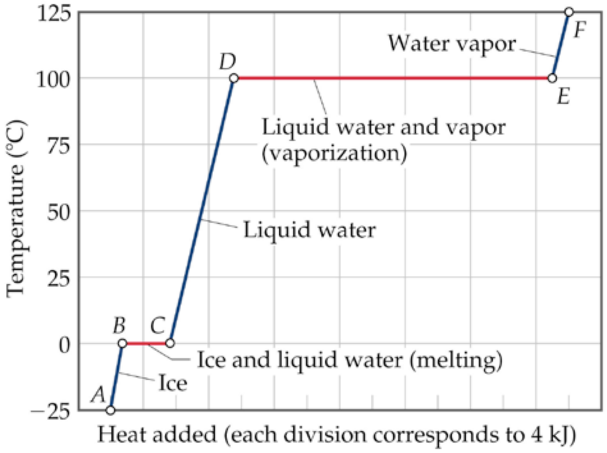
Comparing enthalpy changes for fusion and vaporization.

Heats of fusion (violet bars) and heats of vaporization (blue bars) for several substances. Notice that the heat of vaporization for a substance is always larger than its heat of fusion. The heat of sublimation is the sum of the heats of vaporization and fusion.

- All phase changes are possible under the right conditions (e.g., water sublimes when snow disappears without forming puddles).
  - The following sequence is endothermic:
    heat solid → melt → heat liquid → boil → heat gas
  - The following sequence is exothermic:
    cool gas → condense → cool liquid → freeze → cool solid

Heating Curves

- Plot of temperature change versus heat added is a *heating curve*.



Heating curve for water.

This graph indicates the changes that occur when 1.00 mol of water is heated from 25 °C to 125 °C at a constant pressure of 1 atm. Blue lines show the heating of one phase from a lower temperature to a higher one. Red lines show the conversion of one phase to another at constant temperature.

- During a phase change adding heat causes no temperature change.
  - The added energy is used to break intermolecular bonds rather than cause a temperature change.
  - These points are used to calculate ΔH_{fus} and ΔH_{vap}.

- *Supercooling*: When a liquid is cooled below its freezing point and it still remains a liquid.

Sample Exercise 11.4 (p. 451)

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, ΔH_{fus} = 6.01 kJ/mol, and ΔH_{vap} = 40.67 kJ/mol.

(56.0 kJ)

Practice Exercise 11.4

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? (Use the specific heats and enthalpies for phase changes given in Sample Exercise 11.4.)

(-60.4 kJ)

Critical Temperature and Pressure

- Gases may be liquefied by increasing the pressure at a suitable temperature.

- **Critical temperature** is the highest temperature at which a substance can exist as a liquid.

- **Critical pressure** is the pressure required for liquefaction at this critical temperature.
  - The greater the intermolecular forces, the easier it is to liquefy a substance.
    - Thus the higher the critical temperature.

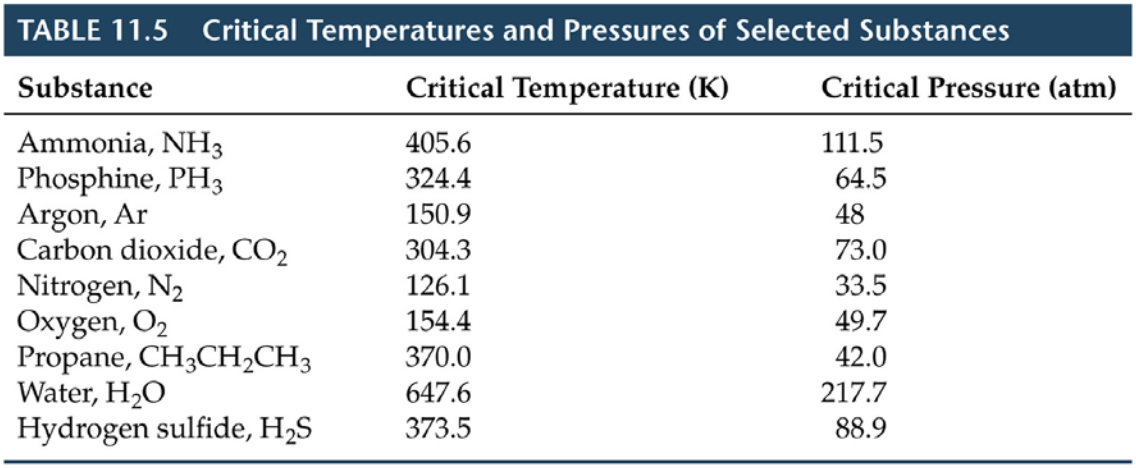
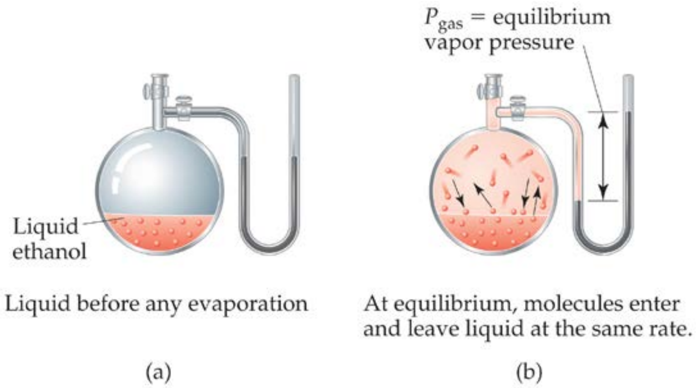


TABLE 11.5 Critical Temperatures and Pressures of Selected Substances

Substance	Critical Temperature (K)	Critical Pressure (atm)
Ammonia, NH_3	405.6	111.5
Phosphine, PH_3	324.4	64.5
Argon, Ar	150.9	48
Carbon dioxide, CO_2	304.3	73.0
Nitrogen, N_2	126.1	33.5
Oxygen, O_2	154.4	49.7
Propane, $CH_3CH_2CH_3$	370.0	42.0
Water, H_2O	647.6	217.7
Hydrogen sulfide, H_2S	373.5	88.9

11.5 Vapor Pressure

Explaining Vapor Pressure on the Molecular Level



- Some of the molecules on the surface of a liquid have enough energy to escape the attraction of the bulk liquid.
  - These molecules move into the gas phase.

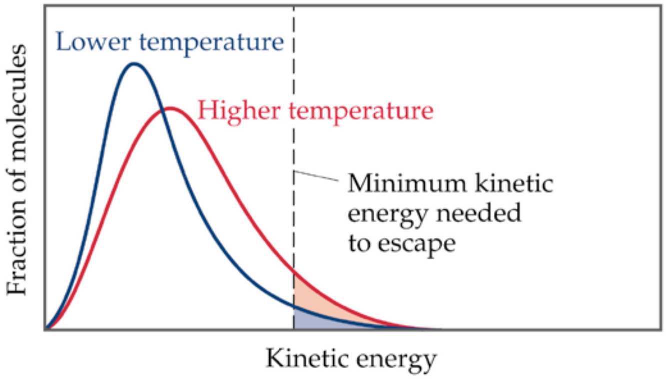
- As the number of molecules in the gas phase increases, some of the gas phase molecules strike the surface and return to the liquid.

- After some time the pressure of the gas will be constant.
  - A **dynamic equilibrium** has been established:
    - Dynamic equilibrium is a condition in which two opposing processes occur simultaneously at equal rates.
    - In this case, it is the point when as many molecules escape the surface as strike the surface.
  - **Vapor pressure** is the pressure exerted when the liquid and vapor are in dynamic equilibrium.
    - The pressure of the vapor at this point is called the equilibrium vapor pressure.

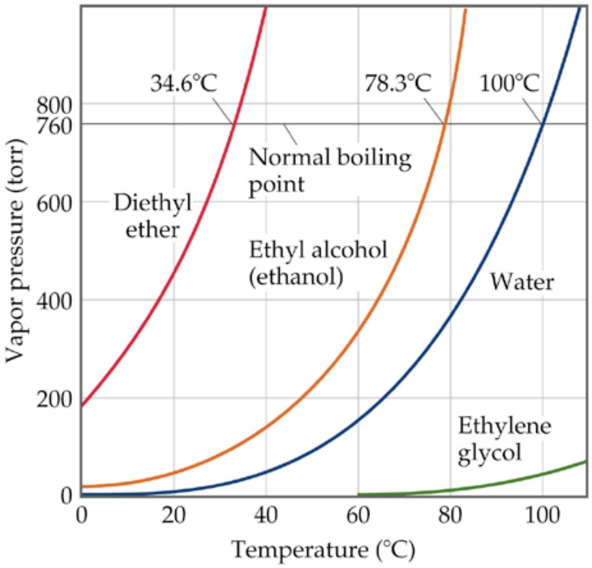
Volatility, Vapor Pressure, and Temperature

- If equilibrium is never established the vapor continues to form.
  - Eventually, the liquid evaporates to dryness.

- Liquids that evaporate easily are said to be **volatile**.
  - The higher the temperature, the higher the average kinetic energy, the faster the liquid evaporates.



Vapor Pressure and Boiling Point



- Liquids boil when the external pressure at the liquid surface equals the vapor pressure.
  - The **normal boiling point** is the boiling point at 760 mm Hg (1 atm).

- The temperature of the boiling point increases as the external pressure increases.

- Two ways to get a liquid to boil:
  - Increase temperature or decrease pressure.
    - Pressure cookers operate at high pressure.
    - At high pressure the boiling point of water is higher than at 1 atm.
    - Therefore, food is cooked at a higher temperature.

Sample Exercise 11.5 (p. 455)

Use the preceding figure to estimate the boiling point of diethyl ether under an external pressure of 0.80 atm.

Practice Exercise 11.5

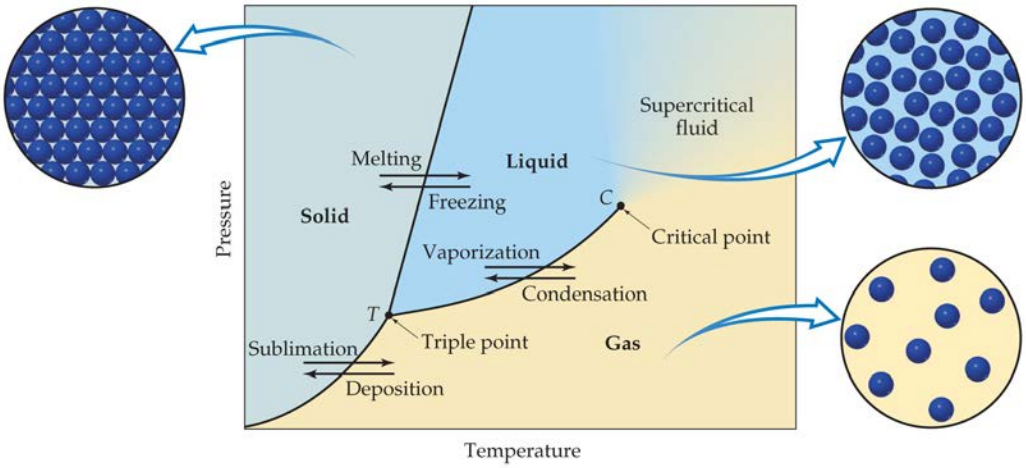
At what external pressure will ethanol have a boiling point of 60^{o}C?

11.6 Phase Diagrams

- **Phase diagram**: plot of pressure vs. temperature summarizing all equilibria between phases.

- Phase diagrams tell us which phase will exist at a given temperature and pressure.

- Features of a phase diagram include:
  - Vapor-pressure curve: generally as temperature increases, vapor pressure increases.
  - *Critical point*: critical temperature and pressure for the gas.
  - **Normal melting point**: melting point at 1 atm.
  - **Triple point**: temperature and pressure at which all three phases are in equilibrium.
  - Any temperature and pressure combination not on a curve represents a single phase.



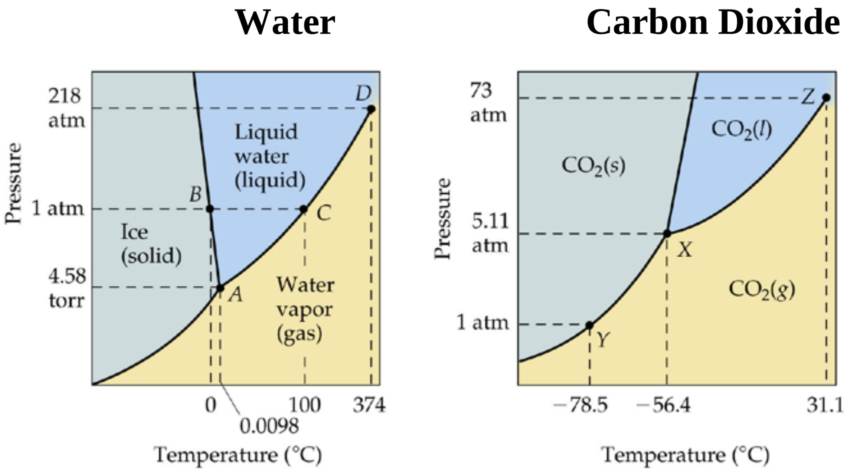
Phase diagram for a three-phase system.

In this generic diagram, the substance being investigated can exist as a solid, a liquid, or a gas, depending on pressure and temperature. Beyond the critical point (C), the distinction between liquid and gas is lost, and the substance is a supercritical fluid.

Phase Diagrams of H_2O and CO_2

- *Water*:
  - In general, an increase in pressure favors the more compact phase of the material.
    - This is usually the solid.
  - Water is one of the few substances whose solid form is less dense than the liquid form.
    - The melting point curve for water slopes to the left.
  - The triple point occurs at 0.0098 ^{o}C and 4.58 mm Hg.
  - The normal melting (freezing) point is 0^{o}C.
  - The normal boiling point is 100 ^{o}C.
  - The critical point is 374^{o}C and 218 atm.

- *Carbon Dioxide*:
  - The triple point occurs at -56.4^{o}C and 5.11 atm.
  - The normal sublimation point is -78.5^{o}C. (At 1 atm CO_2 sublimes, it does not melt.)
  - The critical point occurs at 31.1^{o}C and 73 atm.
  - Freeze drying: Frozen food is placed in a low pressure (< 4.58 torr) chamber.
    - The ice sublimes.



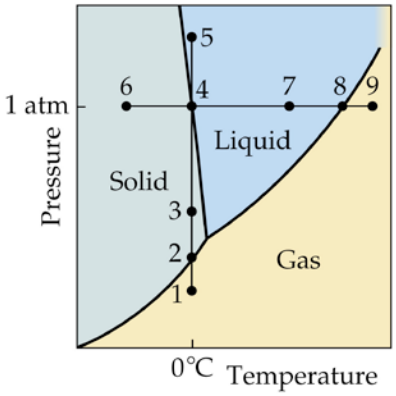
Phase diagrams of H_2O and CO_2.

The axes are not drawn to scale in either case. In (a), for water, note the triple point *T* at 0.0098 °C and 0.00603 atm, the normal melting (or freezing) point of 0 °C at 1 atm, the normal boiling point of 100 °C at 1 atm, and the critical point *C* (374.4 °C and 217.7 atm). In (b), for carbon dioxide, note the triple point *T* at –56.4 °C and 5.11 atm, the normal sublimation point of –78.5 °C at 1 atm, and the critical point *c* (31.1 °C and 73.0 atm).

Sample Exercise 11.6 (p. 458)

Referring to the figure below, describe any changes in the phases present when H_2O is

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



Practice Exercise 11.6

Using the phase diagram of CO_2, describe what happens when the following changes are made in a CO_2 sample initially at 1 atm and -60°C:

a) pressure increases at constant temperature of -60°C from 1 atm to 60 atm,

b) temperature increases from -60°C to -20°C at constant 60 atm pressure.

11.7 Structures of Solids

- **Crystalline solid:** well-ordered, definite arrangements of molecules, atoms or ions.
  - Examples: quartz, diamond, salt, sugar.
  - The intermolecular forces are similar in strength.
    - Thus they tend to melt at specific temperatures.

- **Amorphous solid**: molecules, atoms or ions do not have an orderly arrangement.
  - Examples: rubber, glass.
  - Amorphous solids have intermolecular forces that vary in strength.
    - Thus they tend to melt over a range of temperatures.

11.8 Bonding in Solids

- The physical properties of crystalline solids depend on the:
  - Attractive forces between particles and on
  - The arrangement of the particles.

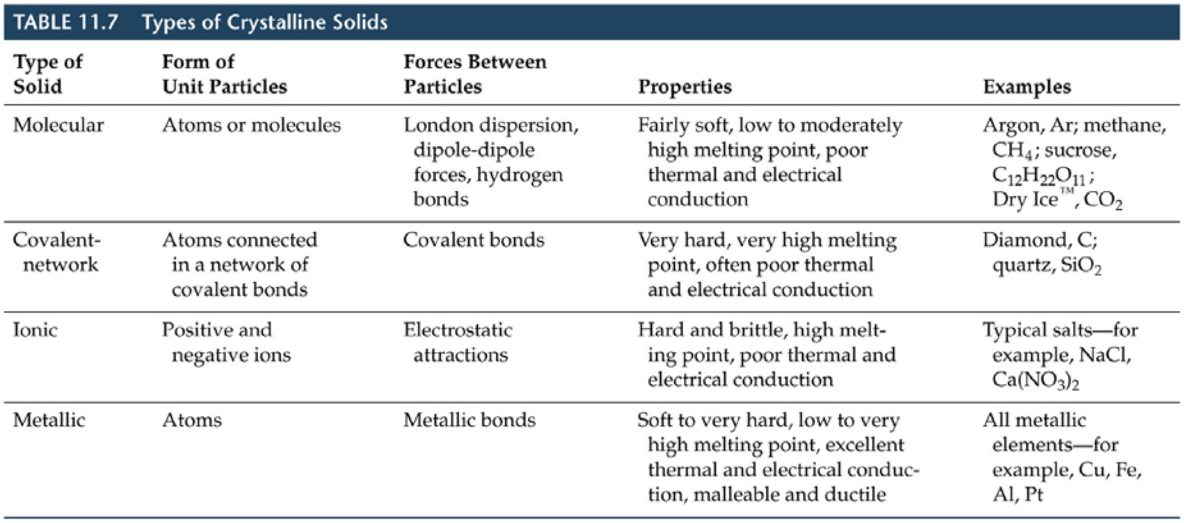


TABLE 11.7 Types of Crystalline Solids

Type of Solid	Form of Unit Particles	Forces Between Particles	Properties	Examples
Molecular	Atoms or molecules	London dispersion, 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

Molecular Solids

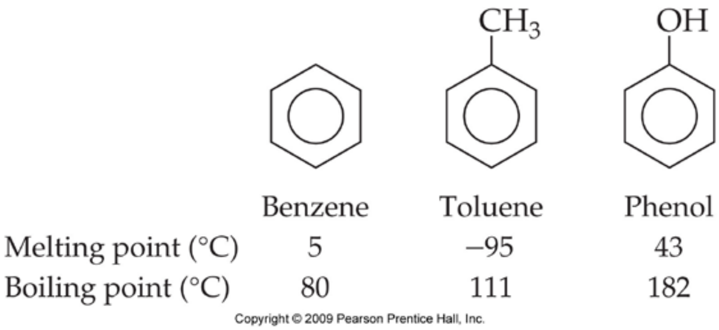
- **Molecular solids** consist of atoms or molecules held together by intermolecular forces.

- Weak intermolecular forces give rise to low melting points.
  - Intermolecular forces: dipole-dipole, London dispersion and H-bonds.
  - Molecular solids are usually soft.
  - They are often gases or liquids are room temperature.

- Efficient packing of molecules is important (since they are not regular spheres).

- Molecular solids show poor thermal and electrical conductivity.

- Examples: Ar(*s*), CH_4(*s*), CO_2(*s*), sucrose.



	Benzene	Toluene	Phenol
Melting point (°C)	5	−95	43
Boiling point (°C)	80	111	182

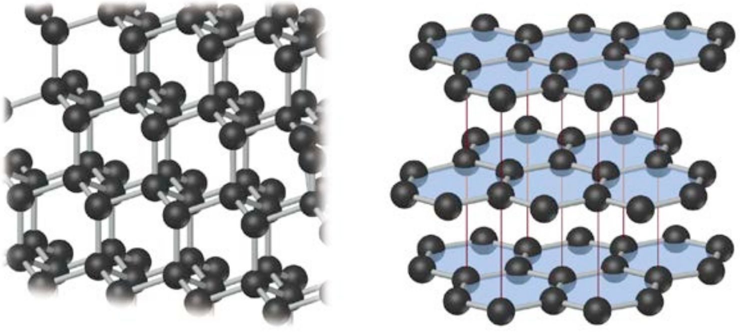
Comparative melting and boiling points for benzene, toluene, and phenol.

Covalent-Network Solids

- **Covalent-network solids** consist of atoms held together, in large networks or chains, with covalent bonds.

- They have much higher melting points and are much harder than molecular solids.
  - This is a consequence of the strong covalent bonds that connect the atoms.

- Examples: diamond, graphite, quartz (SiO_2), and silicon carbide (SiC).



(a) Diamond (b) Graphite

Ionic Solids

- **Ionic solids** consist of ions held together by ionic bonds.
  - They are hard, brittle and have high melting points.

- Ions (spherical) are held together by electrostatic forces of attraction.

- Recall:

$$E = k\frac{Q_1 Q_2}{d}$$

- The larger the charges (Q_1, Q_2) and smaller the distance (d) between ions, the stronger the ionic bond.

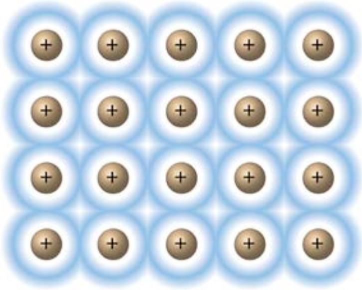
- The structure of the ionic solid depends on the charges on the ions and on the relative sizes of the atoms.

Metallic Solids

- **Metallic solids** consist entirely of metal atoms.
  - Metallic solids are soft or hard.
  - They have high melting points.
  - They show good electrical and thermal conductivity.
  - They are ductile and malleable.
    - Examples: all metallic elements (i.e., Al, Cu, Fe, Au)

- Problem that needs to be explained:
  - The bonding is too strong to be explained by London dispersion forces and there are not enough electrons for covalent bonds.

- Resolution:
  - The metal nuclei float in a sea of delocalized valence electrons.
  - Metals conduct heat and electricity because the valence electrons are delocalized and are mobile.



Sample Integrative Exercise (p. 469)

The substance CS_2 has a melting point of -110.8^{o}C and a boiling point of 46.3^{o}C. Its density at 20^{o}C is 1.26 g/cm^3. It is highly flammable.

a) What is the name of this compound?

b) List the intermolecular forces that CS_2 molecules would have with each other.

c) Predict what type of crystalline solid $CS_{2(s)}$ would form.

d) Write a balanced equation for the combustion of this compound in air. (You will have to decide on the most likely oxidation products.)

e) The critical temperature and pressure for CS_2 are 552 K and 78 atm, respectively. Compare these values with those for CO_2 and discuss the possible origins of the differences.

f) Would you expect the density of CS_2 at 40^{o}C to be greater or less than at 20^{o}C? What accounts for the difference?