

Many of the substances that we encounter are molecular. Virtually all substances that are liquids at room temperature are molecular.

Covalent bonds, which are forces *within* molecules, influence molecular shape, bond energies, and many aspects of chemical behavior.

The physical properties of molecular liquids and solids, however, are due largely to intermolecular forces, the forces that exist *between* molecules.

TABLE 11.1 Some Characteristic Properties of the States of Matter

Gas	Assumes both the volume and shape of container Is compressible Diffusion within a gas occurs rapidly Flows readily
Liquid	Assumes the shape of the portion of the container it occupies Does not expand to fill container Is virtually incompressible Diffusion within a liquid occurs slowly Flows readily
Solid	Retains its own shape and volume Is virtually incompressible Diffusion within a solid occurs extremely slowly Does not flow

The lack of strong attractive forces between molecules allows a gas to expand to fill its container.

In liquids the intermolecular attractive forces are strong enough to hold molecules close together.

In solids the intermolecular attractive forces are so strong that the molecules are locked in place.



Because the particles in a solid or liquid are fairly close together compared with those of a gas, we often refer to solids and liquids as condensed phases.

Watch movie

Many properties of liquids, including their boiling points, reflect the strengths of the intermolecular forces.

A liquid boils when bubbles of its vapor form within the liquid. The molecules of a liquid must overcome their attractive forces in order to separate and form a vapor. The stronger the attractive forces, the higher is the temperature at which the liquid boils.

Similarly, the melting points of solids increase with an increase in the strengths of the intermolecular forces.

Three types of intermolecular attractive forces are known to exist between neutral molecules: dipole-dipole, London dispersion forces, and hydrogen bonding forces.

The above forces are also called vander Waals forces after Johannes vander Waals, who developed the equation for predicting the deviation of gases from ideal behavior.

ION-DIPOLE FORCES

An ion-dipole force exists between an ion and the partial charge on the end of a polar molecule. Polar molecules are dipoles; they have a positive and a negative end.

Positive ions are attracted to the negative end of a dipole, whereas negative ions are attracted to the positive end.

Ion-dipole forces are especially important for solutions of ionic substances in polar liquids

(watch movie).

DIPOLE-DIPOLE FORCES

A dipole-dipole force exists between neutral polar molecules. Polar molecules attract each other when the positive end of one molecule is near the negative end of another.

Dipole-dipole forces are effective only when polar molecules are very close together, and are generally weaker than ion-dipole forces.

Table 11.2 Molecular Masses, Dipole Moments, and Boiling Points of Several Simple Organic Substances

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

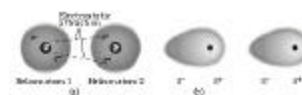
When we examine various liquids, we find that for molecules of approximately equal mass and size the strengths of intermolecular attractions increase with increasing polarity

LONDON DISPERSION FORCES

What kind of interparticle forces can exist between nonpolar atoms or molecules?

The fact that nonpolar gases can be liquefied tells us that there must be some kind of attractive interactions between the particles.

In 1930 a German-American physicist, Fritz London, recognized that the motion of electrons in an atom or molecule can create an *instantaneous* dipole moment.



In a collection of helium atoms the average distribution of the electrons about each nucleus is spherically symmetrical. The atoms are nonpolar and possess no permanent dipole moment. The instantaneous distribution of the electrons can be different from the average distribution.

Because electrons repel one another, the motions of electrons on one atom influence the motions of electrons on its neighbors. Thus, the temporary dipole on one atom can induce a similar dipole on an adjacent atom, causing the atoms to be attracted to each other.



This attractive interaction is called the London dispersion force (or merely the dispersion force)

The ease with which the charge distribution in a molecule can be distorted by an external electric field is called its polarizability. One can think of the polarizability of a molecule as a measure of the "squashiness" of its electron cloud.

TABLE 11.3 Boiling Points of the Halogens and the Noble Gases

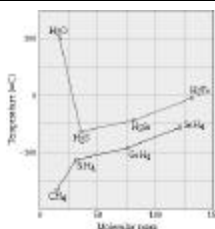
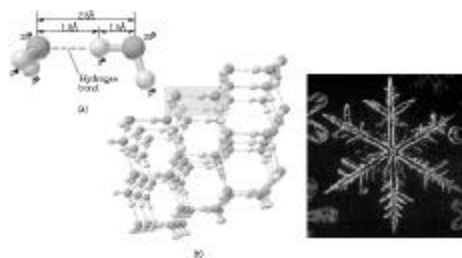
Halogen	Molecular Weight (amu)	Boiling Point (K)	Noble Gas	Molecular Weight (amu)	Boiling Point (K)
F_2	38.0	85.1	He	4.0	4.6
Cl_2	71.0	238.6	Ne	20.2	27.3
Br_2	159.8	332.0	Ar	39.9	87.5
I_2	253.8	457.6	Kr	83.8	120.9
			Xe	131.3	166.1

In general, Larger molecules tend to have greater polarizabilities because they have a greater number of electrons and their electrons are farther from the nuclei.

London dispersion forces tend to increase with increasing molecular size.

Hydrogen bonding is a special type of intermolecular attraction that exists between the hydrogen atom in a polar bond (particularly and H-F, H-O, or H-N bond) and an unshared electron pair on a nearby small electronegative ion or atom.

The energies of hydrogen bonds vary from about 4kJ/mol to 25kJ/mol or so.



In general, the boiling point increases with increasing molecular weight, owing to increased dispersion forces. The notable exception to this trend is H₂O, whose boiling point is much higher than one would expect on the basis of its molecular weight.

The compounds NH₃ and HF also have abnormally high boiling points. These compounds also have many other characteristics that distinguish them from other substances of similar molecular weight and polarity. Ex: water has a high m.p., a high specific heat, and high ΔH_{vap} . Each of these properties indicates that the intermolecular forces between H₂O molecules are strong.

Phase Changes

Each phase change is accompanied by a change in the energy of the system. Whenever a phase change involves going to a less ordered state, energy must be supplied to overcome intermolecular forces.

The melting process for a solid is also referred to as fusion. Thus, the enthalpy change associated with melting a solid is called the enthalpy of fusion, or **heat of fusion**, which is denoted ΔH_{fus} .

The heat needed for the vaporization of a liquid is called the **heat of vaporization** which is denoted ΔH_{vap} .

Critical Temperature and Pressure

For every substance, there exists a temperature above which the gas cannot be liquefied, regardless of the applied pressure. The highest temperature at which a substance can exist as a liquid is called its **critical temperature**. The **critical pressure** is the pressure required to bring about liquefaction at this critical temperature. The greater the intermolecular attractive forces, the more readily a gas is liquefied, and thus the higher is the critical temperature of the substance.

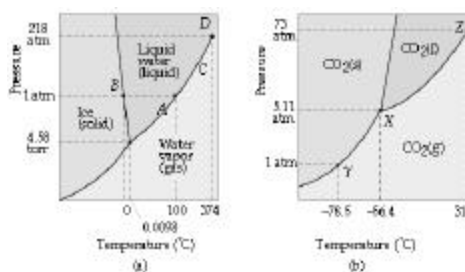
VAPOR PRESSURE

The conditions which two opposing processes are occurring simultaneously at equal rates is called a **dynamic equilibrium**. A liquid and its vapor are in equilibrium when evaporation and condensation occur at equal rates.

The pressure exerted by a vapor in equilibrium with its liquid or solid phase is called **vapor pressure**.

PHASE DIAGRAMS

The equilibrium between a liquid and its vapor is not the only dynamic equilibrium that can exist between states of matter. Under appropriate conditions of temperature and pressure a solid can be in equilibrium with its liquid state or vapor state. A **phase diagram** is a graphical way to summarize the conditions under which equilibria exist between the different states of matter. It also allows one to predict the phase of substances that is stable at any given temperature and pressure.



All three phases coexist in equilibrium at the temperature and pressure of the triple point.

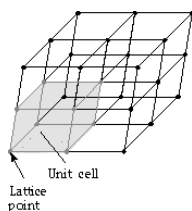
STRUCTURES OF SOLIDS

Solids can be either crystalline or amorphous. A crystalline solid is a solid whose atoms, ions, or molecules are ordered in well-defined arrangements. Solid ordered SiO_2 molecules from quartz.

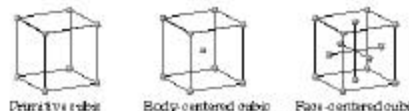
An amorphous solid is a solid whose particles have no orderly structure. Amorphous SiO_2 is glass.

We can think of a crystalline solid as being built up by stacking together identical building blocks much like a brick wall is made by stacking individual, identical bricks.

In a crystalline solid the repeating unit is known as the **unit cell**.



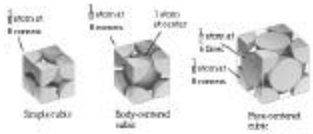
A crystalline solid can be represented by a three-dimensional array of points, each of which represents an identical environment with the crystal. Such an array of points is called a **crystal lattice**.



In a cubic lattice there are three kinds of unit cells. When lattice points are at the corners only, the unit cell is described as **primitive cubic**. When a lattice point also occurs at the center of the unit cell, the cell is known as **body-centered cubic**. A third type of cubic cell has lattice points at the center of each face, as well as at each corner, this cell is known as **face-centered cubic**.



Notice that the particles at corners, edges and faces are shared by other unit cells.

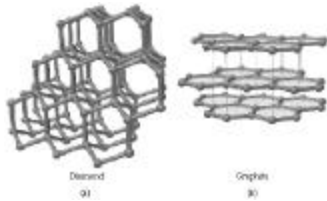


Fraction in unit cell

- Center 1
- Face 1/2
- Edge 1/4
- Corner 1/8

TABLE 11.6 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, W



Metallic solids consist entirely of metal atoms. Each sphere represents the nucleus and inner-core electrons of a metal atom. The surrounding colored "fog" represents the mobile sea of electrons that binds the atoms together.