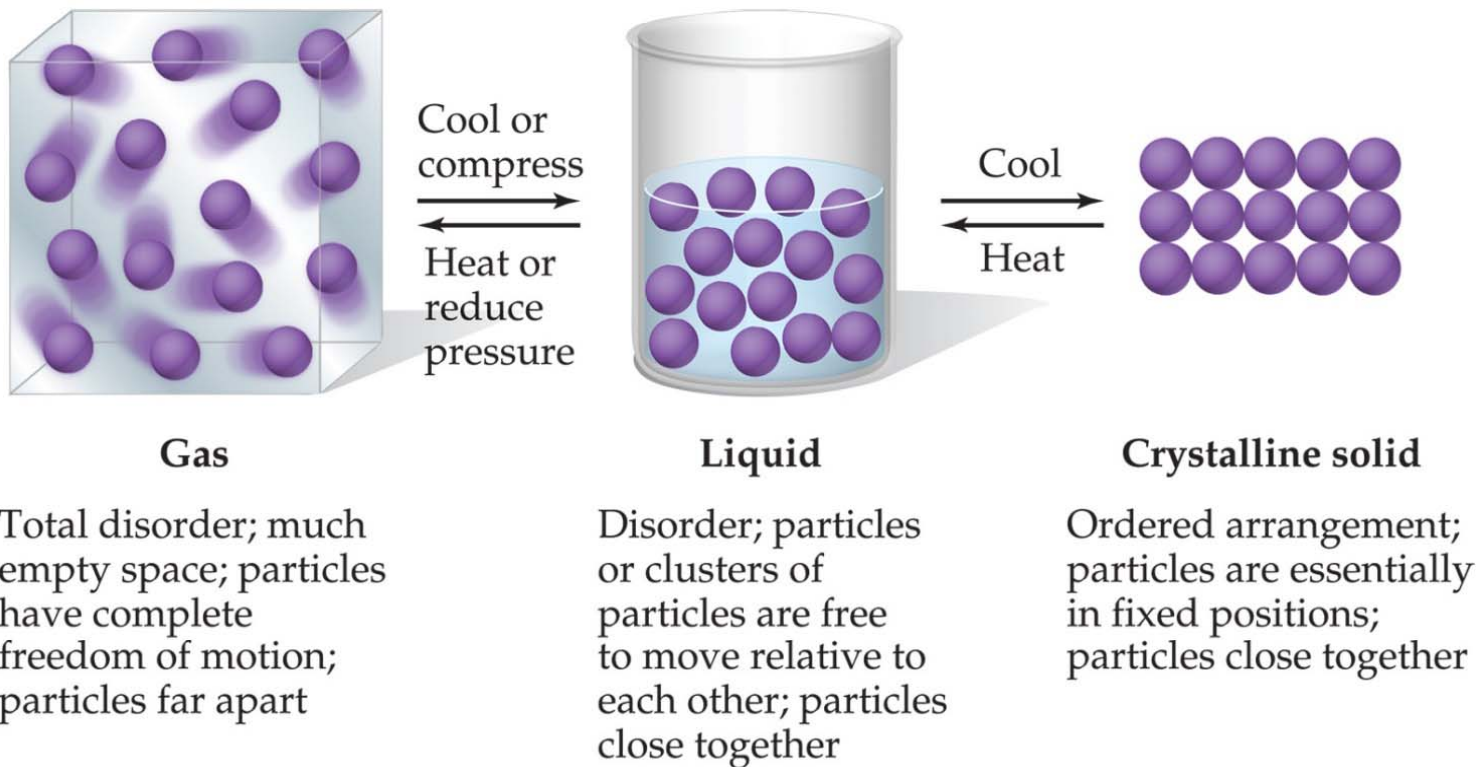# Gases, Liquids and Solids

David A. Katz

Department of Chemistry

Pima Community College
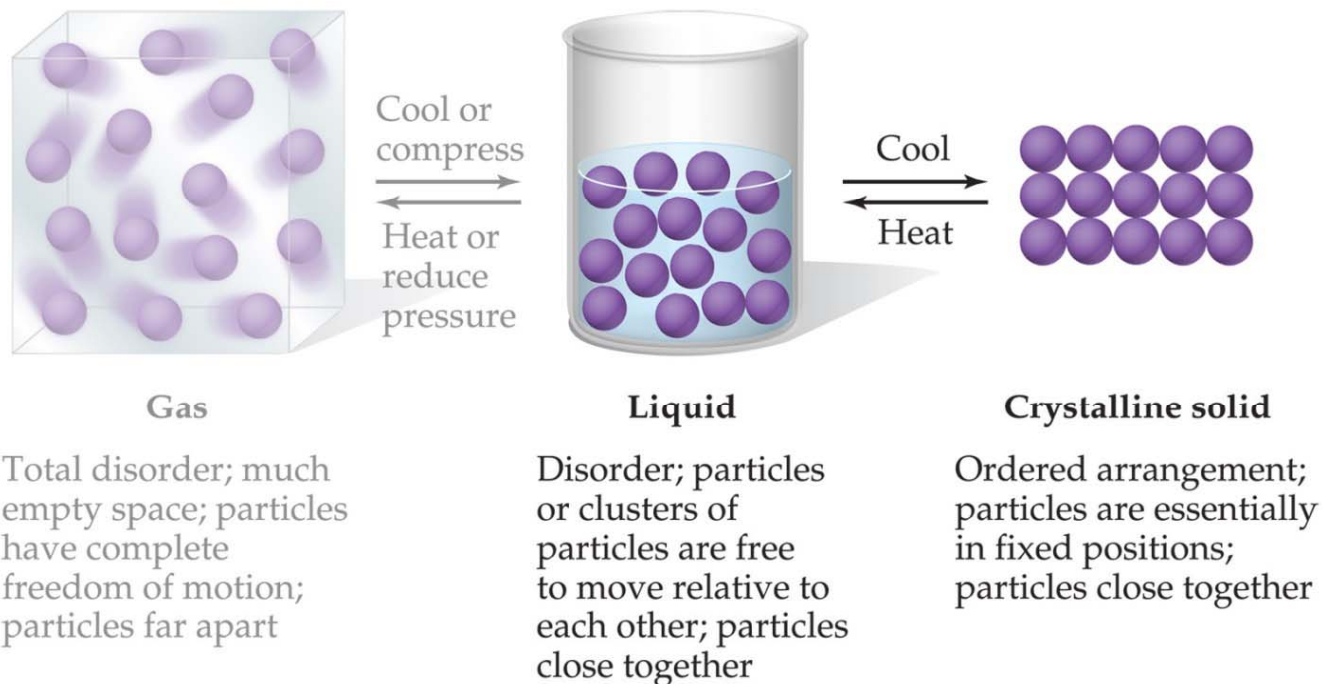
States of Matter

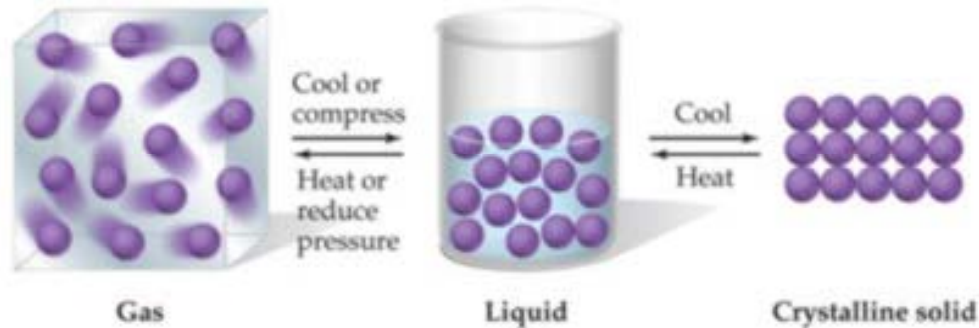**The fundamental difference between states of matter is the distance between particles.**

Gas		Liquid		Crystalline solid
	Cool or compress → ← Heat or reduce pressure		Cool → ← Heat	

Gas

Total disorder; much empty space; particles have complete freedom of motion; particles far apart

Liquid

Disorder; particles or clusters of particles are free to move relative to each other; particles close together

Crystalline solid

Ordered arrangement; particles are essentially in fixed positions; particles close together

States of Matter

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

Gas		Liquid		Crystalline solid
	Cool or compress → ← Heat or reduce pressure		Cool → ← Heat	
Total disorder; much empty space; particles have complete freedom of motion; particles far apart		Disorder; particles or clusters of particles are free to move relative to each other; particles close together		Ordered arrangement; particles are essentially in fixed positions; particles close together

The States of Matter

Gas — Cool or compress / Heat or reduce pressure — Liquid — Cool / Heat — Crystalline solid

- **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**

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

Pressure

- **Pressure is the amount of force applied to a unit of area.**

$$P = \frac{F}{A}$$

- *Atmospheric pressure is the weight of air per unit of area.*

1 m² column of air (mass = 10^4 kg)

Gravitational force

1 atm pressure at surface
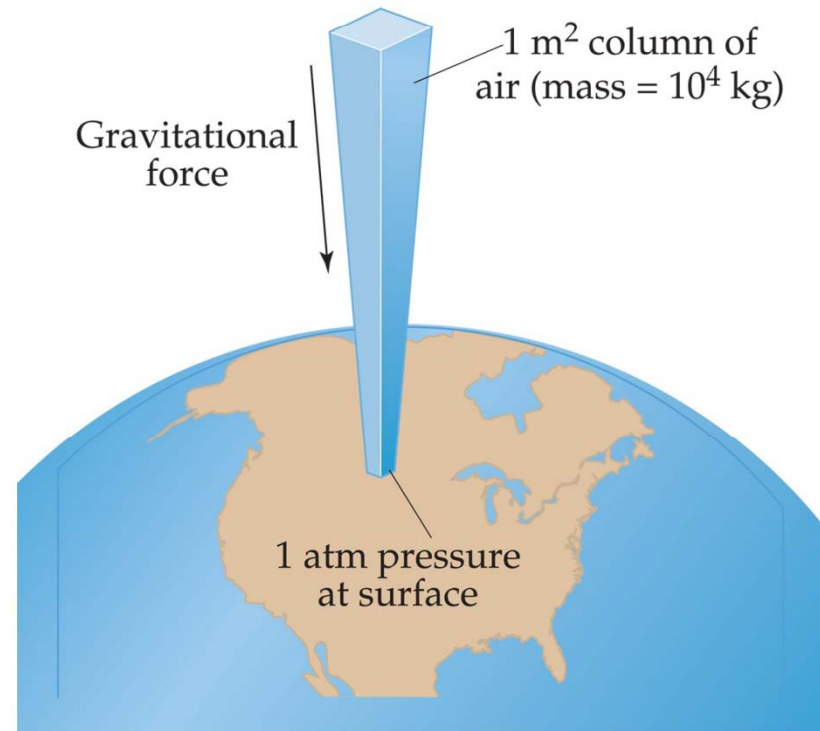
Pressure

- **most commonly measured in millimeters of mercury (mm Hg), atmospheres (atm), and torr.**

$$1\ atm = 760\ mm\ Hg$$
$$= 760\ torr$$
$$= 101{,}325\ pascals$$
$$= 28.96\ in.\ Hg$$

- **Pressure is measured using a barometer**
- **Difference in pressure is measured using a manometer**

Gas Pressure

- **In chemistry we use mm Hg or torr**

  These units based on the height of a mercury column in a barometer.

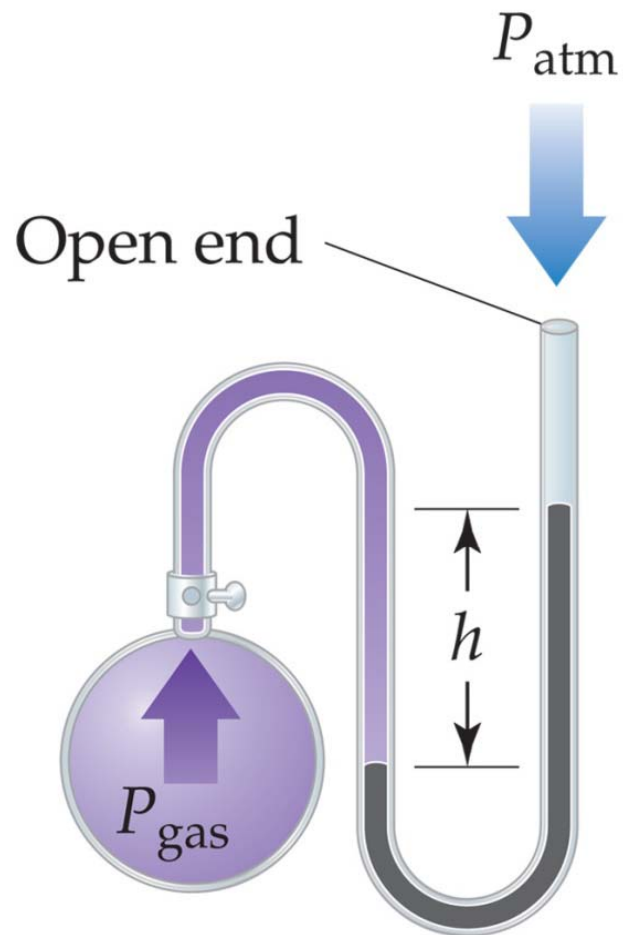 The mercury barometer was invented by Evangelista Torricelli about 1643

Vacuum

Height (mm)

Mercury surface

Atmospheric pressure
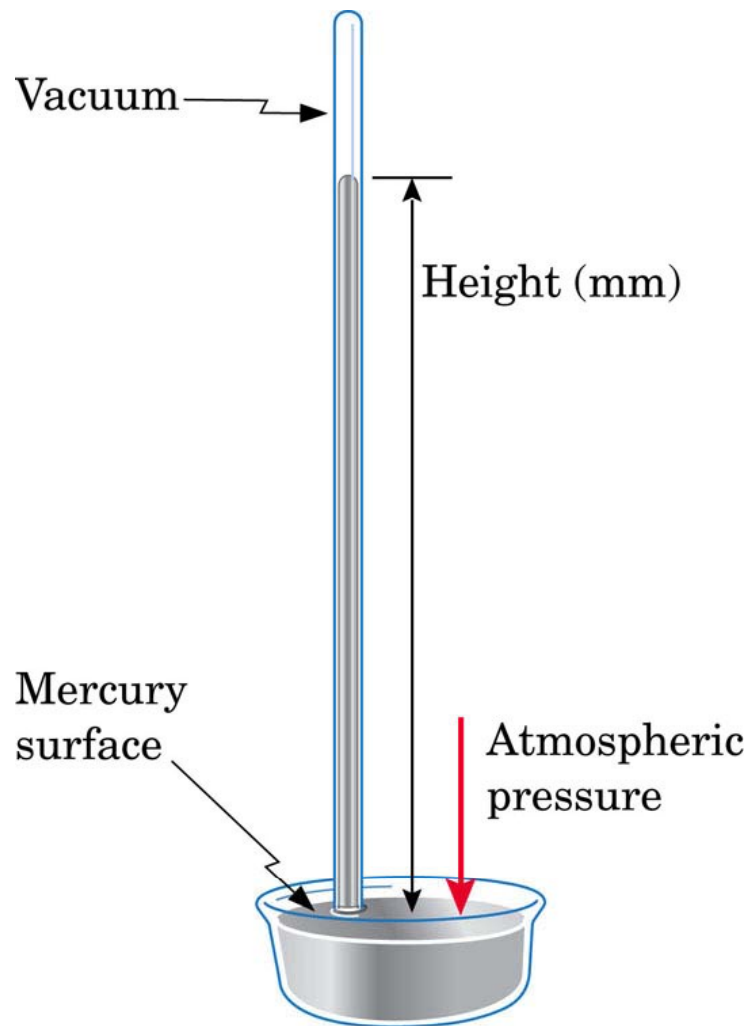
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Atmospheric pressure at sea level:

1.00 atm = 760 torr

Manometer

P_{atm}

Open end

P_{gas}

h

$$P_{gas} = P_{atm} + P_h$$

Used to measure the difference in pressure between atmospheric pressure and that of a gas in a vessel.

The pressure is the atmospheric pressure ± the difference in heights, measured in mm (h), of two connected columns of mercury.

Standard Pressure

- **Normal atmospheric pressure at sea level:**

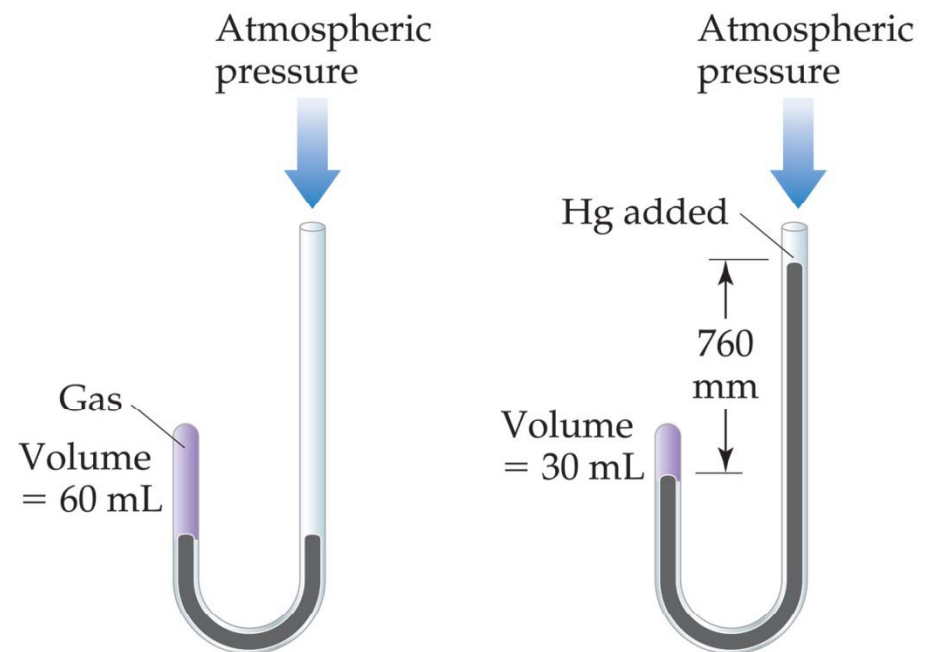   - *1.00 atm*
    - *760 torr (760 mm Hg)*
    - *101.325 kPa*

    - *Standard temperature and pressure, designated as STP, is 1.00 atm and 0°C*

Boyle's Law

Robert Boyle, 1662

The volume of a fixed quantity of gas at constant temperature is inversely proportional to the pressure.
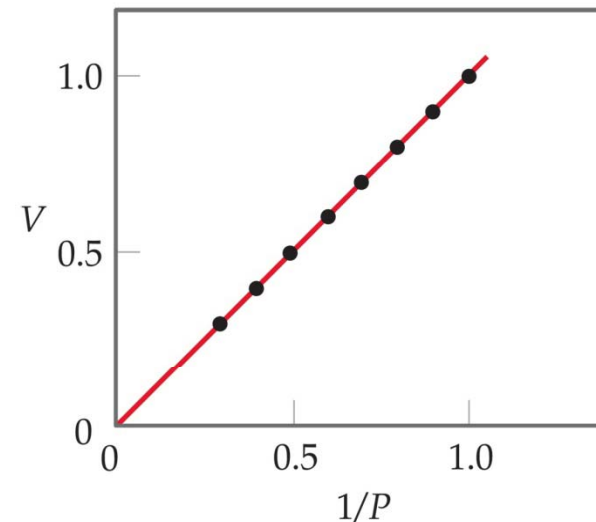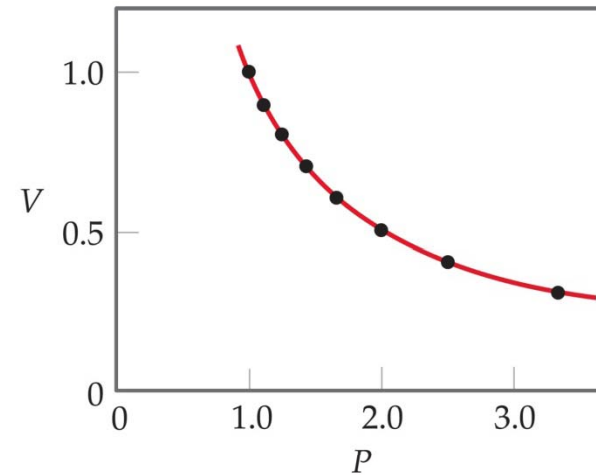
As *P* and *V* are inversely proportional

A plot of *V* versus *P* results in a curve.

Since **PV = k**

V = k (1/P)

This means a plot of V versus 1/P will be a straight line.

Boyle's Law

$$P_1V_1 = P_2V_2$$

Where:

P_1 = initial pressure

V_1 = initial volume

P_2 = final pressure

V_2 = final volume

Pressure can be in atm, torr or kPa

Volume can be in L or mL

Units must be the same on both sides of the equation

Charles' Law

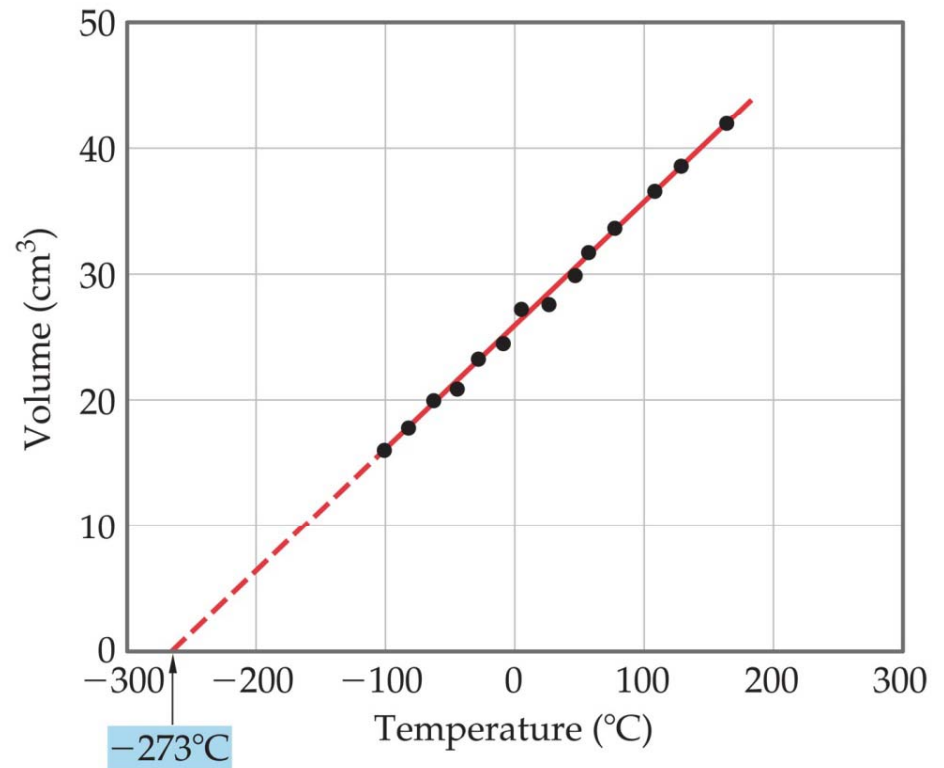**Jacques Charles, 1787**

The volume of a fixed amount of gas at constant pressure is directly proportional to its absolute temperature.

Charles' Law

$$\frac{V}{T} = k$$

A plot of V versus T will be a straight line.

Charles observed that the volume of a gas changed by 1/273rd of its volume at 0°C for each 1°C change in temperature

Charles' Law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Where:

V_1 = initial volume

T_1 = initial temperature

V_2 = final volume

T_2 = final temperature

Volume can be in L or mL

Temperature MUST be in K

Units must be the same on both sides of the equation

Gas Law

- **Gay-Lussac's Law:** for a fixed mass of gas at constant volume, the pressure is directly proportional to the temperature in kelvins (K).

$$\frac{P}{T} = a\ constant \qquad or \qquad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

- in summary:

Name	Expression	Constant
Boyle's law	$P_1 V_1 = P_2 V_2$	T
Charles's Law	$\frac{V_1}{T_1} = \frac{V_2}{T_2}$	P
Gay-Lussac's law	$\frac{P_1}{T_1} = \frac{P_2}{T_2}$	V

The Combined Gas Law

- **Boyle's, Charles', and Gay-Lussac's Laws can be combined in a single equation**

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Gas Laws

- **Problem: a gas occupies 3.00 L at 2.00 atm. Calculate its volume when the pressure is 10.15 atm at the same temperature.**

Initial: $P_1 = 2.00$ atm $V_1 = 3.00$ L

Final: $P_2 = 10.15$ atm $V_2 = ?$

- **because the temperature is constant $T_1 = T_2$**

$$V_2 = \frac{P_1 V_1 \cancel{T_2}}{\cancel{T_1} P_2} = \frac{(2.00 \, \cancel{\text{atm}})(3.00 \, \text{L})}{10.15 \, \cancel{\text{atm}}} = 0.591 \, \text{L}$$

Avogadro's Law

- **Amadeo Avogadro, 1811**
- **The volume of a gas at constant temperature and pressure is directly proportional to the number of moles of the gas.**
  - *Mathematically, this means* $V = kn$

Observation	Two volumes hydrogen	One volume oxygen	Two volumes water vapor

Equation	$2\,H_2(g)$	$+$	$O_2(g)$	$\longrightarrow$	$2\,H_2O(g)$
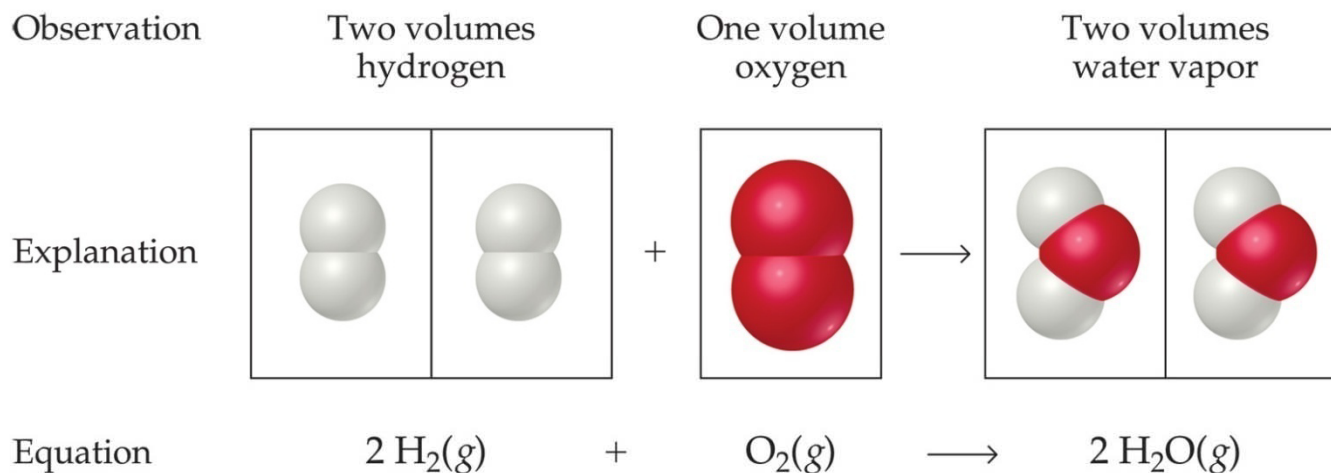
Gas Laws

- **Avogadro's law: equal volumes of gas at the same temperature and pressure contain the same numbers of molecules.**
  - **The actual temperature and pressure at which we compare two or more gases does not matter.**
  - **For convenience in making comparisons, chemists have selected one pressure as a standard pressure, and one temperature as a standard pressure.**
  - **The standard temperature and pressure (STP) selected are 0°C (273 K) and 1 atm pressure.**

Gas Laws

- All gases at STP or any other combination of pressure and temperature contain the same number of molecules in a given volume. But how many is that?
- One mole contains 6.022×10^{23} formula units; what volume of gas at STP contains this many molecules?
- This volume has been measured and found to be 22.4 L.
- Thus, one mole of any gas at STP occupies 22.4 L

Ideal Gas Law

- **Avogadro's law allows us to write a gas law that is valid not only for any P, V, and T but also for any mass of gas.**

- **Ideal gas law:**

$$PV = nRT$$

P = pressure of the gas in atmospheres (atm)

V = volume of the gas in liters (L)

n = moles of the gas (mol)

T = temperature in kelvins (K)

R = ideal gas constant (a constant for all gases)

Ideal Gas Law

- **We find the value of R by using the fact that 1.00 mol of any gas at STP occupies 22.4 L**

$$R = \frac{PV}{nT} = \frac{(1.00\ \text{atm})(22.4\ \text{L})}{(1.00\ \text{mol})(273\ \text{K})} = 0.0821\ \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$$

- **Problem: 1.00 mol of CH_4 gas occupies 20.0 L at 1.00 atm. What is the temperature of the gas in kelvins?**

- **Solution: solve the ideal gas law for T and plug in the given values:**

$$T = \frac{PV}{nR} = \frac{(1.00\ \text{atm})(20.0\ \text{L})}{(1.00\ \text{mol})(0.0821\ \text{L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})} = 244\ \text{K}$$

Gas Laws

- **Dalton's law of partial pressures:** the total pressure, P_T, of a mixture of gases is the sum of the partial pressures of each individual gas:

$$P_T = P_1 + P_2 + P_3 + \cdots$$

- **Problem:** to a tank containing N_2 at 2.0 atm and O_2 at 1.0 atm we add an unknown quantity of CO_2 until the total pressure in the tank is 4.6 atm. What is the partial pressure of CO_2?

- **Solution:**

4.6 atm	=	2.0 atm	+	1.0 atm	+	1.6 atm
Total pressure		Partial pressure of N_2		Partial pressure of O_2		Partial pressure of CO_2

Kinetic Molecular Theory

- **Assumptions of the kinetic molecular theory:**

  1. **Gases consist of particles constantly moving through space in random directions and with various speeds.**

  2. **Gas particles have no volume (compared with the volume of the gas).**

  3. **Gas particles have no attraction between them.**

  4. **The average kinetic energy (KE) of gas particles is proportional to the temperature in kelvins.**

Kinetic Molecular Theory

- **Assumptions of the kinetic molecular theory (continued):**

    5. Molecular collisions are elastic; when molecules collide, they may exchange KE but the total KE remains constant.

    6. Molecules collide with the walls of their container; these collisions constitute the pressure of the gas.

Kinetic Molecular Theory

- **Ideal gas:**
  - **Behave according to the six assumptions of the Kinetic Molecular Theory**

- **Real gases**
  - **their atoms or molecules do occupy some volume.**
  - **there are forces of attraction between their atoms or molecules.**

- **In reality, no gases are ideal**
  - **at pressures above 1 to 2 atm and temperatures well above their boiling points, most real gases behave in much the same way as predicted by the KMT.**
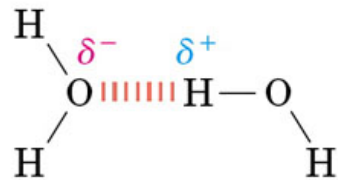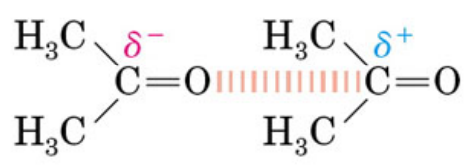
Intermolecular Forces

- **The strength of attractive forces between molecules determines whether any sample of matter is a gas, liquid, or solid.**
  - **At or near STP, the forces of attraction between molecules of most gases are so small that they can be ignored.**
  - **When T decreases or P increases or both, the forces of attraction become important to the point that they cause condensation (gases to liquids) and ultimately solidification (liquids to solids).**

Intermolecular Forces

In order to understand the properties of liquids and solids, we must look at the nature of the intermolecular forces of attraction.

Table 6.2 Forces of Attraction Between Molecules and Ions

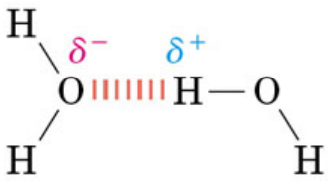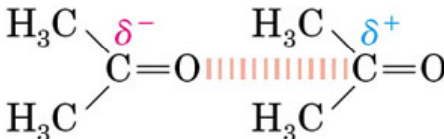| Attractive Force	Example	Typical Energy (kcal/mol)
Ionic bonds	Na^+ ⫴⫴⫴ Cl^-, Mg^{2+} ⫴⫴⫴ O^{2-}	170–970
Single, double, and triple covalent bonds	$C—C$ $C=C$ $C\equiv C$ $O—H$	80–95 175 230 90–120
Hydrogen bonding	H δ^- δ^+ O ⫴⫴⫴ $H—O$ H H	2–10
Dipole-dipole interaction	H_3C δ^- H_3C δ^+ $C=O$ ⫴⫴⫴ $C=O$ H_3C H_3C	1–6
London dispersion forces	Ne ⫴⫴⫴ Ne	0.01–2.0

For purposes of comparison, the strengths of single, double, and triple covalent bonds are also given.

Intermolecular Forces

Ionic Bonds: Electrostatic attraction between positive and negative ions

**Covalent Bonds:** Sharing electrons between atoms

Table 6.2   Forces of Attraction Between Molecules and Ions

Attractive Force	Example	Typical Energy (kcal/mol)
Ionic bonds	Na^+ ||||||| Cl^-, Mg^{2+} ||||||| O^{2-}	170–970
Single, double, and triple covalent bonds	$C-C$	80–95
	$C=C$	175
	$C\equiv C$	230
	$O-H$	90–120
Hydrogen bonding	H $O^{\delta-}$ |||||| $H^{\delta+}-O$ H $\qquad$ H	2–10
Dipole-dipole interaction	H_3C $C^{\delta-}=O$ ||||||||||| $C^{\delta+}=O$ H_3C $\qquad$ H_3C	1–6
London dispersion forces	Ne ||||||| Ne	0.01–2.0

For purposes of comparison, the strengths of single, double, and triple covalent bonds are also given.

London Dispersion Forces

- **London dispersion forces are the attraction between temporary induced dipoles.**

δ^- δ^+ δ^- δ^+

(a) (b)
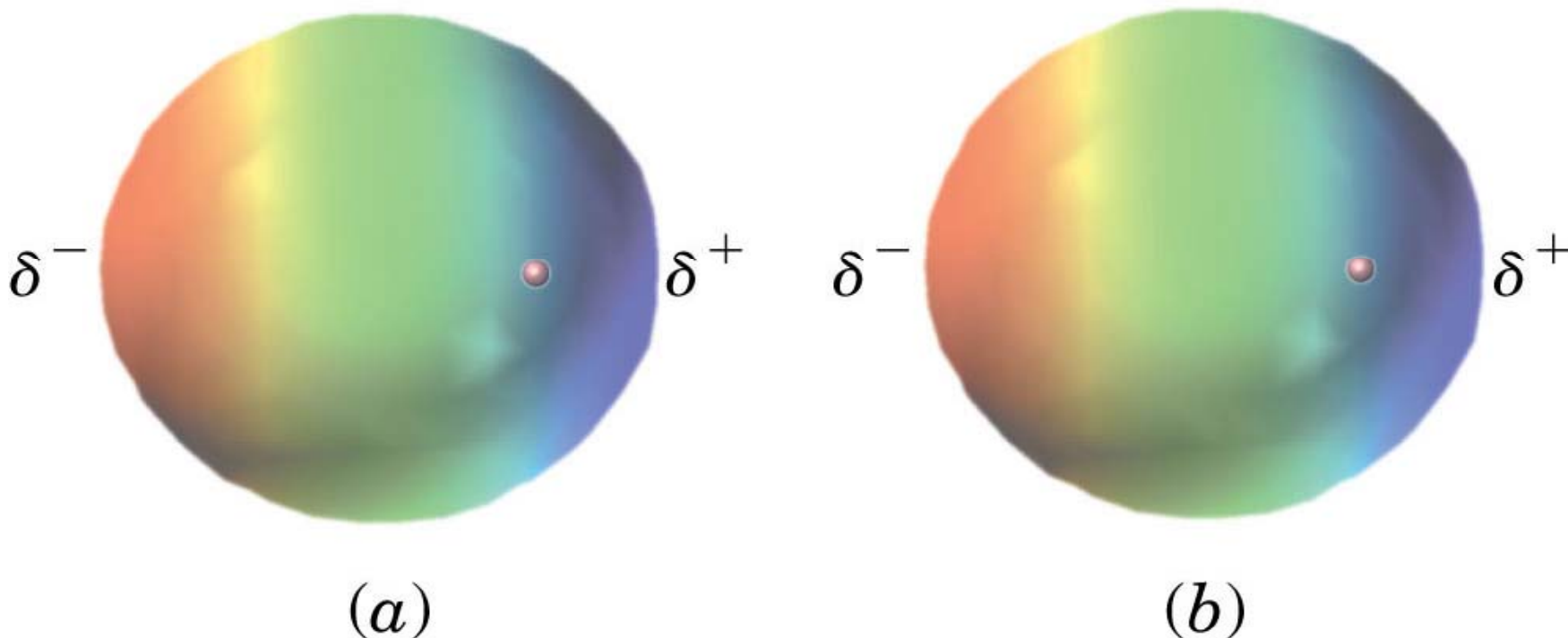
London Dispersion Forces

- London dispersion forces exist between all atoms and molecules.

- They are the only forces of attraction between atoms and nonpolar molecules.

- They range in strength from 0.01 to 2 kcal/mol depending on mass, size, and shape of the interacting molecules.

- In general, their strength increases as the mass and number of electrons in a molecule increases.

- Even though these forces are very weak, they contribute significantly to the attractive forces between large molecules because they act over large surface areas.

Dipole-Dipole Interactions

- **Dipole-dipole interactions; the electrostatic attraction between positive and negative dipoles.**
  - **consider butane and acetone, compounds of similar molecular weight**

$$CH_3\,CH_2\,CH_2\,CH_3 \qquad\qquad \overset{\delta-}{\underset{\delta+}{\underset{|}{CH_3 - \overset{O}{\overset{||}{C}} - CH_3}}}$$
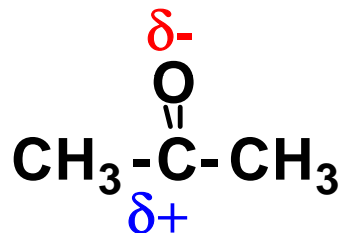
Butane
**(bp 0.5°C)**

Acetone
(bp 58°C)

- **Butane is a nonpolar molecule; the only interactions between butane molecules are London forces.**

- **Acetone is a polar molecule; its molecules are held together in the liquid state by dipole-dipole interactions.**
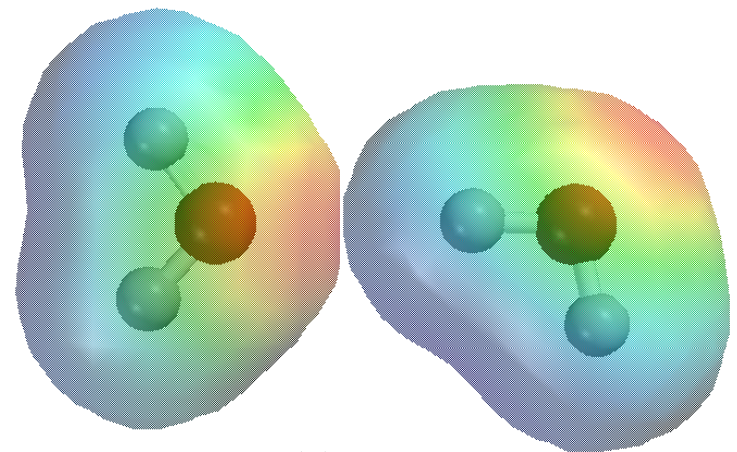
Hydrogen Bonds

- **Hydrogen bond: a special case of dipole-dipole interactions**
  - Occurs when the molecule contains a hydrogen bonded to an atom of high electronegativity, most commonly O, N, or F
  - Bond is between the hydrogen and the partial negative charge on a nearby O or N.
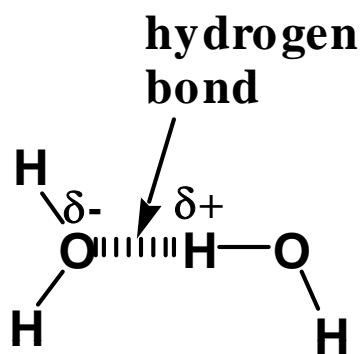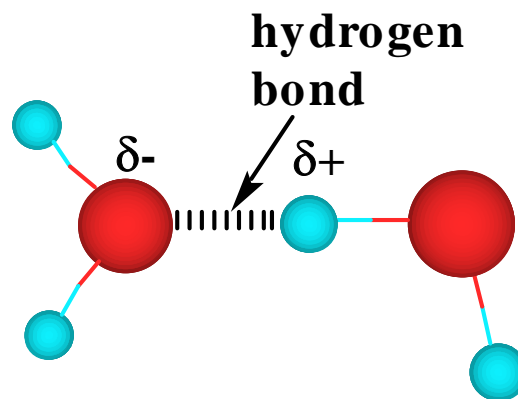
(a)   (b)   (c)

Hydrogen Bonds

- **The strength of hydrogen bonds ranges from 2 to 10 kcal/mol.**
- **In liquid water bond strength is approximately 5.0 kcal/mol**
- **By comparison, the strength of an O-H covalent bond in a water molecule is 119 kcal/mol.**
- **Hydrogen bonding in liquid water has an important effect on the physical properties of water.**
  - **The relatively high boiling point of water is due to hydrogen bonding between water molecules; extra energy is required to separate a water molecule from its neighbors.**
  - **The high surface tension of water**
  - **The effectiveness of water as a solvent**

Liquids

- As pressure increases in a real gas, its molecules come closer and closer with the result that attractions between molecules become important.
- When distances decrease so that almost all molecules touch or almost touch, a gas condenses to a liquid.
- In liquids, there is very little space between molecules; consequently, liquids are difficult to compress.
- The density of liquids is much greater than that of gases because the same mass occupies a much smaller volume in the liquid state.
- The position of molecules in a liquid is random and there is irregular space between them into which other molecules can slide; this causes liquids to be fluid.

Surface Tension

- **Surface tension:** the layer on the surface of a liquid produced by uneven intermolecular attractions at its surface:
  - Molecules in the interior of a liquid have equal intermolecular forces in all directions.
  - Molecules at the liquid-gas interface experience a greater attraction toward the interior of the liquid than toward the gas phase above it.
  - Therefore, there is preferential pull of molecules on the surface toward the interior of the liquid.
  - This preferential pull crowds the molecules on the surface, and creates a thin elastic skin-like layer.
  - Surface tension is directly related to strength of the intermolecular attraction between molecules.

Surface Tension

Typical molecule in liquid

Surface molecule

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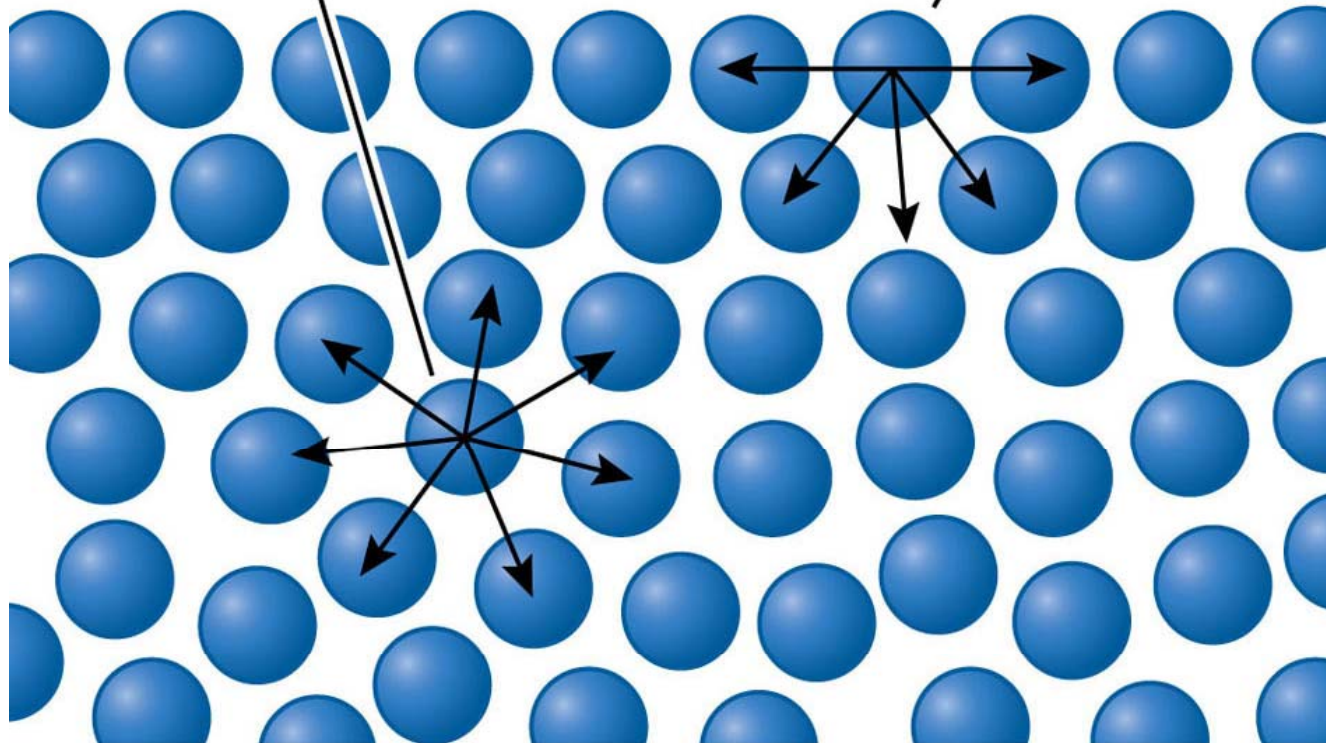
Evaporation/Condensation

- **An important property of liquids is that they evaporate:**
  - **In a liquid there is a distribution of kinetic energies (KE) among its molecules.**
  - **Some have high KE and move rapidly; others have low KE and move more slowly.**
  - **If a molecule at the surface is moving slowly (has a low KE), it cannot escape from the liquid because of the attractions of neighboring molecules.**
  - **If, however, it is moving more rapidly (has a higher KE) and moving upward, it can escape the liquid and enter the gaseous space above it.**

Evaporation/Condensation

- If the container is open, this process continues until all molecules escape.
- If the container is closed, molecules remain in the air space above the liquid.
- At equilibrium, molecules continue to escape from the liquid while an equal number are recaptured by it.
- The partial pressure of the vapor in equilibrium with the liquid is called the vapor pressure of the liquid.
- Vapor pressure is a function of temperature.
- Vapor pressure increases with temperature until it equals the atmospheric pressure.
- Boiling point: the temperature at which the vapor pressure of a liquid equals the atmospheric pressure.

Evaporation/Condensation

- **Normal boiling point:** the temperature at which the vapor pressure of a liquid equals the atmospheric pressure.


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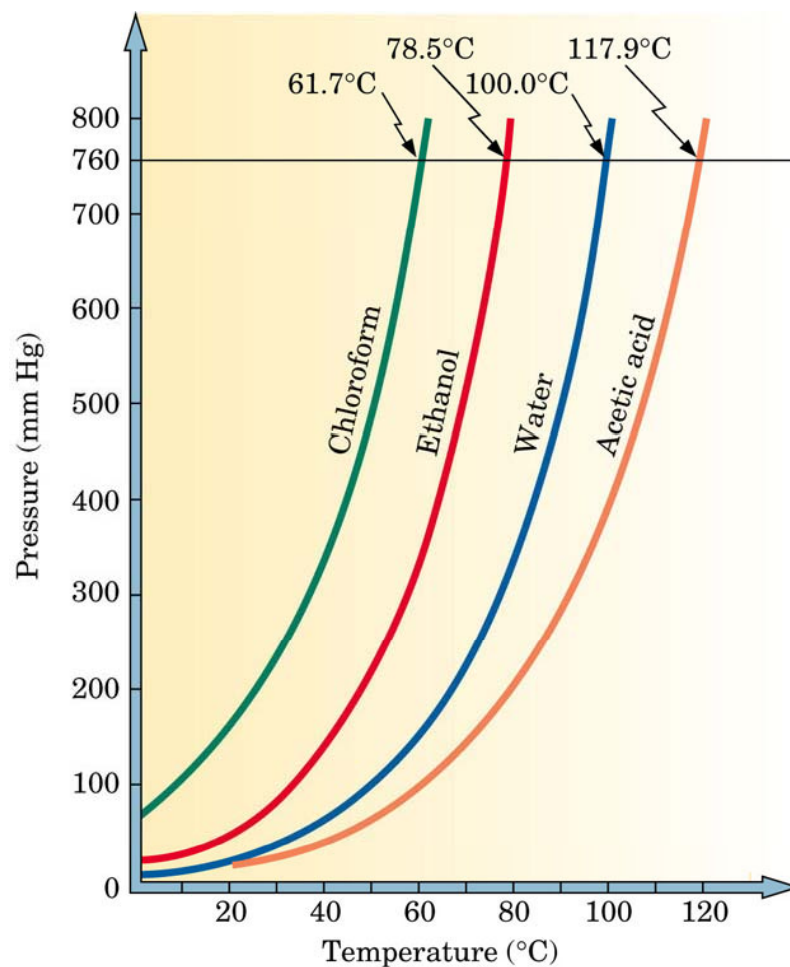
Boiling Point

Name	Molecular Formula	Molecular Weight (amu)	Boiling Point (°C)
Chloroform	$CHCl_3$	120	62
Hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	86	69
Ethanol	CH_3CH_2OH	46	78
Water	H_2O	18	100
Acetic acid	CH_3COOH	60	118

- Boiling points of covalent compounds depend primarily on two factors: (1) the nature and strength of intermolecular forces and (2) molecular size and shape.
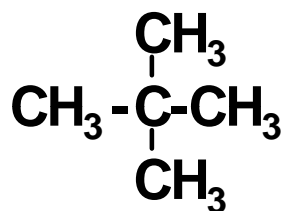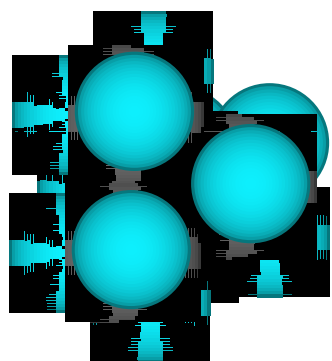
Boiling Points

- **Intermolecular forces**
  - **Consider CH_4 (MW 16, bp -164°C) and H_2O (MW 18, bp 100°C). The difference in boiling points between them is due to the greater strength of hydrogen bonding in water compared with the much weaker London dispersion forces in methane.**
  - **Consider methane, CH_4 (MW 16, bp -164°C), and hexane C_6H_{14} (MW 86, bp 69°C). Because of its larger surface area, London dispersion forces are stronger between hexane molecules than between methane molecules.**
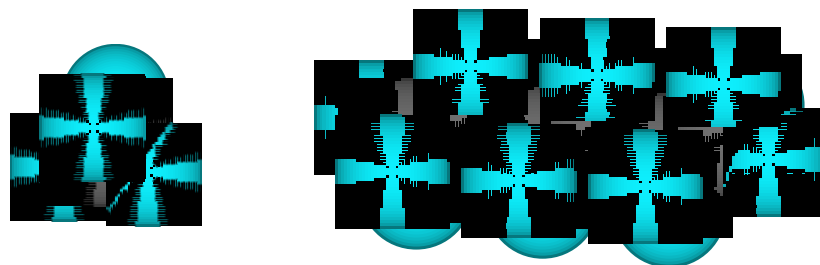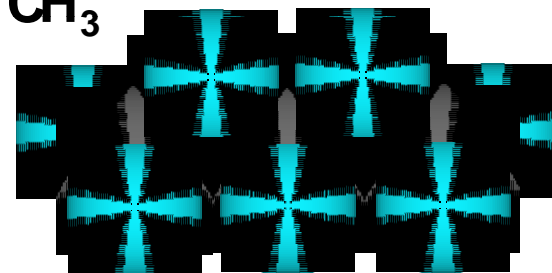
Boiling Points

- **Molecular shape**
  - **when molecules are similar in every way except shape, the strength of London forces determines boiling point**

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

2,2-Dimethylpropane
(bp 9.5°C)

$$CH_3\,CH_2\,CH_2\,CH_2\,CH_3$$

Pentane
(bp 36.2°C)

  - **Both are C_5H_{12} and have the same molecular weight.**
  - **2,2-dimethylpropane is roughly spherical while pentane is a linear molecule.**
  - **Pentane has the higher boiling point because it has the larger surface area and stronger London dispersion forces between its molecules.**

Solids

- **When liquids are cooled, their molecules come so close together and attractive forces between them become so strong that random motion stops and a solid is formed.**

- **Crystallization (solidification): formation of a solid from a liquid.**
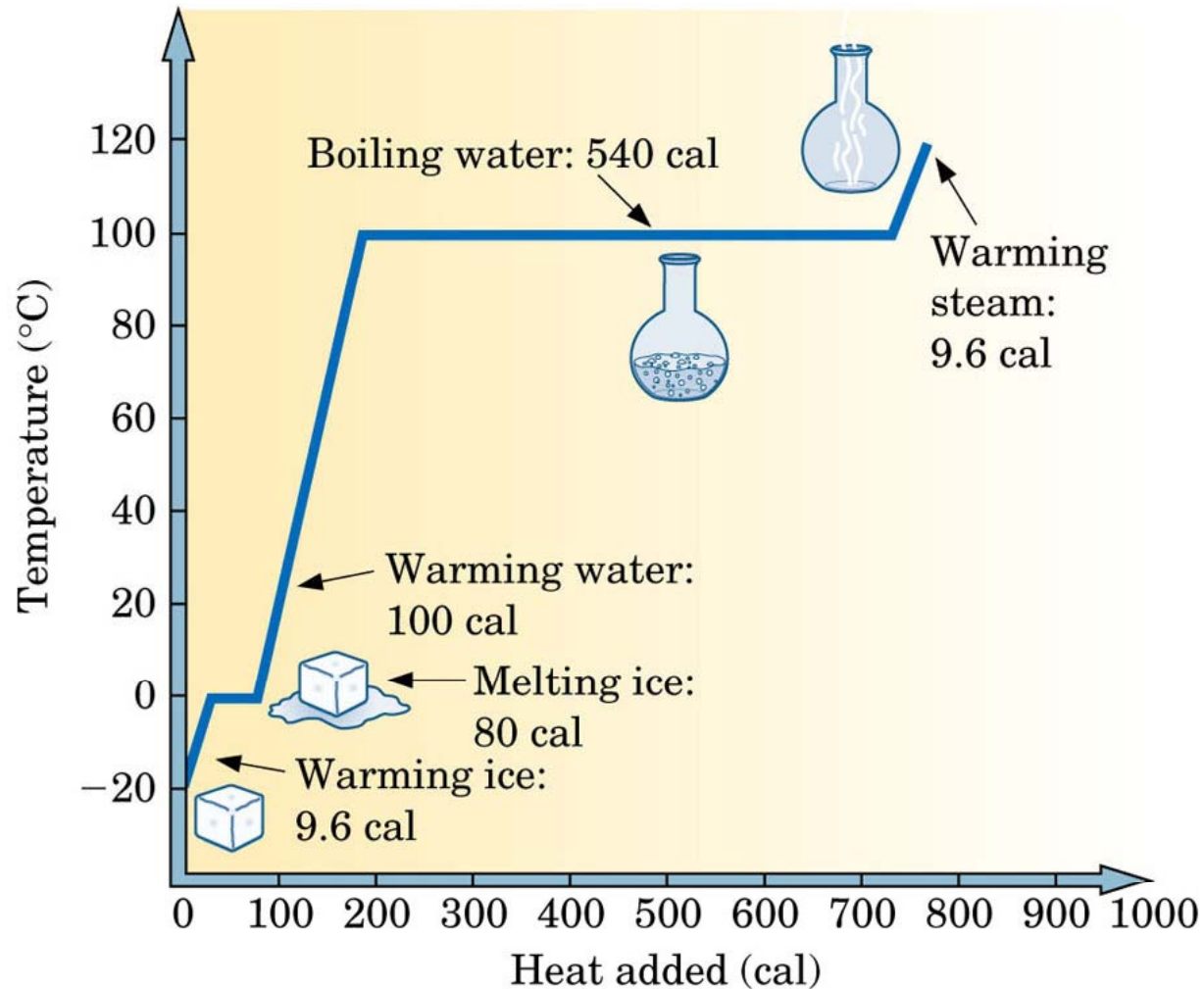
Types of Solids

Type	Made up of	Characteristics	Examples
Ionic	Ions in a crystal lattice	High melting points	NaCl, K_2SO_4
Molecular	Molecules in a crystal lattice	Low melting points	Ice, aspirin
Polymeric	Giant molecules; can be crystalline, semicrystalline, or amorphous	Low melting points or cannot be melted; soft or hard	Rubber, plastics, proteins
Network	A very large number of atoms connected by covalent bonds	Very hard; very high melting or cannot be melted	Diamond, quartz
Amorphous	Randomly arranged atoms or molecules	Mostly soft, can be made to flow, but no melting point	Soot, tar, glass

Phase Changes

- **Phase:** any part of a system that looks uniform throughout.
  - examples: solid water (ice), liquid water, and gaseous water (steam)
- **Phase change:** a change from one physical state (gas, liquid, or solid) to another.

Phase Changes

- **Figure 6.17 The heating curve of ice**

Boiling water: 540 cal

Warming steam: 9.6 cal

Warming water: 100 cal

Melting ice: 80 cal

Warming ice: 9.6 cal

Phase Changes

- **Calculation of energy required to heat 1.0 gram of solid water from -20°C to 120°C**

Physical change	Energy (cal/g)	Basis for Calculation of Energy Required*
warm ice from -20°C to 0°C	9.6	SH of ice = 0.48 cal/g•°C
melt ice; temp = 0°C	80	Heat of fusion of ice = 80 cal/g
warm water from 0°C to 100°C	100	SH of liquid water = 1.0 cal/g•°C
boil water; temp = 100°C	540	Heat of vaporization = 540 cal/g
warm steam from 100°C to 120°C	9.6	SH of steam = 0.48 cal/g•°C

*SH = specific heat

Phase Changes

- **All phase changes for any substance can be shown on a phase diagram**

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