Chemistry 120 Fall 2016

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Office Hours: M,W,F 9:30-11:30 am T,R 8:00-10:00 am or by appointment;

Test Dates:

September 23, **2016 (Test 1): Chapter 1,2 &3**
October 13, **2016 (Test 2): Chapter 4 & 5**
October 31, **2016 (Test 3): Chapter 6, 7 & 8**
November 15, **2016 (Test 4): Chapter 9, 10 & 11**
November 17, **2016 (Make-up test) comprehensive: Chapters 1-11**

Chapter 7. Gases, Liquids, and Solids

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7-2 Kinetic Molecular Theory and Physical States

7-3 Gas Law Variables

Pressure Readings and Significant Figures

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Chapter 7. Gases, Liquids, and Solids

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- Rate of Evaporation and Temperature

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- Conditions That Affect Boiling Point

7-13 Intermolecular Forces in Liquids

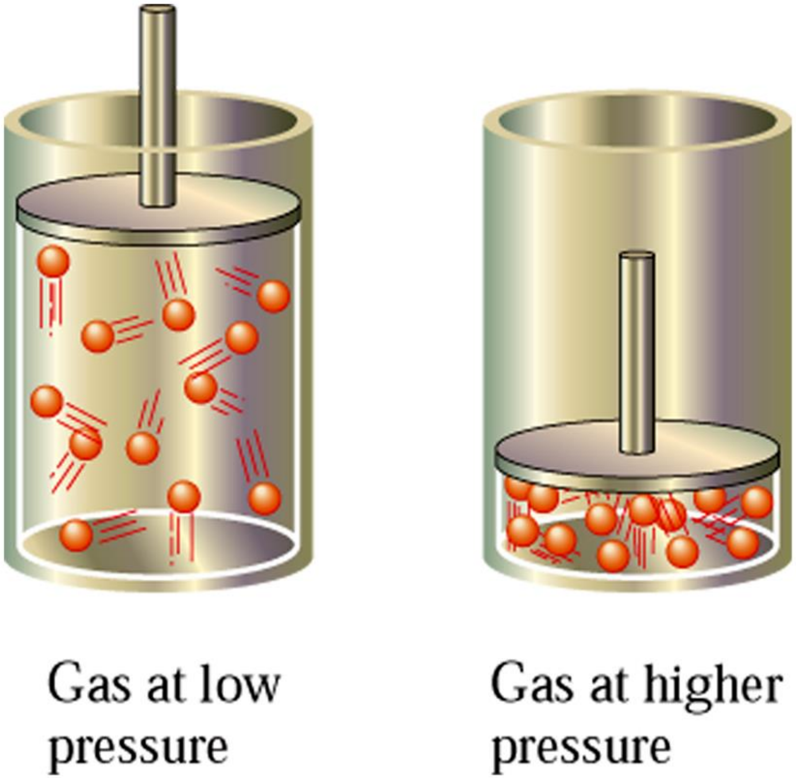
- Dipole–Dipole Interactions
- Hydrogen Bonds
- London Forces

Chapter 7

Gases, liquids, and solids

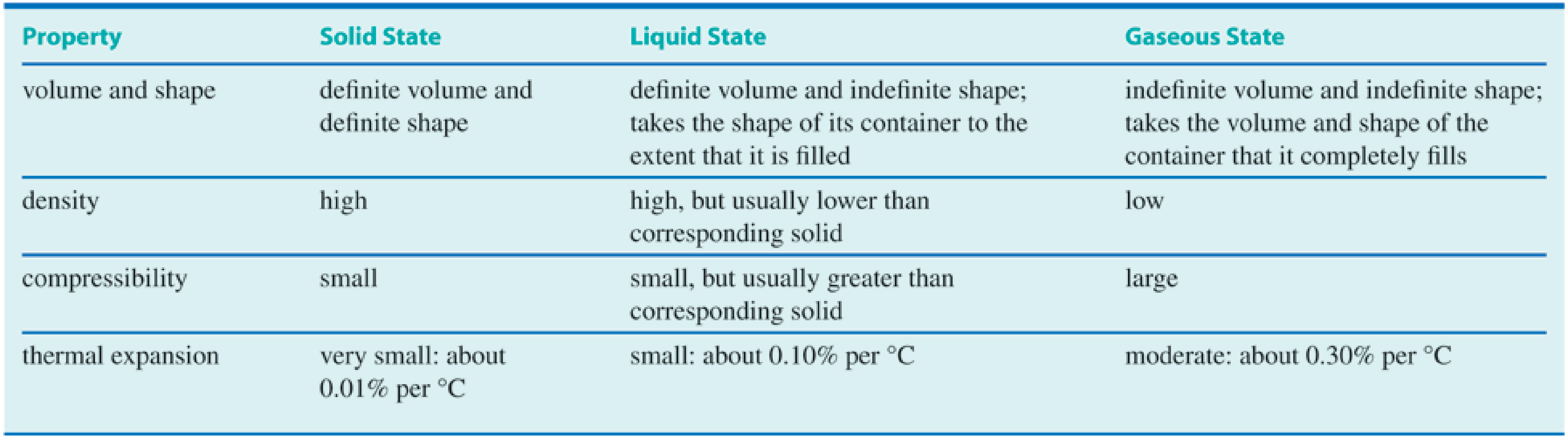
The kinetic molecular theory of matter

- It is easy to distinguish solids, liquids, and gases, using the following characteristics:
  - Volume/shape (see chapter 1)
  - Density (chapter 1)
  - Compressibility: a measure of the change in the volume of a sample of matter resulting from a pressure change
  - Thermal expansion: a measure of the change in volume of a sample of matter resulting from a temperature change

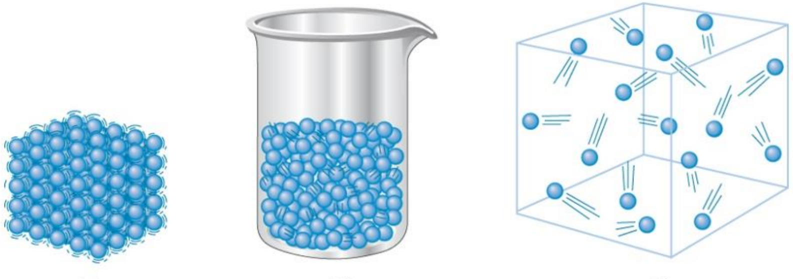


Compressibility of a gas

The kinetic molecular theory of matter



Property	Solid State	Liquid State	Gaseous State
volume and shape	definite volume and definite shape	definite volume and indefinite shape; takes the shape of its container to the extent that it is filled	indefinite volume and indefinite shape; takes the volume and shape of the container that it completely fills
density	high	high, but usually lower than corresponding solid	low
compressibility	small	small, but usually greater than corresponding solid	large
thermal expansion	very small: about 0.01% per °C	small: about 0.10% per °C	moderate: about 0.30% per °C



(a) (b) (c)

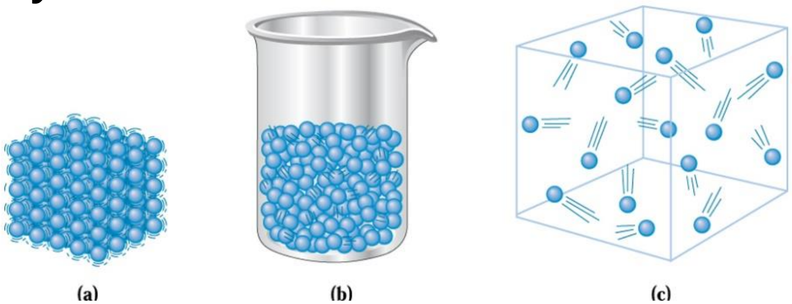
The kinetic molecular theory of matter

- The physical behavior of the three states of matter (solids, liquids, gases) can be explained by a set of five statements, called kinetic molecular theory, the basic idea being that particles that make up any substance are continually in random motion.

  - 1) Matter is composed of tiny particles (atoms, ions, or molecules) that have definite and characteristic sizes (volume, mass) that do not change
  - 2) The particles in a substance are in constant, random motion, and therefore possess kinetic energy (the energy an object possesses because of its motion)
  - 3) Particles interact with one another through attractions and repulsions, and therefore possess potential energy (the energy that matter possesses by virtue of its position, condition, and/or composition). The most significant potential energy we'll consider in most exercises is *electrostatic attraction*.
  - 4) The kinetic energy of the particles in a substance increase *in proportion to an increase in the absolute temperature*
  - 5) Particles in a substance transfer energy to other particles in the substance through elastic collisions

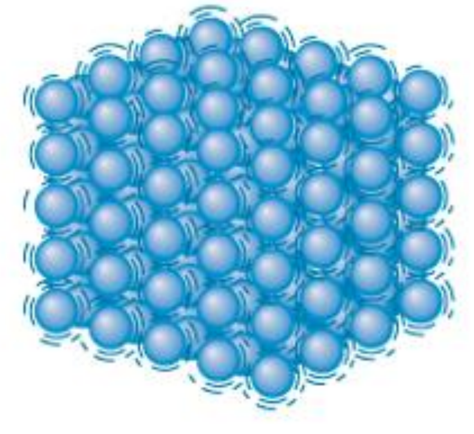
The kinetic molecular theory of matter

- Potential and kinetic energies of the particles that make up a substance are what determines the physical state of that substance (solid, liquid, or gas)
  - Kinetic energy results from particles’ motions and can be thought of as a <u>disruptive force</u> that tends to cause particles to behave increasingly independently
  - Potential energy that exists between particles can be thought of as <u>cohesive</u>, yielding more ordered systems
- The physical state of the substance is results from a competition between these forces. Kinetic energy is temperature-dependent, so as temperature increases, the particles that make up a substance tend to move increasingly independently.



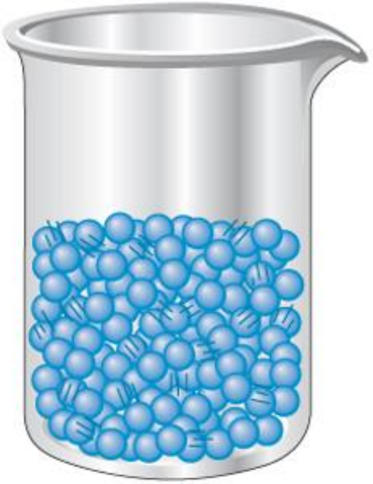
Kinetic molecular theory and physical states

- Particles in solids are dominated by the cohesive forces that exist between them. This draws the particles close together so that they occupy fixed positions (can still vibrate as a result of kinetic energy).
- Properties of solids:
    - Definite volume and shape
    - High density
    - Small compressibility
    - Very small thermal expansion



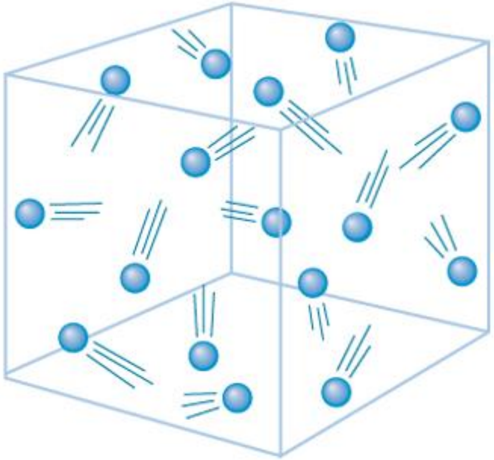
Kinetic molecular theory and physical states

- In liquids, disruptive (kinetic energy) and cohesive (potential energy) forces are of about the same magnitude. Particles (molecules, atoms, ions) remain closely packed, but are capable of motion (random), moving past other particles but not with enough energy to become separated from other particles nearby.
- Properties:
  - Definite volume and indefinite shape
  - High density
  - Small compressibility
  - Small thermal expansion



Kinetic molecular theory and physical states

- Gases are characterized by complete dominance of disruptive forces (kinetic energy) over cohesive (potential energy) forces, resulting in a state in which the particles behave independently of one another. Attractive forces here are very weak.
- Properties:
  - Indefinite volume and indefinite shape
  - Low density
  - Large compressibility
  - Moderate thermal expansion



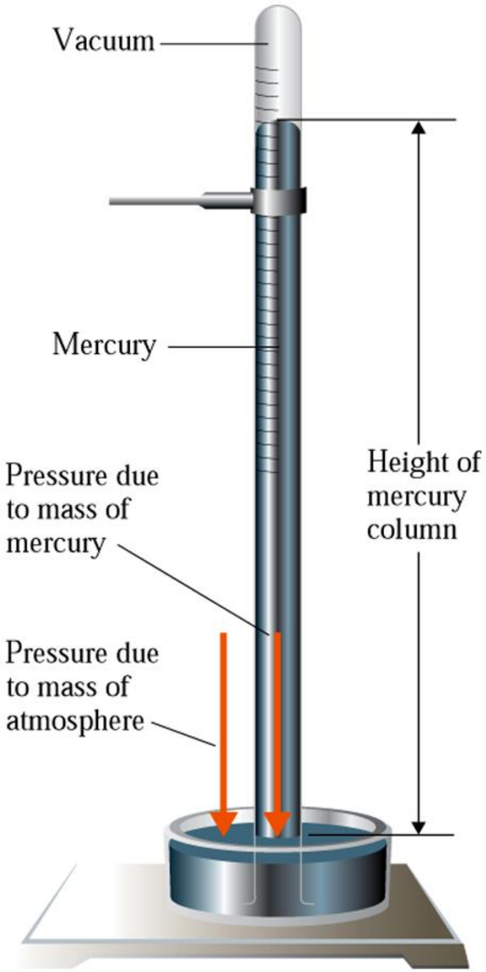
Gas law variables

- Gas behavior is described reasonably well by simple quantitative relationships called gas laws, which describe, in mathematical terms, relationships between the pressure and temperature that a gas is subjected to, as well as the volume the gas occupies.
- The gas laws will involve the use of conversion factors that will *typically* involve combinations of the following units:
  - Moles, mol
  - Liters, L (milliliters, mL)
  - Kelvin, K
  - Millimeters of mercury in a barometer (mm Hg, also called torr)

Four variables are needed to completely discuss a gas: pressure, temperature, volume, and amount of gas

Gas law variables

- Pressure is a key descriptor of a gas. The pressure that a gas generates results from collisions of gas molecule with the walls of the container the gas occupies.
- These collisions create a force, which is distributed over a surface area:



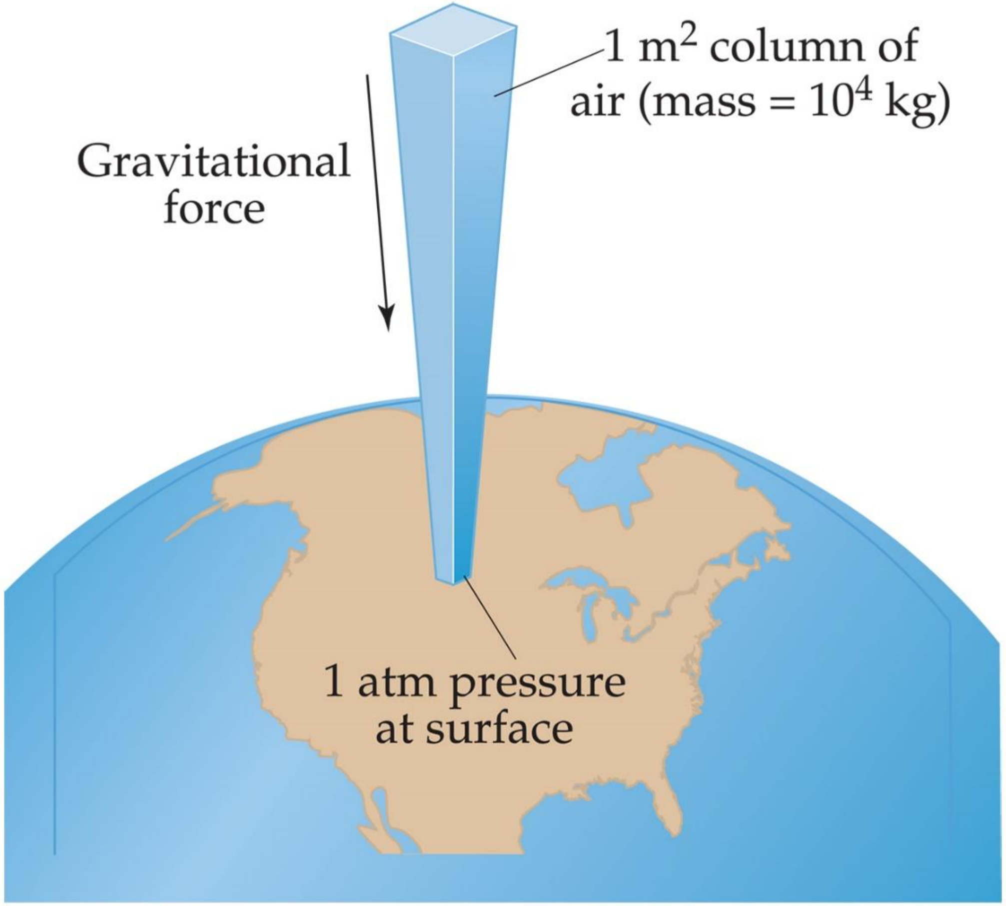
$$P(pressure) = \frac{F(force)}{A(area)}$$

1mm Hg = 1 torr

760 mm Hg = 1 atm = 14.7 psi (pounds-per-square-inch)

At sea-level, atmospheric pressure is 760 mm Hg (or 1 atmosphere

Gas law variables

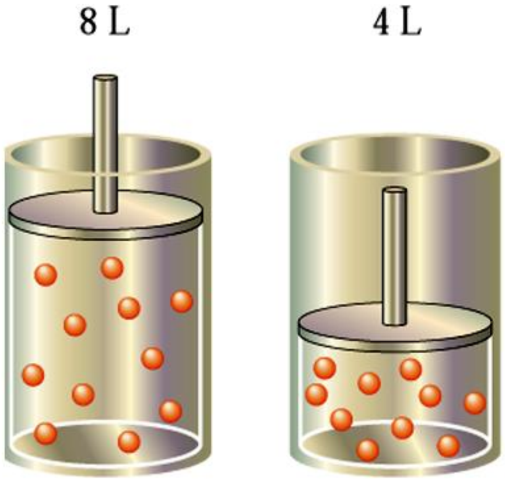


Gas law variables

- Standard procedure for reporting pressures reading barometers is to record the pressure to the nearest mm Hg. Thus, when you see pressures reported in the text as 750 mm Hg or 700 mm Hg, the uncertainty in the number is in the "ones column"
- These figures are understood to have three significant digits.

Boyle’s law: a pressure-volume relationship

- Boyle’s law states that the volume of a fixed amount of gas (at constant temperature) is proportional to the pressure applied to it.
- Example: a gas in an 8 L container has a pressure of 5 atm. If the volume of the container is changed to 4 L (half the initial volume) then the pressure of the gas will double (it will become 10 atm), provided the temperature of the gas is held constant.



P = 5 atm **P = 10 atm**

Boyle’s law: a pressure-volume relationship

- The equation that expresses Boyles law is:

$$P_1V_1 = P_2V_2$$

Equation holds as long as T (temperature) is constant

P_1 = pressure of the gas under the first set of conditions
V_1 = volume of the gas under the first set of conditions
P_2 = pressure of the gas under the second set of conditions
V_2 = volume of the gas under the second set of conditions

Boyle's law: a pressure-volume relationship

- A sample of H_2 gas occupies a volume of 2.25 L at a pressure of 628 mm Hg and a temperature of 35°C. What volume will it occupy (L) if the pressure is decreased to 428 mm Hg while the temperature is held constant?

$$P_1V_1 = P_2V_2$$

Sets of conditions:

1) Pressure = 628 mm Hg; V = 2.25 L
2) Pressure = 428 mm Hg, V = ?

$$(628mm\_Hg)(2.25L) = (428mm\_Hg)V_2$$

$$\frac{(628mm\_Hg)(2.25L)}{(428mm\_Hg)} = V_2$$

$$V_2 = 3.30L$$

Charles's law: a temperature-volume relationship

- Charles's law tells us that the volume of a fixed amount of gas is proportional to the absolute (Kelvin) temperature of the gas, provided the pressure of the gas is held constant.

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

- V_1 = volume of gas in first set of conditions
- T_1 = temperature of gas (in K), first set of conditions
- V_2 = volume of gas, second set of conditions
- T_2 = temperature of gas (in K), second set of conditions

Charles's law: a temperature-volume relationship

- A sample of dry air with a volume of 125 mL at a temperature of 53°C is heated at a constant pressure to 95°C. What is the new volume (mL) of the sample?

Conditions:

1) Volume = 125 mL; temperature = 53°C (= 326K)
2) Volume = ?; temperature = 95°C (= 368K)

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

$$\frac{(125mL)}{326K} = \frac{V_2}{368K}$$

$$\frac{(125mL)(368K)}{(326K)} = V_2$$

Going from the first set of conditions to the second, the temperature increased. Charles's law tells us that the volume will increase in proportion to the increase in the absolute temperature of the gas.

$$V_2 = 141mL$$

Combined gas law

- Boyle's law tells us that the volume occupied by a gas is inversely proportional to the pressure of the gas (constant T and n)
- Charles's law tells us that the volume of a gas is directly proportional to the temperature of the gas (constant P and n)
- If both pressure and temperature vary, the volume of a gas can be calculated using the combined gas law:

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

Combined gas law

- A helium-filled balloon, when released, has a volume of 10.0 L at 27^{o}C and a pressure of 663 mm Hg. What volume, in liters, will the balloon occupy at an altitude where the pressure is 96 mm Hg and the temperature -30.0^{o}C?

Conditions:
1) Volume = 10.0 L; temperature = 27^{o}C (= 300K); pressure = 663 mm Hg
2) Volume = ?; temperature = -30.0^{o}C (= 243K); pressure = 96 mm Hg

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

$$\frac{(663mm\_Hg)(10.0L)}{(300K)} = \frac{(96mm\_Hg)V_2}{(243K)}$$

$$\frac{(663mm\_Hg)(10.0L)}{(300K)}\frac{(243K)}{(96mm\_Hg)} = V_2$$

$$56L = V_2$$

The ideal gas equation

- The ideal gas equation describes the relationships between pressure, volume, temperature, and amount of gas (moles).

$$PV = nRT$$

- A constant, R, permits conversion of units. Its value depends on the units of pressure and volume used:

$$R = 0.0821 \frac{L \cdot atm}{mol \cdot K}$$

$$R = 62.4 \frac{L \cdot torr}{mol \cdot K}$$

The ideal gas equation

- Calculate the volume (L) occupied by 3.25 moles of $Cl_2(g)$ at 1.54 atm pressure and a temperature of 213^oC.

$213^oC + 273 = 486K$

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$V = \frac{(3.25 mol)\left(0.0821 \frac{L.atm}{mol \cdot K}\right)(486K)}{(1.54 atm)}$$

$$V = 84.2L$$

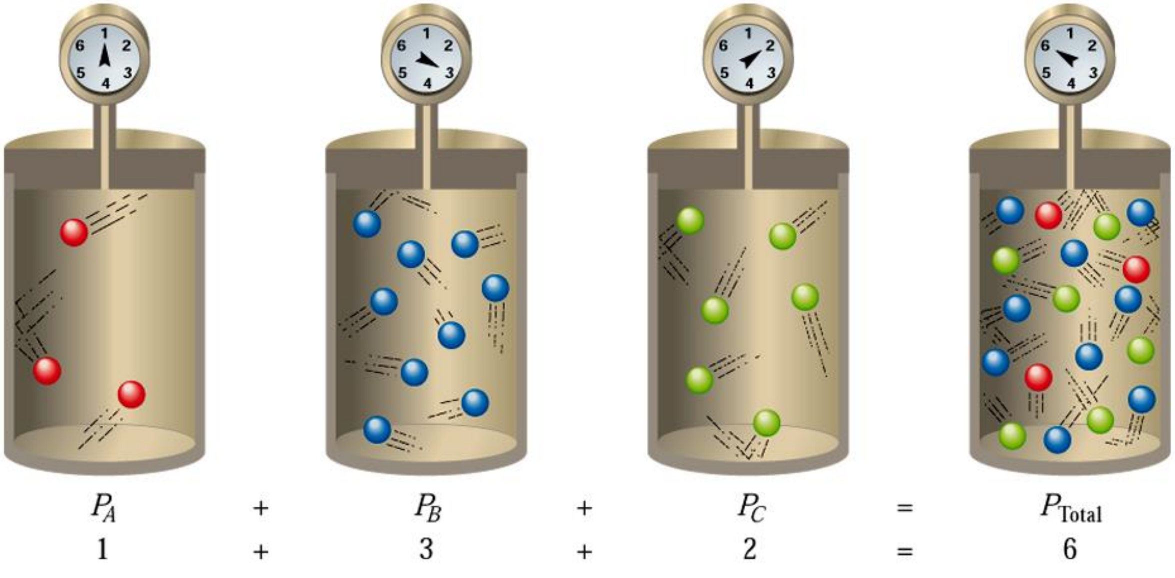
Dalton’s law of partial pressures

- The collisions of gas molecules with the container walls creates gas pressure.
- It doesn’t matter what *kind* of gas molecule creates this pressure.
- Thus, in a mixture of gases, the total pressure exerted by the gas mixture is the sum of the pressures exerted by each of the gases in the mixture.

$$P_{total} = P_A + P_B + P_C + \dots$$

Dalton’s law of partial pressures

- The pressures exerted by each gas in the mixture are called partial pressures.
- The *partial pressure* of a gas is the pressure that would be exerted by a gas in a mixture of gases if it were present alone under the same conditions

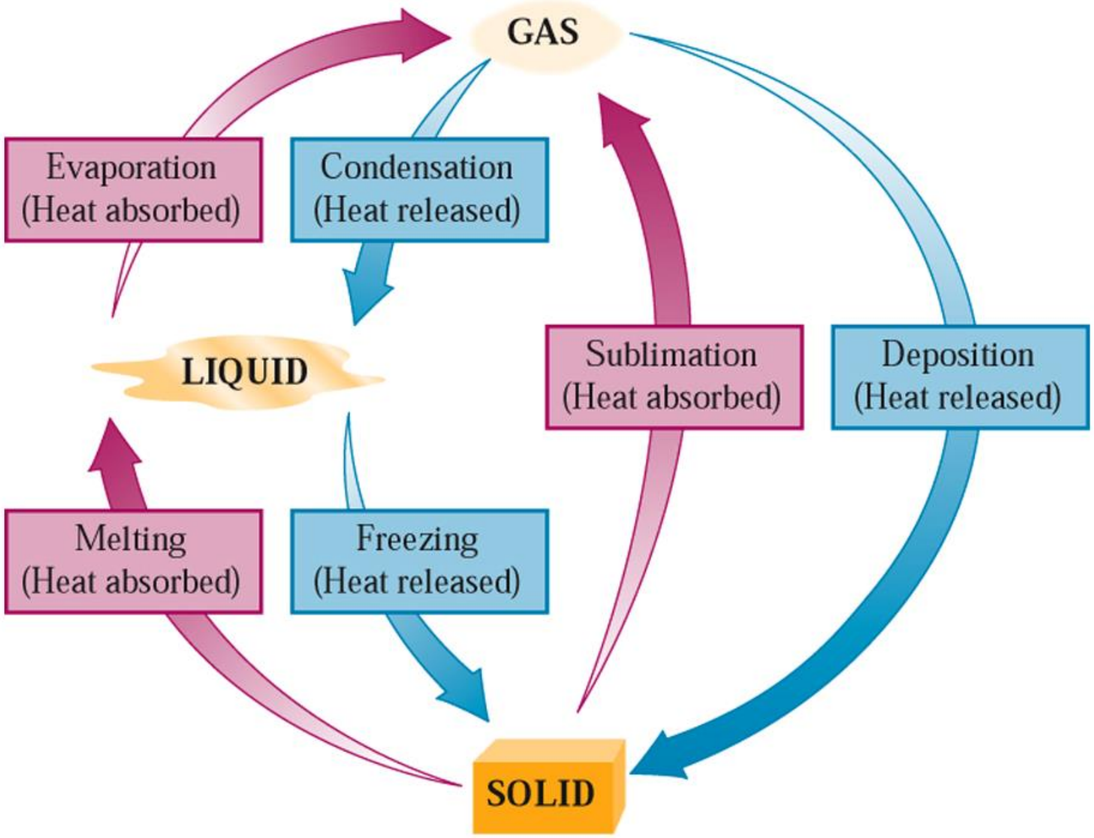


Dalton's law of partial pressures

- In this week's lab, you'll collect H_2(g) over water (makes it easier to determine the volume of gas).
- Water evaporates at temperatures above 0^oC. Thus, in the experiment, the pressure of the gas you'll collect will partially be due to H_2(g), and partially due to H_2O(g)

$$P_{total} = P_{H2} + P_{H2O}$$

Changes of state



Endothermic: heat is absorbed by a substance (or reaction) as some process happens
Exothermic: heat is released by a substance (or reaction) as some process occurs

Evaporation of liquids

- Evaporation is the process by which liquids escape from the liquid state to the gas state
- Molecules in the liquid state must acquire enough kinetic energy to overcome their attractions to other molecules in the liquid. They can obtain this energy from heat (and collisions with other molecules)
- Evaporation happens at the interface of a liquid and a gas (at the surface) – there are fewer attractions to other liquid molecules at the surface

Evaporation of liquids

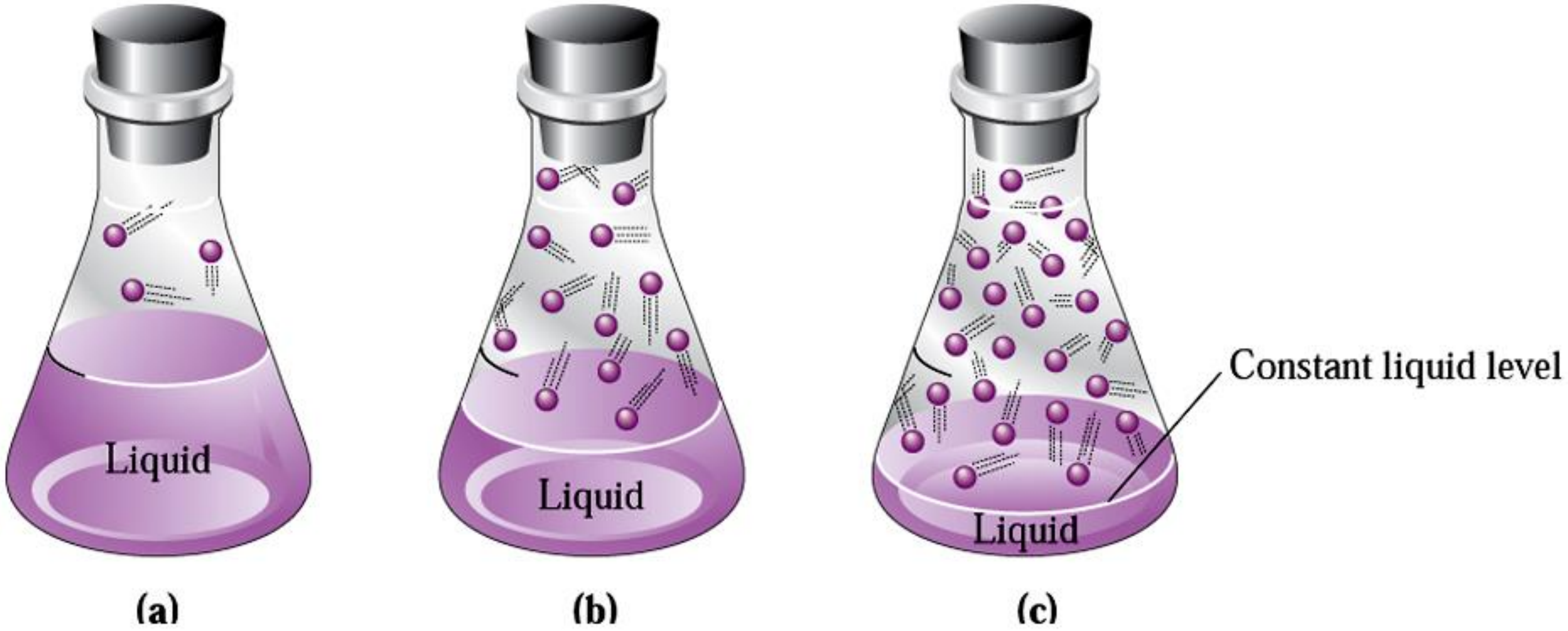
- Evaporation cools a liquid. As the most energetic molecules of the liquid (the ones at the highest temperature) exit to the gas phase, the temperature of the liquid drops.
- Vapor is a gas that exists as a liquid at temperatures and pressures at which it would normally be thought of as a liquid (or solid)

Vapor pressure of liquids

- A glass of water left on a countertop overnight will slowly evaporate. We know this because the level of the water in the glass drops with time
- In a closed container, evaporation still happens, but the gas molecules formed cannot leave the container. They *can* be re-captured by the liquid phase and brought back into that phase
- A *cycle of evaporation-condensation* occurs.
- Initially, the rate of evaporation is fast (and condensation is slow), but as more gas is formed, collisions between the gas molecules and the surface of the liquid are more frequent, resulting in an increasing rate of condensation
- At some point, these rates become equal (equilibrium)

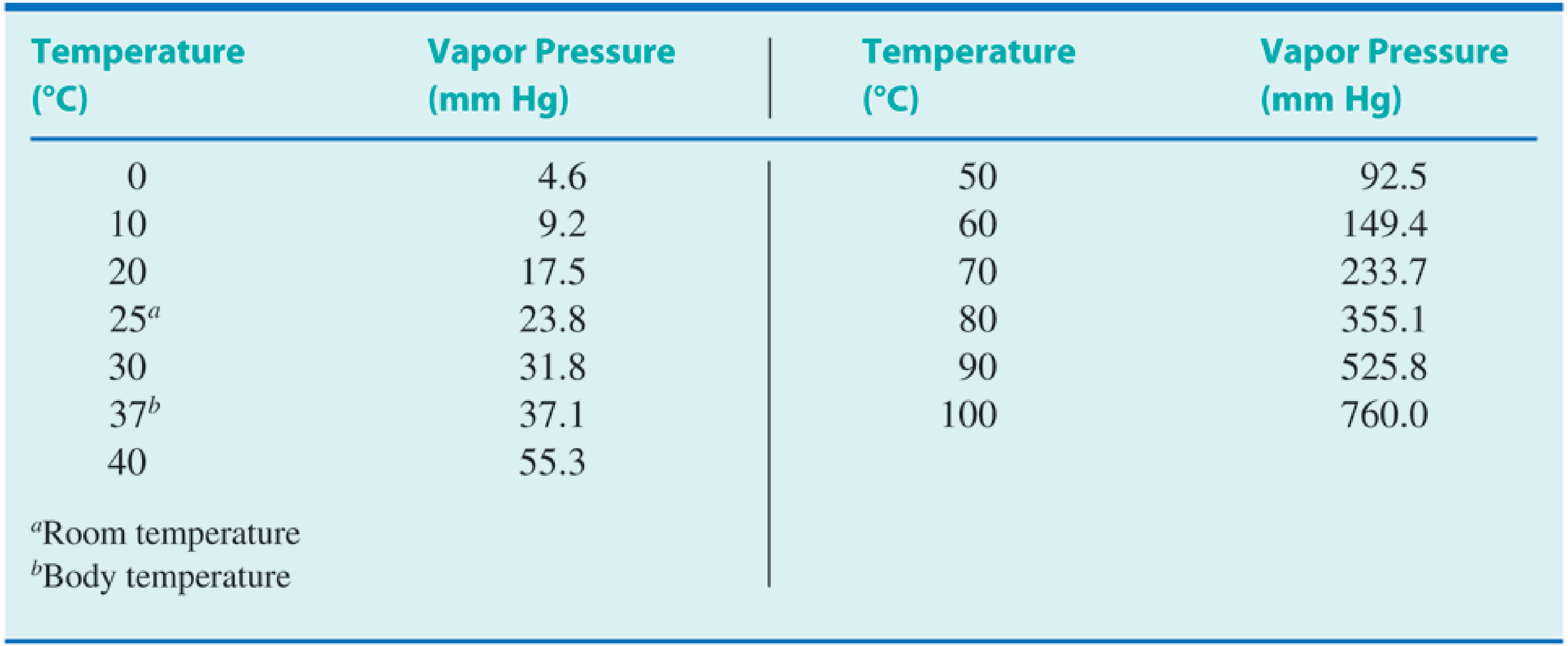
Equilibrium: a condition in which two opposed processes have the same rate

Vapor pressure of liquids



- The pressure exerted by a vapor in equilibrium with a liquid in a closed container is constant and is called the vapor pressure.
- Vapor pressure is influenced by temperature and also by the nature of the liquid.
- Some liquids consist of molecules that have very weak attractive forces between them.
- These liquids evaporate easily. They have high vapor pressures (called volatile)

Vapor pressure of liquids



Temperature (°C)	Vapor Pressure (mm Hg)	Temperature (°C)	Vapor Pressure (mm Hg)
0	4.6	50	92.5
10	9.2	60	149.4
20	17.5	70	233.7
25[a]	23.8	80	355.1
30	31.8	90	525.8
37[b]	37.1	100	760.0
40	55.3		

[a] Room temperature

[b] Body temperature

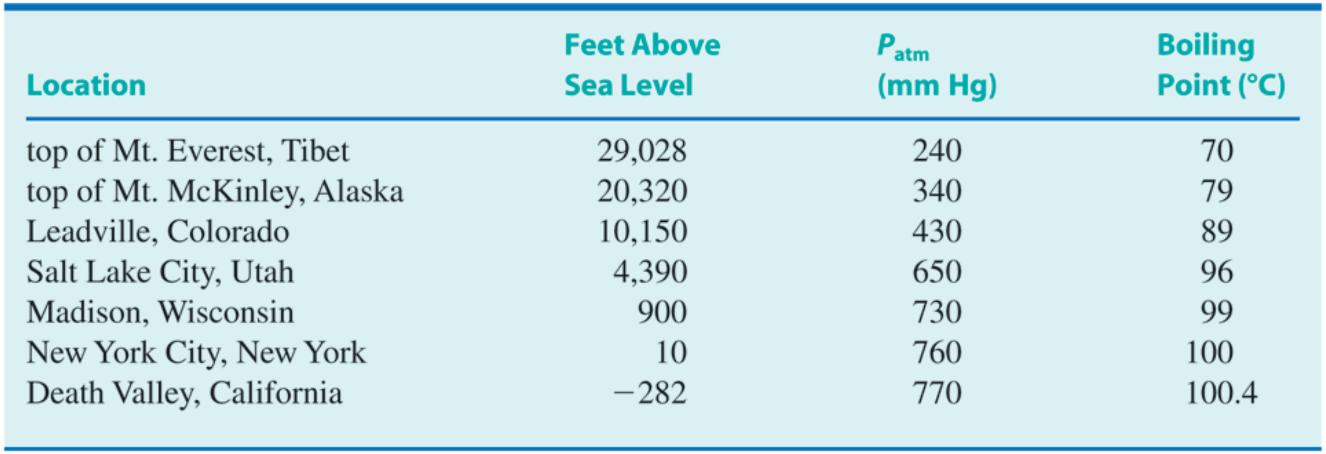
Vapor pressure increases with increasing temperature

Boiling and boiling point

- Evaporation occurs at the air-liquid interface.
- If the temperature of the liquid is made high enough, evaporation from the interior of the liquid can be made to occur (in bubbles)
- Boiling is a kind of evaporation in which the liquid-to-gas change of state occurs within the body of the liquid
- This transformation happens when the vapor pressure of the liquid becomes equal to the external (room) pressure above the liquid
- The boiling point is the temperature at which the liquid’s vapor pressure equals the external pressure

Boiling and boiling point

- The factor that has the greatest influence on a liquid's boiling point is the external pressure.
- Increasing the external pressure causes the boiling point to increase, while decreasing it will lower the boiling point.



Location	Feet Above Sea Level	P_{atm} (mm Hg)	Boiling Point (°C)
top of Mt. Everest, Tibet	29,028	240	70
top of Mt. McKinley, Alaska	20,320	340	79
Leadville, Colorado	10,150	430	89
Salt Lake City, Utah	4,390	650	96
Madison, Wisconsin	900	730	99
New York City, New York	10	760	100
Death Valley, California	−282	770	100.4

Intermolecular forces in liquids

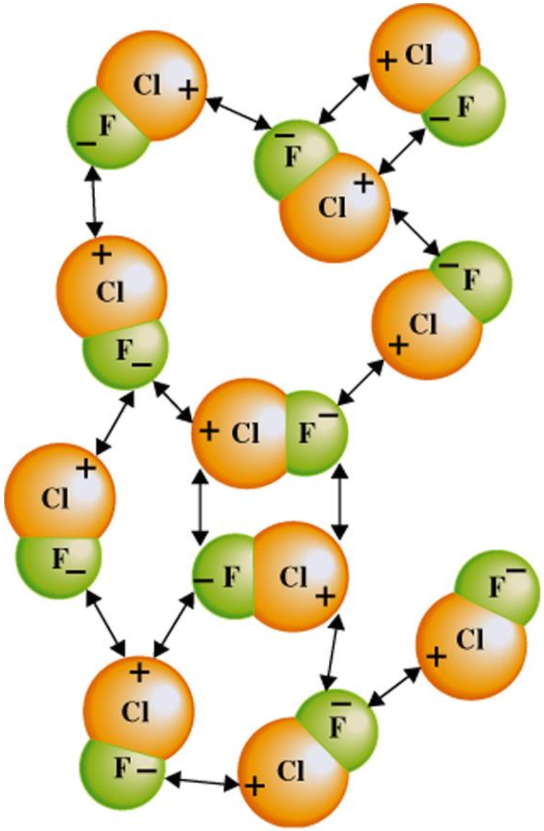
- *Inter*molecular forces are attractive forces that operate between molecules. They consist of:
  - Dipole-dipole forces
  - Hydrogen bonding
  - London forces
  - Ion-dipole forces (we won’t examine these)
- *Intra*molecular forces operate within a single molecule. We already looked at one of these (covalent bonding)
- In terms of relative strengths, intramolecular forces are usually much stronger than intermolecular forces

Intermolecular forces in liquids

- Intermolecular forces are cohesive forces – they hold molecules close to each other. Therefore, if the intermolecular forces in a liquid are strong, it is difficult for these molecules to evaporate
- For these liquids, boiling points are high (and they are considered to be non-volatile)

Intermolecular forces in liquids

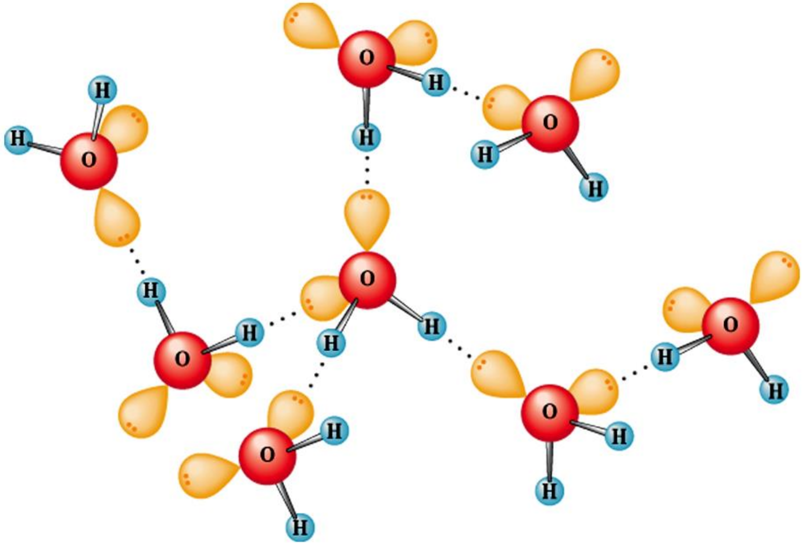
- Dipole-dipole interactions are intermolecular forces that result from interactions between polar molecules
- The negative “pole” of a polar molecule interacts with the positive “pole” of a second molecule. (The resulting electrostatic attraction is the dipole-dipole interaction)
- The more polar the molecule, the stronger are the dipole-dipole forces



To have dipole-dipole forces, molecules of the liquid must be polar

Intermolecular forces in liquids

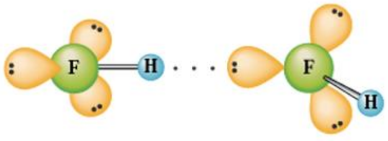
- Hydrogen bonding is a special case of dipole-dipole interaction, *occurring in hydrogen-containing molecules where hydrogen is bonded to either O, N, or F* (all very electronegative atoms)
- This makes for a very polar bond in which the hydrogen side is essentially a bare nucleus
- The H-atom inn such a bond can interact very strongly with the non-bonding pairs on O, N, and F-atoms of other molecules
- **H-bonding is the strongest intermolecular force**



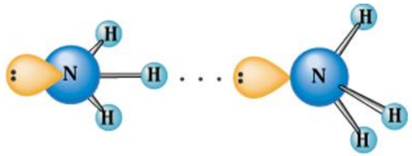
To exhibit H-bonding, molecules must possess H-X bonds, where X = O, N, or F.

Intermolecular forces in liquids

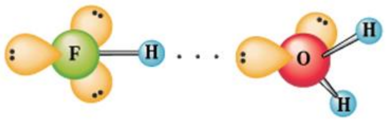
- H-bonding doesn’t need to occur between atoms of the same type. The H-bond just needs to involve:
  - A H-atom bonded to O, N, or F
  - A non-bonding pair of electrons on a second O, N, or F-atom



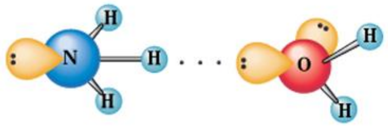
Hydrogen fluoride—hydrogen fluoride



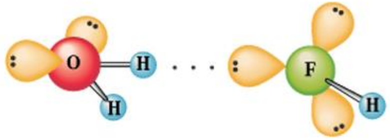
Ammonia—ammonia



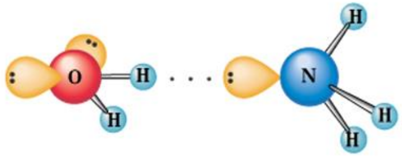
Hydrogen fluoride—water



Ammonia—water



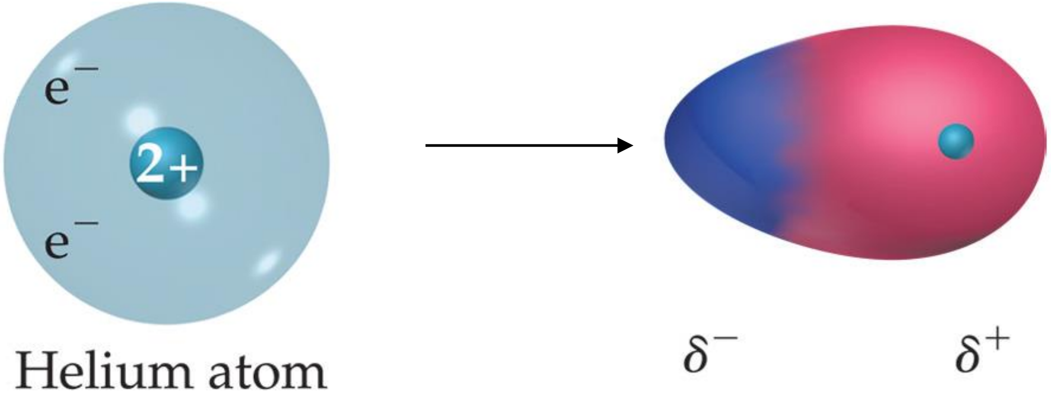
Water—hydrogen fluoride



Water—ammonia

Intermolecular forces in liquids

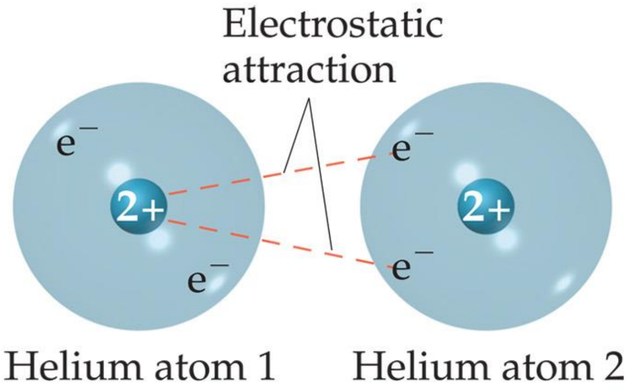
- London forces are the weakest type of intermolecular force (and the most difficult to understand)

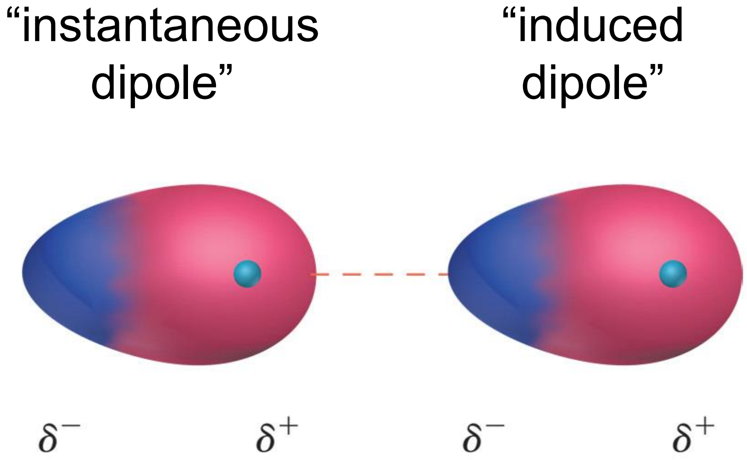


The movement of electrons around nuclei in atoms and molecules can create a very brief (temporary) dipole.

Intermolecular forces in liquids

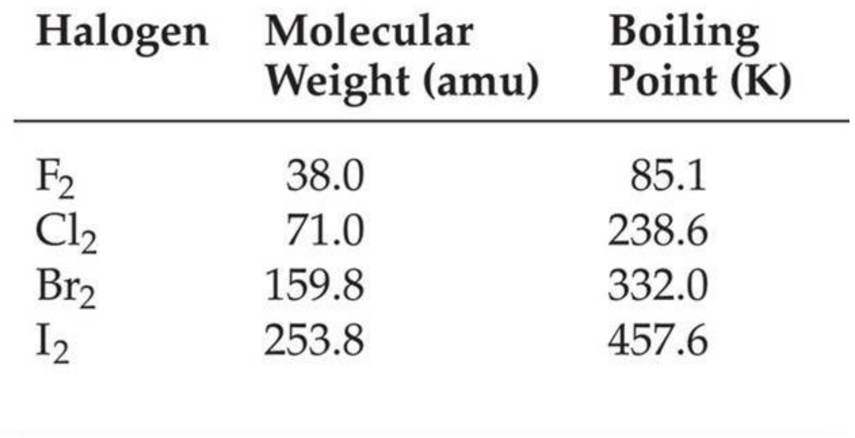
- These “instantaneous dipoles” can cause other molecules around them to become polar for an instant. The resulting interaction is attractive (London force)





Intermolecular forces in liquids

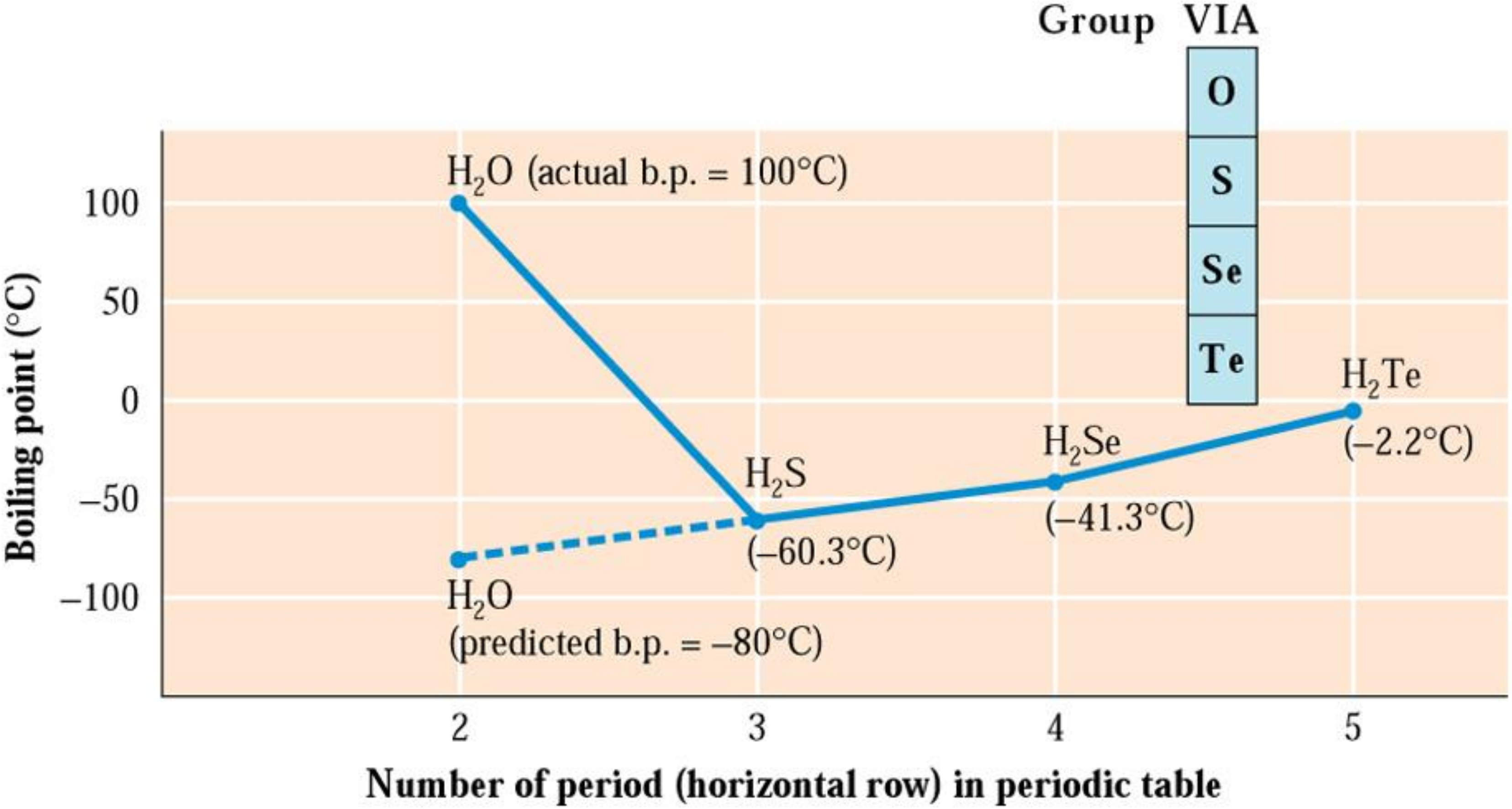
- London forces are stronger between larger atoms. Thus London forces become stronger with increasing molar mass.



Halogen	Molecular Weight (amu)	Boiling Point (K)
F_2	38.0	85.1
Cl_2	71.0	238.6
Br_2	159.8	332.0
I_2	253.8	457.6

London forces are present in all molecules

Intermolecular forces in liquids



of central atom (O, S, Se, Te)