States of Matter: Gases, Liquids and Solids

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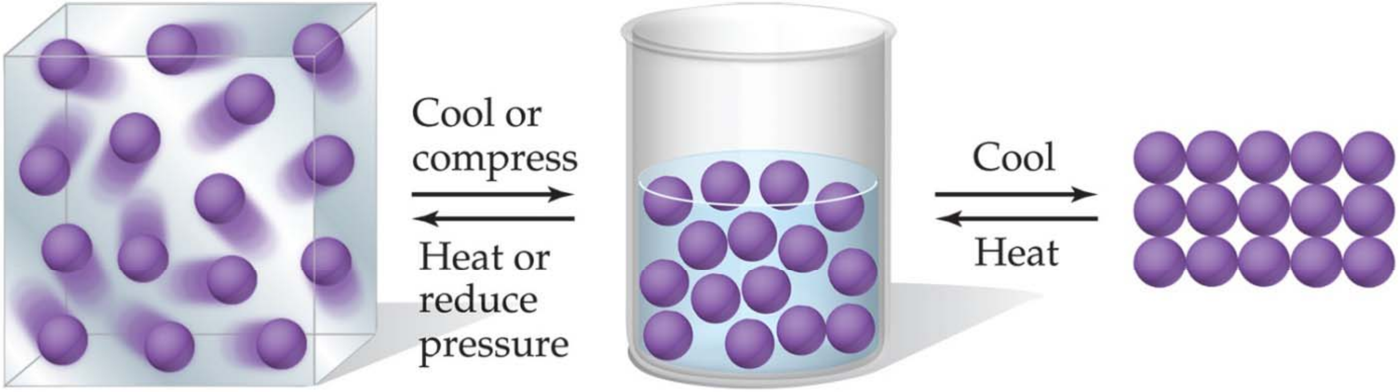
Original source: *Chemistry, The Central Science*, 10th edition
Theodore L. Brown; H. Eugene LeMay, Jr.; and Bruce E. Bursten

States of Matter

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



Gas

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

Liquid

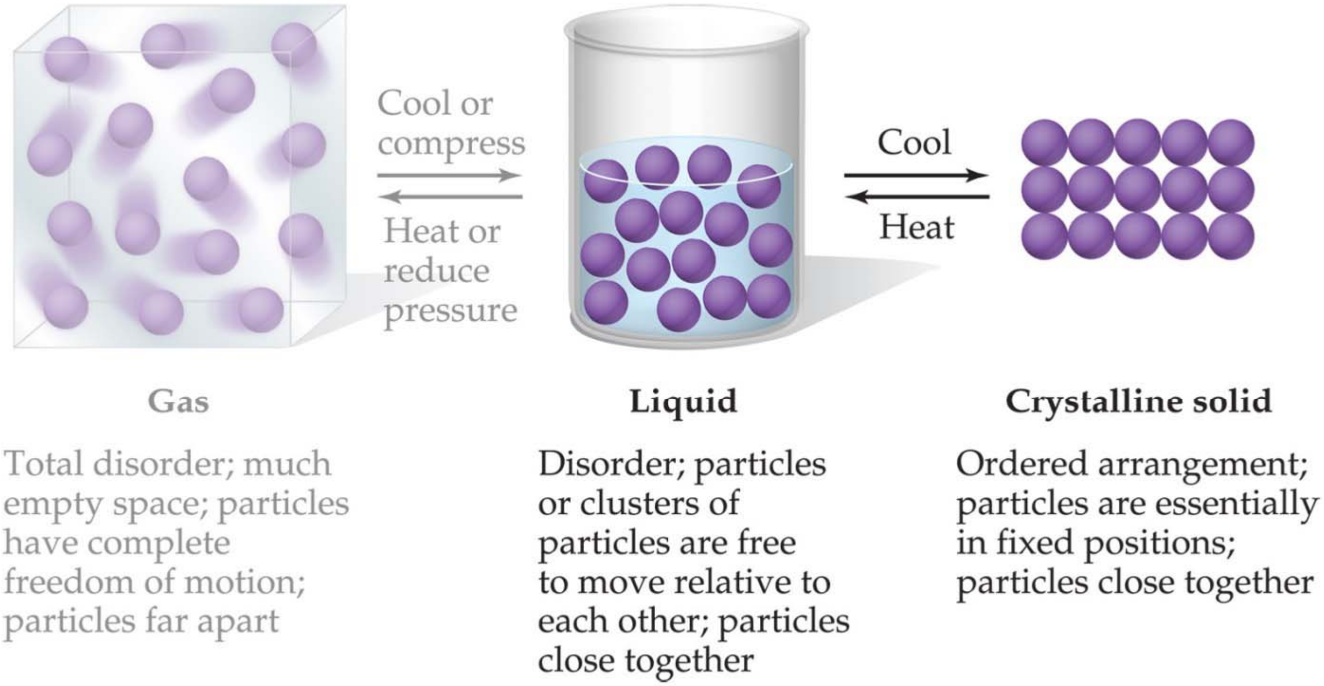
Disorder; particles or clusters of particles are free to move relative to each other; particles close together

Crystalline solid

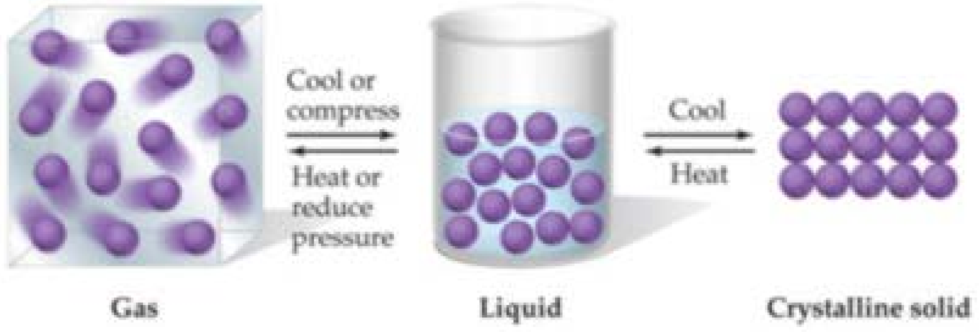
Ordered arrangement; particles are essentially in fixed positions; particles close together

States of Matter

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



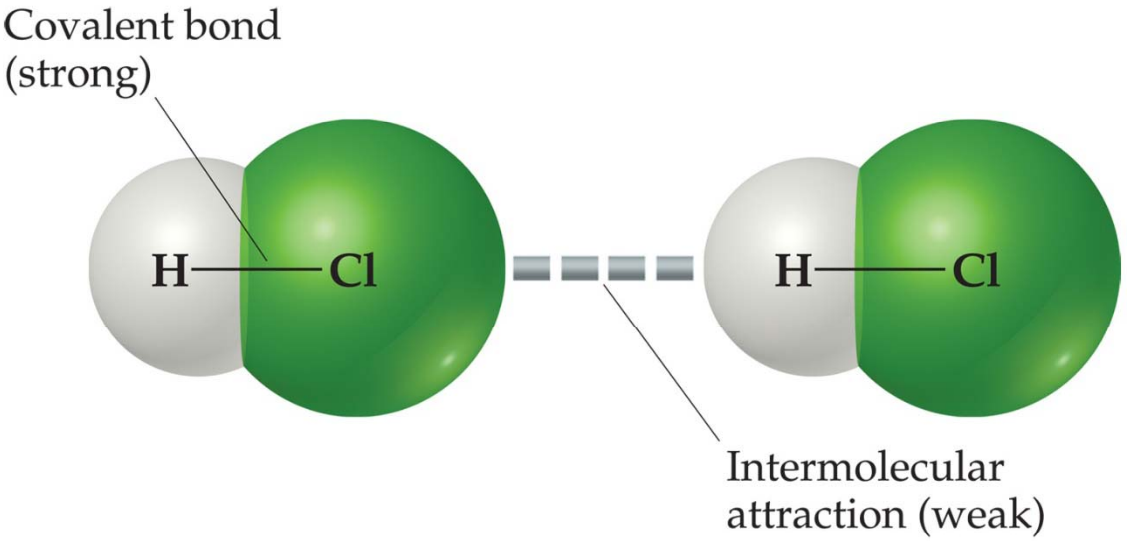
The States of Matter



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

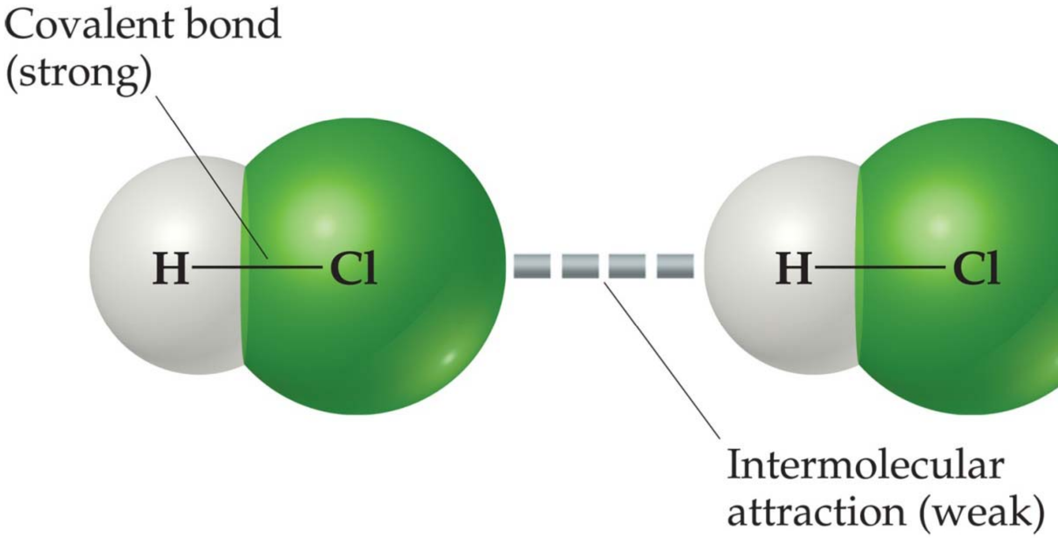
- The state a substance is in at a particular temperature and pressure depends on two antagonistic entities
  - The kinetic energy of the particles
  - The strength of the attractions between the particles

Intermolecular Forces



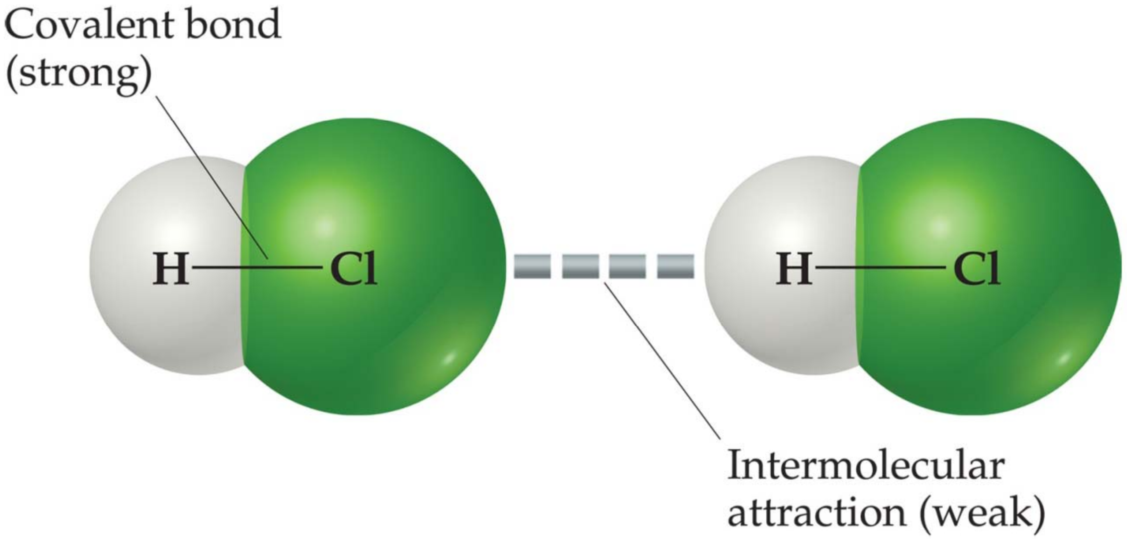
The attractions between molecules are not nearly as strong as the intramolecular attractions that hold compounds together.

Intermolecular Forces



They are, however, strong enough to control physical properties such as boiling and melting points, vapor pressures, viscosities, surface tension, and related properties.

Intermolecular Forces

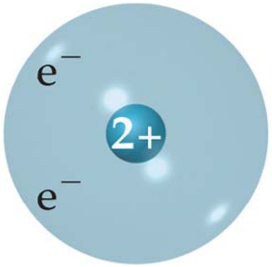


These intermolecular forces as a group are referred to as van der Waals forces.

Intermolecular Forces

- London dispersion forces
- Dipole-induced dipole interactions
- Dipole-dipole interactions
- Hydrogen bonding
- Ion-induced dipole interactions
- Ion-dipole interactions

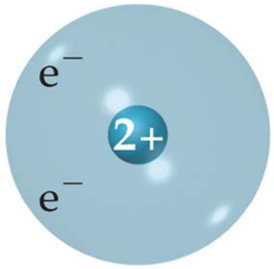
London Dispersion Forces



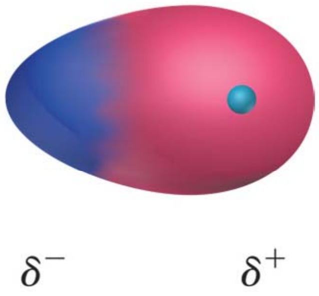
Helium atom 2

While the electrons in the 1*s* orbital of helium would repel each other (and, although they are paired, tend to stay away from each other), it does happen that they occasionally wind up on the same side of the atom.

London Dispersion Forces



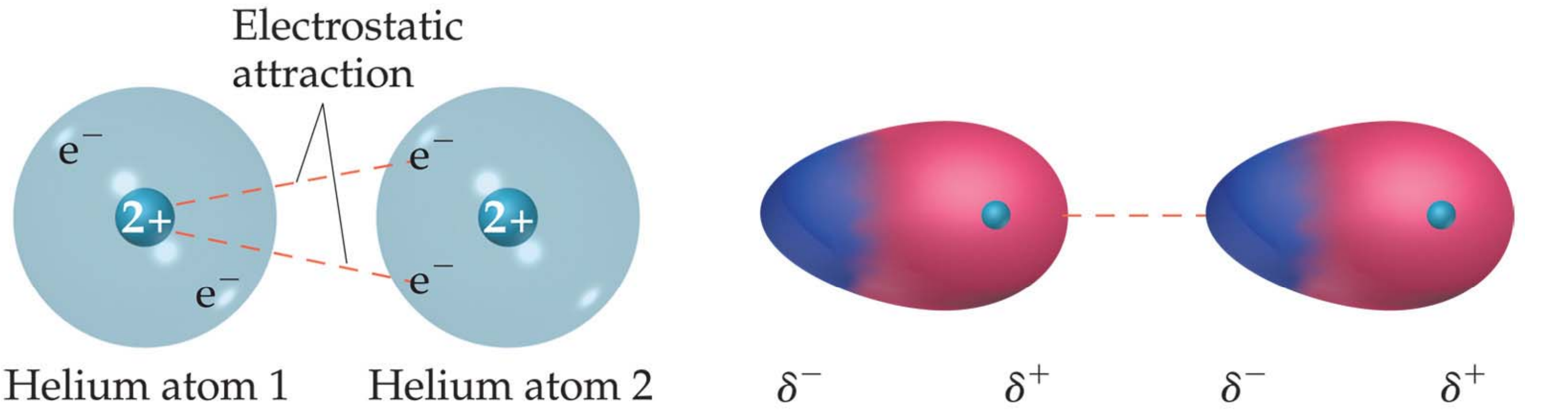
Helium atom 2



At that instant, then, the helium atom is polar, with an excess of electrons on the left side and a shortage on the right side.

This is called an instantaneous dipole

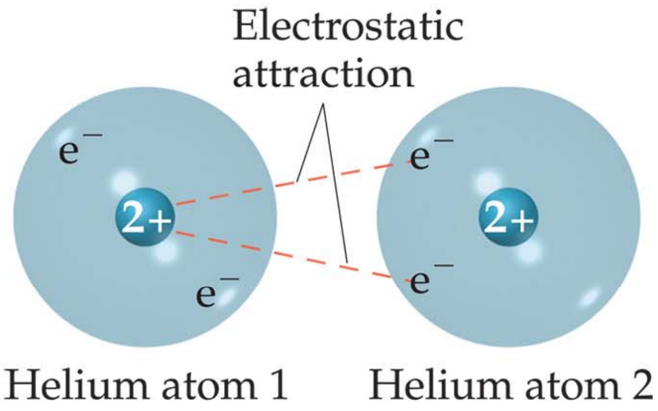
London Dispersion Forces

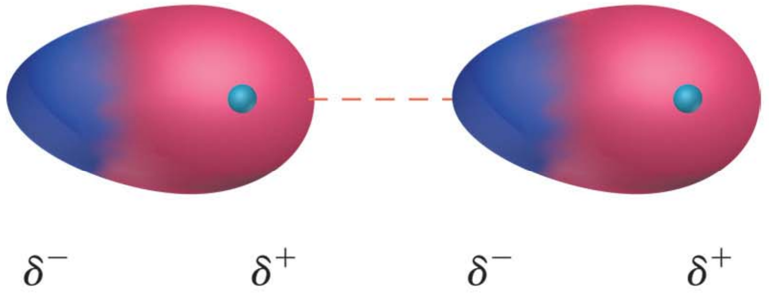


Another helium nearby, then, would have a dipole induced in it, as the electrons on the left side of helium atom 2 repel the electrons in the cloud on helium atom 1.

The second helium atom has an induced dipole

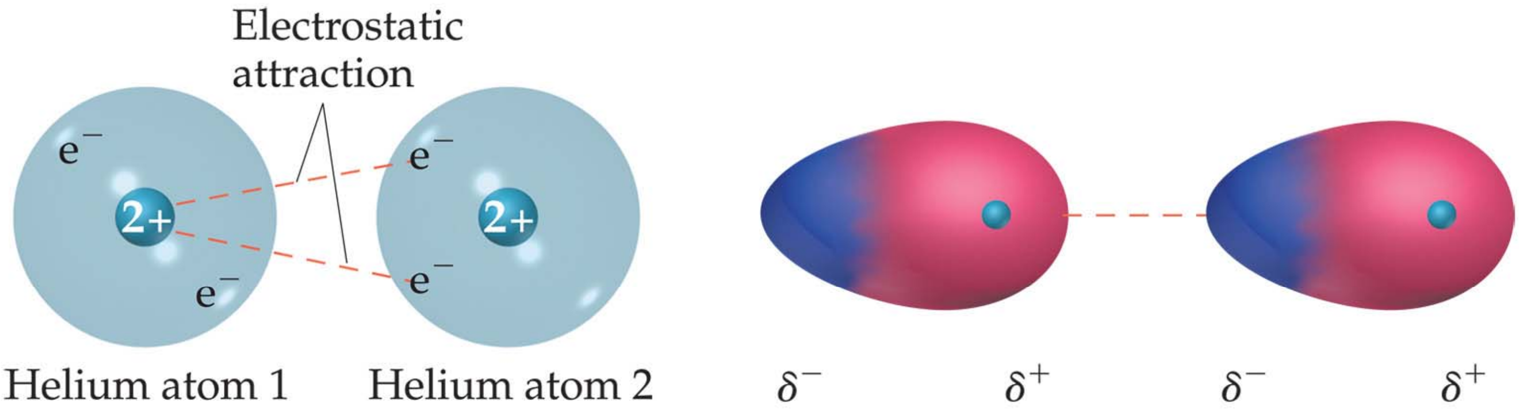
London Dispersion Forces





London dispersion forces, or dispersion forces, are attractions between an instantaneous dipole and an induced dipole.

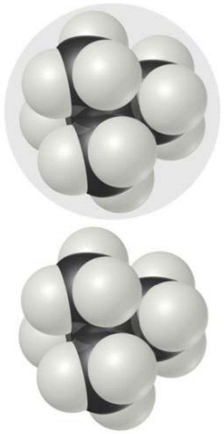
London Dispersion Forces



- These forces are present in *all* molecules, whether they are polar or nonpolar.
- The tendency of an electron cloud to distort in this way is called polarizability.

Factors Affecting London Forces

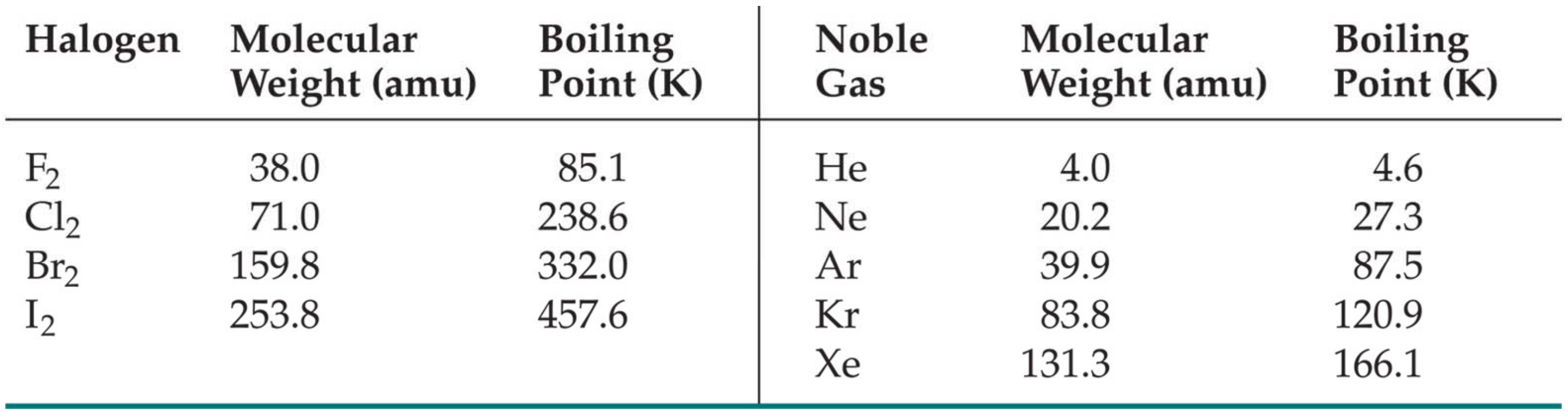
n-Pentane
(bp = 309.4 K)



Neopentane
(bp = 282.7 K)

- The shape of the molecule affects the strength of dispersion forces: long, skinny molecules (like *n*-pentane tend to have stronger dispersion forces than short, fat ones (like neopentane, 2,2-dimethylpropane).
- This is due to the increased surface area in *n*-pentane.

Factors Affecting London Forces

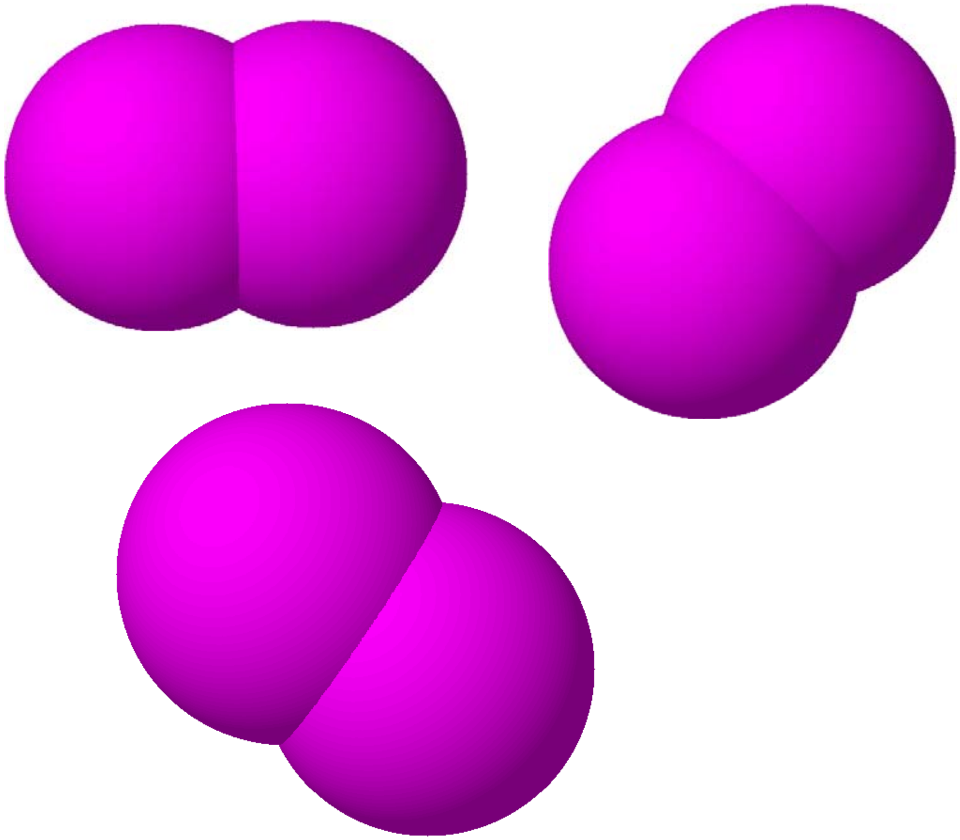


Halogen	Molecular Weight (amu)	Boiling Point (K)	Noble Gas	Molecular Weight (amu)	Boiling Point (K)
F_2	38.0	85.1	He	4.0	4.6
Cl_2	71.0	238.6	Ne	20.2	27.3
Br_2	159.8	332.0	Ar	39.9	87.5
I_2	253.8	457.6	Kr	83.8	120.9
			Xe	131.3	166.1

- The strength of dispersion forces tends to increase with increased molecular weight.
- Larger atoms have larger electron clouds, which are easier to polarize.

Intermolecular forces in I_2

1. Iodine vapor
2. Iodine-hexane: Nonpolar interactions (London forces)

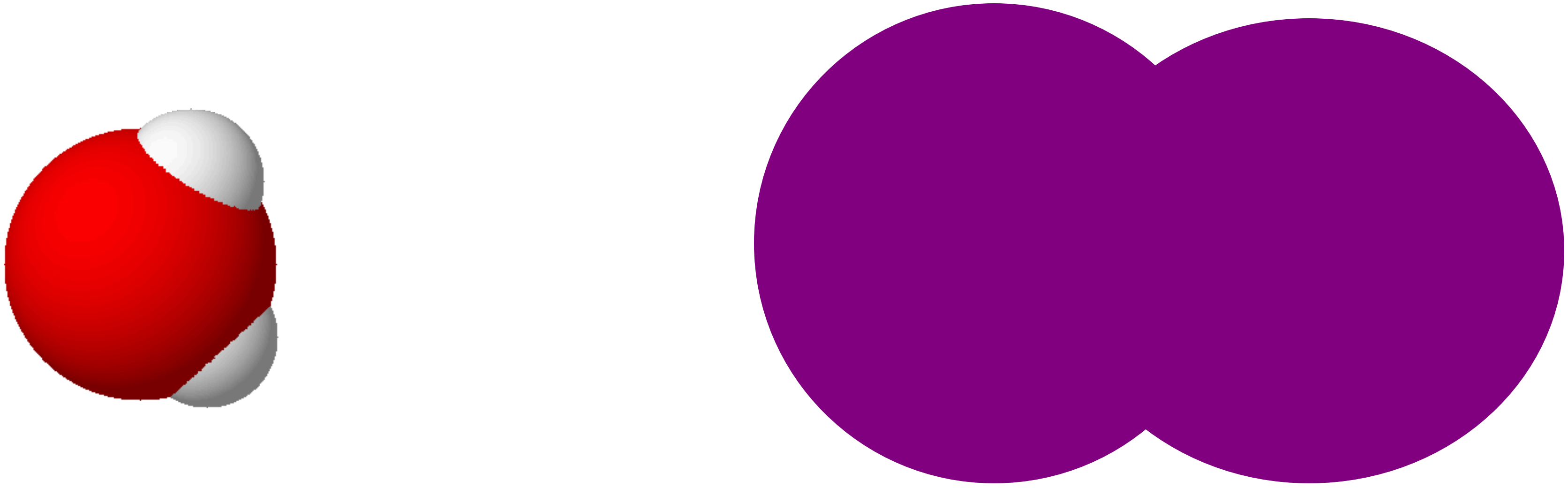


Dipole-Induced Dipole Interactions

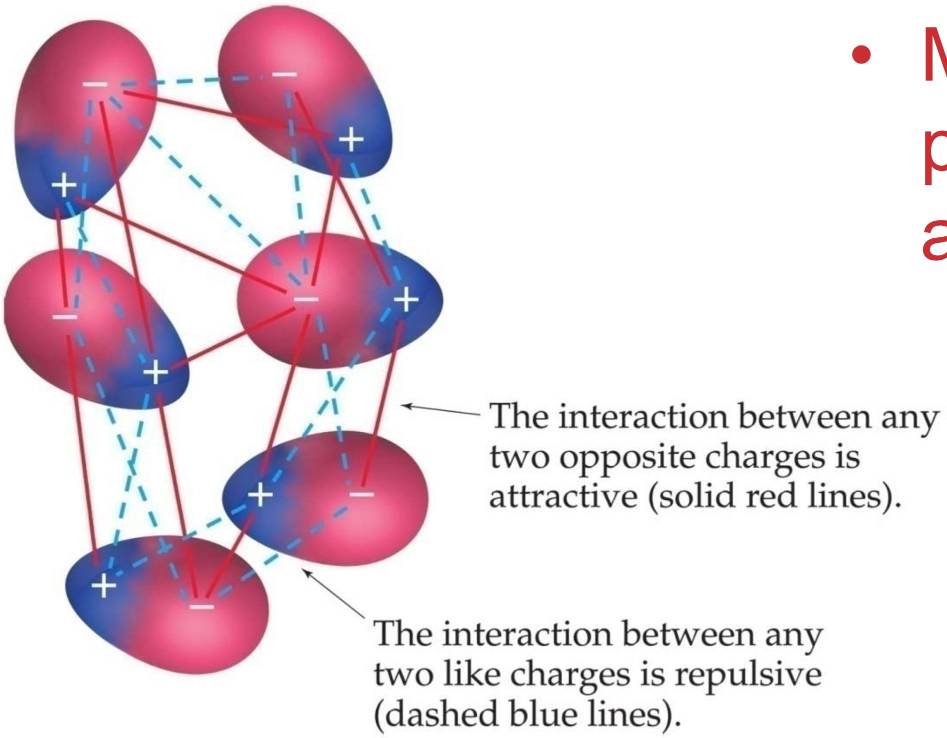
Intermolecular forces using I_2

Molecules that have permanent dipoles can induce a dipole on a non-polar atom or molecule

Demonstration: iodine in water



Dipole-Dipole Interactions

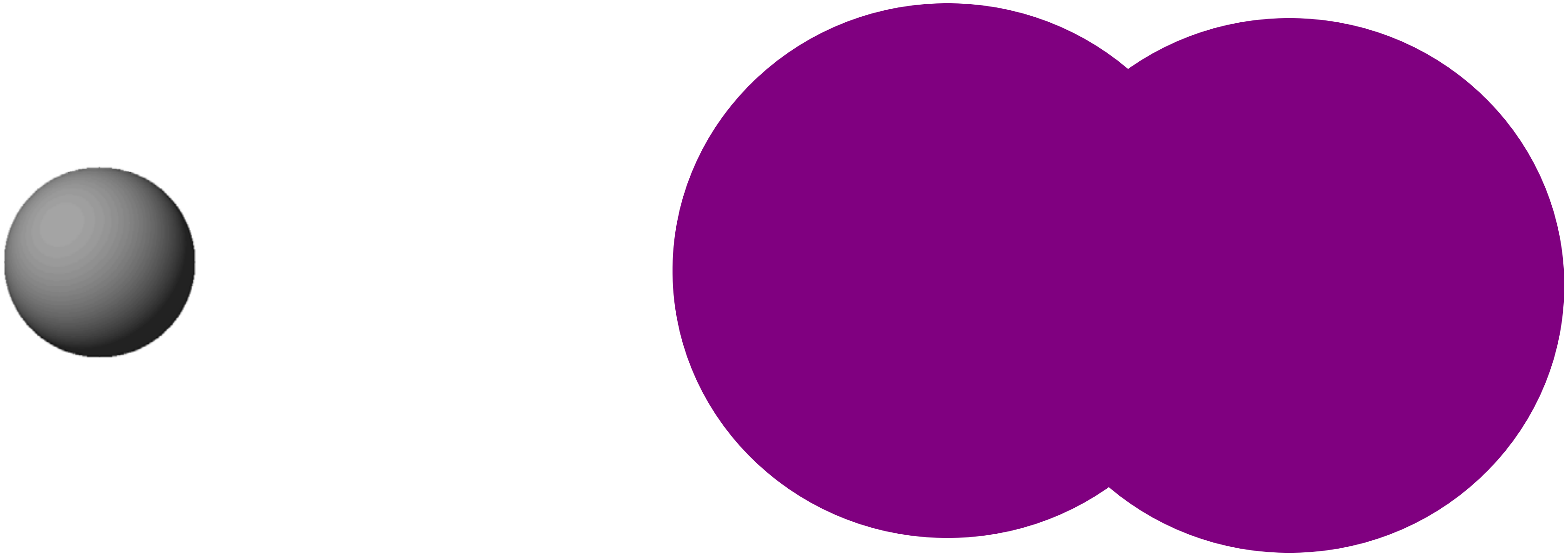


- Molecules that have permanent dipoles are attracted to each other.
  - The positive end of one is attracted to the negative end of the other and vice-versa.
  - These forces are only important when the molecules are close to each other.

Ion-Induced Dipole Interactions
Intermolecular forces using I_2

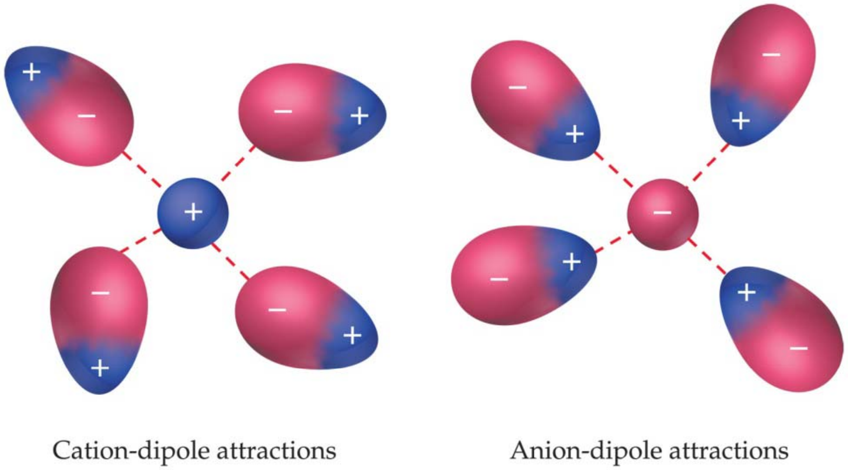
Ions can induce a dipole on a non-polar atom or molecule

Demonstration: Add potassium iodide to iodine in water



Ion-Dipole Interactions

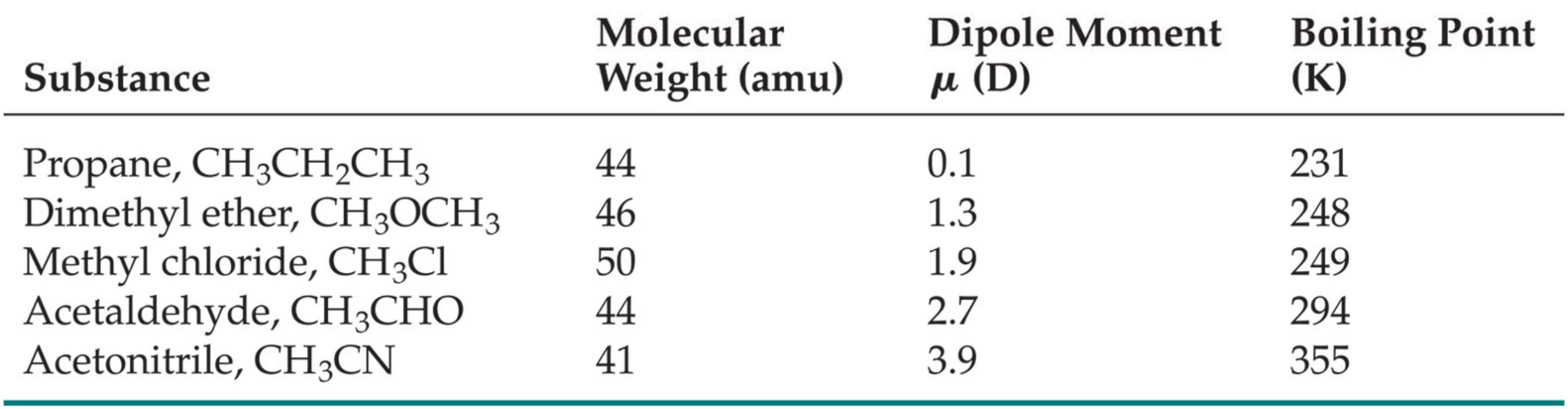
- Ion-dipole interactions are an important force in solutions of ions.
- The strength of these forces are what make it possible for ionic substances to dissolve in polar solvents.



Cation-dipole attractions

Anion-dipole attractions

Dipole-Dipole Interactions



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

The more polar the molecule, the higher is its boiling point.

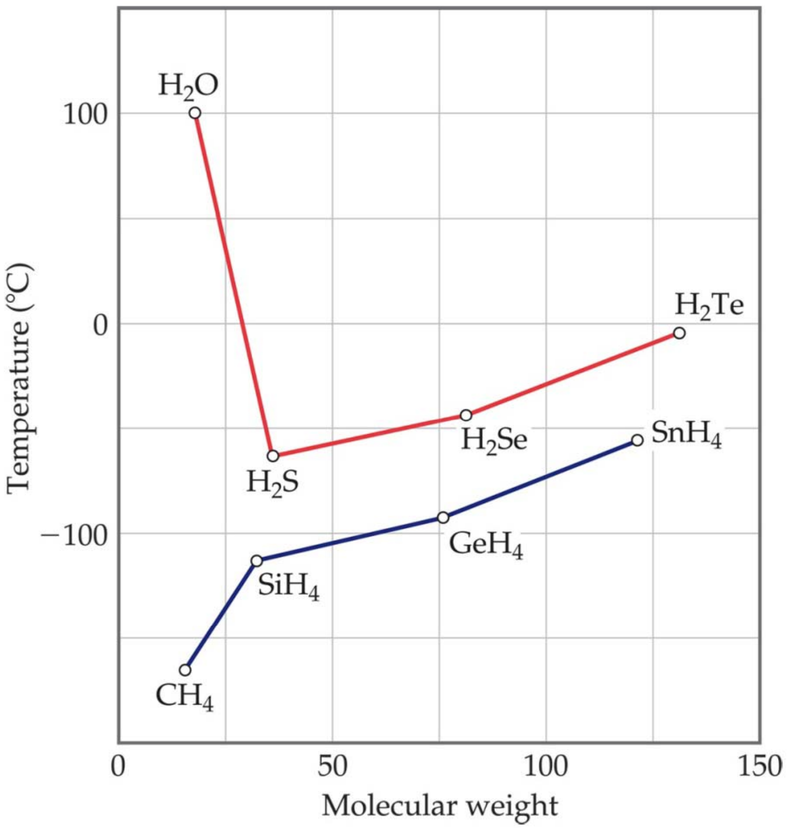
NOTE: To better see the polarity of these molecules, draw their structures.

Which Have a Greater Effect:

Dipole-Dipole Interactions or Dispersion Forces?

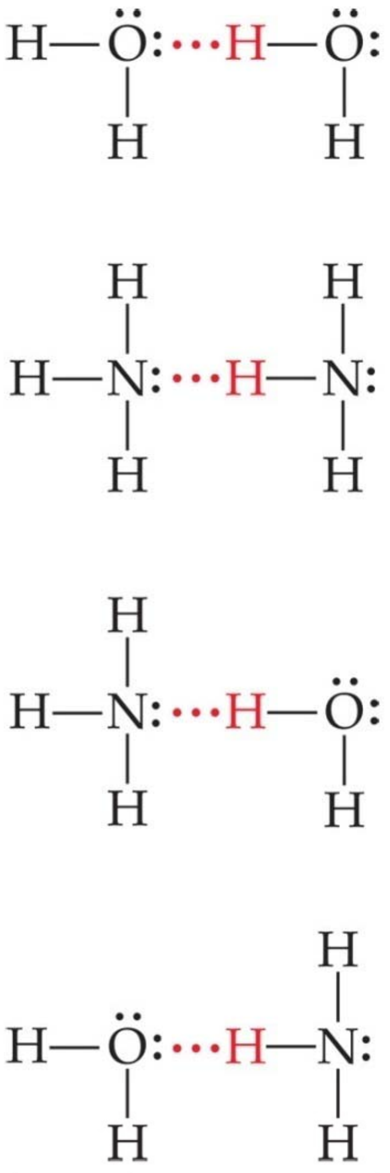
- If two substances have molecules that are of comparable size and shape
    - Dispersion forces are approximately equal in the two substances
    - If there is any polarity in the molecules, then dipole-dipole interactions will be the dominating force.
- If two substances differ where one molecule is much larger than another
    - If they are non-polar, substances, dispersion forces in the substance consisting of larger molecules will be stronger.

How Do We Explain This?



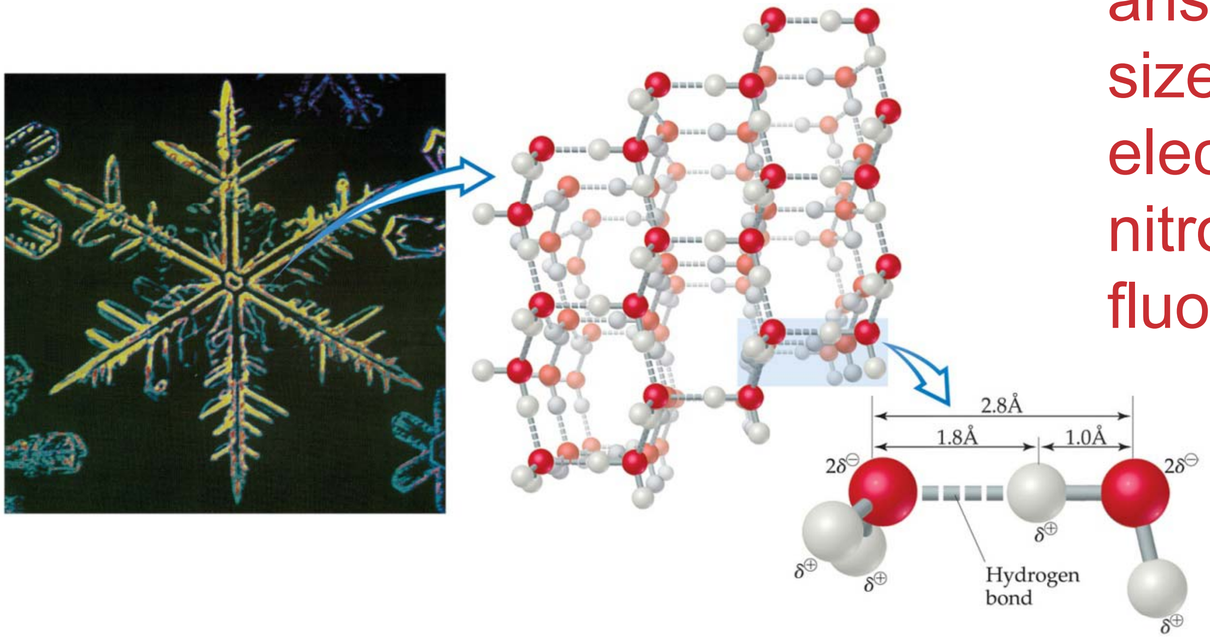
- The nonpolar series (SnH_4 to CH_4) follow the expected trend.
- The polar series follows the trend from H_2Te through H_2S, but water is quite an anomaly.

Hydrogen Bonding



- The dipole-dipole interactions experienced when H is bonded to N, O, or F are unusually strong.
- We call these interactions hydrogen bonds.

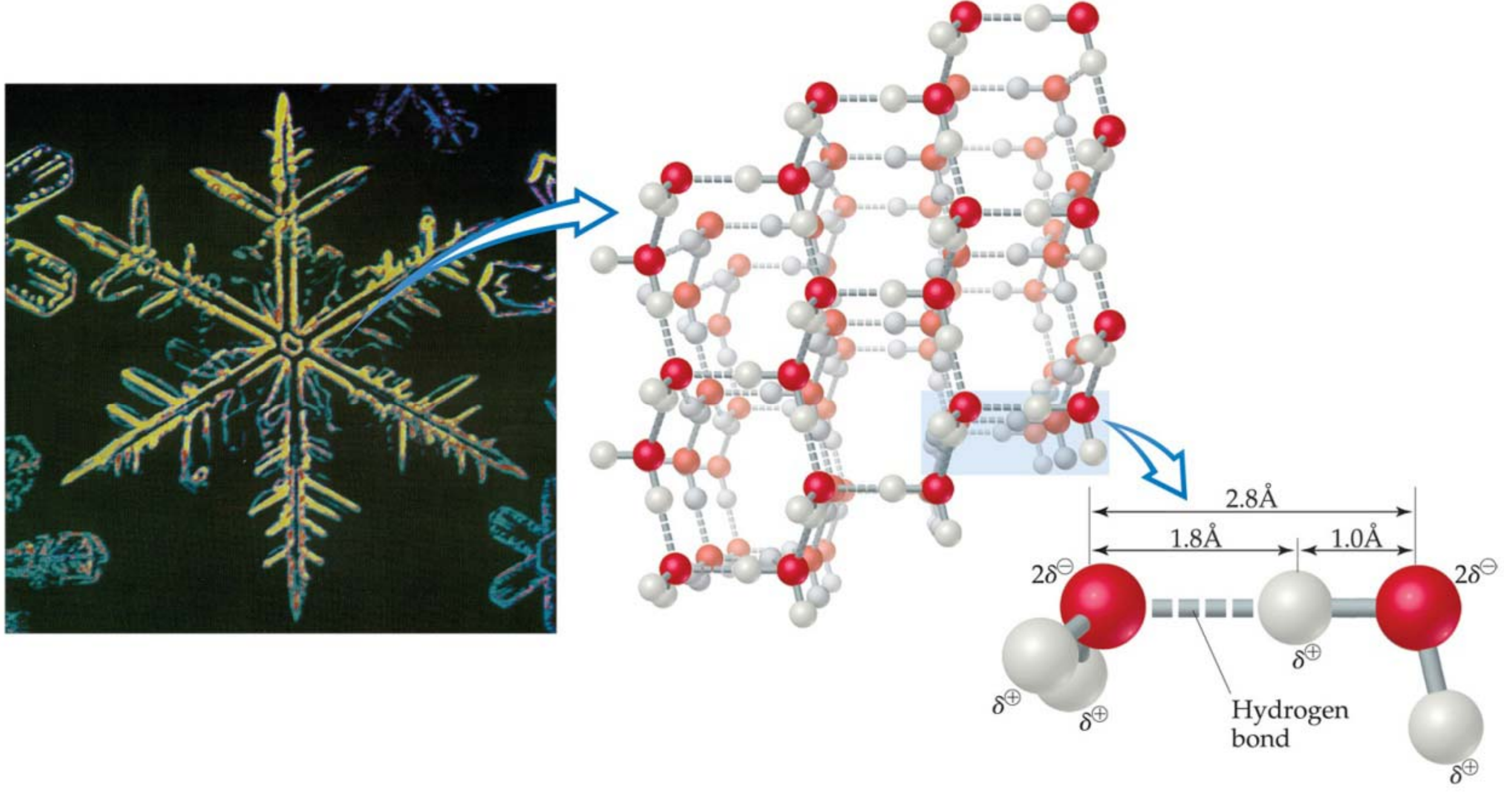
Hydrogen Bonding



Hydrogen bonding arises from the small size and high electronegativity of nitrogen, oxygen, and fluorine.

Also, when hydrogen is bonded to one of those small, electronegative elements, the hydrogen nucleus is essentially exposed.

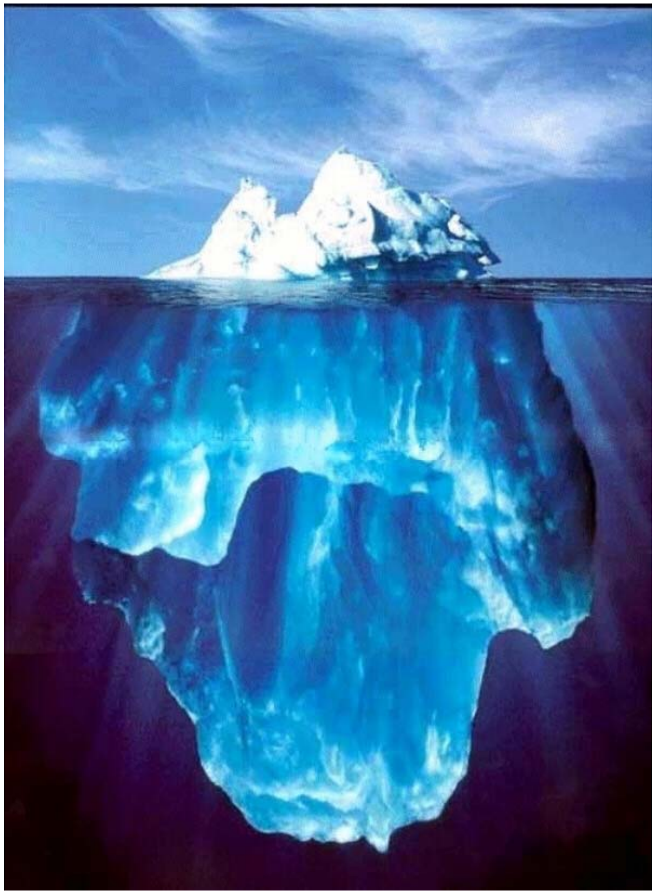
Hydrogen Bonding



The hexagonal shape of a snowflake is a result of the hexagonal, non-planar rings formed by water molecules in ice.

When water is cooled below 4°C, the molecules slow down sufficiently so repulsions between the water molecules cause the molecules to move apart causing the density of the cold water or ice to decrease.

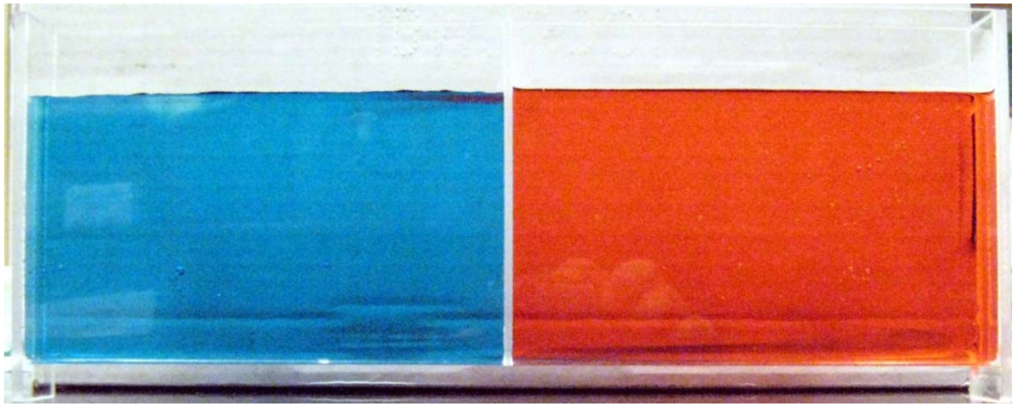
Water expands on freezing



Ice is less dense than liquid water

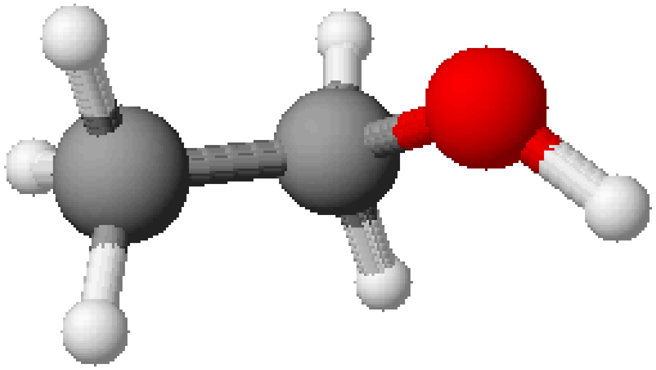
Hot and Cold

Separate water by density

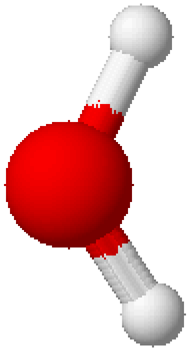


Hydrogen Bonding

Decrease in Volume

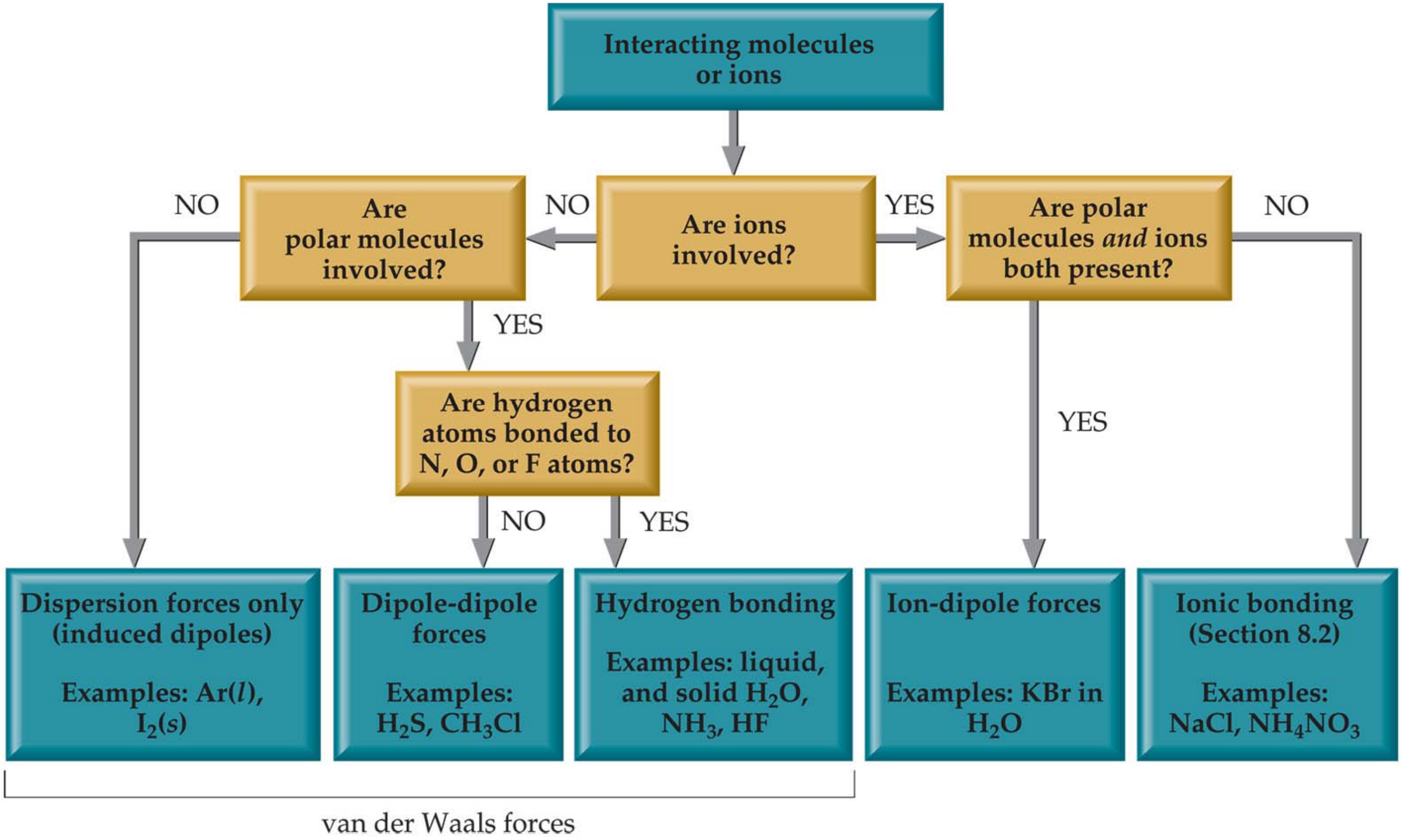


ethanol



water

Summarizing Intermolecular Forces



Interacting molecules or ions

Are ions involved?

NO → **Are polar molecules involved?**

- NO → **Dispersion forces only (induced dipoles)**
  Examples: Ar(l), I_2(s)
- YES → **Are hydrogen atoms bonded to N, O, or F atoms?**
  - NO → **Dipole-dipole forces**
    Examples: H_2S, CH_3Cl
  - YES → **Hydrogen bonding**
    Examples: liquid, and solid H_2O, NH_3, HF

YES → **Are polar molecules *and* ions both present?**

- YES → **Ion-dipole forces**
  Examples: KBr in H_2O
- NO → **Ionic bonding (Section 8.2)**
  Examples: NaCl, NH_4NO_3

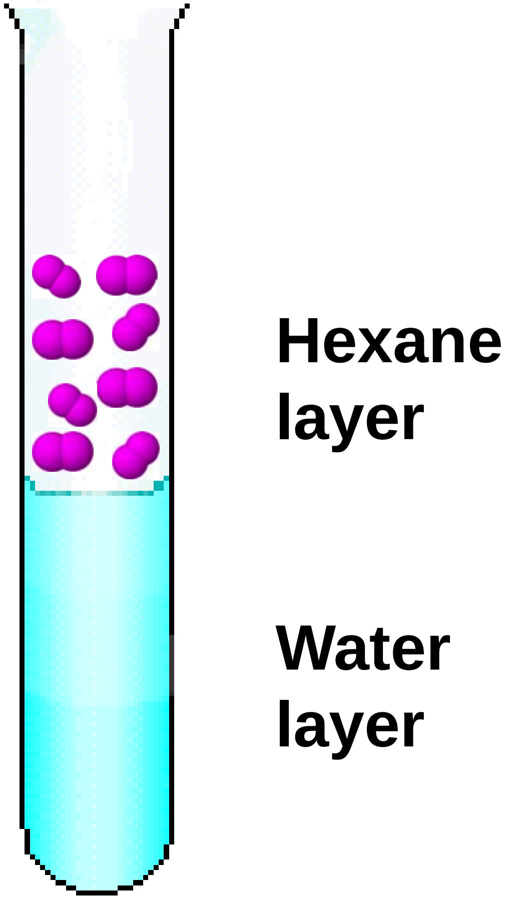
van der Waals forces

Intermolecular forces Intermolecular forces using I_2

Even though there are these different forces of attraction between particles, there are still preferences.

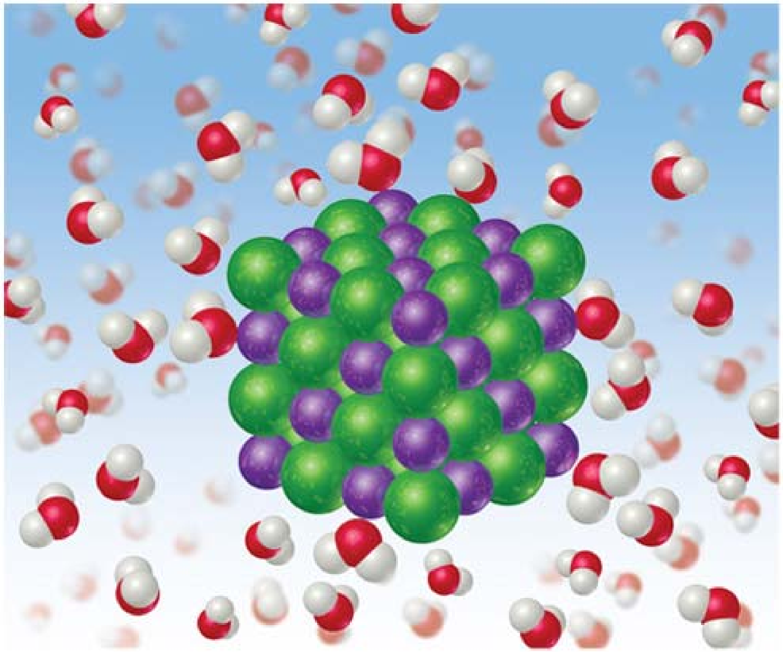
When given the proper conditions, iodine prefers a non-polar solvent:

Like dissolves like



Intermolecular Forces
Why does a substance dissolve?

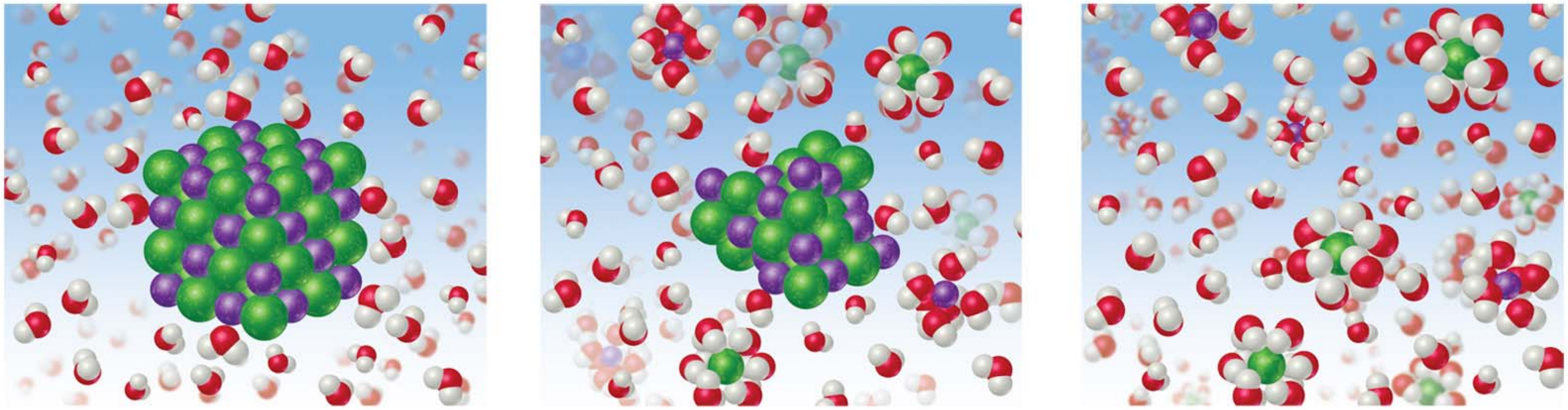
The intermolecular forces between solute and solvent particles must be strong enough to compete with those between solute particles and those between solvent particles.



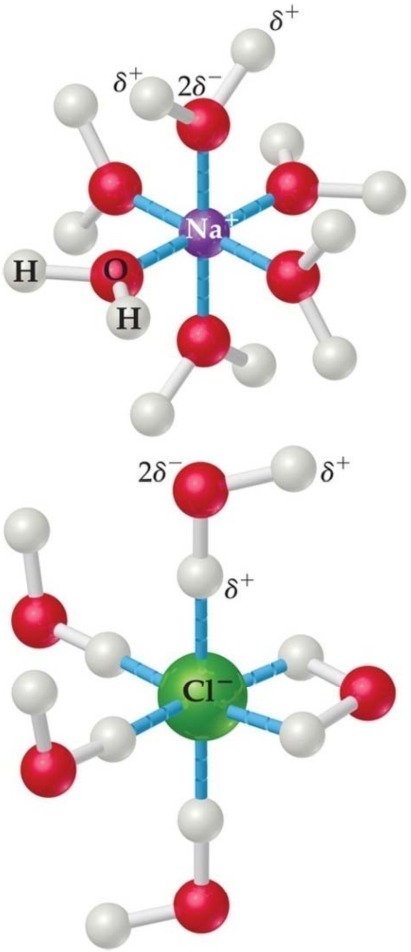
How Does a Solution Form?

In this example, we have an ionic solid, NaCl, and a polar solvent, H_2O.

The solution forms because the solvent pulls solute particles apart and surrounds, or **solvates**, them. In water this is called **hydration**.



How Does a Solution Form



If an ionic salt is soluble in water, it is because the ion-dipole interactions are strong enough to overcome the lattice energy of the salt crystal.

Factors Affecting Solubility

- Chemists use the axiom "like dissolves like":
  - Polar and ionic substances tend to dissolve in polar solvents.
  - Nonpolar substances tend to dissolve in nonpolar solvents.

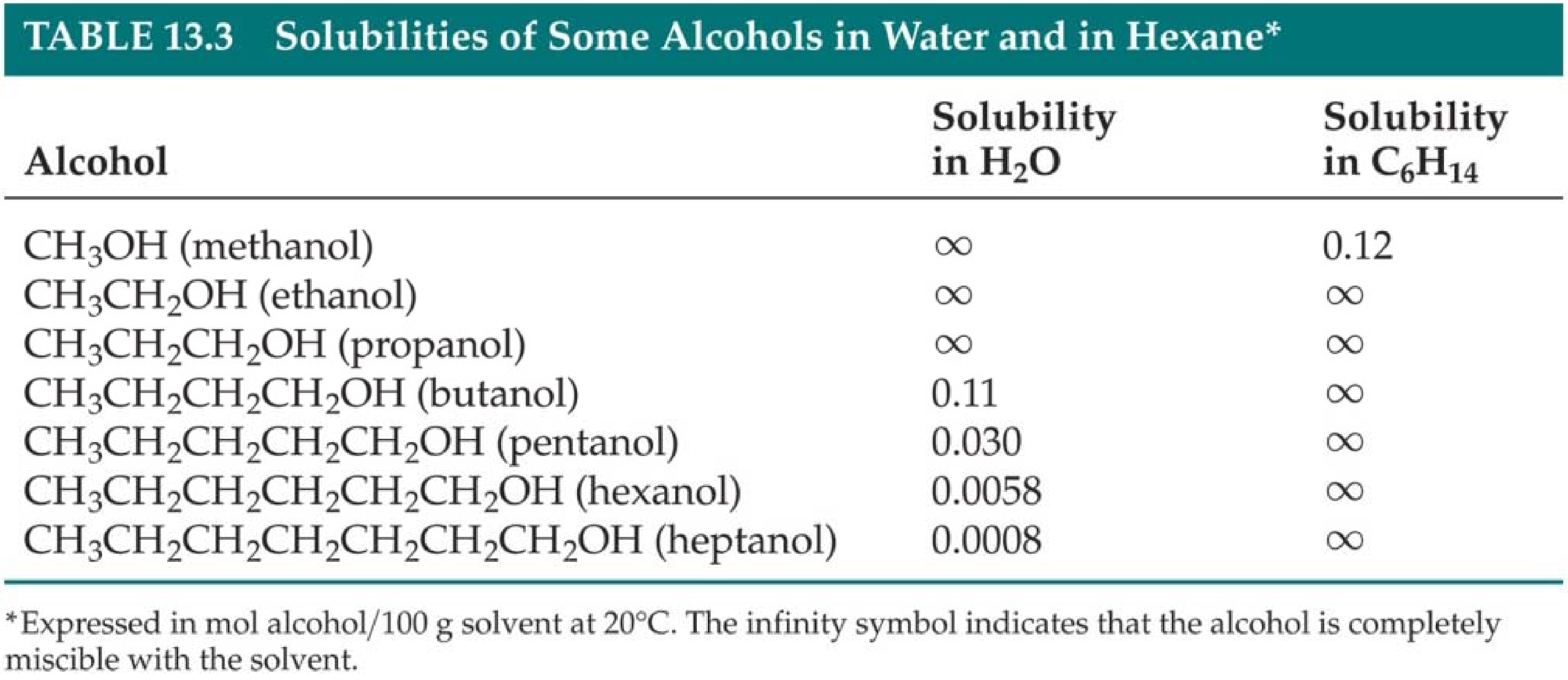


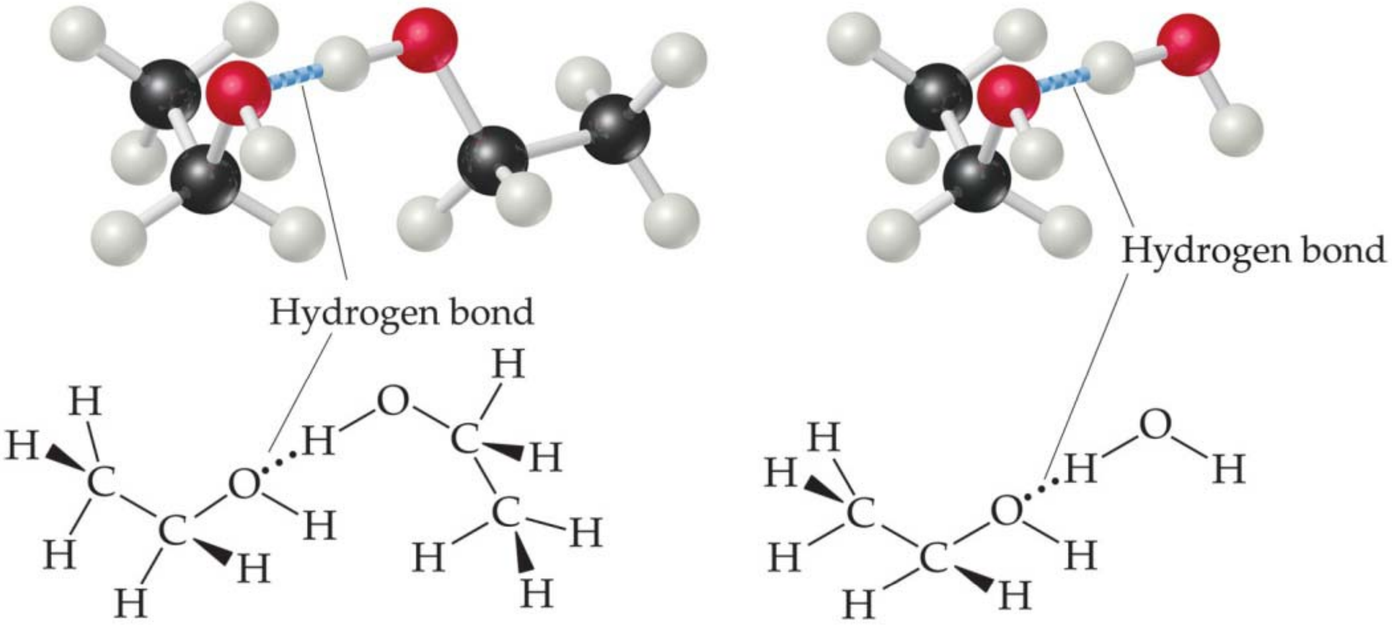
TABLE 13.3 Solubilities of Some Alcohols in Water and in Hexane*

Alcohol	Solubility in H_2O	Solubility in C_6H_{14}
CH_3OH (methanol)	∞	0.12
CH_3CH_2OH (ethanol)	∞	∞
$CH_3CH_2CH_2OH$ (propanol)	∞	∞
$CH_3CH_2CH_2CH_2OH$ (butanol)	0.11	∞
$CH_3CH_2CH_2CH_2CH_2OH$ (pentanol)	0.030	∞
$CH_3CH_2CH_2CH_2CH_2CH_2OH$ (hexanol)	0.0058	∞
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$ (heptanol)	0.0008	∞

*Expressed in mol alcohol/100 g solvent at 20°C. The infinity symbol indicates that the alcohol is completely miscible with the solvent.

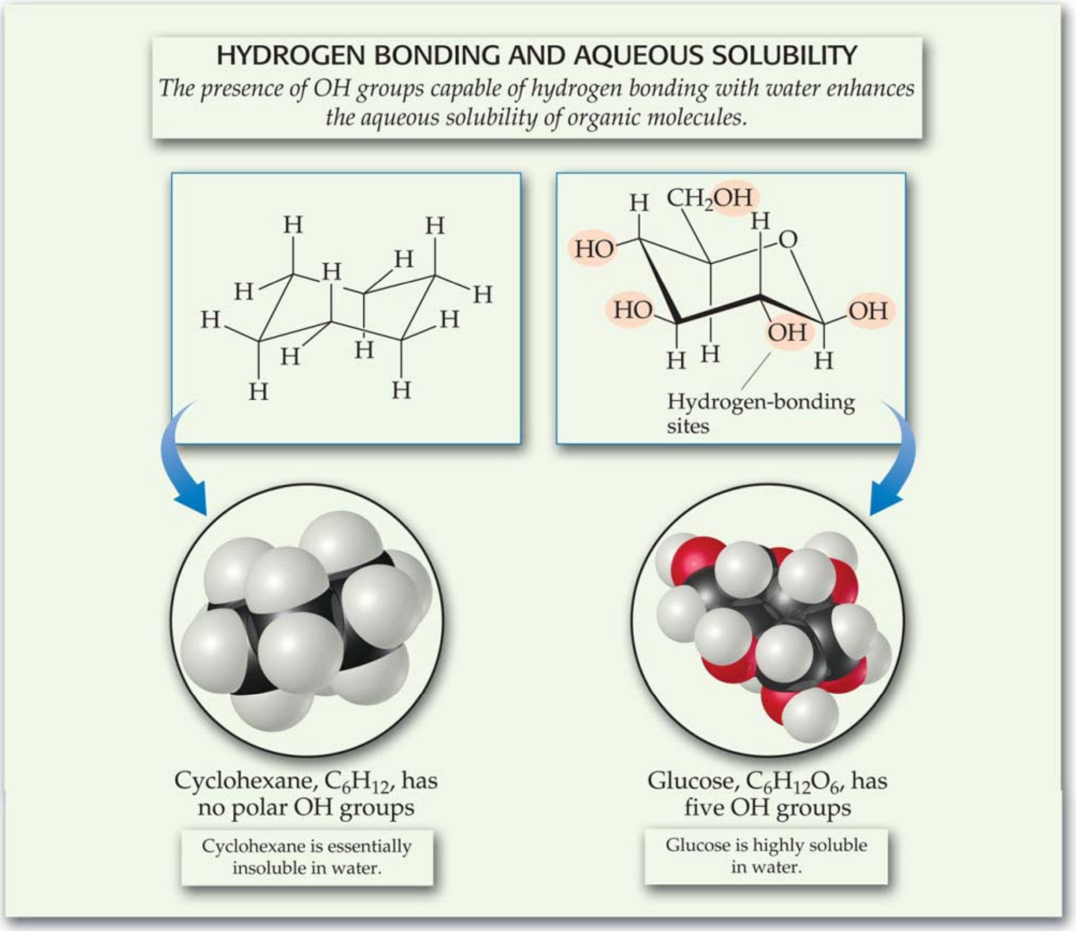
Factors Affecting Solubility

The more similar the intermolecular attractions, the more likely one substance is to be soluble in another.



Factors Affecting Solubility

Glucose (which has hydrogen bonding) is very soluble in water, while cyclohexane (which only has dispersion forces) is not.



HYDROGEN BONDING AND AQUEOUS SOLUBILITY

The presence of OH groups capable of hydrogen bonding with water enhances the aqueous solubility of organic molecules.

Cyclohexane, C_6H_{12}, has no polar OH groups

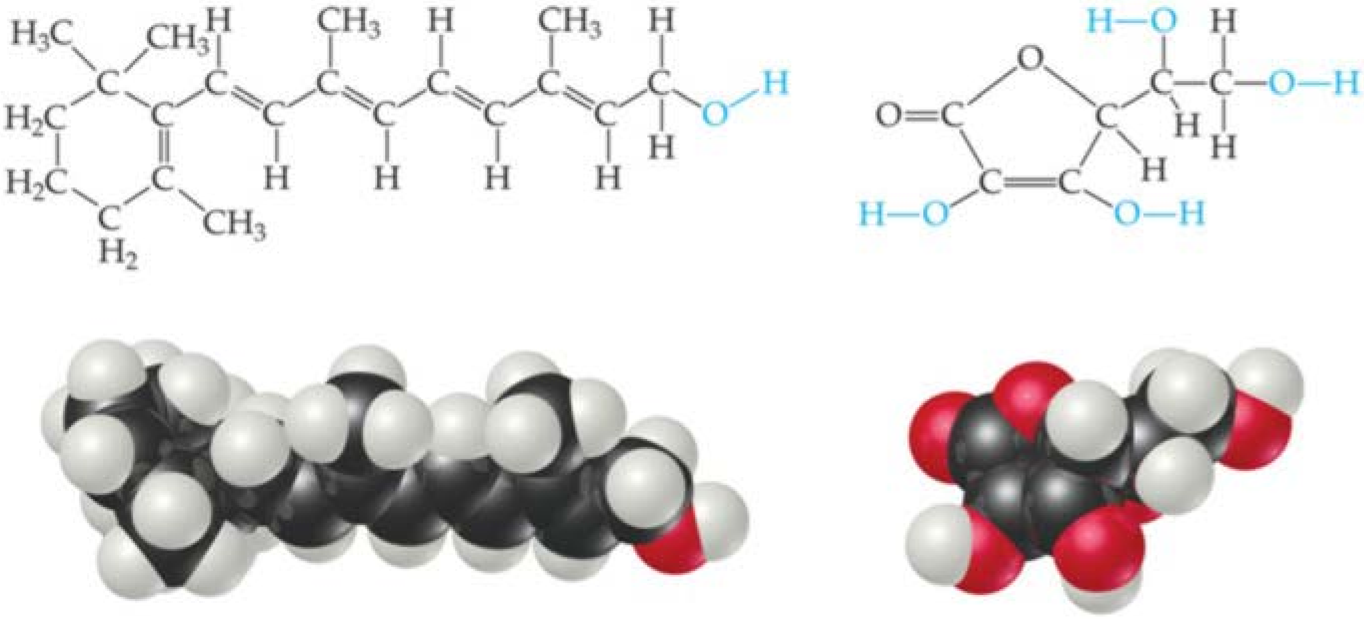
Cyclohexane is essentially insoluble in water.

Glucose, $C_6H_{12}O_6$, has five OH groups

Glucose is highly soluble in water.

Factors Affecting Solubility

- Vitamin A is soluble in nonpolar compounds (like fats).
- Vitamin C is soluble in water.



Vitamin A

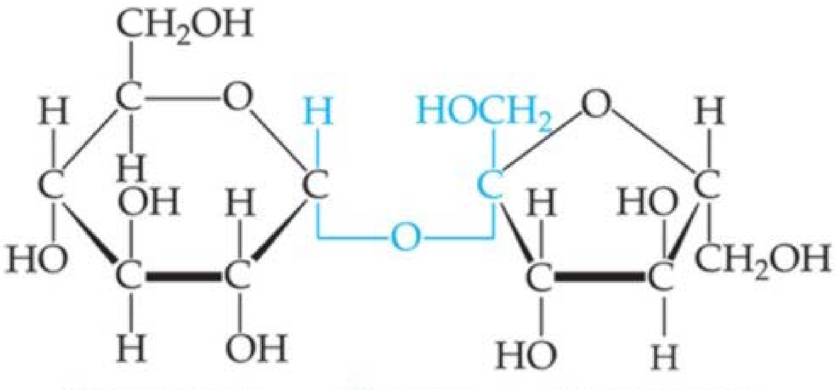
(a)

Vitamin C

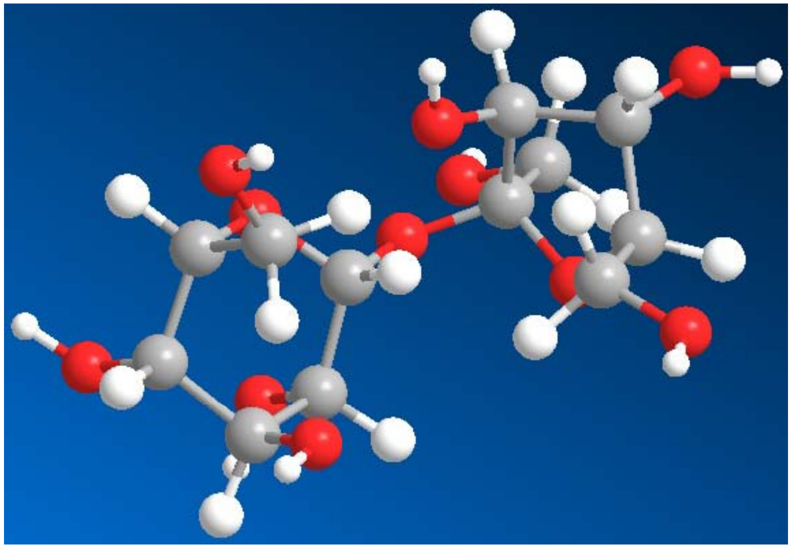
(b)

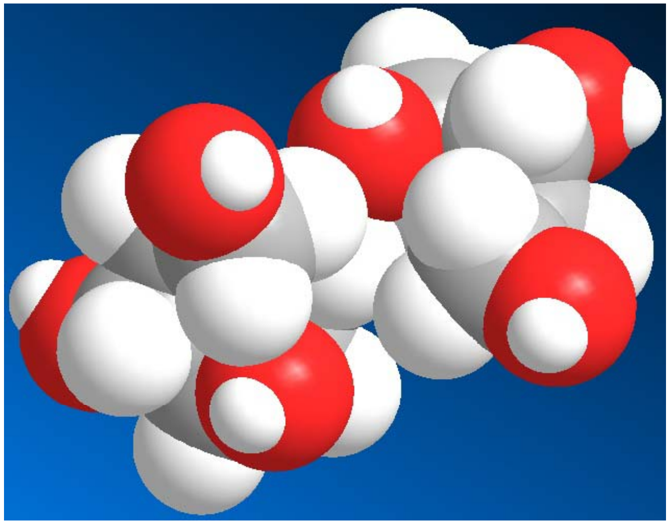
Intermolecular Forces

Why does a substance dissolve?



Glucose unit Sucrose Fructose unit

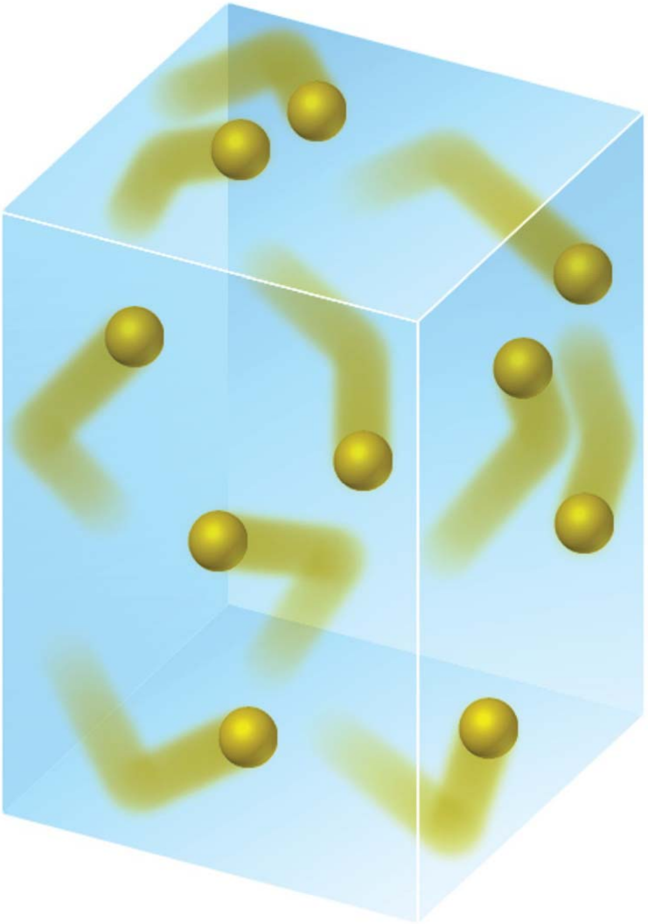




States of Matter

How does a solid, liquid, and gas differ at the atomic-molecular level?

Kinetic-Molecular Theory



This is a model that aids in our understanding of what happens to particles as environmental conditions change.

Kinetic-Molecular Theory

- History:
  - 1856, August Krönig created a simple gas-kinetic model, which only considered the translational motion of the particles.
  - 1857 Rudolf Clausius developed a more sophisticated version of the theory which included translational, rotational and vibrational molecular motions.
  - 1859, James Clerk Maxwell formulated the Maxwell distribution of molecular velocities. In an 1875 article, Maxwell stated: “we are told that an 'atom' is a material point, invested and surrounded by 'potential forces' and that when 'flying molecules' strike against a solid body in constant succession it causes what is called pressure of air and other gases.”
  - More modern developments are based on the Boltzman equation, developed by Ludwig Boltzman.

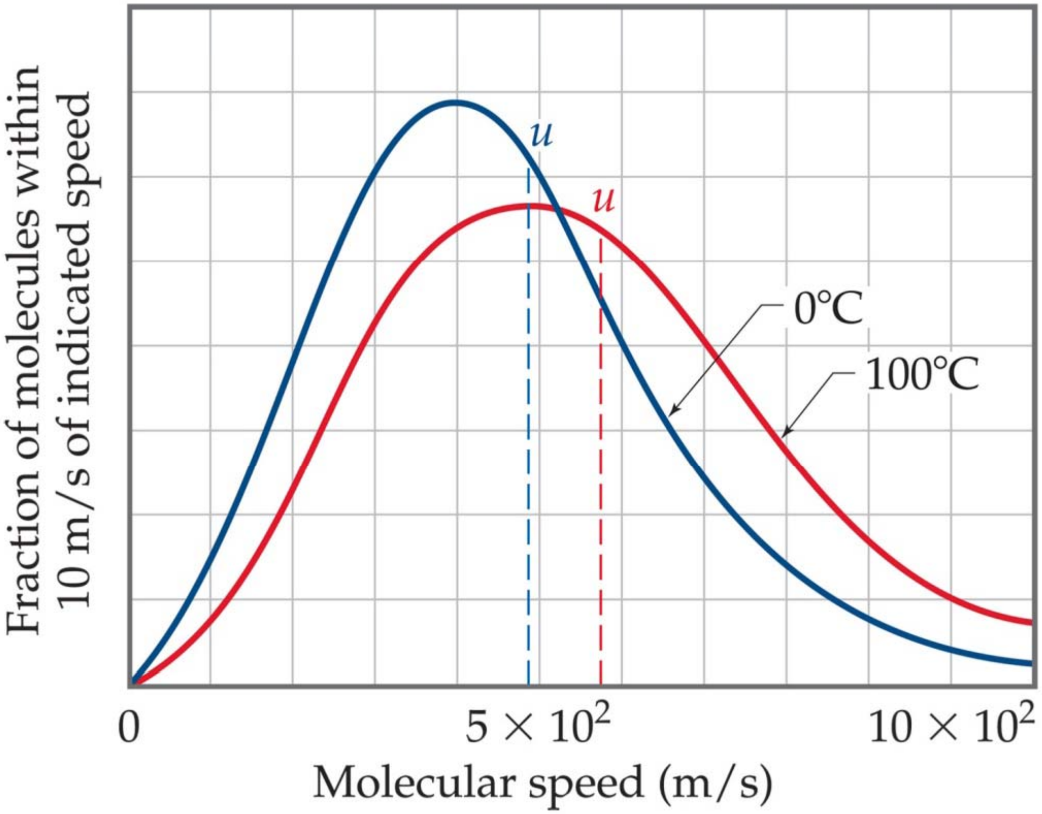
Rudolf Clausius

James Clerk Maxwell

Ludwig Boltzman

Kinetic-Molecular Theory

According to Boltzmann, the average kinetic energy of molecules is proportional to the absolute temperature.

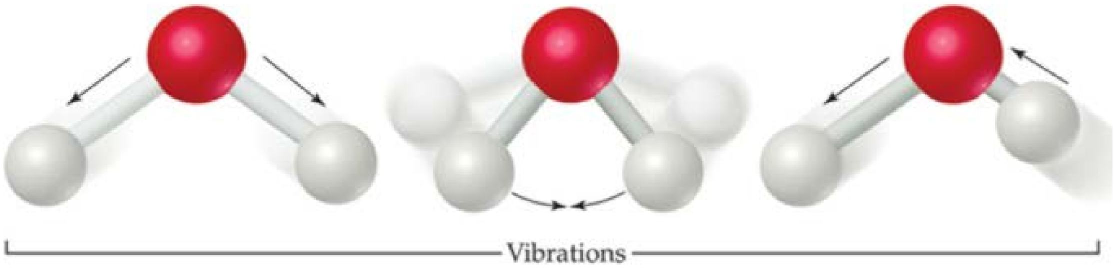


An animation of the Maxwell-Boltzman distribution for molecular speeds in a gas can be found at http://www.chm.davidson.edu/chemistryapplets/KineticMolecularTheory/Maxwell.html

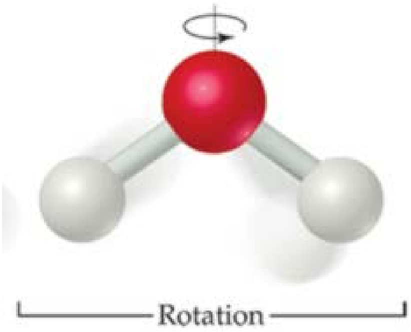
Molecular Motion

- Molecules exhibit several types of motion:

Vibrational: Periodic motion of atoms within a molecule.



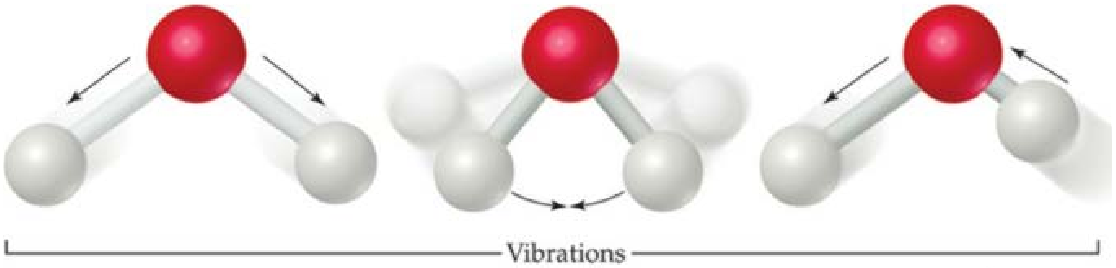
Rotational: Rotation of the molecule on about an axis or rotation about σ bonds.



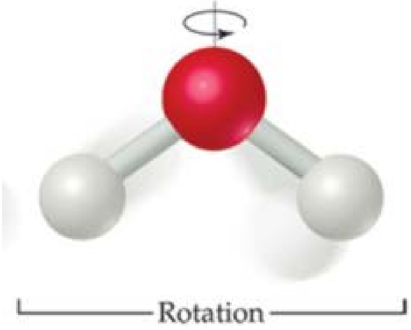
Translational: Movement of the entire molecule from one place to another.

Molecular Motion

- At 0 K, all substances are solids.
  - Molecules have vibrational motion.
  - Their energy is called zero-point energy.



- As temperature increases
  - Molecules exhibit rotational motion.

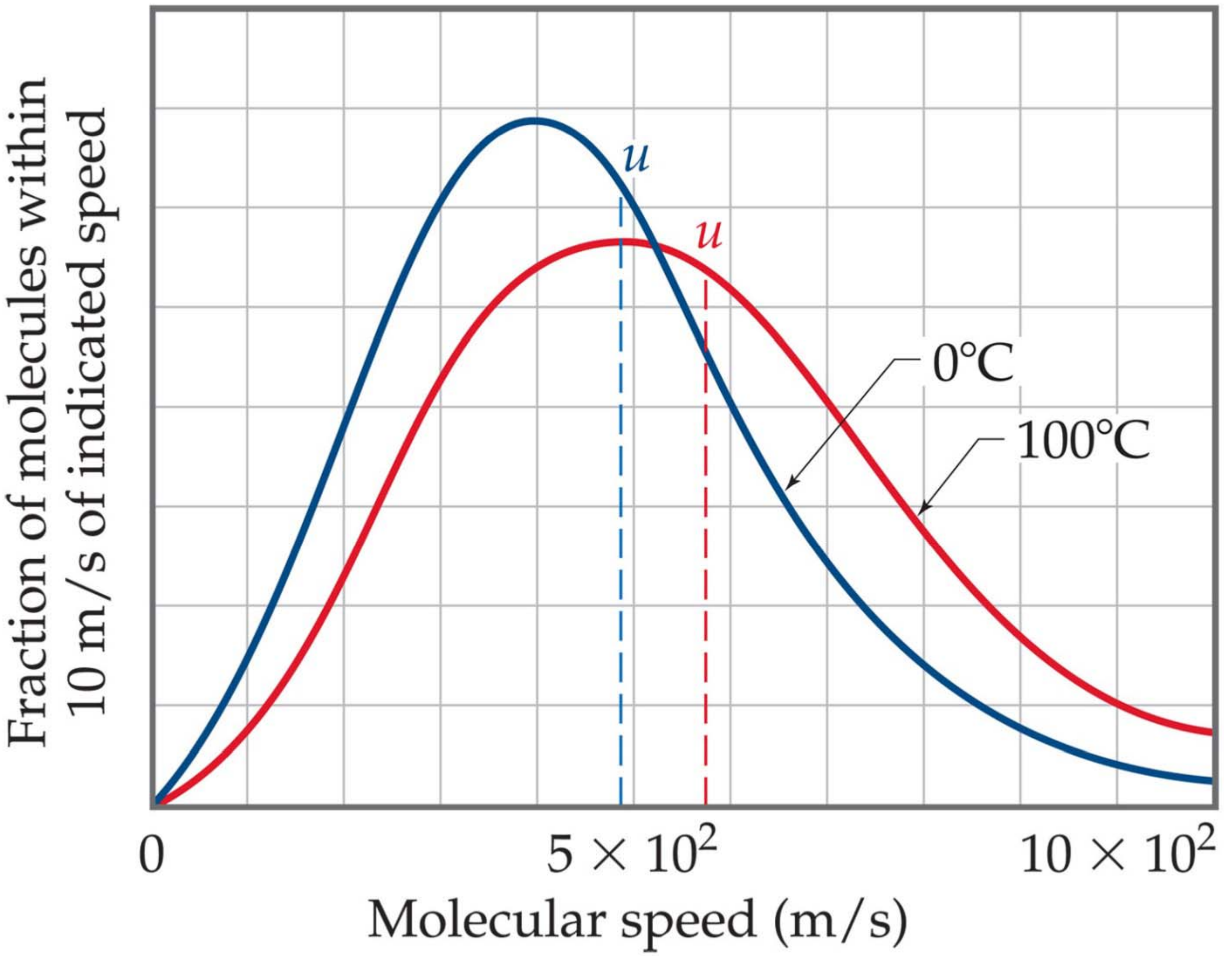


- Eventually, the solid melts
  - Molecules exhibit translational motion.

Kinetic-Molecular Theory

- **As applied to gases**
  - The gas consists of very small particles, widely separated in space.
  - Gas particles are in constant, rapid, random motion
  - Gas particles constantly collide with each other and with the walls of the container.
    - Collisions with objects or the walls of the container is called **pressure**.
  - Collisions of gas particles with each other and the walls of the container are perfectly elastic.
    - Energy can be transferred between the particles but no energy is lost.
  - The interactions among gas particles are negligible. They exert no forces of attraction or repulsion on one another.
  - The total volume of the individual gas particles is negligible compared to the volume of the container.
  - The average kinetic energy of the gas particles depends only on the absolute temperature of the system

The effect of temperature on molecular speeds



Where μ is the root-mean-square (rms) speed

GASES

Characteristics of Gases

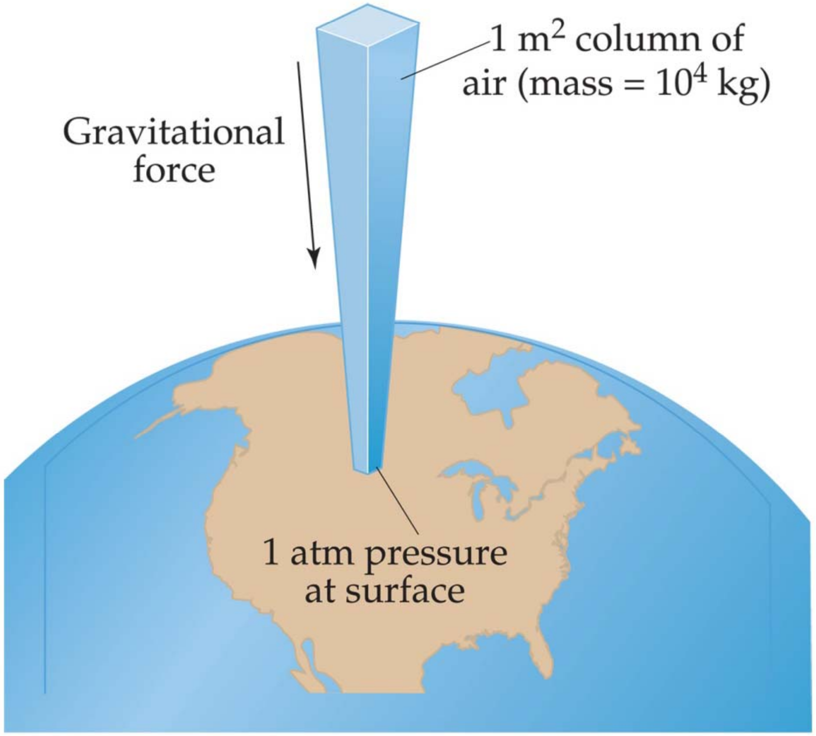
- Particles are far apart in space.
- Expand to fill their containers.
- Are highly compressible.
- Have extremely low densities.

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.

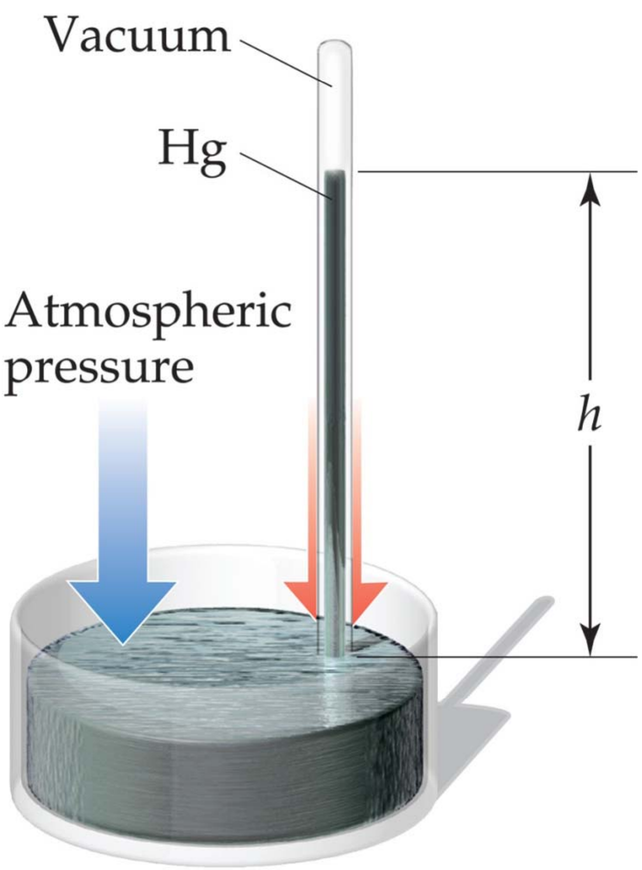


Units of Pressure

- Pascals
  - 1 Pa = 1 N/m^2
- Bar
  - 1 bar = 10^5 Pa = 100 kPa

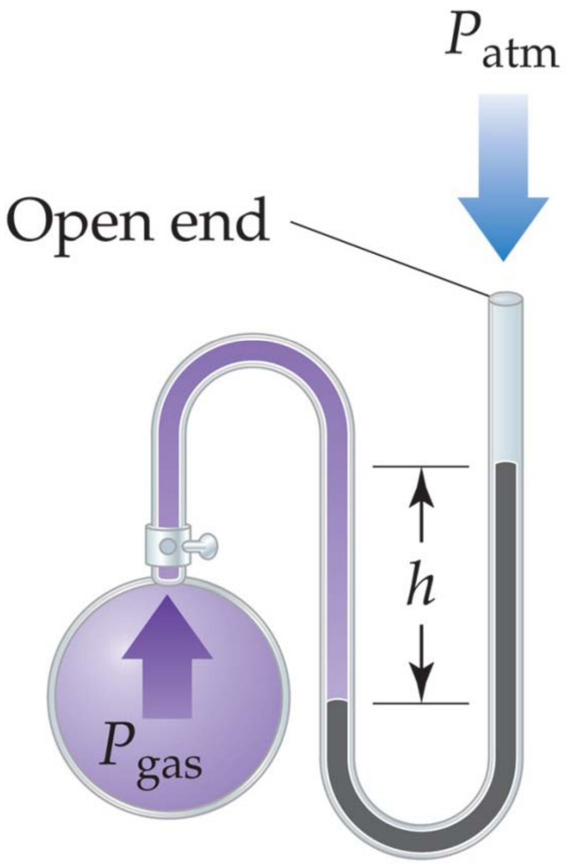
Units of Pressure

- 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



Atmospheric pressure at sea level:
1.00 atm = 760 torr

Manometer



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

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

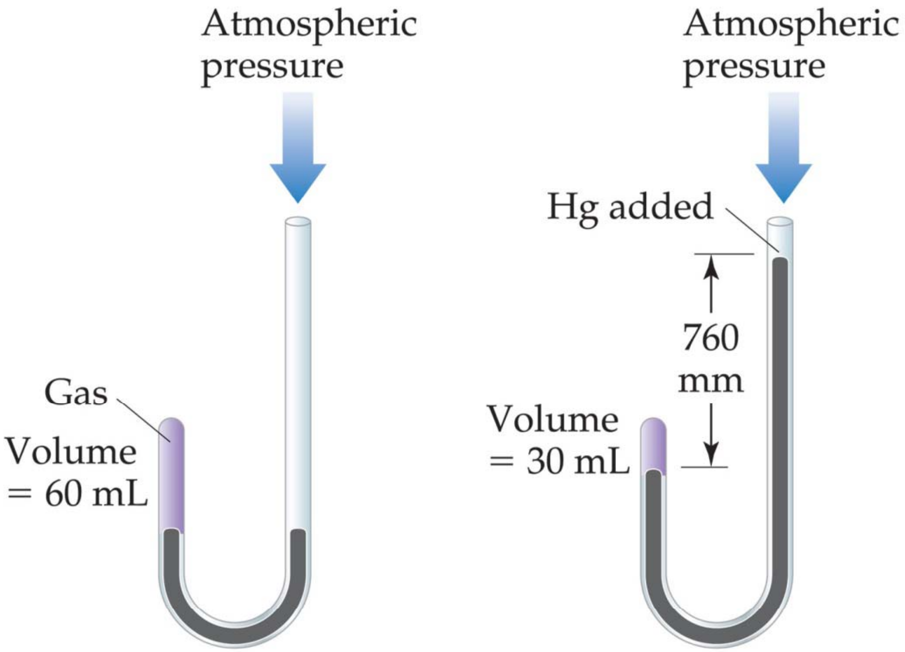
- Normal atmospheric pressure at sea level:
  - 1.00 atm
  - 760 torr (760 mm Hg)
  - 101.325 kPa

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

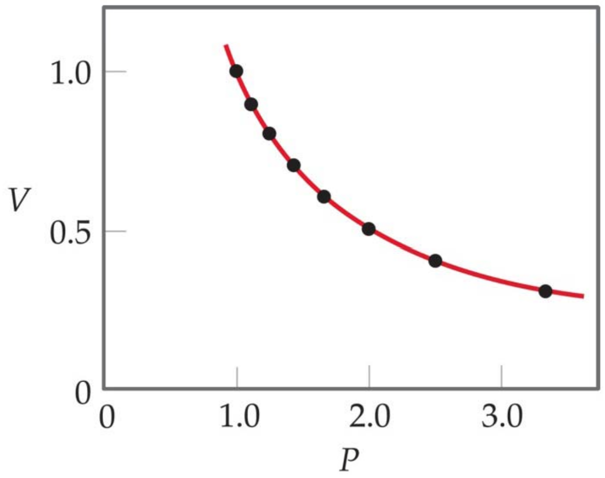
Boyle’s Law

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

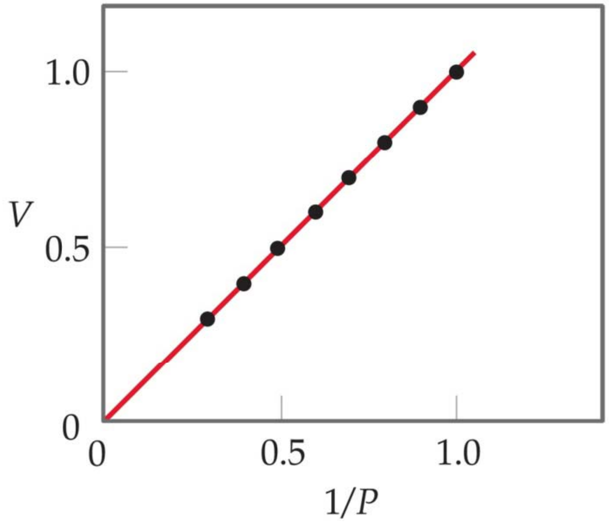


A plot of *V* versus *P* results in a curve.

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

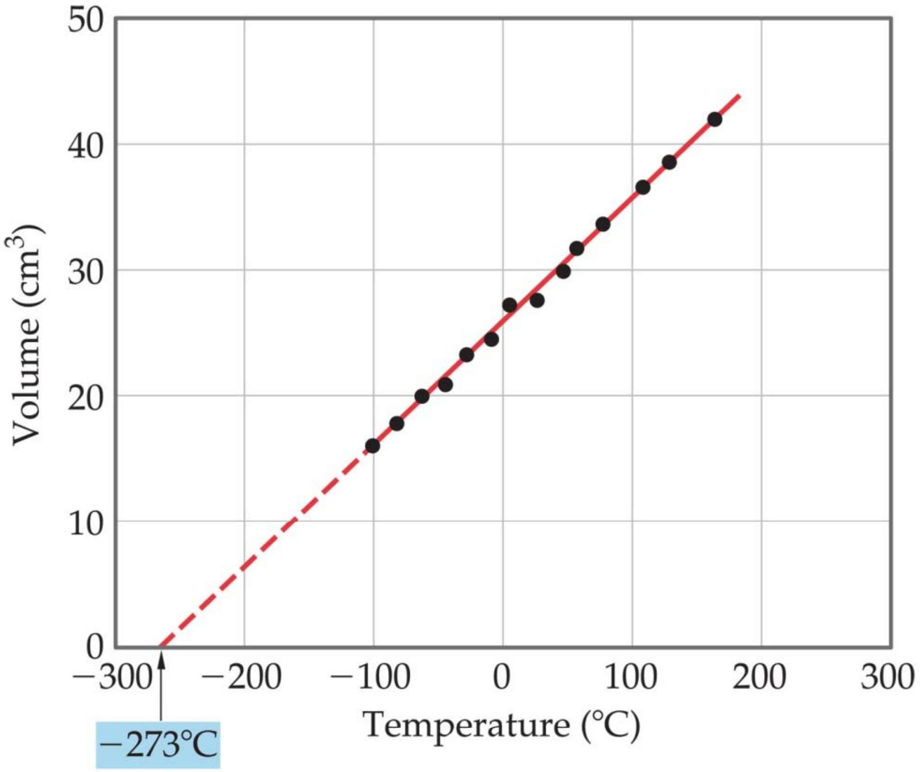
Jacques Charles, 1787

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

The Combined Gas Law

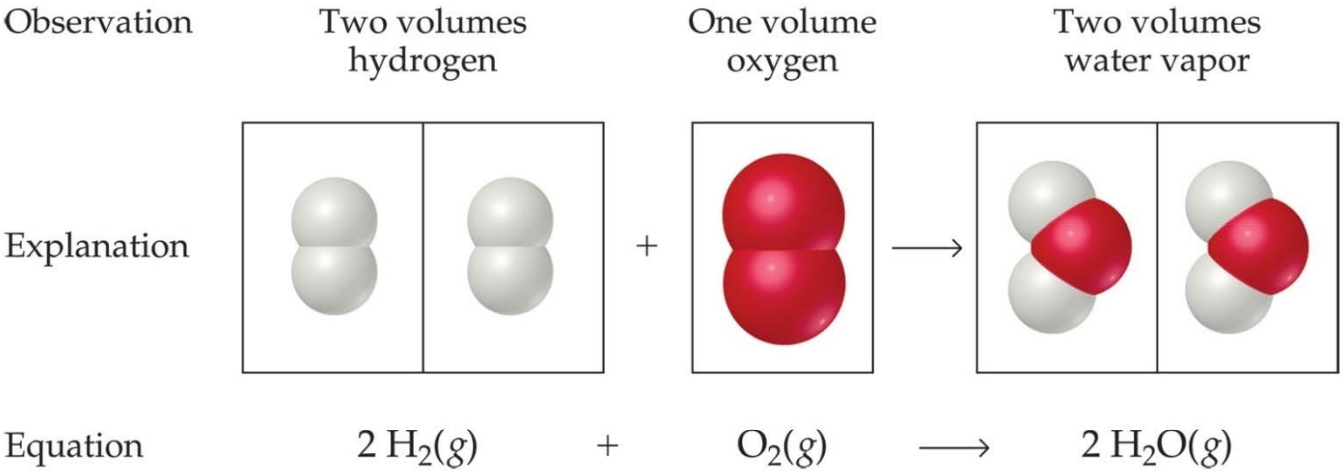
- Boyle’s and Charles’ Laws can be combined in a single equation

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

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 $V = kn$



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

Ideal-Gas Equation

- So far we've seen that

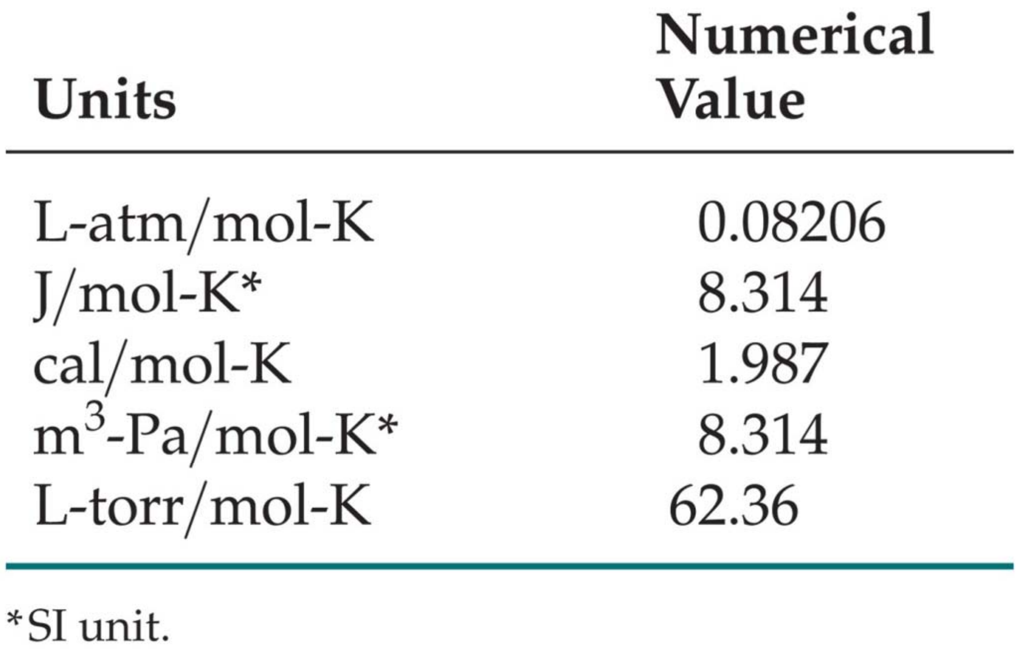
$V \propto 1/P$ (Boyle's law)
$V \propto T$ (Charles's law)
$V \propto n$ (Avogadro's law)

- Combining these, we get

$$V \propto \frac{nT}{P}$$

Ideal-Gas Equation

The constant of proportionality is known as *R*, the gas constant.



Units	Numerical Value
L-atm/mol-K	0.08206
J/mol-K*	8.314
cal/mol-K	1.987
m^3-Pa/mol-K*	8.314
L-torr/mol-K	62.36

*SI unit.

Ideal-Gas Equation

The relationship

$$V \propto \frac{nT}{P}$$

then becomes

$$V = R\,\frac{nT}{P}$$

or

$$PV = nRT$$

Ideal-Gas Equation: Densities of Gases

If we divide both sides of the ideal-gas equation by *V* and by *RT*, we get

$$\frac{n}{V} = \frac{P}{RT}$$

Ideal-Gas Equation: Densities of Gases

- We know that
  - moles × molecular mass = mass

$$n \times M = m \quad \text{or} \quad n = \frac{m}{M}$$

- So substitute for n *and rearrange the equation to get*

$$\frac{m}{V} = \frac{PM}{RT}$$

Densities of Gases

- Mass ÷ volume = density
- So, $d = \frac{m}{V} = \frac{P\mathcal{M}}{RT}$
- Note: One only needs to know the molecular mass, the pressure, and the temperature to calculate the density of a gas.

Molecular Mass

The final equation is:

$$d = \frac{PM}{RT}$$

We can rearrange the density equation to solve for the molecular mass of a gas:

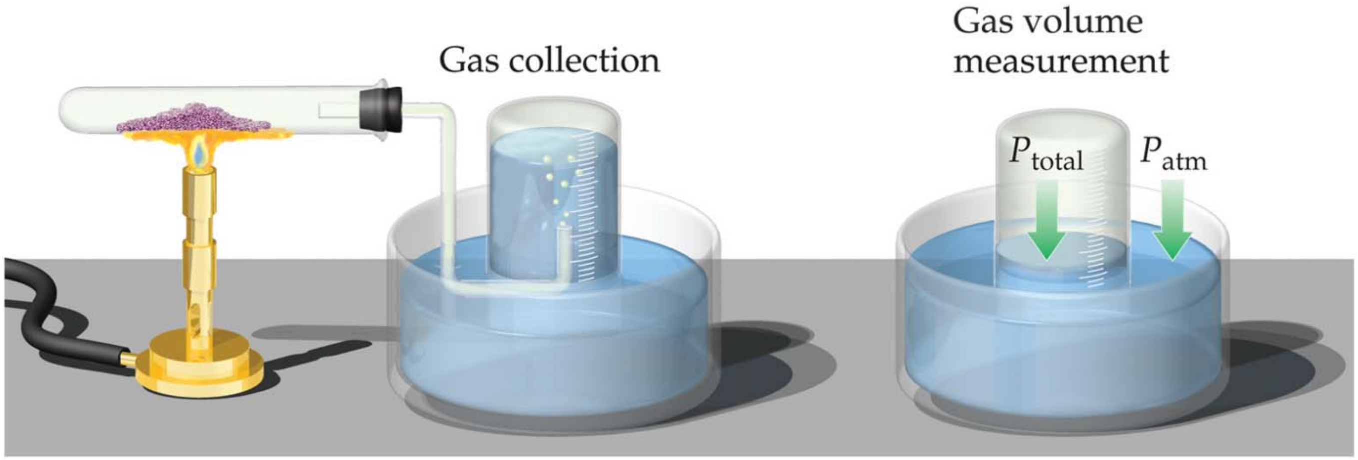
$$M = \frac{dRT}{P}$$

Dalton's Law of Partial Pressures

- John Dalton, 1801
- The total pressure of a mixture of gases equals the sum of the pressures that each would exert if it were present alone.

$$P_{\text{total}} = P_1 + P_2 + P_3 + \ldots$$

Partial Pressures



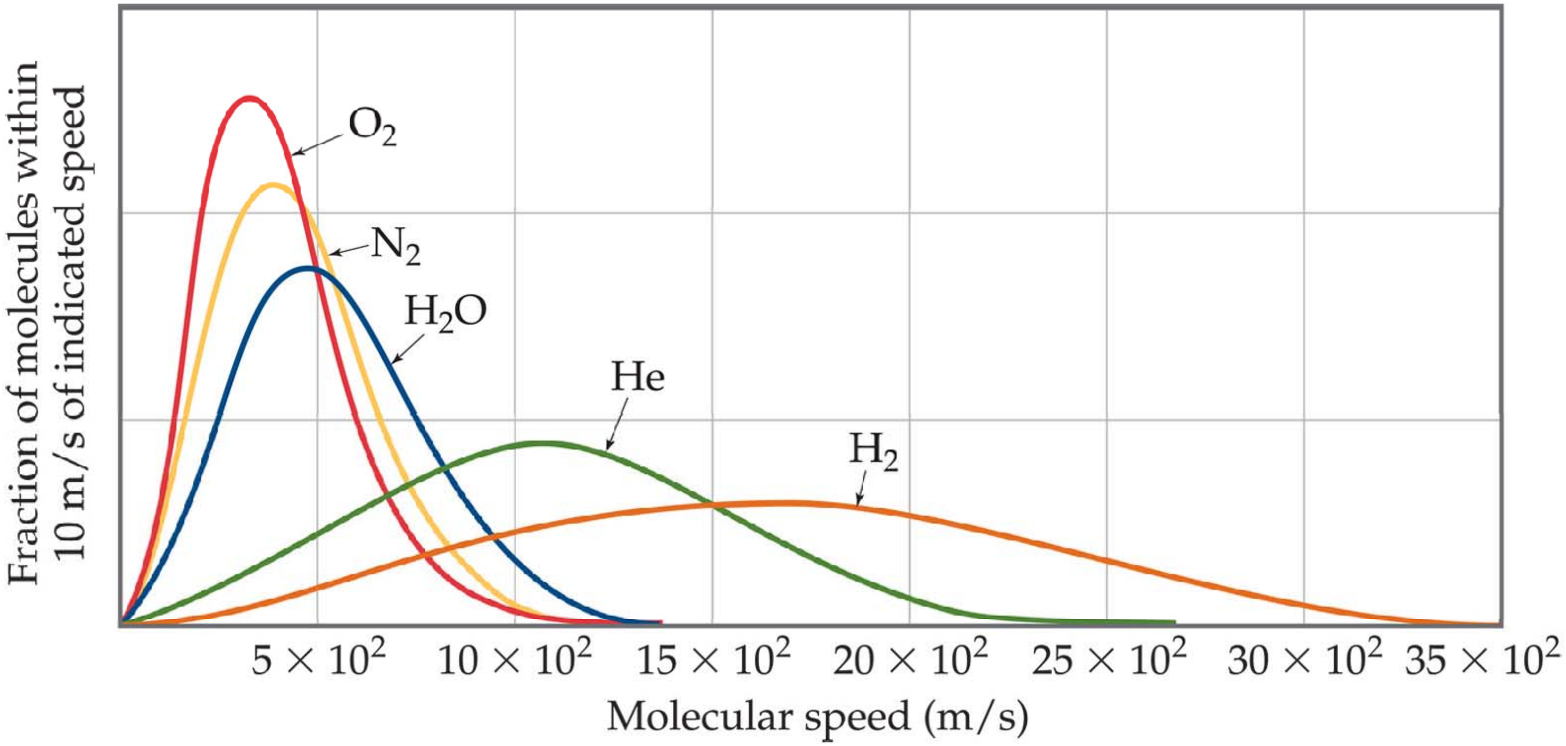
- When one collects a gas over water, there is water vapor mixed in with the gas.
- To find only the pressure of the desired gas, one must subtract the vapor pressure of water from the total pressure.

Effusion and Diffusion

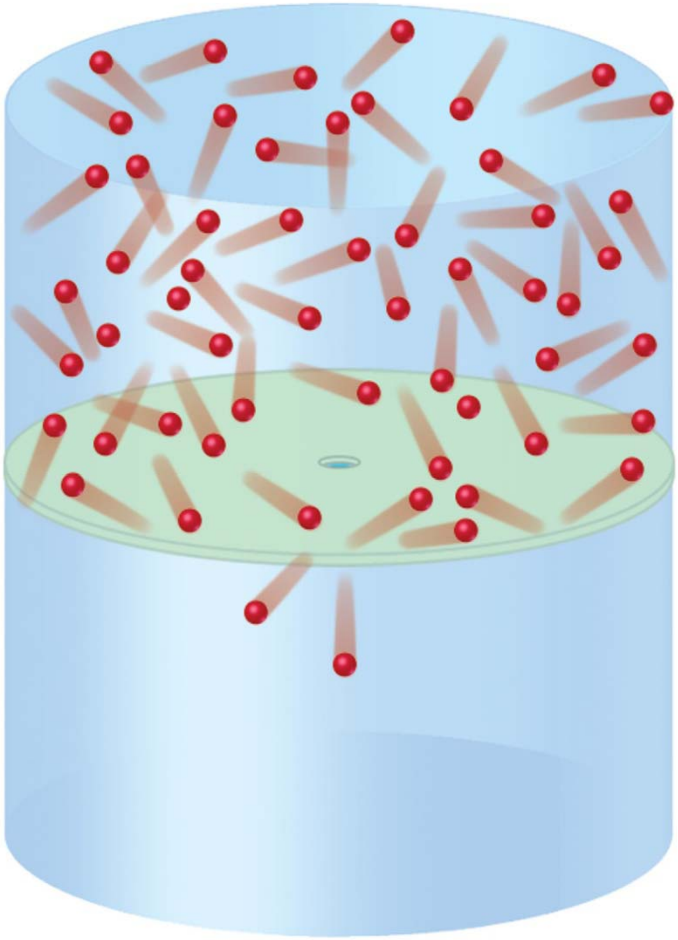
The rms speed of a molecule is related to its molar mass

$$\mu = \sqrt{\frac{3RT}{M}}$$

μ = root-mean-speed
R = Ideal gas constant
T = absolute temperature
M = molar mass



Effusion

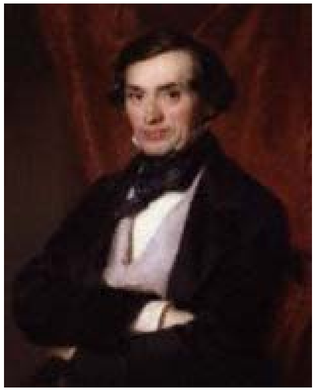


The escape of gas molecules through a tiny hole into an evacuated space.

Diffusion

The spread of one substance throughout a space or throughout a second substance.

Effusion and Diffusion



- Thomas Graham, 1831
- Graham's Law:

$$\frac{Rate_1}{Rate_2} = \sqrt{\frac{M_2}{M_1}}$$

- Where:

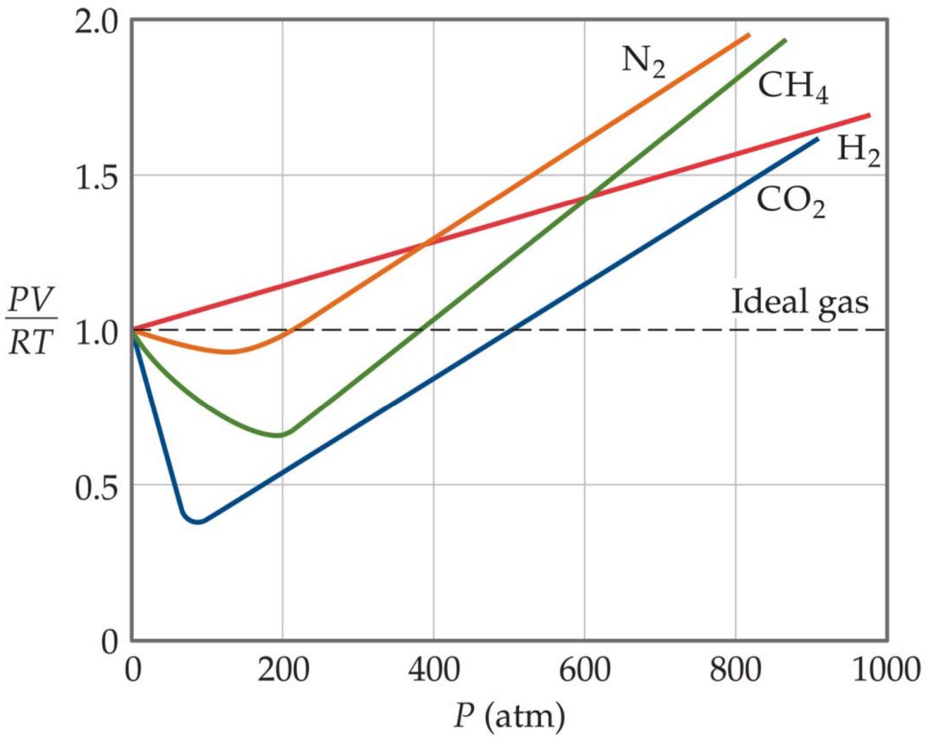
  $Rate_1$ is the rate of effusion of the first gas.

  $Rate_2$ is the rate of effusion for the second gas.

  M_1 is the molar mass of gas 1

  M_2 is the molar mass of gas 2.

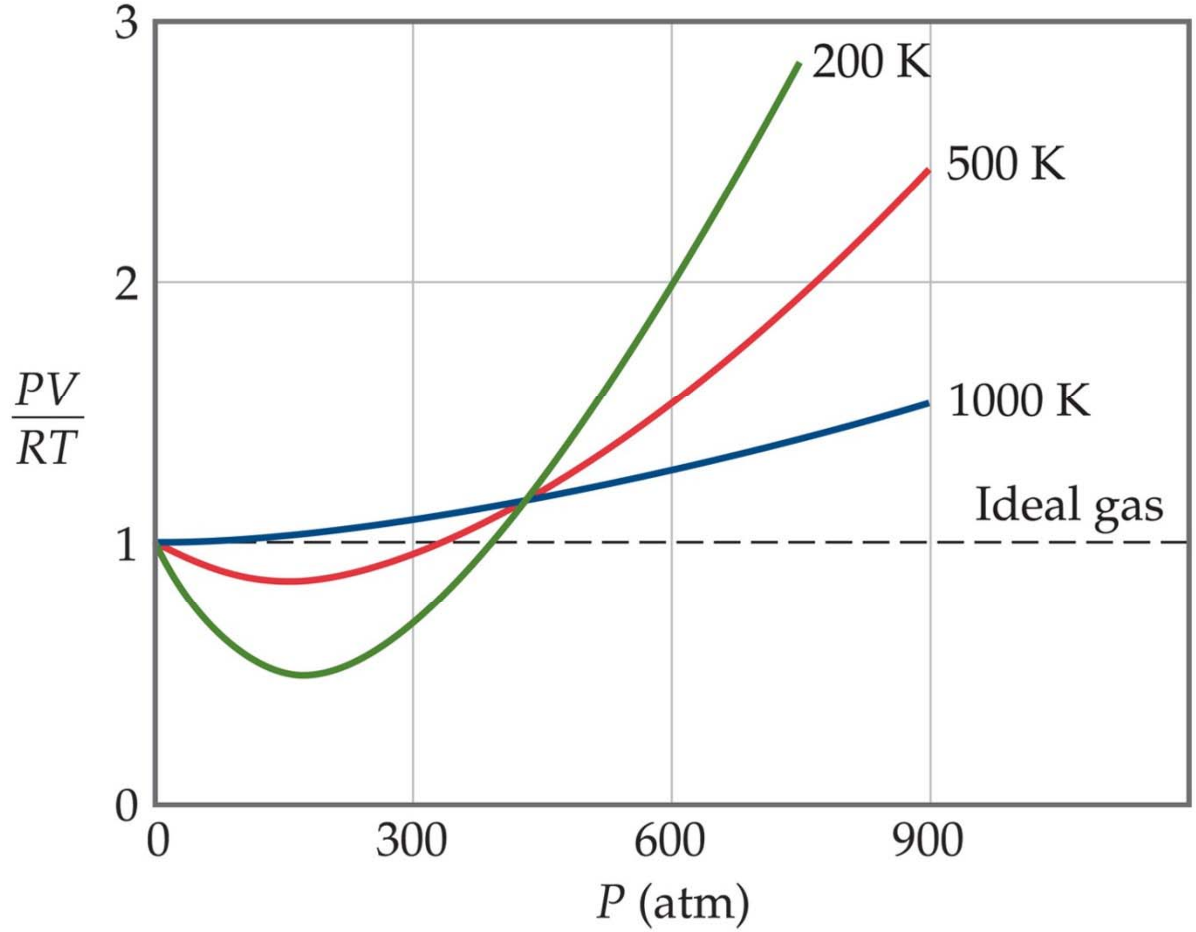
Real Gases



In the real world, the behavior of gases only conforms to the ideal-gas equation at ambient or relatively high temperatures and pressures less than 10 atm.

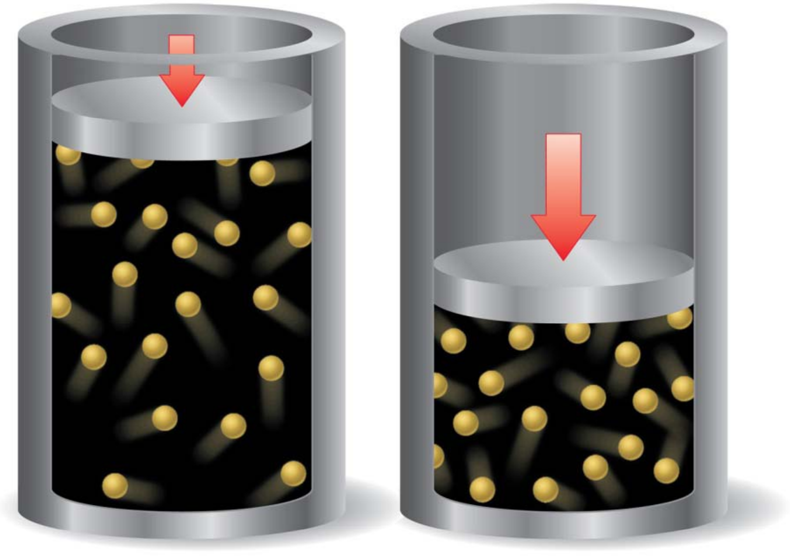
The effect of temperature and pressure on nitrogen gas

At low temperature, attractive forces between gas particles affects ideal behavior.

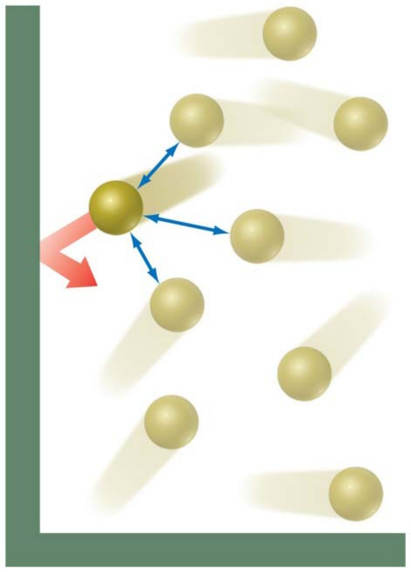


Deviations from Ideal Behavior

The assumptions made in the kinetic-molecular model break down at high pressure and/or low temperature.



At high pressure, the volume of the gas particles themselves become a significant factor in the volume of the gas



At high pressure, the attractive forces between the gas particles affects the pressure of the gas

Corrections for Nonideal Behavior

- The ideal-gas equation can be adjusted to take these deviations from ideal behavior into account.
- The corrected ideal-gas equation is known as the van der Waals equation.

The van der Waals Equation

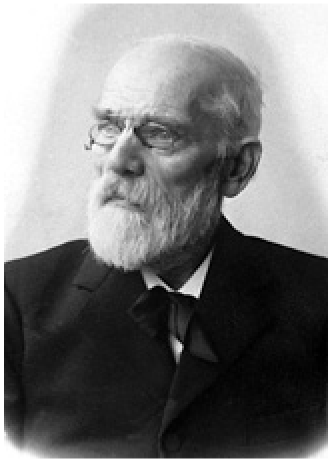
$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

Where:

a = correction for the attractive forces of gas molecules

b = the volume of a mole of gas molecules

Johannes Diderik van der Waals (1837-1923)



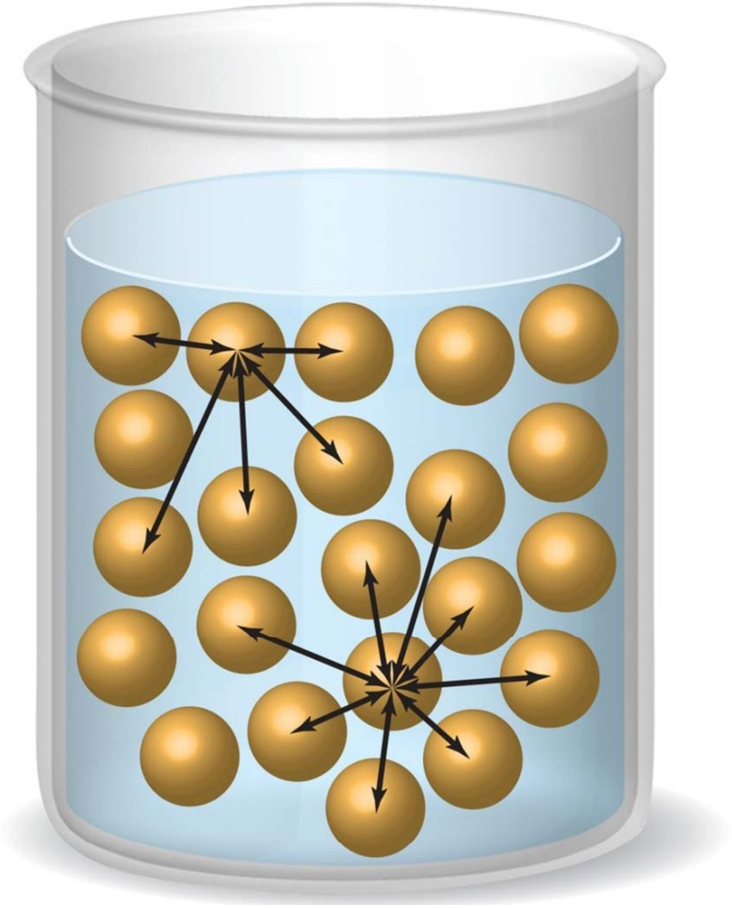
The van der Waals Equation

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

Substance	***a*** **(L^2-atm/mol^2)**	***b*** **(L/mol)**
He	0.0341	0.02370
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0510
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
Cl_2	6.49	0.0562
H_2O	5.46	0.0305
CH_4	2.25	0.0428
CO_2	3.59	0.0427
CCl_4	20.4	0.1383

Liquids

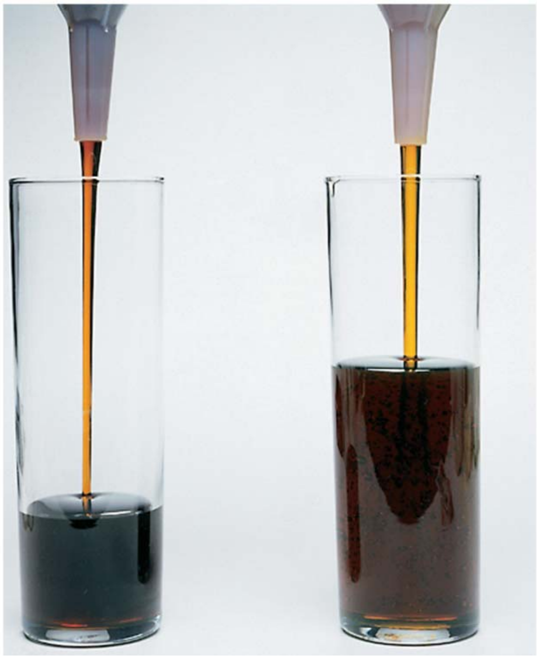
Intermolecular Forces Affect Many Physical Properties



The strength of the attractions between particles can greatly affect the properties of a substance or solution.

Viscosity

- Resistance of a liquid to flow is called viscosity.
- It is related to the ease with which molecules can move past each other.
- Viscosity:
  - Increases with stronger intermolecular forces
  - Increases with the size of the molecules
  - Decreases with increasing temperature.

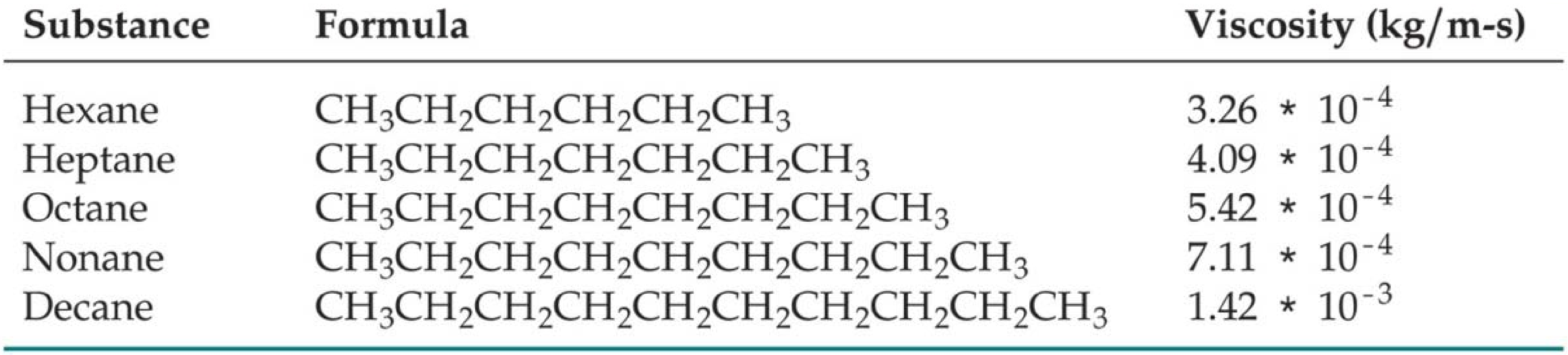


Two methods of measuring viscosity:

1. Timing the flow of a liquid through an opening.
2. A disk or drum type viscometer

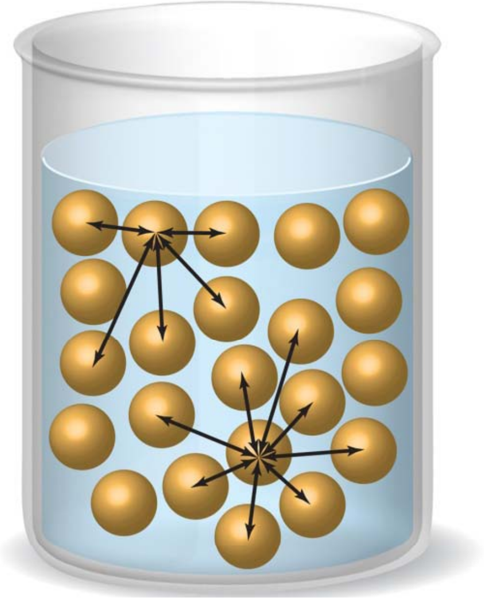
Viscosity

Viscosity of hydrocarbons at 20°C



Substance	**Formula**	**Viscosity (kg/m-s)**
Hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	$3.26 * 10^{-4}$
Heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	$4.09 * 10^{-4}$
Octane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	$5.42 * 10^{-4}$
Nonane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	$7.11 * 10^{-4}$
Decane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	$1.42 * 10^{-3}$

Surface Tension

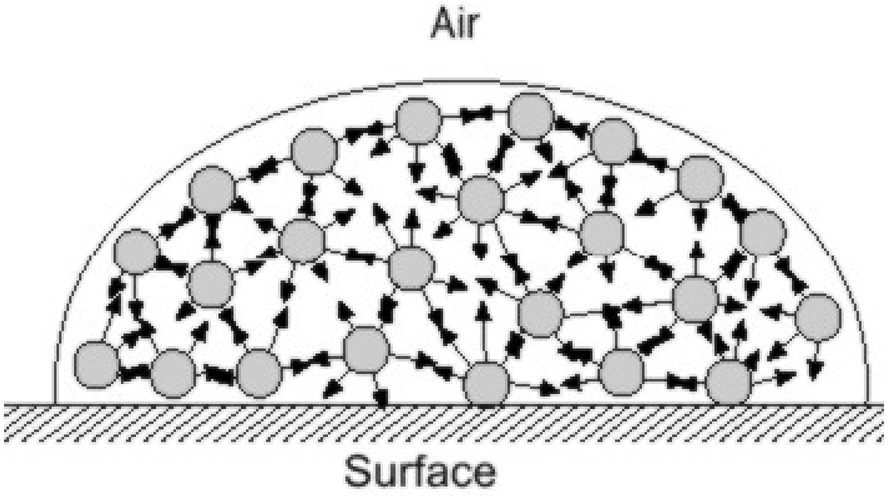


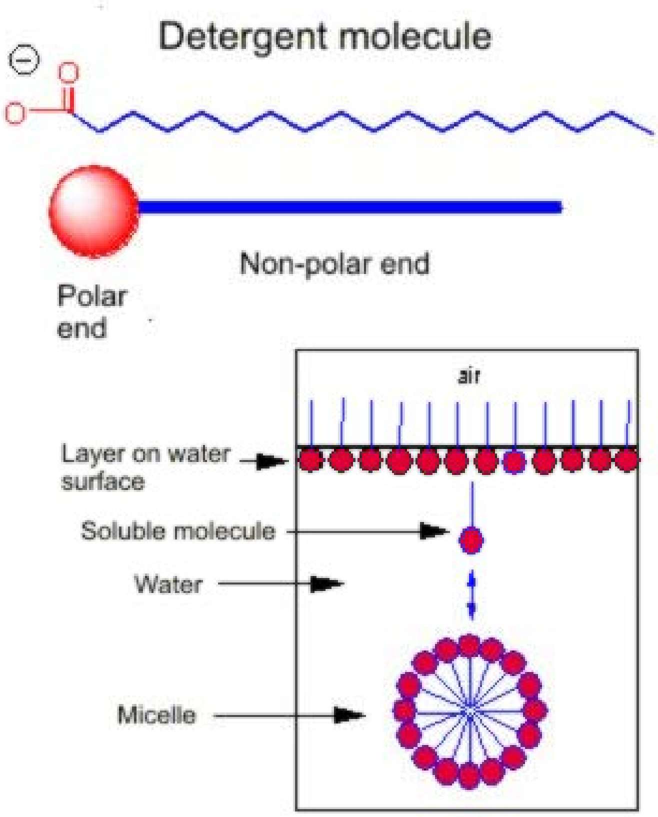
Surface tension results from the net inward force experienced by the molecules on the surface of a liquid.

Surface Tension
Drops of liquid on a coin

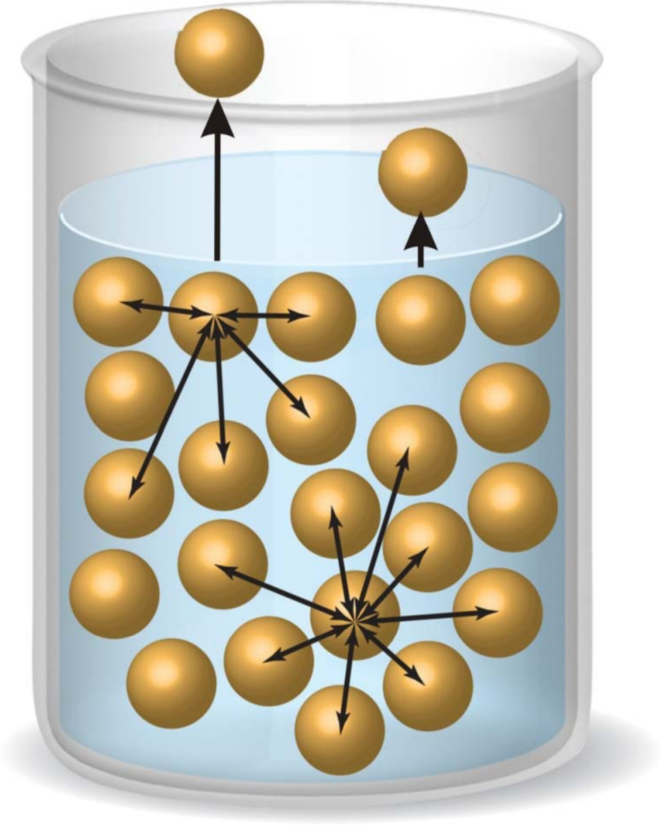
How many drops of liquid can you put on a coin?

Surface Tension
Drops of liquid on a coin





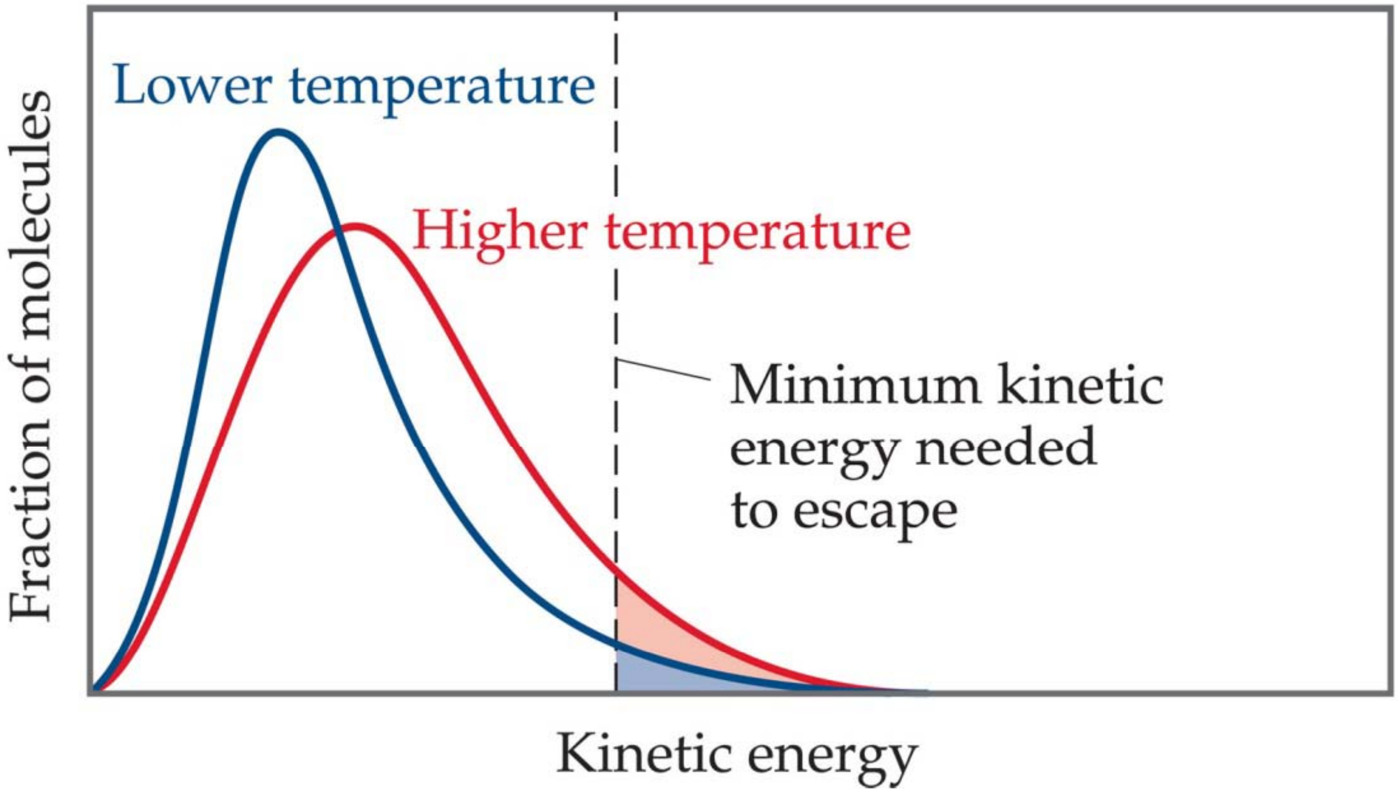
Vapor Pressure



Due to both temperature effects and energy transfers from collisions, molecules on the surface of a liquid are able to gain sufficient kinetic energy to escape into the atmosphere

Vapor Pressure

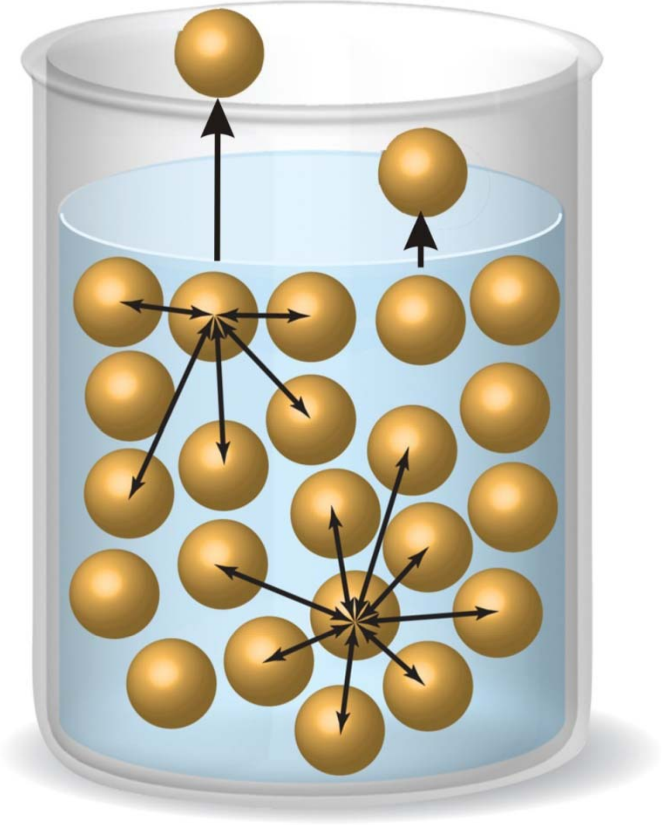
- At any temperature, some molecules in a liquid have enough energy to escape.
- As the temperature rises, the fraction of molecules that have enough energy to escape increases.



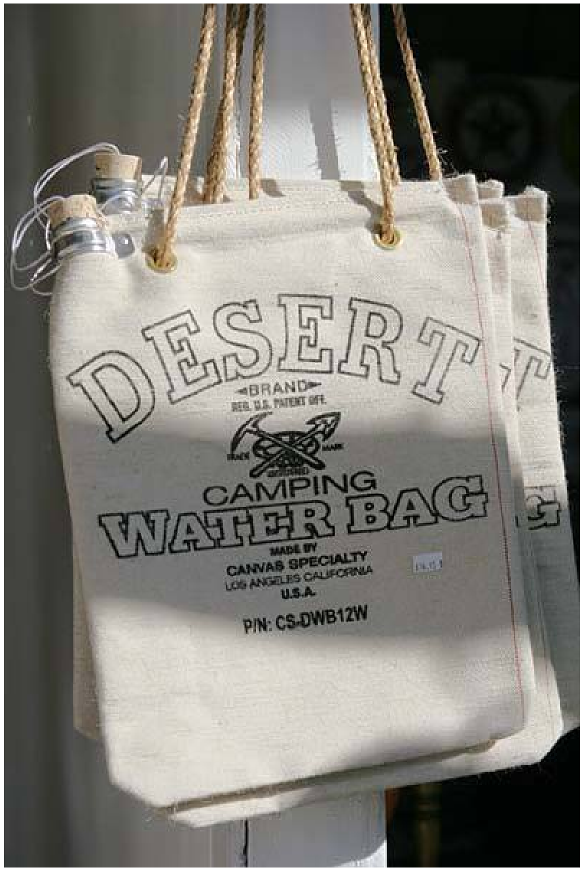
Vapor Pressure

If the container is open to the atmosphere, the molecules simply escape. This process is called evaporation.

As molecules escape from the surface, they take energy with them resulting in a cooling effect on the liquid.



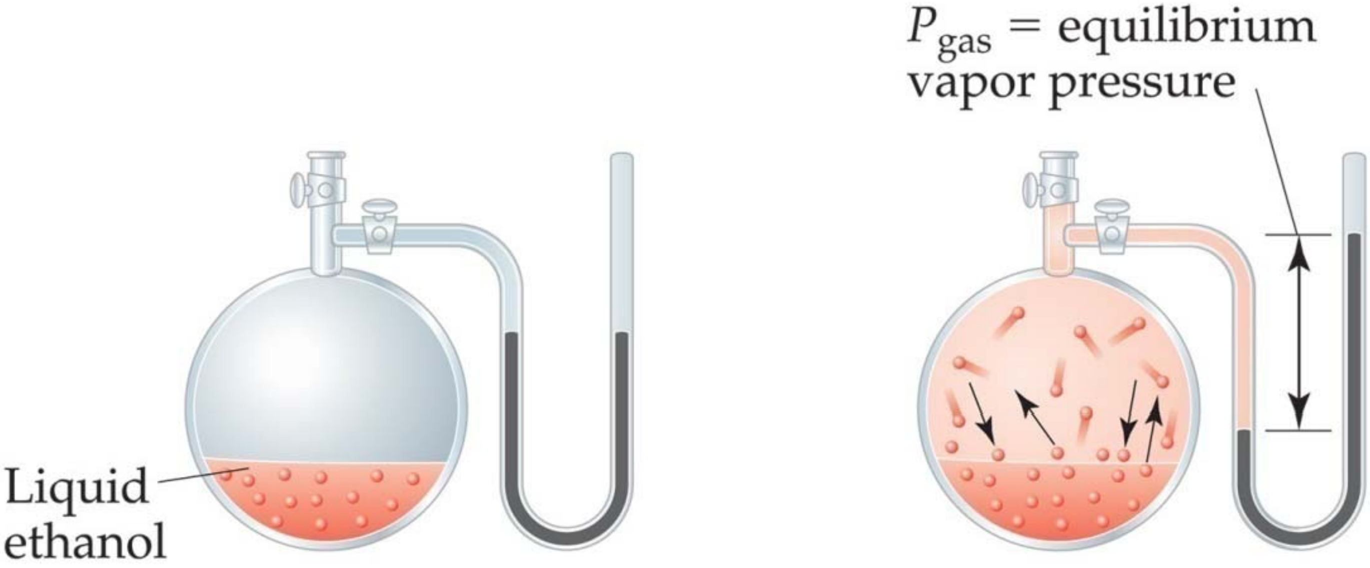
Vapor Pressure



A desert water bag (left)
A desert canteen (center)
An Army canteen (right)

Vapor Pressure

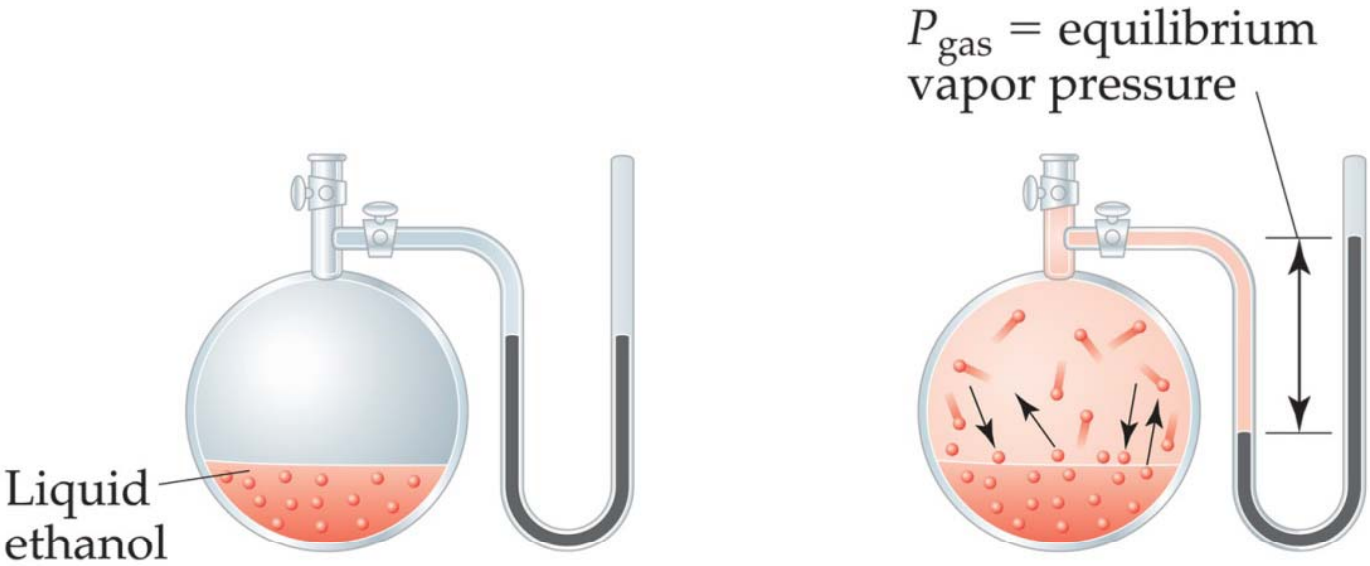
If the container is closed to the atmosphere, as more molecules escape the liquid, the pressure they exert increases.



Vapor Pressure

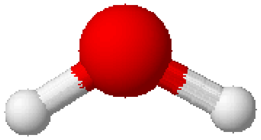
Eventually, the air space in the container becomes saturated with vapor molecules.

The liquid and vapor reach a state of dynamic equilibrium: as liquid molecules evaporate, vapor molecules condense at the same rate. This is called the vapor pressure equilibrium

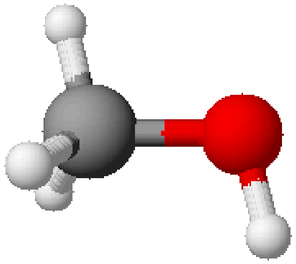


Which Will Evaporate First?

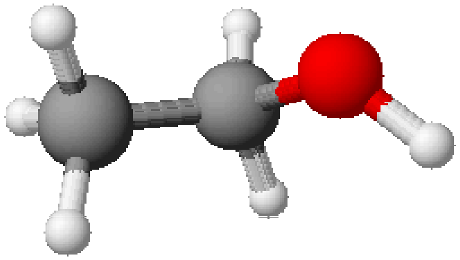
What factors affect evaporation?



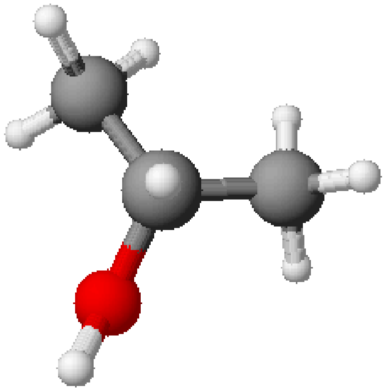
Water



methanol



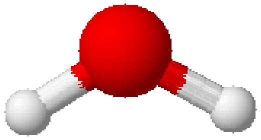
ethanol



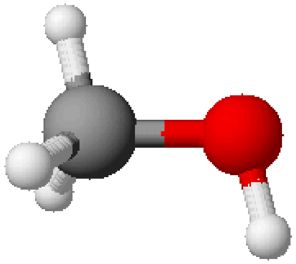
2-propanol

Which Will Evaporate First?

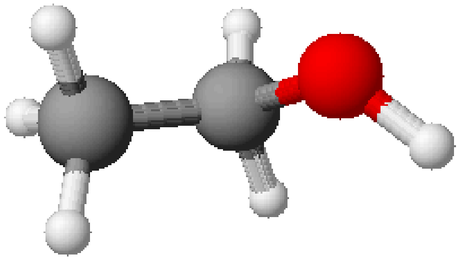
What factors affect evaporation?



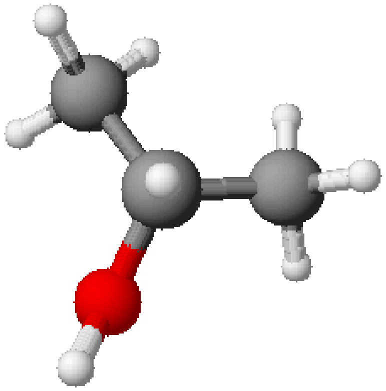
Water



methanol



ethanol



2-propanol

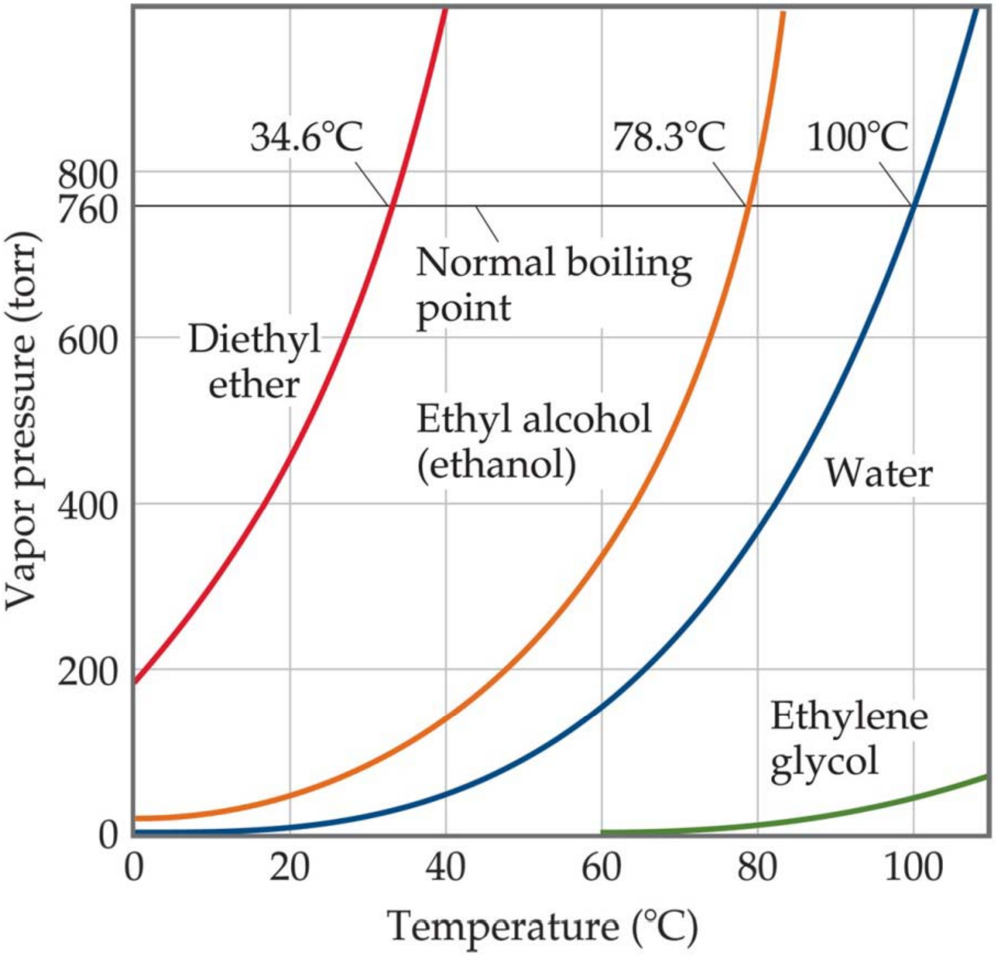
Effect of molecular weight:

H_2O = 18 CH_3OH = 32 C_2H_5OH = 46 C_3H_8OH = 60

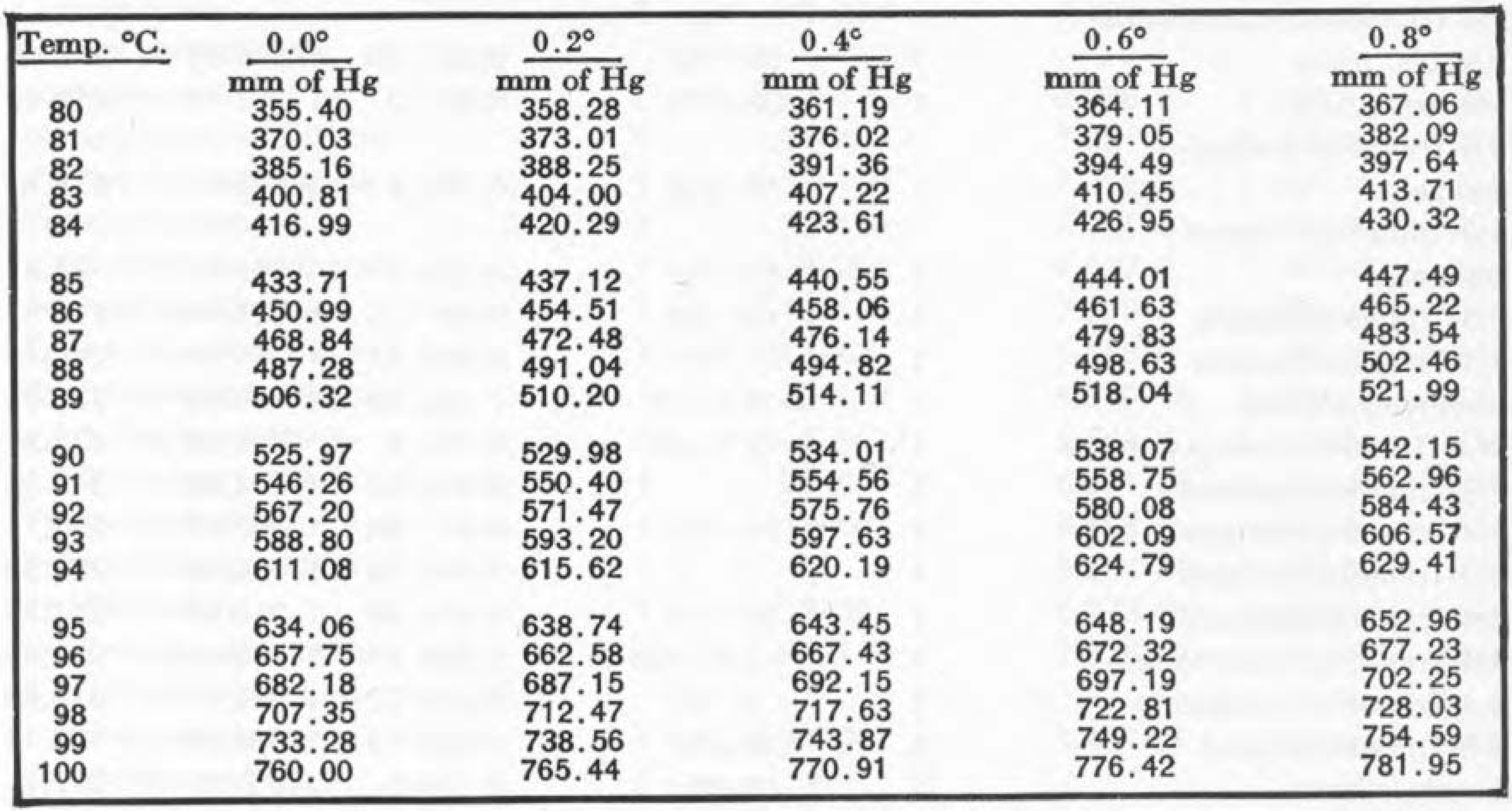
Effect of polarity

Vapor Pressure

- Vapor pressure increases with temperature.
- When the vapor pressure of a liquid equals the atmospheric pressure, the liquid boils.
- The normal boiling point of a liquid is the temperature at which its vapor pressure is 760 torr.



Boiling point of water at various temperatures

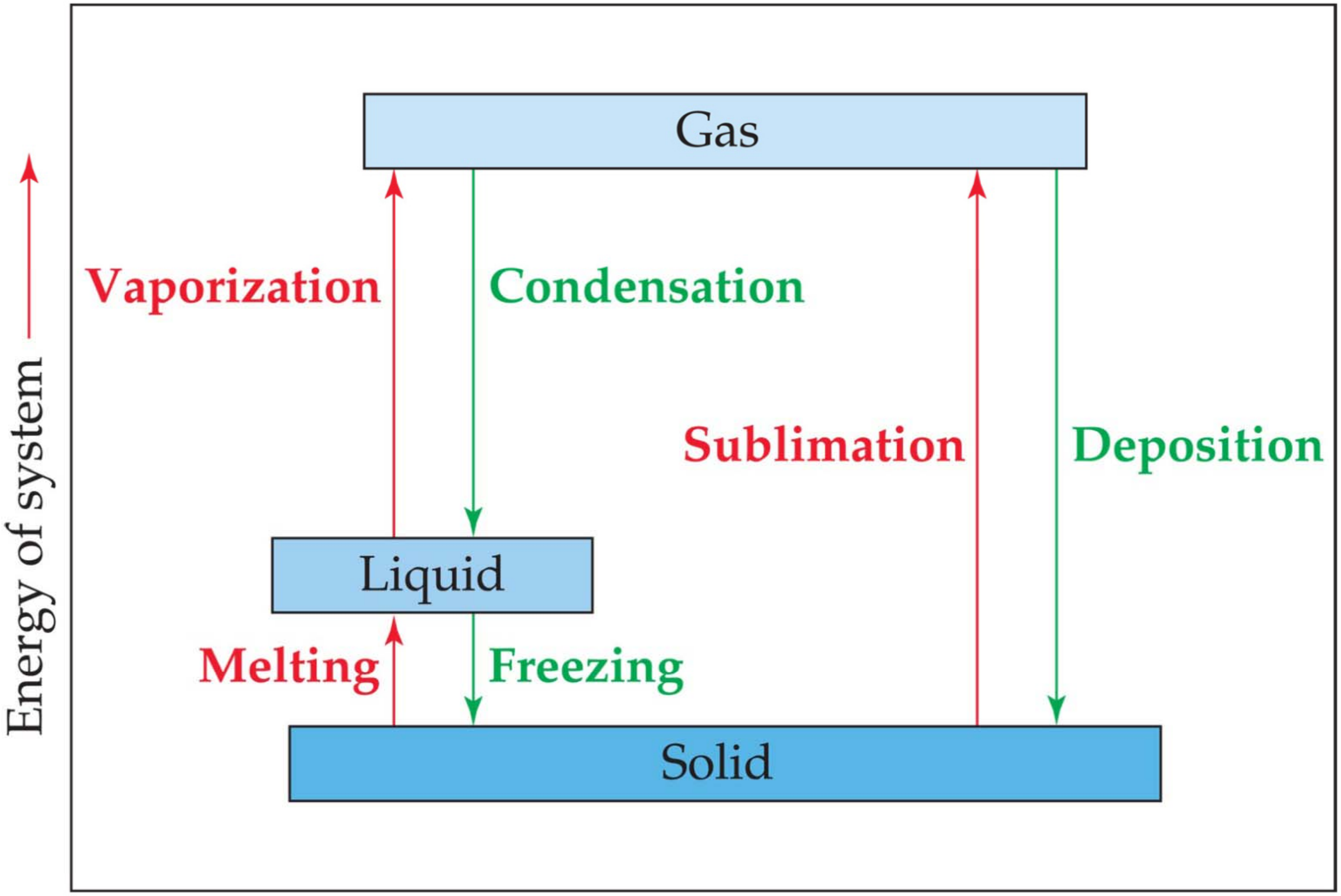


Temp. °C.	0.0°	0.2°	0.4°	0.6°	0.8°
	mm of Hg	mm of Hg	mm of Hg	mm of Hg	mm of Hg
80	355.40	358.28	361.19	364.11	367.06
81	370.03	373.01	376.02	379.05	382.09
82	385.16	388.25	391.36	394.49	397.64
83	400.81	404.00	407.22	410.45	413.71
84	416.99	420.29	423.61	426.95	430.32
85	433.71	437.12	440.55	444.01	447.49
86	450.99	454.51	458.06	461.63	465.22
87	468.84	472.48	476.14	479.83	483.54
88	487.28	491.04	494.82	498.63	502.46
89	506.32	510.20	514.11	518.04	521.99
90	525.97	529.98	534.01	538.07	542.15
91	546.26	550.40	554.56	558.75	562.96
92	567.20	571.47	575.76	580.08	584.43
93	588.80	593.20	597.63	602.09	606.57
94	611.08	615.62	620.19	624.79	629.41
95	634.06	638.74	643.45	648.19	652.96
96	657.75	662.58	667.43	672.32	677.23
97	682.18	687.15	692.15	697.19	702.25
98	707.35	712.47	717.63	722.81	728.03
99	733.28	738.56	743.87	749.22	754.59
100	760.00	765.44	770.91	776.42	781.95

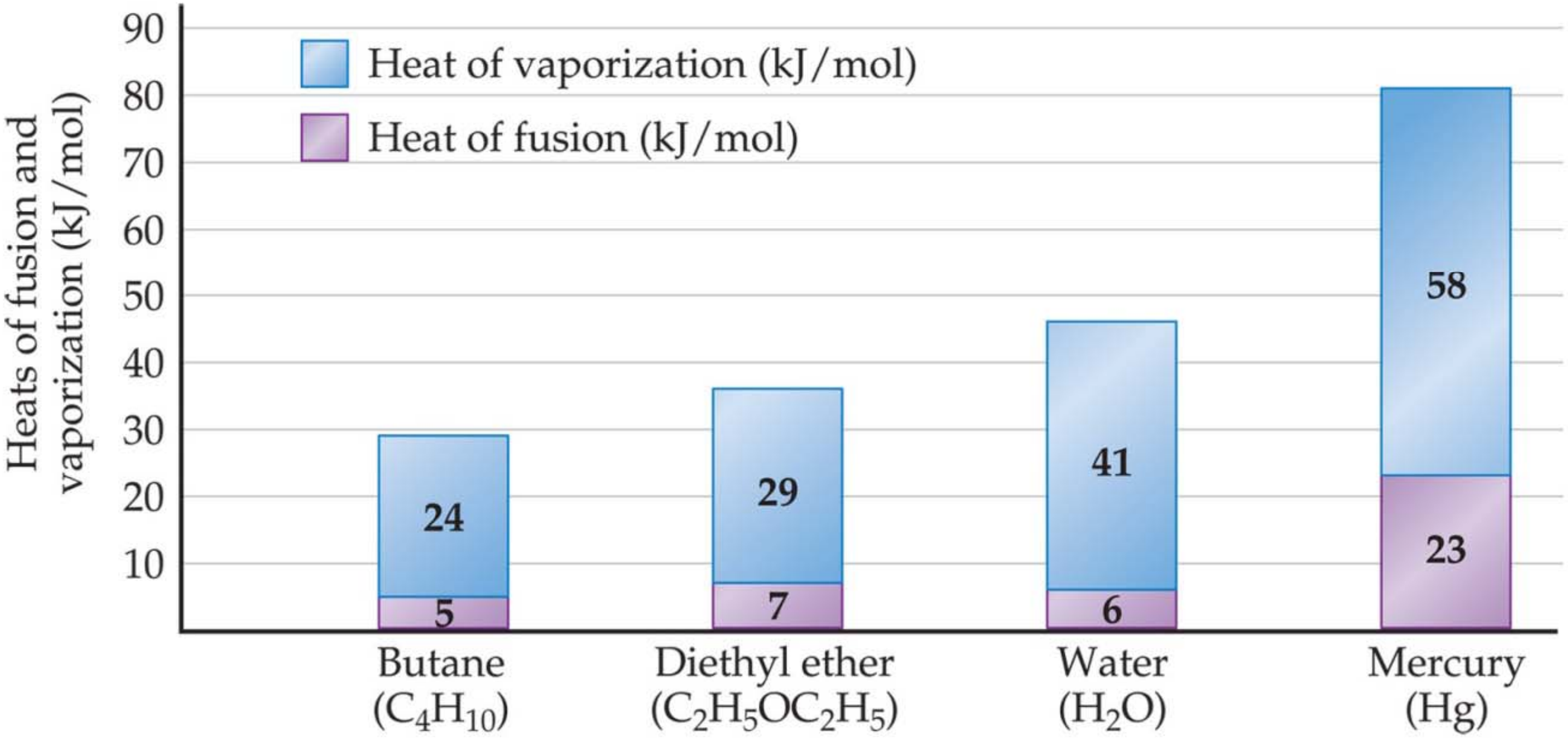
Atmospheric pressure at various altitudes

	Feet	Meters	Atm	Mm Hg
Sea level ➔	0	0	1.00	760
	328	100	0.99	752
	500	150	0.98	747
	656	200	0.97	743
	1000	300	0.96	734
	1312	400	0.95	725
	1500	450	0.94	719
	2000	600	0.93	706
Tucson ➔	2500	750	0.91	694
	3000	900	0.89	681
	3500	1070	0.88	668
	4000	1220	0.86	655
	4500	1370	0.85	645
Denver ➔	5000	1520	0.83	633
	5500	1680	0.81	620
	6000	1830	0.80	610
	6500	1980	0.78	597
	7000	2130	0.77	587
	7500	2290	0.76	577
	8000	2440	0.74	564
	8500	2590	0.73	554

Phase Changes

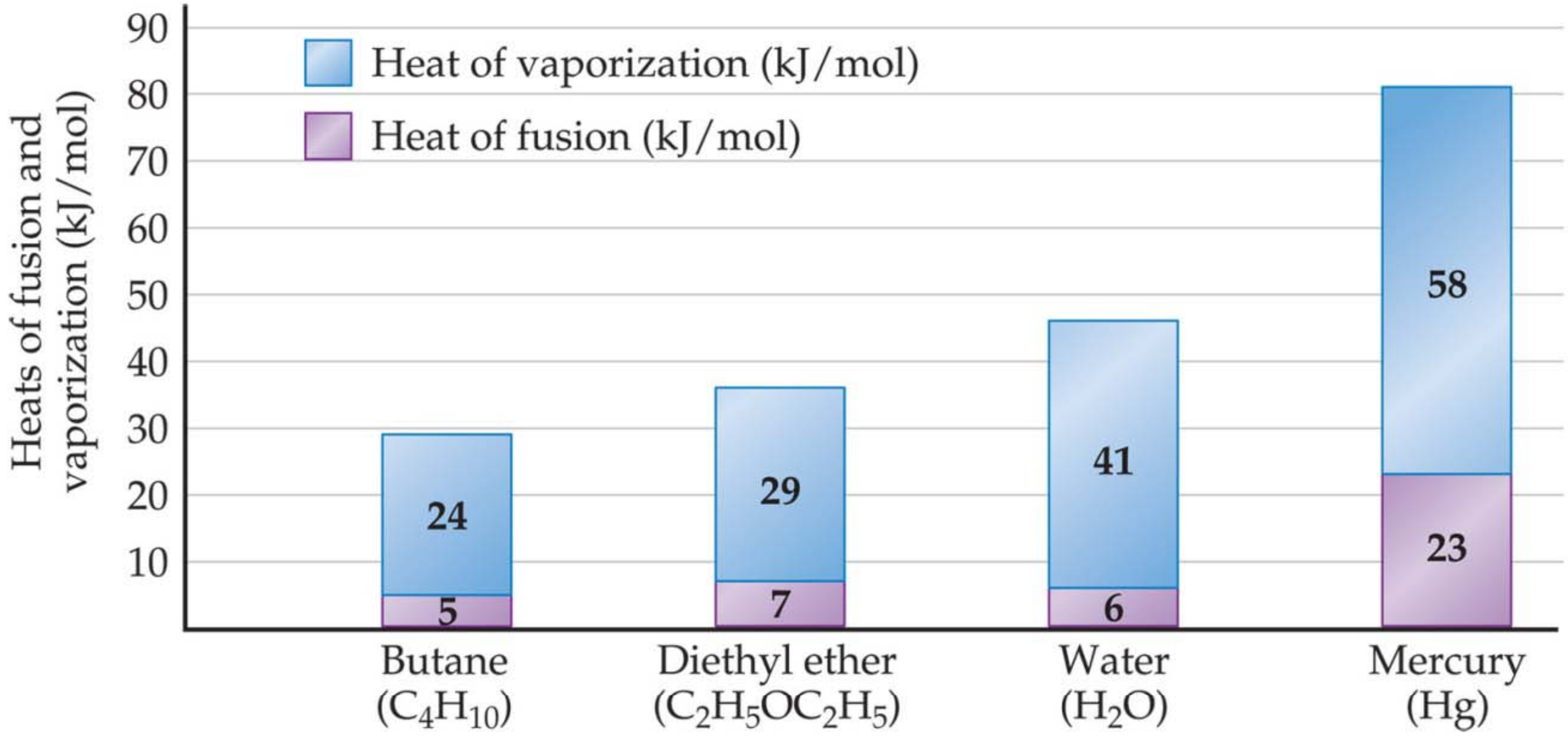


Energy Changes Associated with Changes of State



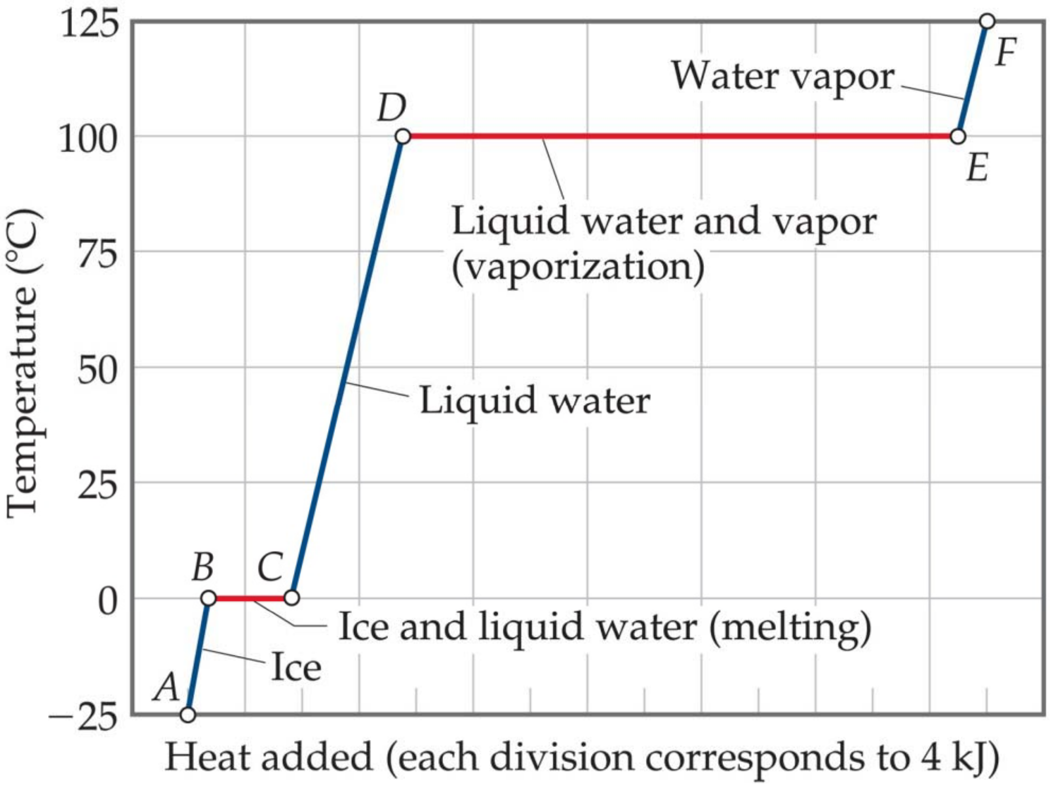
- **Heat of Fusion:** Energy required to change a solid at its melting point to a liquid.

Energy Changes Associated with Changes of State



- Heat of Vaporization: Energy required to change a liquid at its boiling point to a gas.

Energy Changes Associated with Changes of State

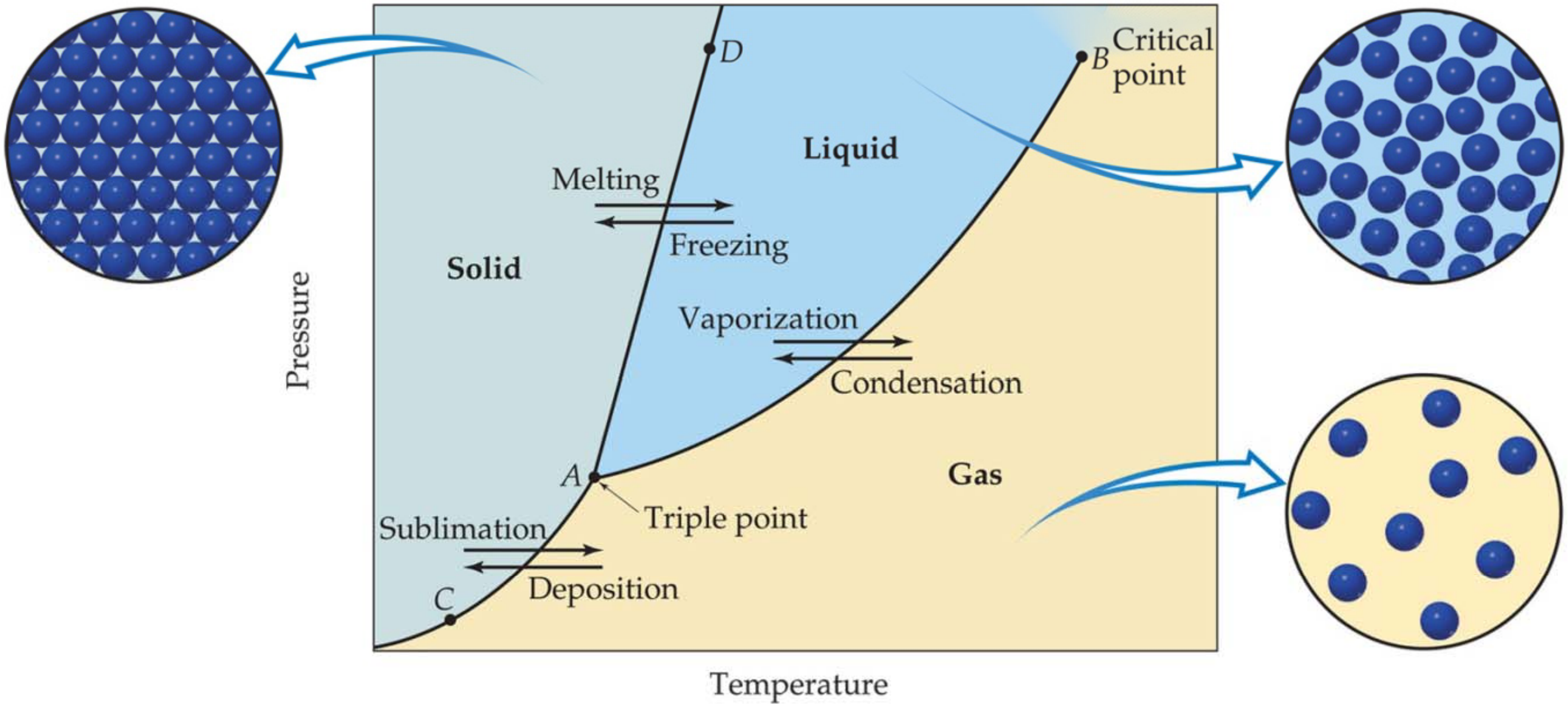


- Temperature remains constant at the melting and boiling points
  - Energy needed to break the intermolecular forces between the molecules.
  - Added kinetic energy for liquid or gaseous states.

Phase Diagrams

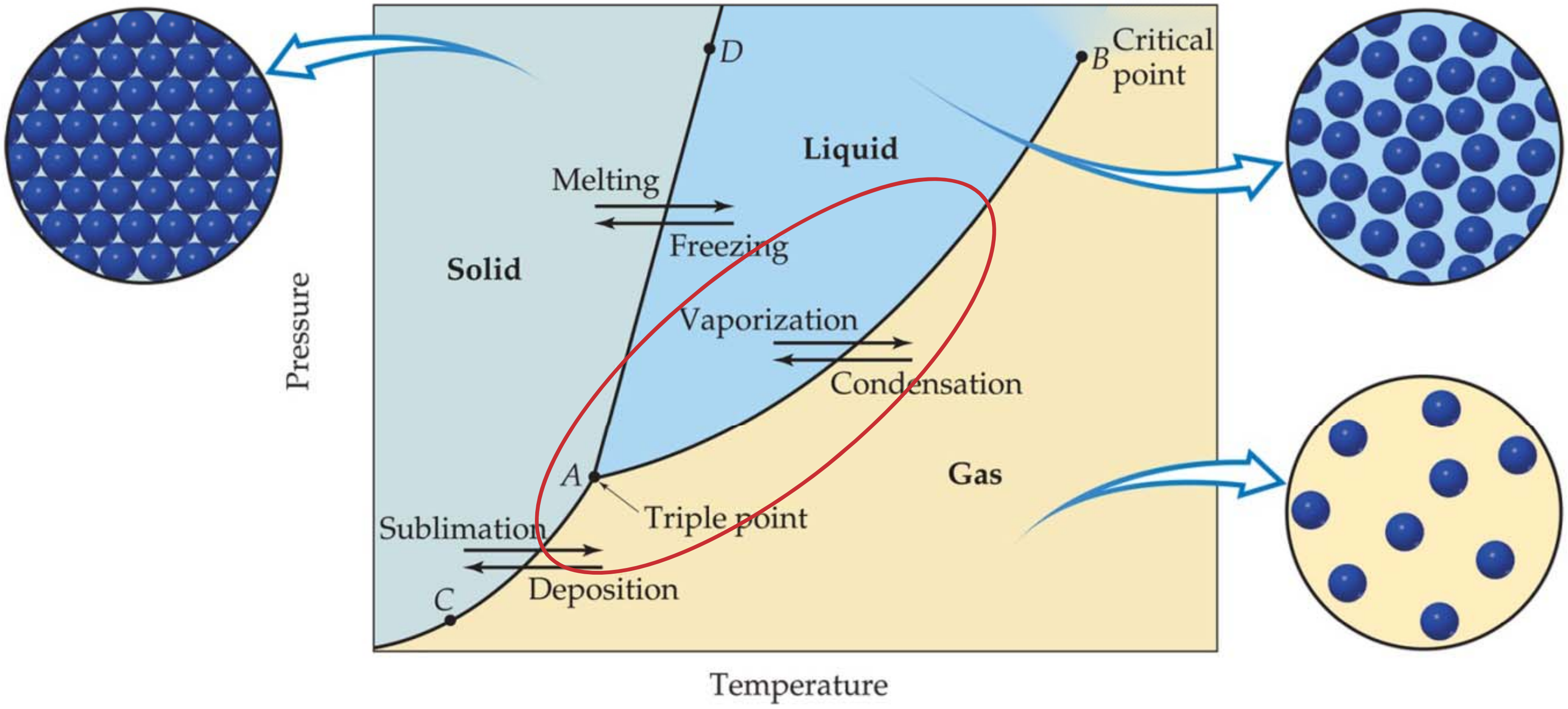
Phase diagrams display the state of a substance at various pressures and temperatures and the places where equilibria exist between phases.

Each substance has its own unique phase diagram.



Phase Diagrams

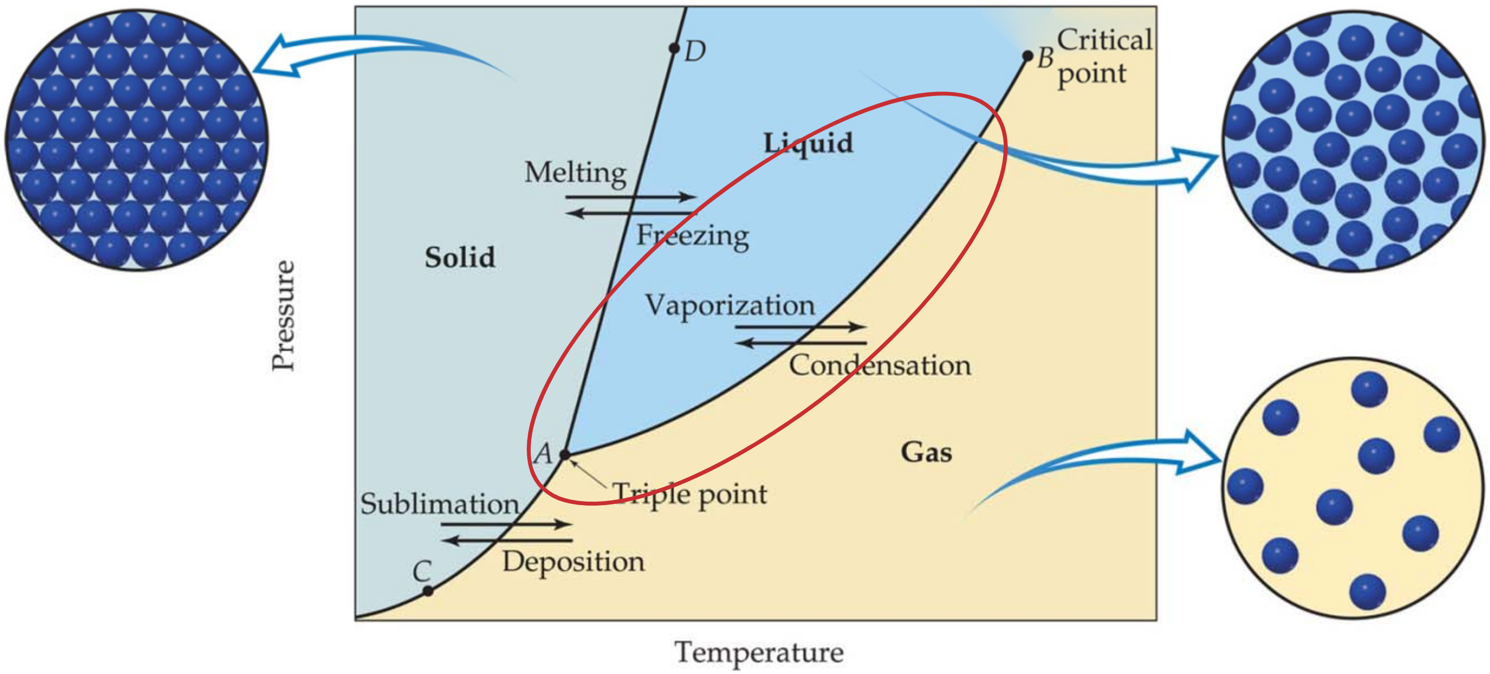
- The *AB* line is the liquid-vapor interface.
- It starts at the triple point (*A*), the point at which all three states are in equilibrium.



Phase Diagrams

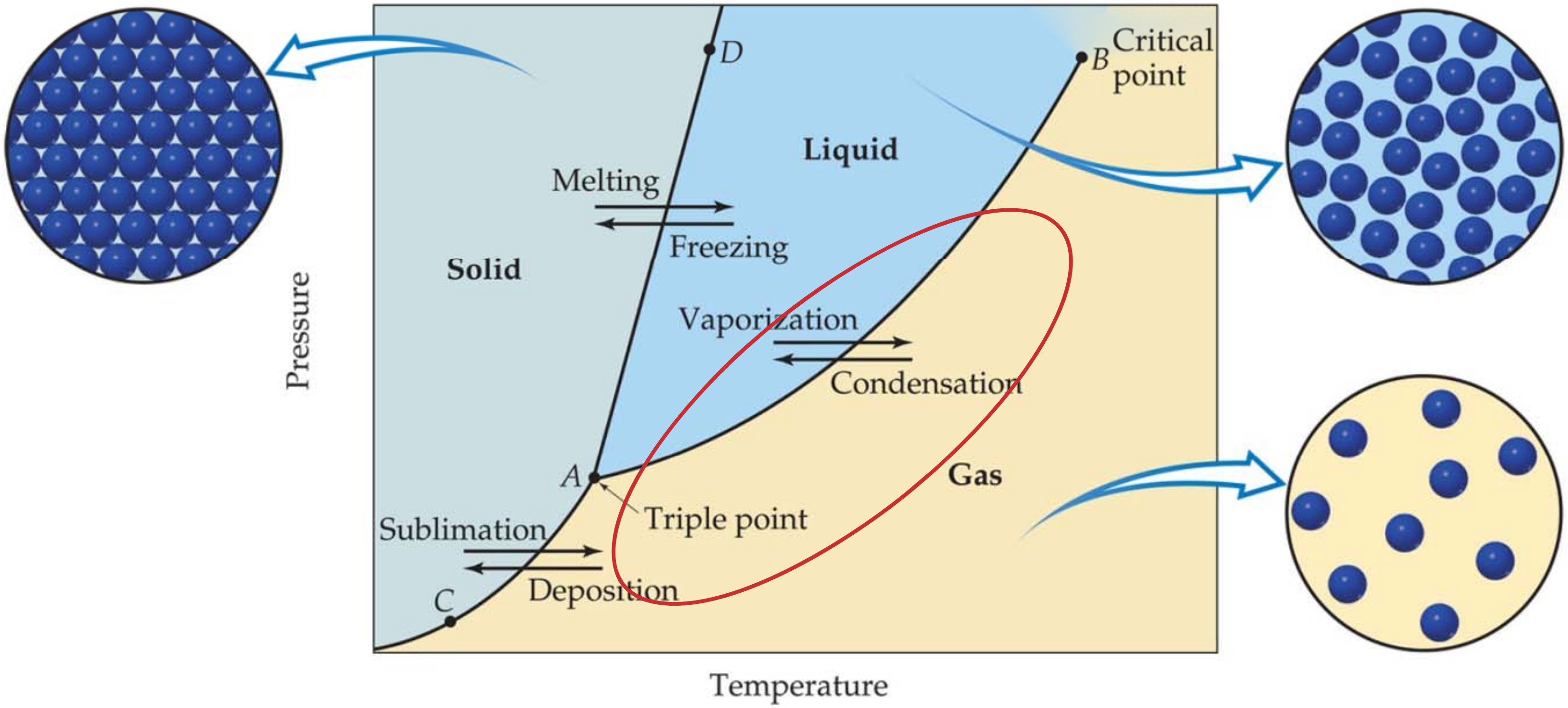
The critical point (*B*) is the highest temperature and pressure where the liquid form of the substance can exist.

Above the critical temperature and critical pressure the liquid and vapor are indistinguishable from each other.



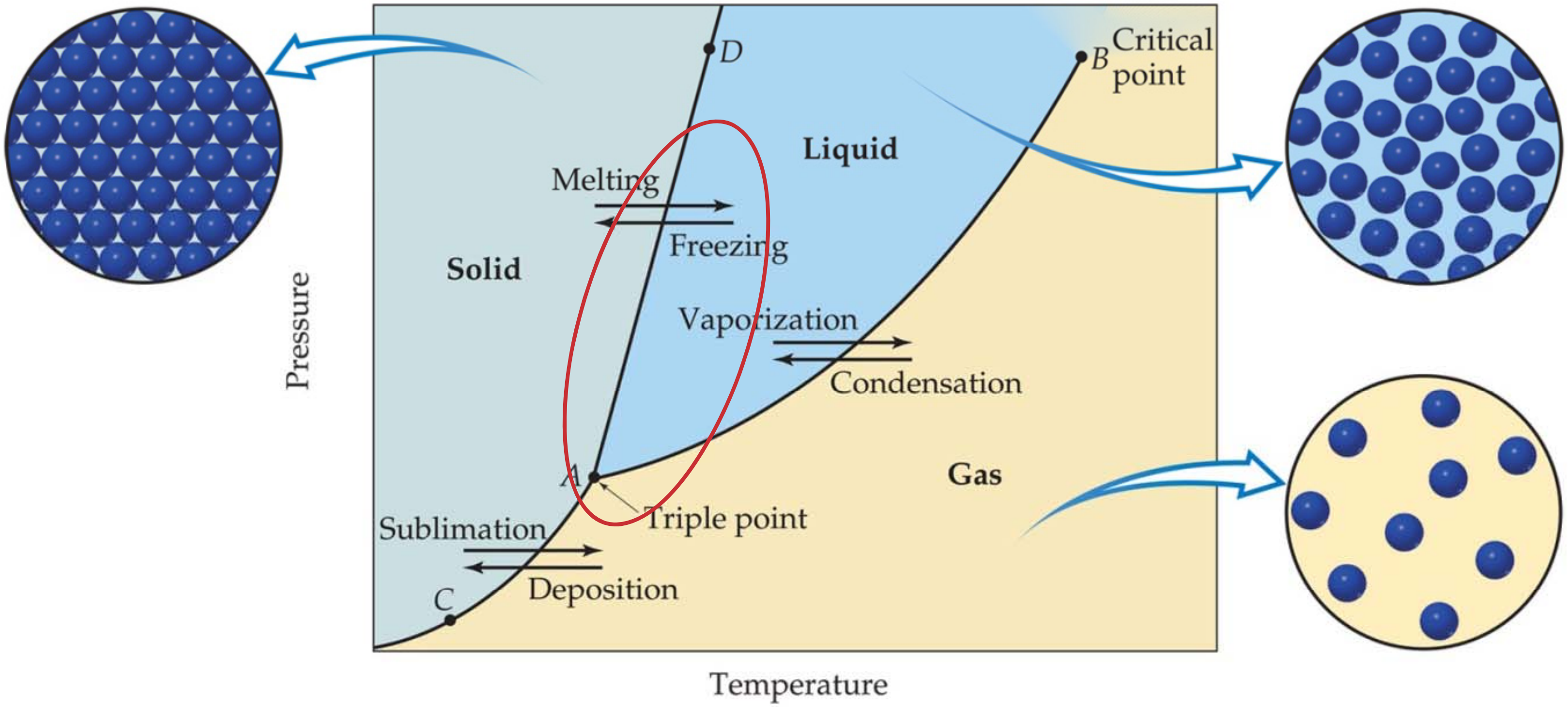
Phase Diagrams

Each point along this line is the boiling point of the substance at that pressure.



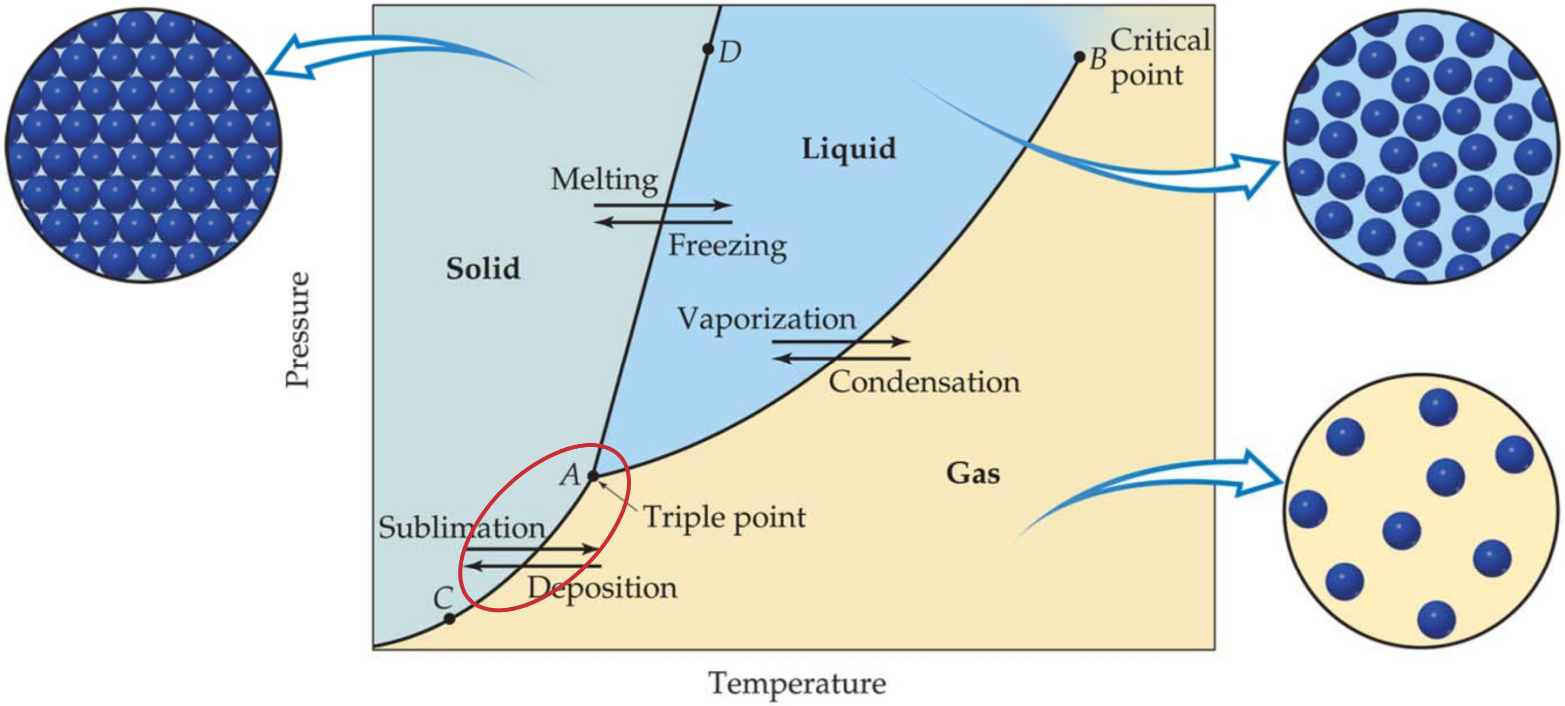
Phase Diagrams

- The *AD* line is the interface between liquid and solid.
- The melting point at each pressure can be found along this line.
- The substance represented in this phase diagram tends to decrease in volume on freezing, the melting point line slants to the right.

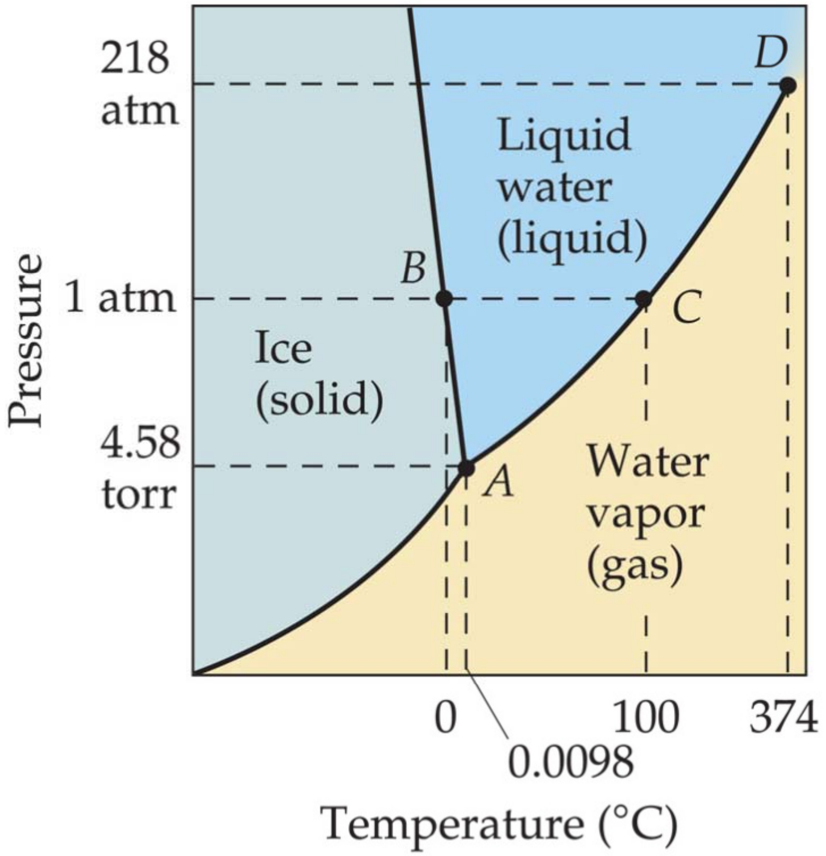


Phase Diagrams

- Below *A* the substance cannot exist in the liquid state.
- Along the *AC* line the solid and gas phases are in equilibrium.
- This is called the sublimation curve.

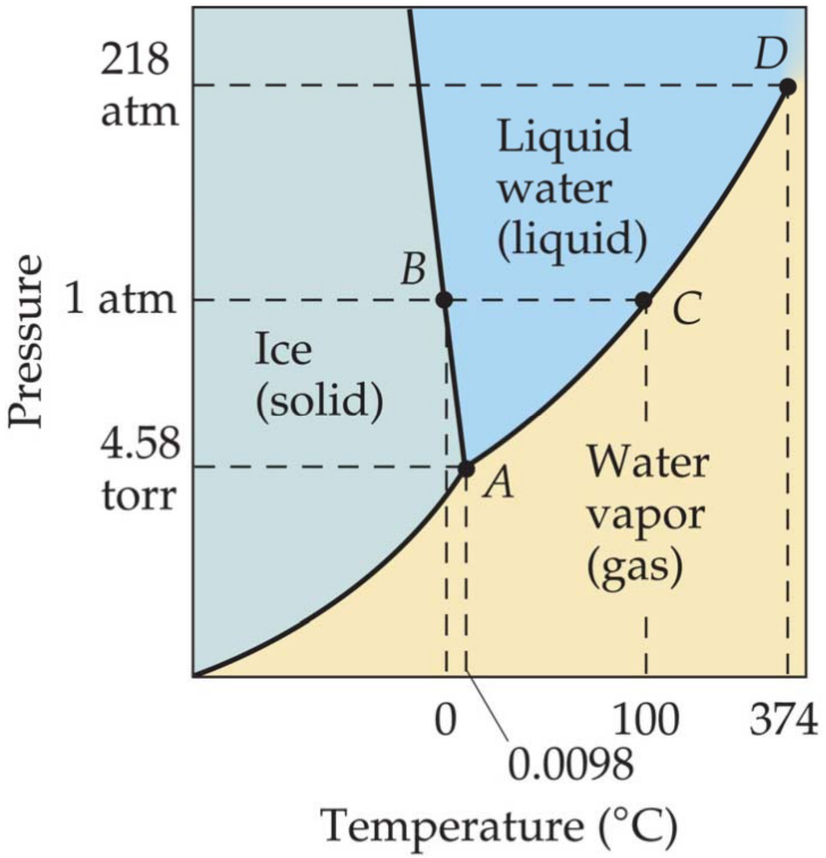


Phase Diagram of Water



- Note the high critical temperature and critical pressure:
  - These are due to the strong polar bonding between water molecules.
- Water expands on freezing, so the melting point line slants to the left.

Phase Diagram of Water

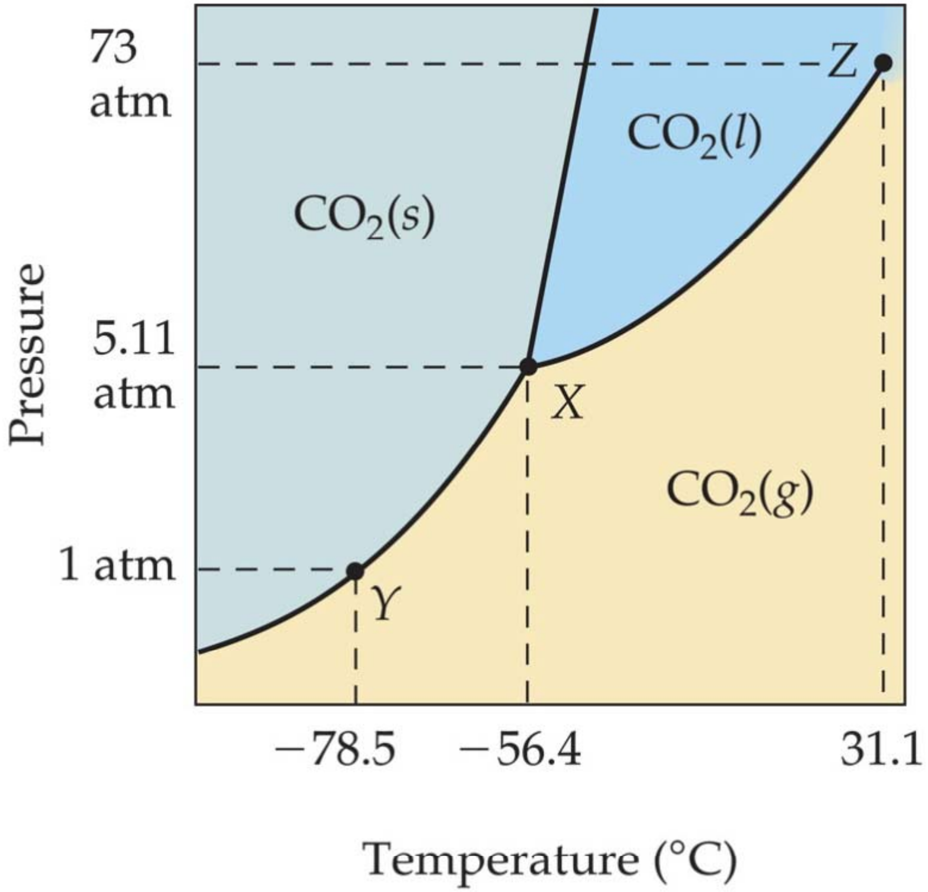


- The slope of the solid–liquid line is negative.
  - This means that as the pressure is increased at a temperature just below the melting point, water goes from a solid to a liquid.
  - This is why an ice skater can skate on ice.

Phase Diagram of Carbon Dioxide

Carbon dioxide cannot exist in the liquid state at pressures below 5.11 atm

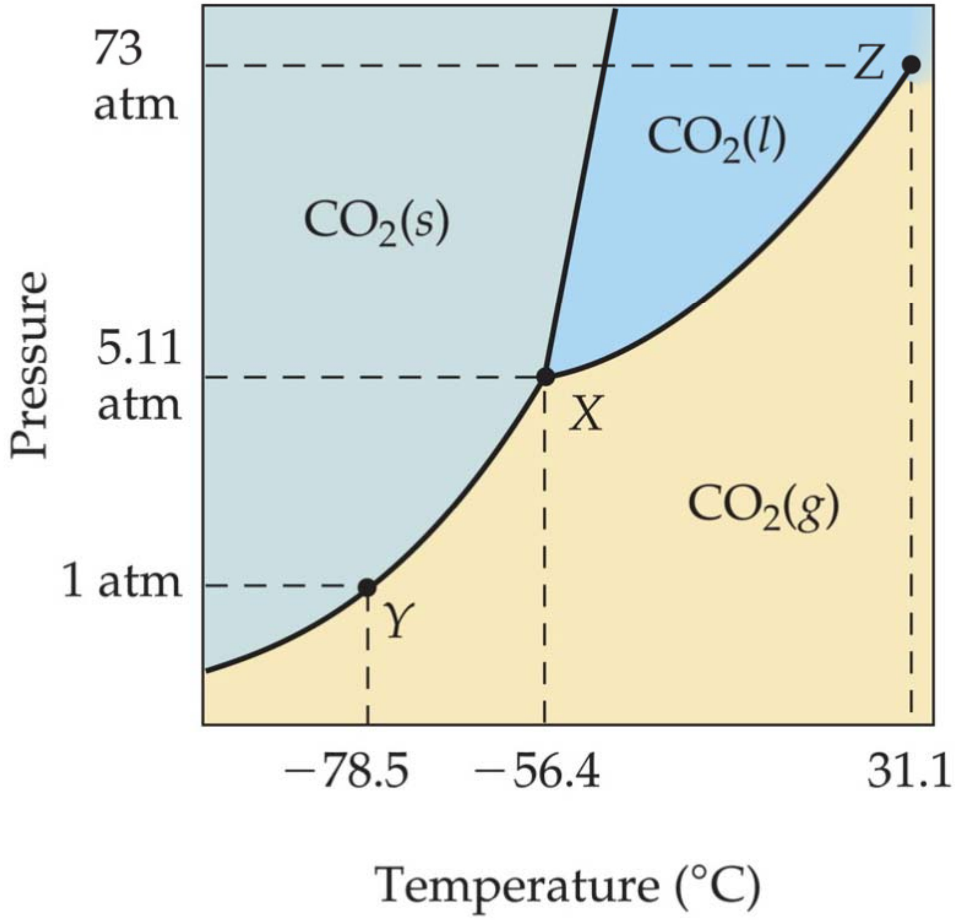
CO_2 sublimes at normal pressures.



Phase Diagram of Carbon Dioxide

The low critical temperature and critical pressure for CO_2 make supercritical CO_2 a good solvent for extracting nonpolar substances (such as caffeine).

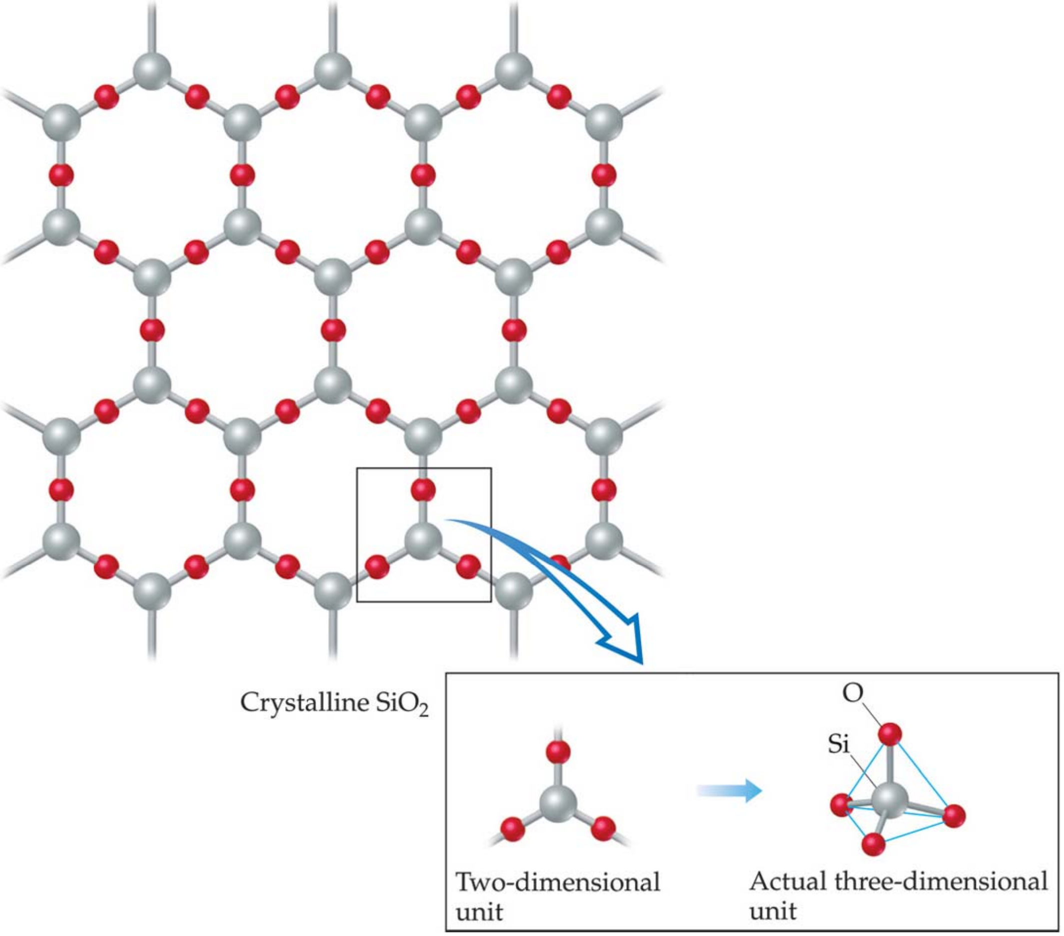
Supercritical CO_2 is being used for dry cleaning of clothing,



Solids

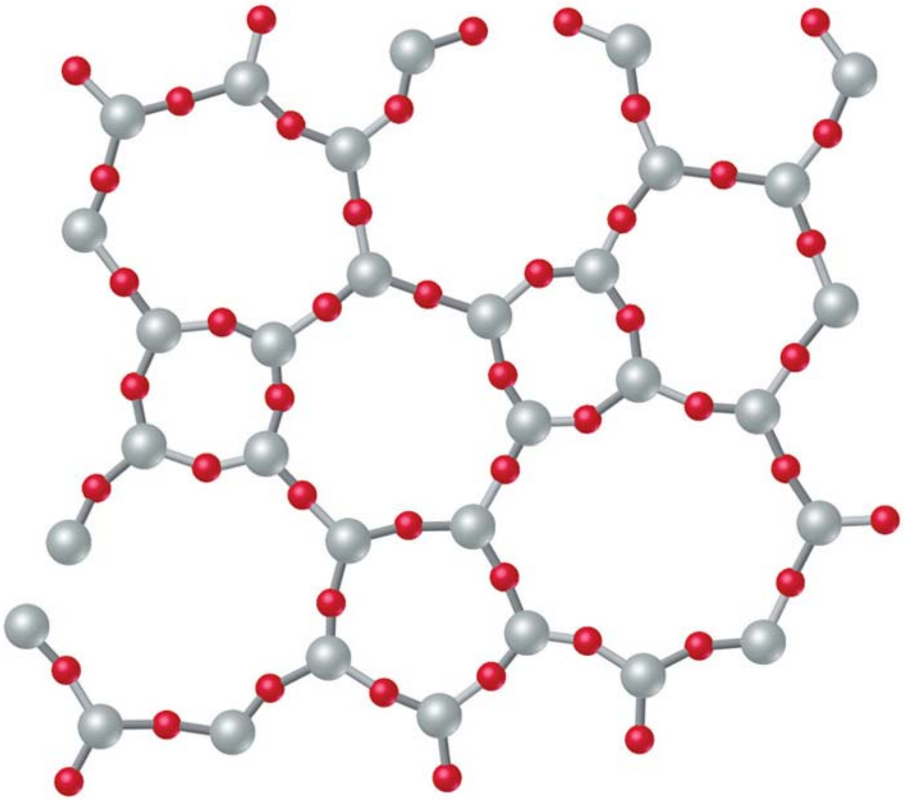
Solids

- We can think of solids as falling into two groups:
  - Crystalline—particles are in highly ordered arrangement.



Although these structures appear to be planar in the drawing, they are actually in a tetrahedral arrangement.

Solids

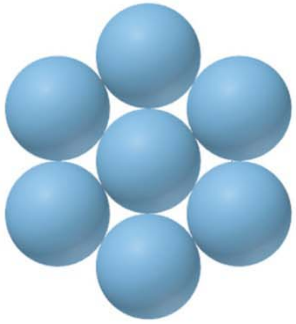


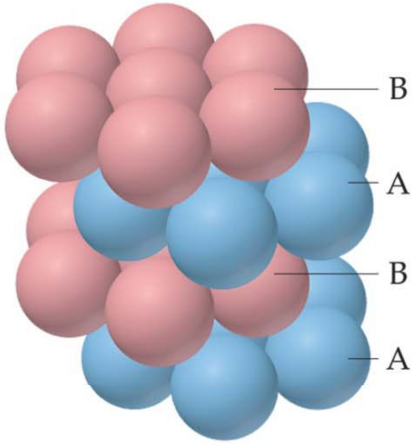
Amorphous SiO_2

- Amorphous—no particular order in the arrangement of particles.

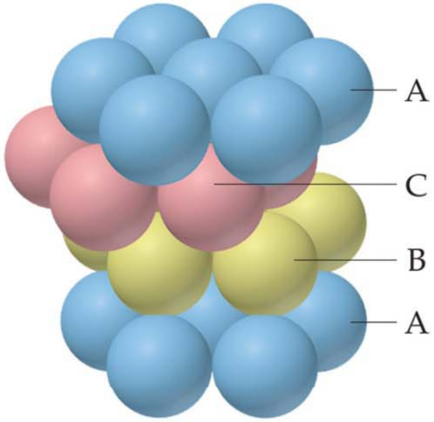
Attractions in Ionic Crystals

In ionic crystals, ions pack themselves so as to maximize the attractions and minimize repulsions between the ions.


Close-packed layer of spheres

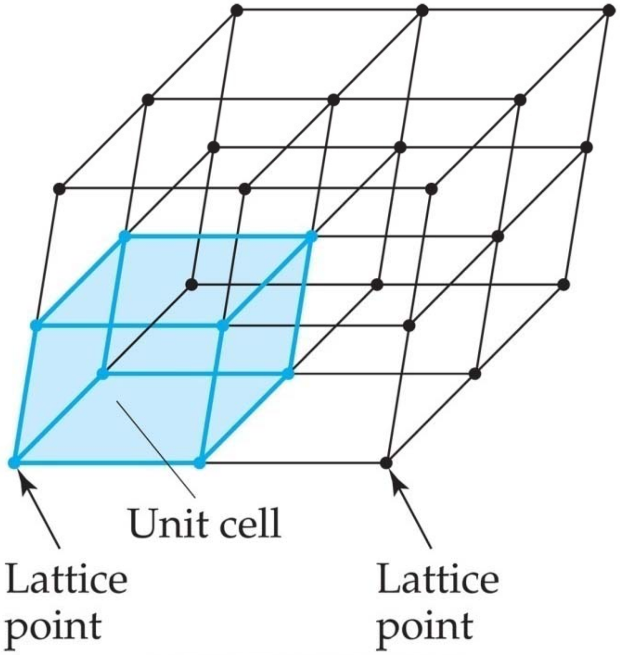


Hexagonal close-packed structure



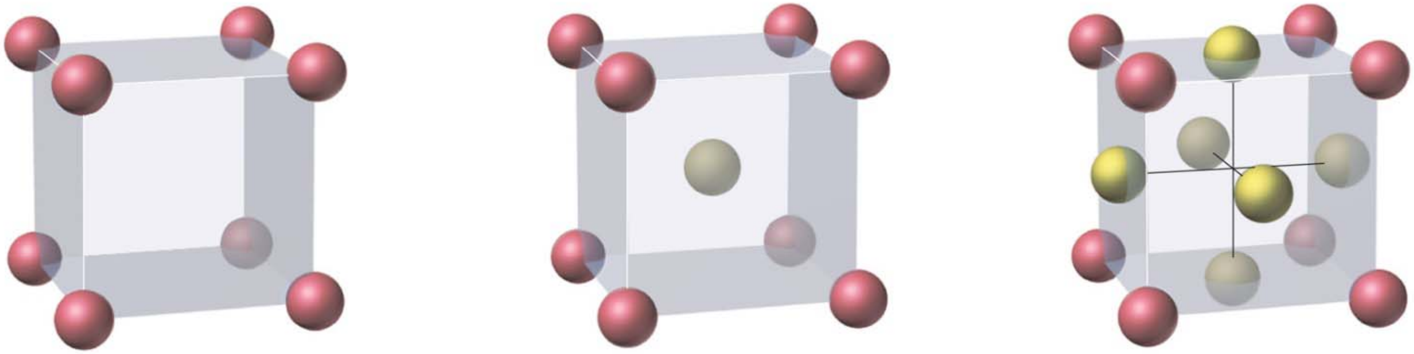
Cubic close-packed structure

Crystalline Solids



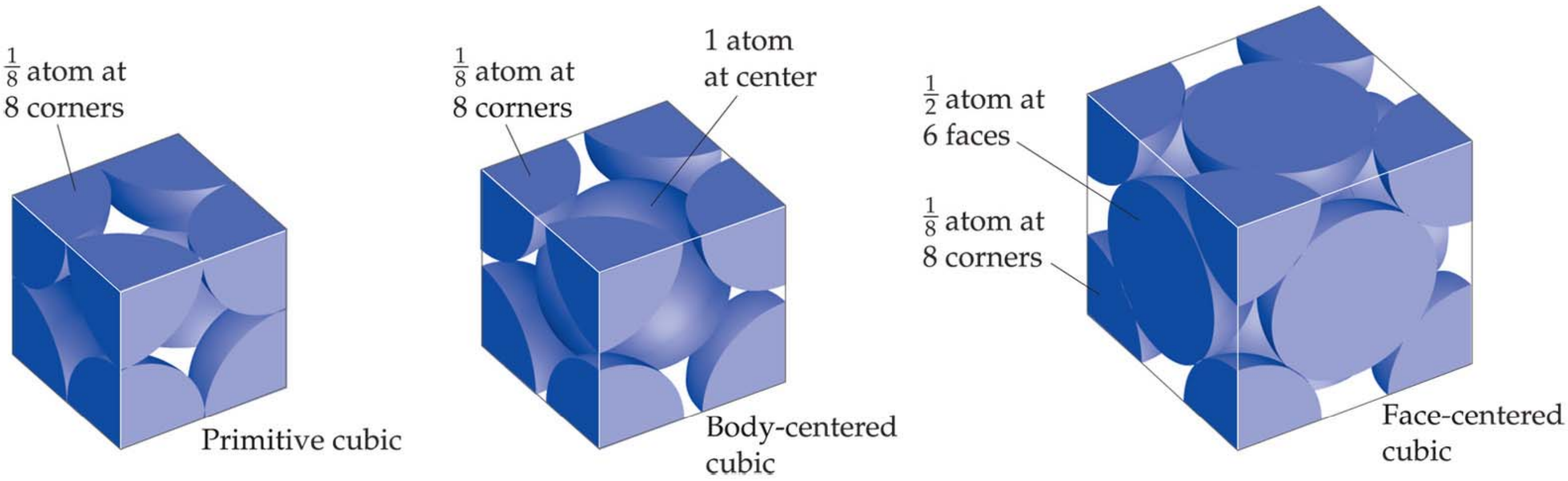
Because of the order in a crystal, we can focus on the repeating pattern of arrangement called the unit cell.

Some variations of a cubic unit cell are diagrammed below.



Primitive cubic Body-centered cubic Face-centered cubic

Crystalline Solids

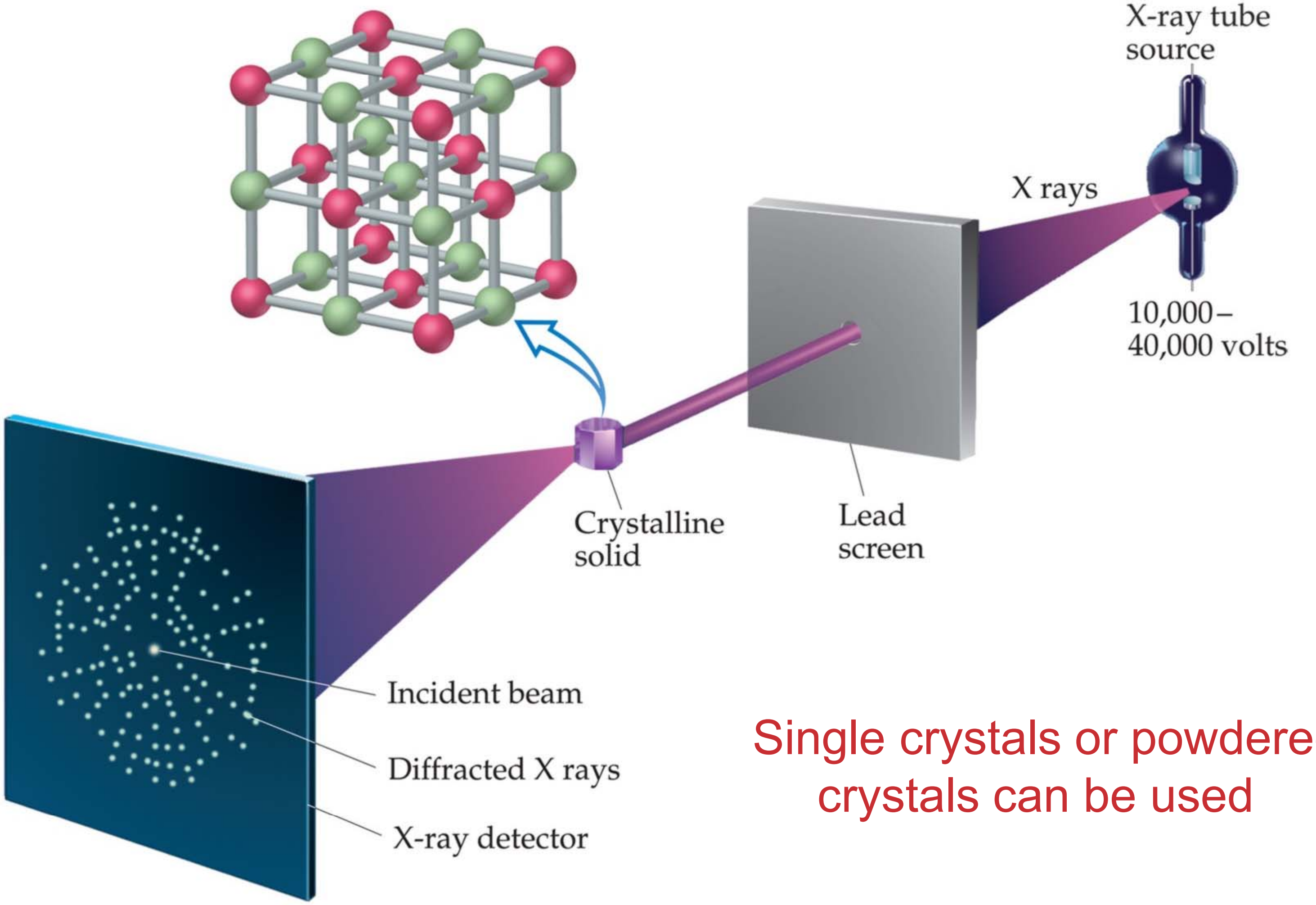


Lattice points in a unit cell are considered to be at the nuclei of the atoms making up the unit cell.

A simple (or primitive) unit cell contains one atom.

Body-centered and face-centered unit cells contain two or more atoms enclosed in the unit cell.

Unit cell structures are determined by x-ray crystallography



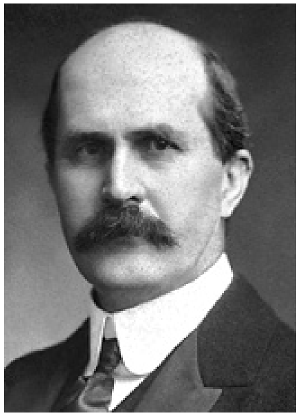
Single crystals or powdered crystals can be used

X-ray Diffraction

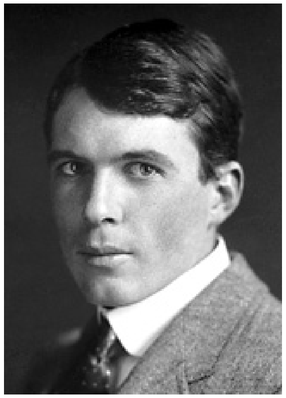
- Sir William Henry Bragg and his son Sir William Lawrence Bragg, 1913
- Bragg's law made it possible to calculate the positions of the atoms within a crystal from the x-ray diffraction of a crystal lattice.

$$n\lambda = 2d \sin\theta$$

where
n = an integer determined by the order of the x-rays
λ = the wavelength of x-rays
d = the spacing between the planes in the atomic lattice
θ = the angle between the incident ray and the scattering planes



W. H. Bragg



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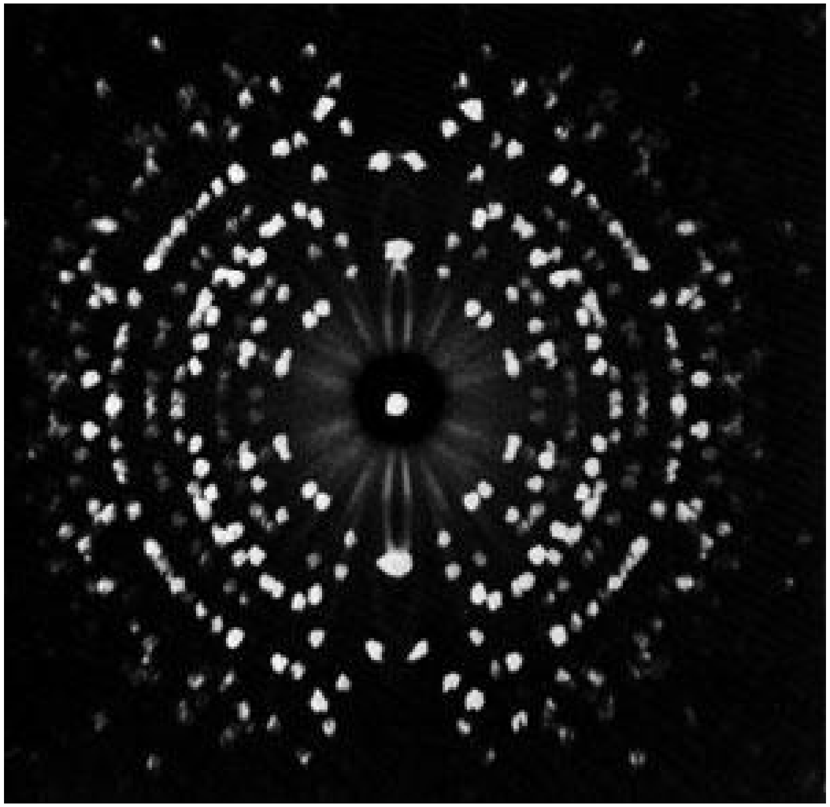
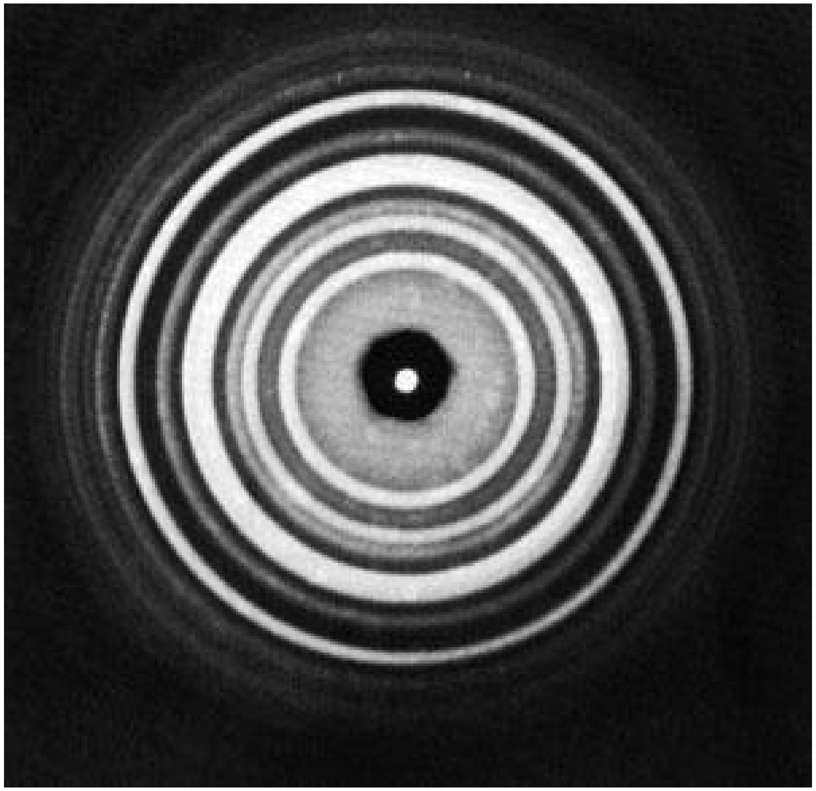


X-ray diffraction pattern
for a single alum crystal



X-ray diffraction pattern
for powdered alum

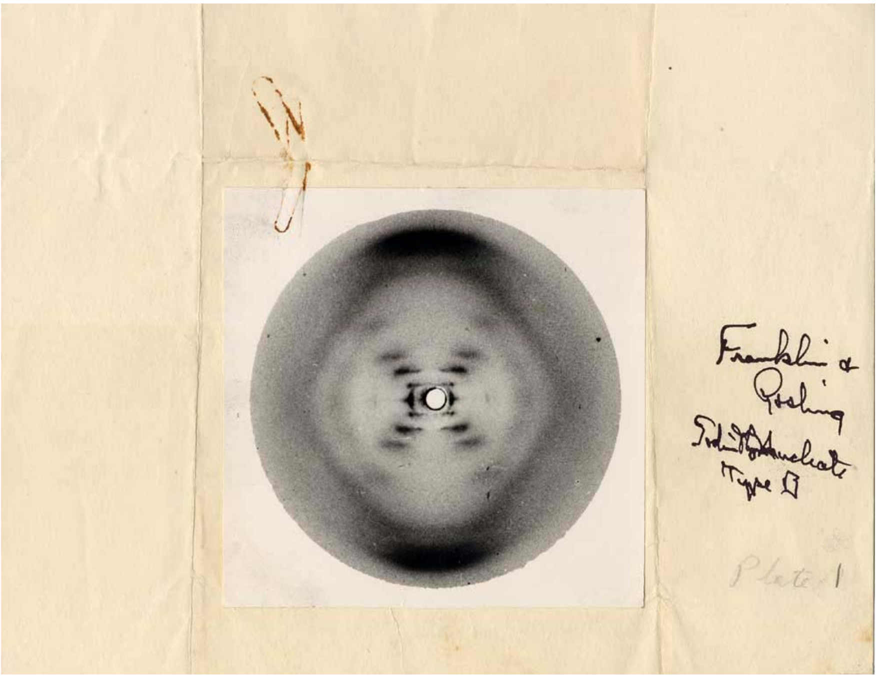
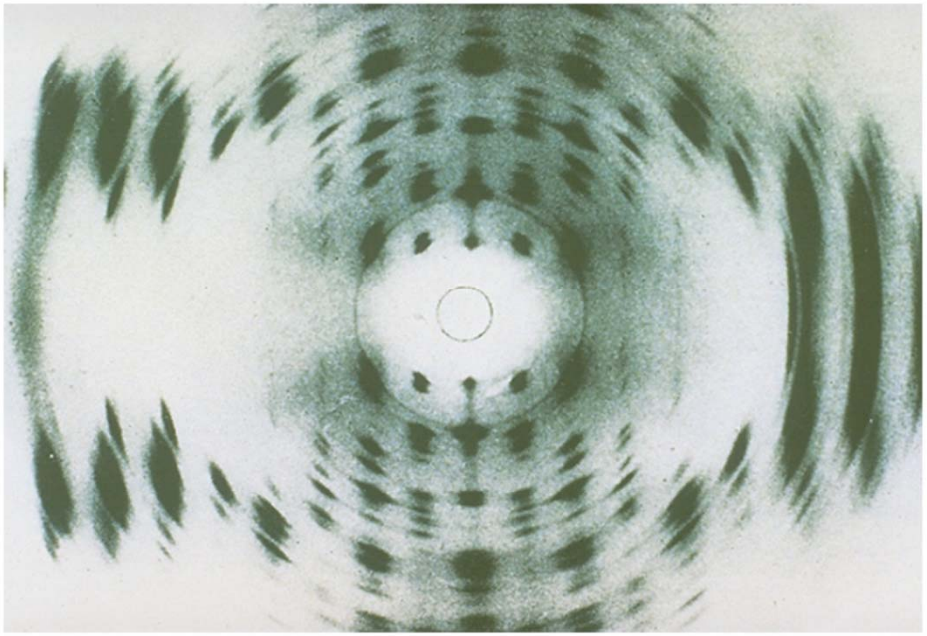


Photo No. 51 of DNA taken
by Rosalind Franklin
This photograph made it
possible for Watson and
Crick to determine the
structure of DNA



Another X-ray diffraction
photograph of one form
of crystalline DNA taken
in the early 1950’s

Solving the Structure of DNA: History

- Rosalind Franklin- physical chemist and x-ray crystallographer who first crystallized and photographed B-DNA
- Maurice Wilkins- collaborator of Franklin
- Watson & Crick- chemists who combined the information from Photo 51 with molecular modeling to solve the structure of DNA in 1953

Rosalind Franklin

Solving the Structure of DNA

- Photo 51 Analysis
  - "X" pattern characteristic of helix
  - Diamond shapes indicate long, extended molecules
  - Smear spacing reveals distance between repeating structures
  - Missing smears indicate interference from second helix

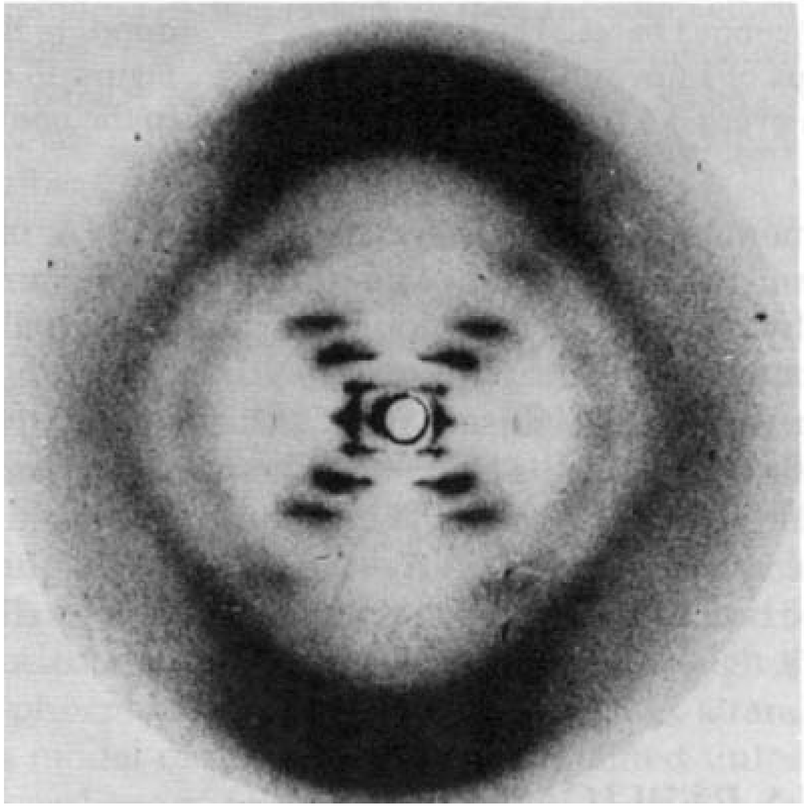


Photo 51- The x-ray diffraction image that allowed Watson and Crick to solve the structure of DNA

www.pbs.org/wgbh/nova/photo51

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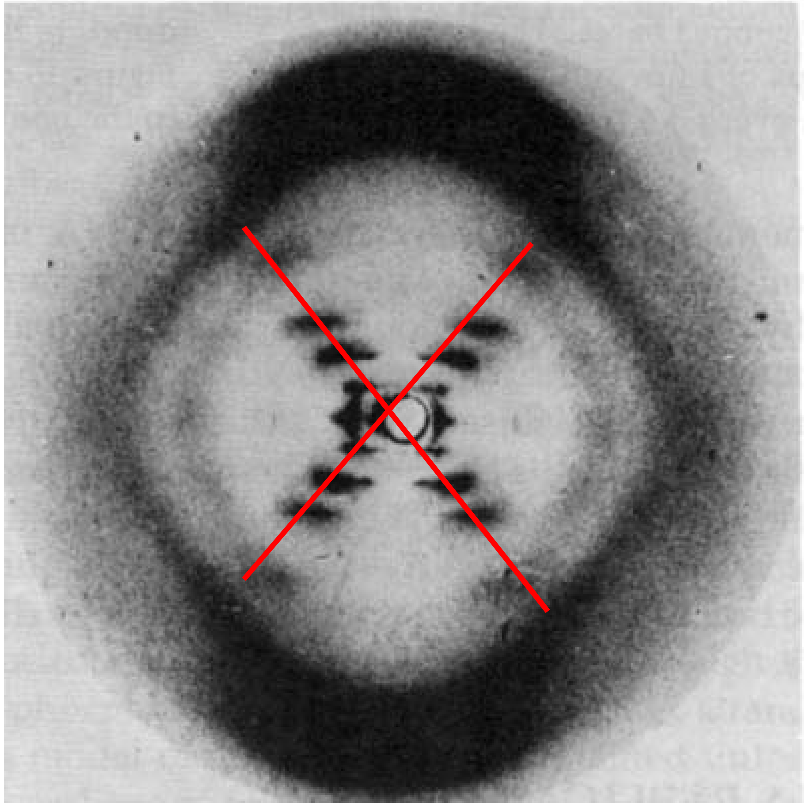

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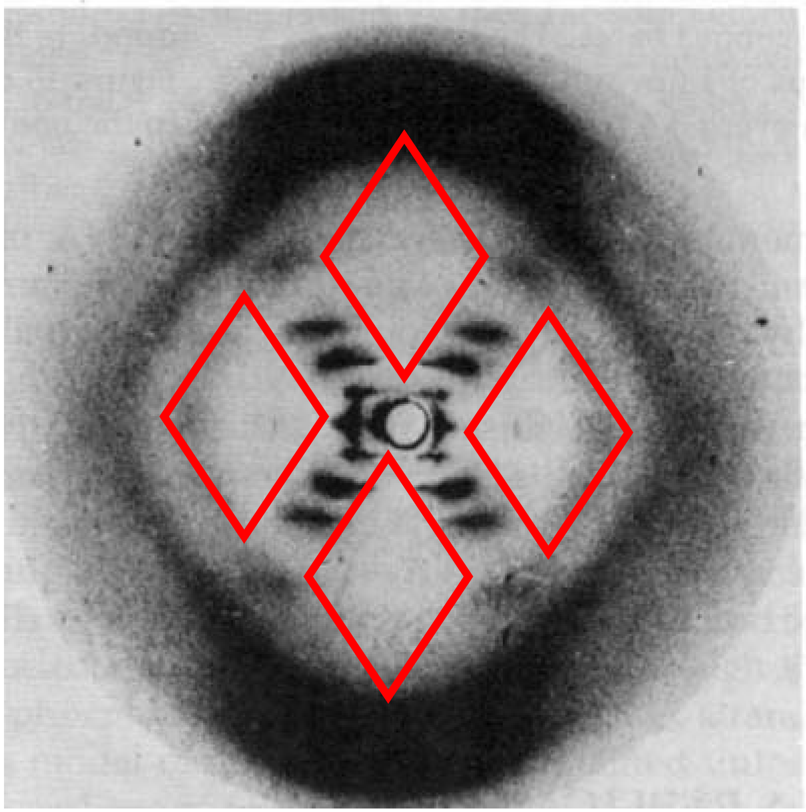

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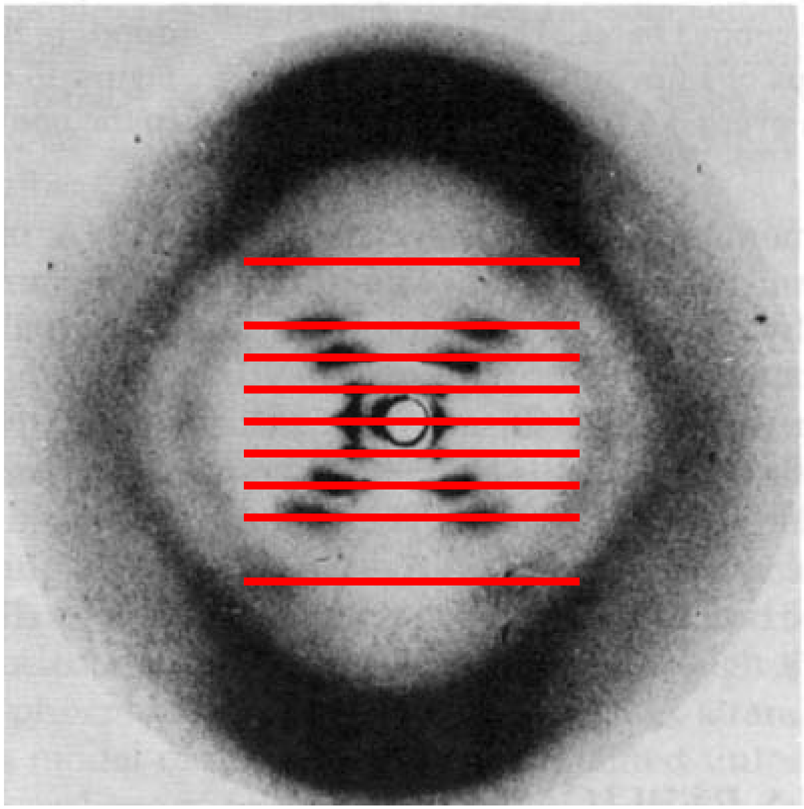

Photo 51- The x-ray diffraction image that allowed Watson and Crick to solve the structure of DNA

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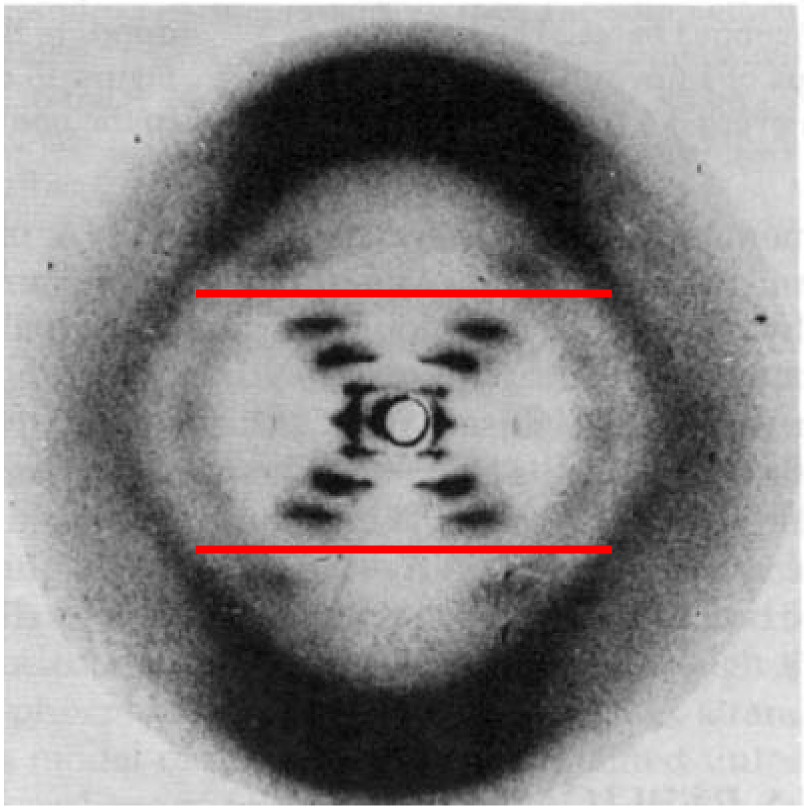


Photo 51- The x-ray diffraction image that allowed Watson and Crick to solve the structure of DNA

www.pbs.org/wgbh/nova/photo51

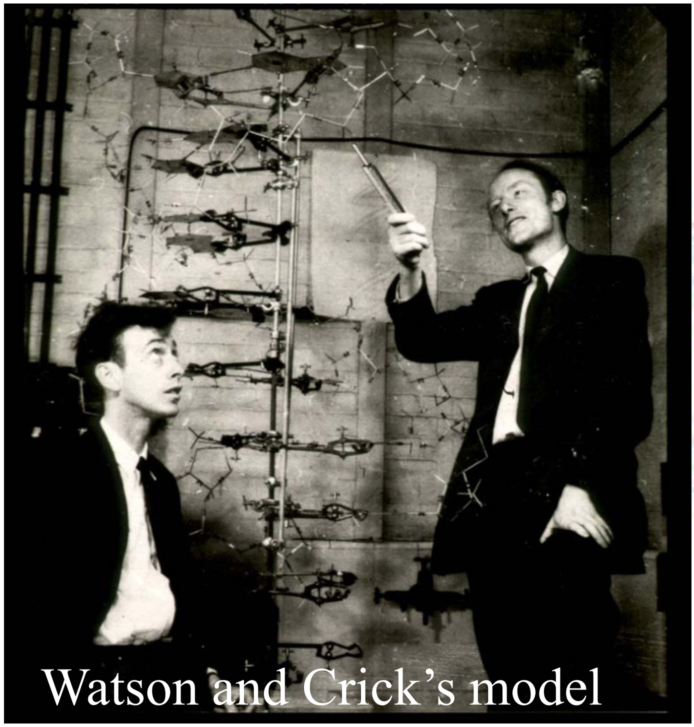
Solving the Structure of DNA

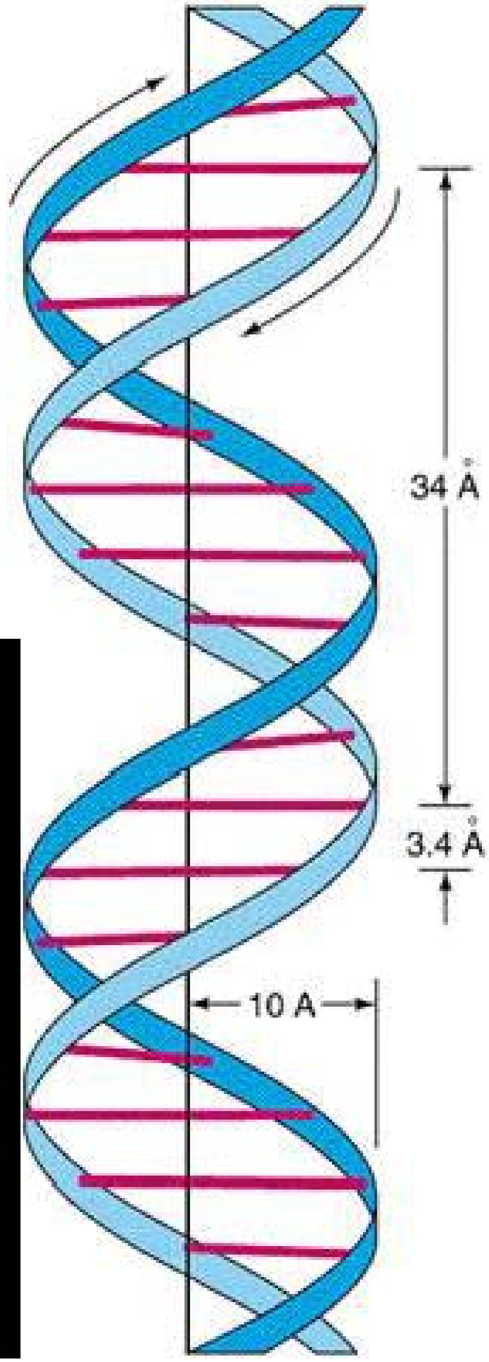
- Information Gained from Photo 51
  - ➢ Double Helix
  - ➢ Radius: 10 angstroms
  - ➢ Distance between bases: 3.4 angstroms
  - ➢ Distance per turn: 34 angstroms
- Combining Data with Other Information
  - ➢ DNA made from:

    sugar

    phosphates

    4 nucleotides (A,C,G,T)
  - ➢ Chargaff's Rules
    - %A=%T
    - %G=%C
  - ➢ Molecular Modeling


Watson and Crick's model

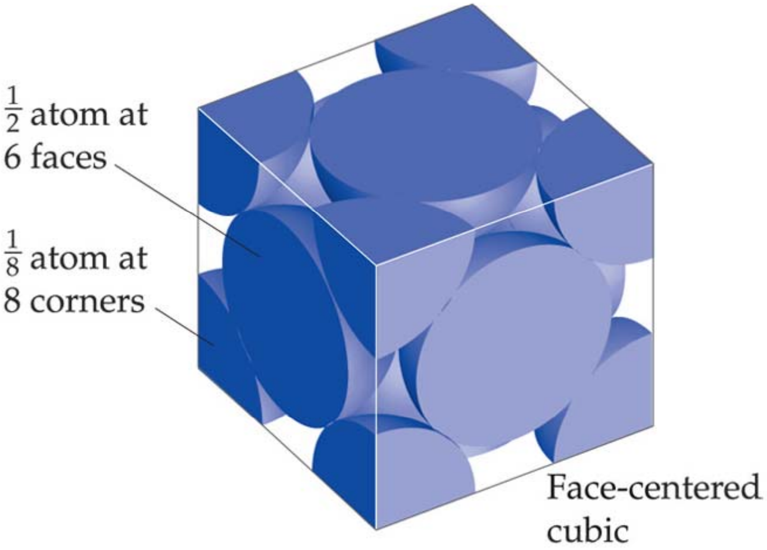


Crystalline Solids

We can determine the empirical formula of an ionic solid by determining how many ions of each element fall within the unit cell.

How many atoms are contained in the unit cell shown on the right?

Position in Unit Cell	Fraction in Unit Cell
Center	1
Face	$\frac{1}{2}$
Edge	$\frac{1}{4}$
Corner	$\frac{1}{8}$



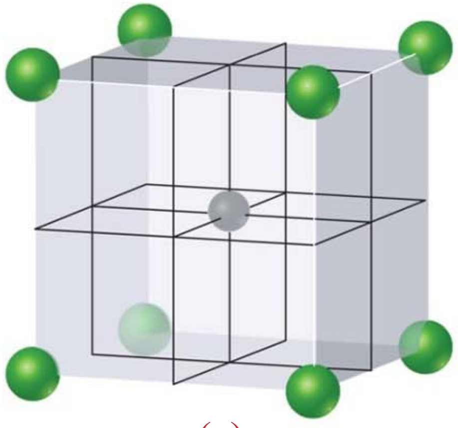
Ionic Solids

What are the empirical formulas for these compounds?

(a) Green: chlorine; Gray: cesium

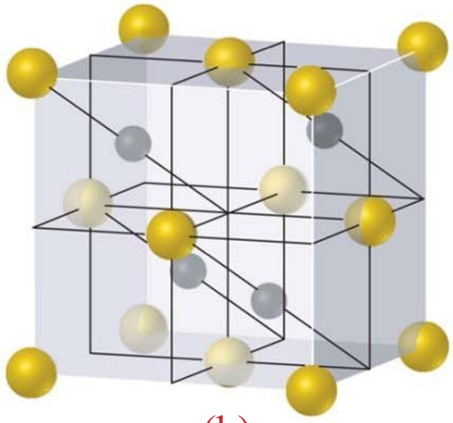
(b) Yellow: sulfur; Gray: zinc

(c) Green: calcium; Gray: fluorine



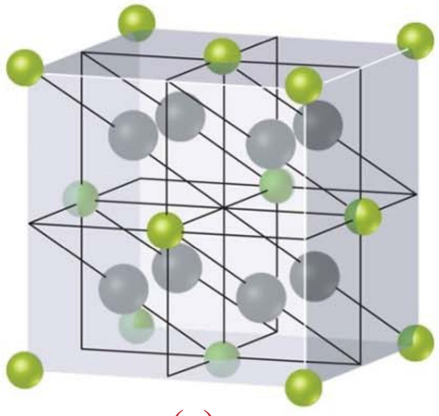
(a)

$CsCl$



(b)

ZnS



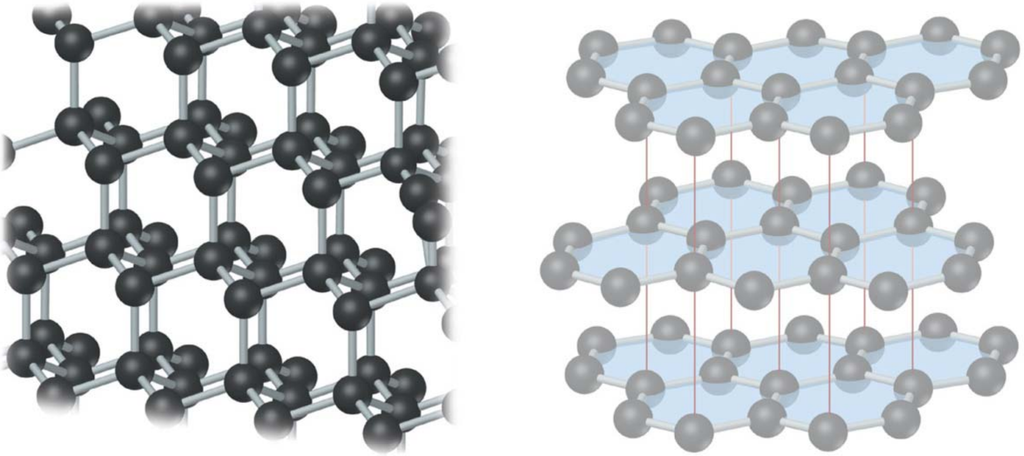
(c)

CaF_2

Types of Bonding in Crystalline Solids

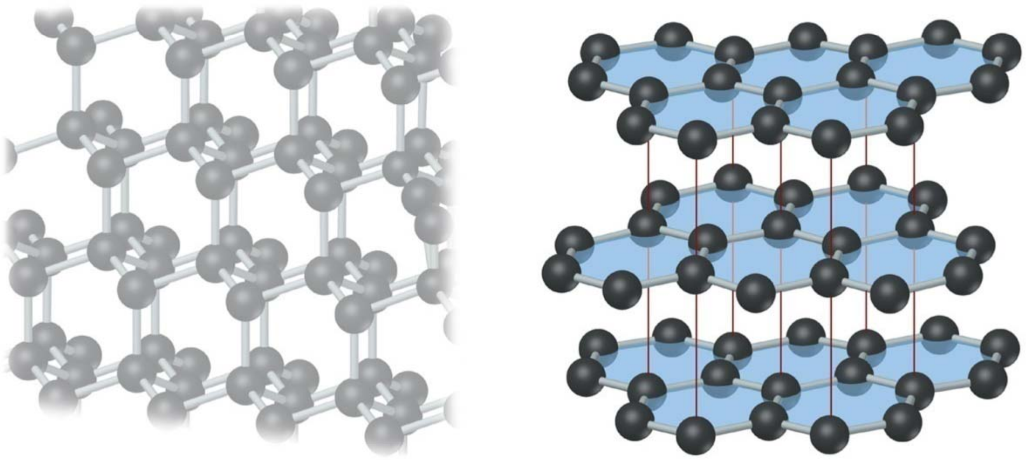
Type of Solid	Form of Unit Particles	Forces Between Particles	Properties	Examples
Molecular	Atoms or molecules	London dispersion forces, dipole-dipole forces, hydrogen bonds	Fairly soft, low to moderately high melting point, poor thermal and electrical conduction	Argon, Ar; methane, CH_4 ;sucrose, $C_{12}H_{22}O_{11}$; 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

Covalent-Network and Molecular Solids



- Diamonds are an example of a covalent-network solid in which atoms are covalently bonded to each other.
  - They tend to be hard and have high melting points.

Covalent-Network and Molecular Solids



- Graphite is an example of a molecular solid in which atoms are held together with van der Waals forces.
  - ➢ They tend to be softer and have lower melting points.

Metallic Solids

- Metals are not covalently bonded, but the attractions between atoms are too strong to be van der Waals forces.
- In metals, valence electrons are delocalized throughout the solid.