Chapter 11 – Liquids & Intermolecular Forces

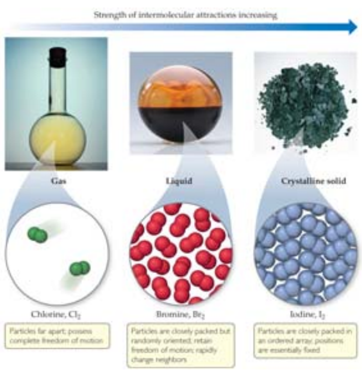
• 11.1 A Molecular Comparison of Gases, Liquids, and Solids

The state of a substance is a balancing act between how fact the molecule is moving (kinetic energy) and interactions between particles (intermolecular forces)

Table 11.1 Some Characteristic Properties of the States of Matter

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

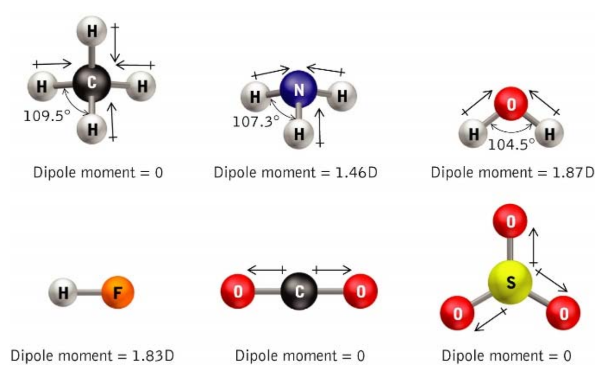
*The atoms in a solid are able to vibrate in place. As the temperature of the solid increases, the vibrational motion increases.



- The fundamental difference between states is the strength of the intermolecular force
- Stronger forces bring molecules closer together
- Solids and liquids are referred to as condensed phases

<Recall Polar Covalent Bonds & Dipole Moments>

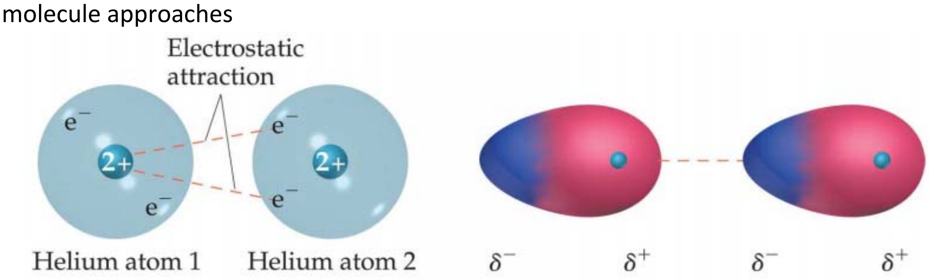
- van der Waals constant for water (a = 5.28 L^2atm/mol^2) vs O_2 (a = 1.36 L^2atm/mol^2)
  - -- water is polar (draw diagram) and O_2 is non-polar
    - --- recall the Electronegativity (EN) Trend
  - -- interaction between water molecules are electrostatic
- polar bonds and polar molecules
  - -- *bond dipole*
    - --- change in EN between 2 atoms makes the bond connecting them polar
    - --- this phenomenon leads to a bond dipole (arrow head points to the more EN atom)
  - -- *permanent dipole moment* (see figure →)
    - --- a molecule has a permanent dipole moment when it possesses an asymmetric orientation of polar bonds



--- molecules that possess a permanent dipole: NH_3, H_2O, SO_2, SF_4, $XeOF_4$
--- molecules that do not possess a permanent dipole: CBr_4, BF_3, $BeCl_2$, PCl_5, I_3^-, SF_6, XeF_4

- **11.2 Intermolecular Forces**

- Intramolecular =inside a single molecule versus Intermolecular = between two or more molecules
  -- Intramolecular forces will impact bond energies (polar versus covalent)
  -- Intermolecular forces will impact things like melting/freezing and boiling points
- Dispersion Forces
  Why do van der Waals constants have nonzero values for nonpolar species?
  -- recall a = 1.36 L^2atm/mol^2 for O_2
  -- polarizability: refers to the distortion of the electron cloud around the atom's nucleus as another atom or molecule approaches



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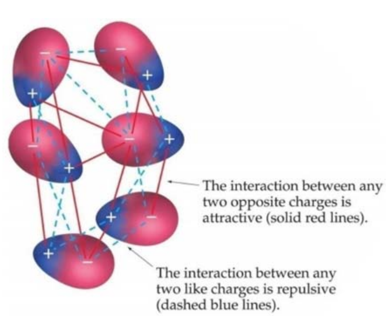
  -- this distortion occurs as a result of electron-electron repulsion btwn the atom and the approaching species
  -- the larger a molecule is the less tightly the electrons are held to the nucleus
    --- this makes it easier to distort the electron cloud
    --- therefore larger molecules are more polarizable
  -- comparison btwn He (a = 0.0341 L^2atm/mol^2) versus Ar (a = 3.59 L^2atm/mol^2)
  -- London or dispersion forces: interactions btwn induced dipoles
    --- when an atom is polarized in the presence of another species this induced dipole occurs
    --- this is the type of interaction which happens btwn two non-polar species - e.g. N_2 molecules
    --- factors that impact the strength of this force:
      ---- molecular weight (aka size) – the larger the more polarizable and therefore the larger the force
      ---- molecular shape – when two molecules have the samemolecular formula then the shape that maximizes surface area will have a greater induced dipole
  -- Usually this intermolecular force is considered to be the weakest
  -- It is also the only force that is present in ALL *neutral* molecules
- Dipole-Dipole



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  -- we have attraction btwn the negative (pink) and positive "poles" in blue shown with solid red lines

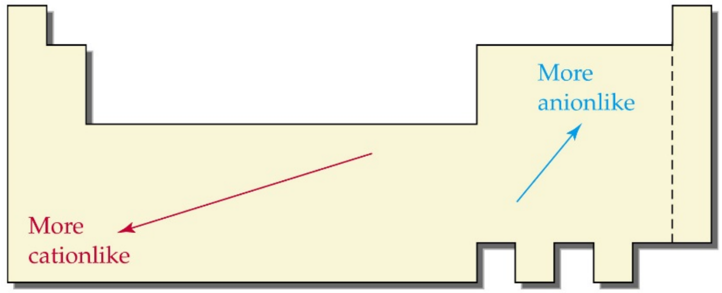
  -- we also have repulsion btwn the "poles" which are charged the sames shown with dashed blue lines

  -- these dipoles happen because electron density is pulled from the less electronegative atoms toward the more electronegative ones

-- recall the Electronegativity trend

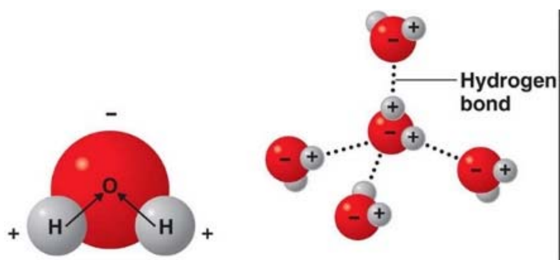
--- the more cationlike atom will have less electron density making it more positive

--- the more anionlike atom will have more electron density thereby appearing more negative



-- Overall two poles are produced which is why we call this IF dipole-dipole

- Hydrogen Bonding



-- defn: dipole-dipole interaction that occurs btwn molecules possessing H and either O, N, or F

-- bond created by the close proximity of the lone pairs from the very EN atoms

-- very strong dipole-dipole interaction

-- contribute to the high boiling point of water

-- lead to the double helical formation of DNA

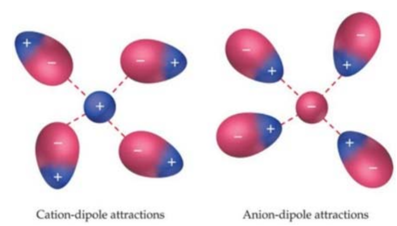
-- they also attribute to other properties that will be discussed later

- Ion-Dipole

-- In this figure

--- On the left we have an positive ion (cation) interacting with a polar species

--- On the right it is an anion interacting with a polar species

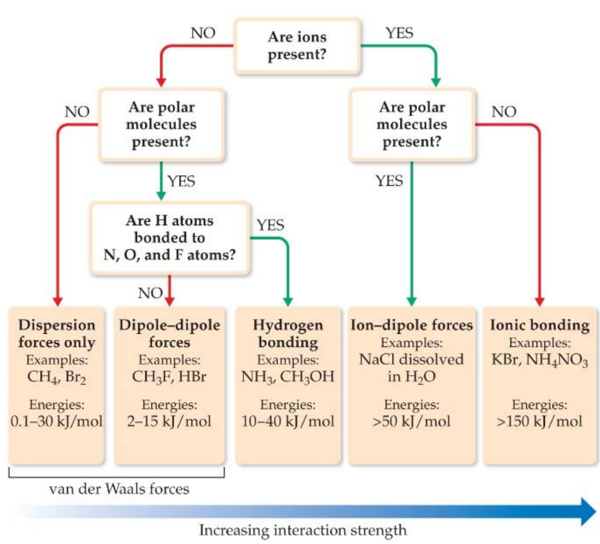


-- attractive forces btwn opposite charges

-- very strong interaction leads to the larger value of the van der Waals a constant

-- the more polar a molecule is the stronger the ion-dipole interaction

- Comparing Intermolecular Forces



-- When looking at a compound you will first determine if ions are present

-- If yes, you will decide it the molecules are polar or ionic

--- If polar we have ion-dipole IF

--- if ionic we have ion-ion IF

-- If no, you will decide if the molecules are polar or nonpolar

--- If polar, ask if they have H with N, O or F

---- If yes we have H-bonding IF

---- If no we have dipole-dipole IF

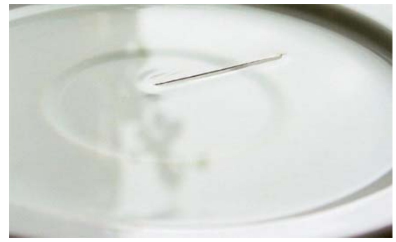
--- If nonpolar we have dispersion forces

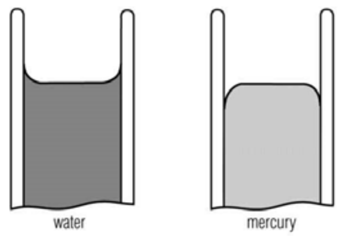
• 11.3 Select Properties of Liquids

- surface tension: energy needed to separate the molecules of unit area on the surface of a liquid

-- the reason a cold needle floats on the surface of water is because it is not dense enough to break the hydrogen bonds btwn the individual water molecules

-- a hot needle will sink because the added temperature is enough to break the H-bonds



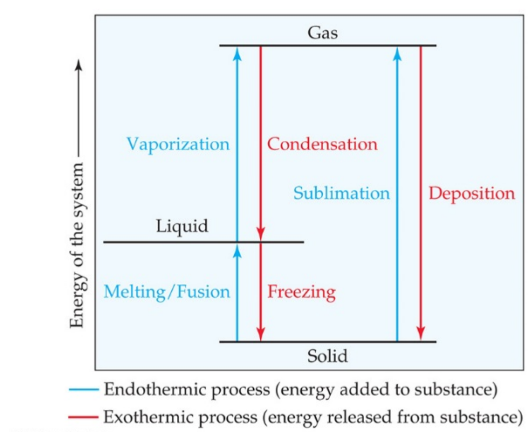


- meniscus: curved surface of a liquid as a result of cohesive (H-bonds - e.g. water with water) or adhesive (dipole-dipole - e.g. water with glass) forces btwn solvent and container molecules

- capillary action: rise of a liquid up a narrow tube
  -- result of cohesive and adhesive forces
    --- cohesive forces occur btwn liquid molecules
    --- adhesive forces occur btwn liquid and solid molecules
  -- the way in which water flows upwards into trees and plants from the soil
- viscosity: resistance of a fluid to flow
  -- molasses is very viscous
  -- water is not
  -- heating a fluid causes the viscosity to lower

• 11.4 Phase Changes

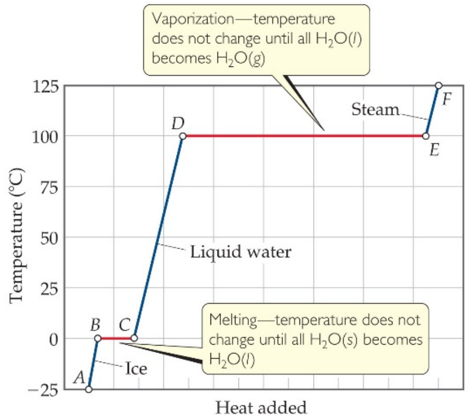
- Energy Changes Accompanying Phase Changes
  -- All phase changes require energy input (endothermic) or release (exothermic)
  -- heat of vaporization, ΔH_{vap} is the energy required to vaporize 1 mole of liquid at a pressure of 1 atm
  -- Other changes of state
    --- aside from going back and forth from liquid to gas we also have solid state transitions
    --- sublimation is another endothermic process in which solid goes to gas
    --- solidification is the opposite effect in which liquid/gas is solidified
    --- a solid may melt to form a liquid



    --- for each one of these processes we have accompanying enthalpies e.g. ΔH_{sub}
    --- one final note: when a change of state is performed the intermolecular forces which led to the initial state must be overcome (e.g. to boil something the intermolecular forces in the

liquid must be overwhelmed with our heat to the point molecules escape from the liquid to the gas phase)

- Heating Curves



-- AB we are heating up to the freezing point of water, T_f (recall Ch 5 q = mCΔT, q = heat, m = mass, C = specific heat of solid, ΔT = change in temperature)

-- BC represents the heat of fusion, ΔH_{fus}, which allows a phase change from s to l

-- CD we are heating up the liquid from T_f to T_b (boiling point, use q=mCΔT where C is for liquid)

-- DE represents the heat of vaporization, ΔH_{vap}, which allows a phase change from l to g

-- EF we are heating up the gas from T_b to final temperature

- Critical Temperature & Pressure
  - -- All substances have a T & P in which the liquid and gas phases are completely indistinguishable this is called the critical point
    - --- the density is the same for both states
    - --- the liquid phase is less dense due to high T
    - --- the gas phase is more dense due to high P
  - -- The name we give to this state is supercritical fluid
  - -- We will talk more about this in 11.6

• 11.5 Vapor Pressure

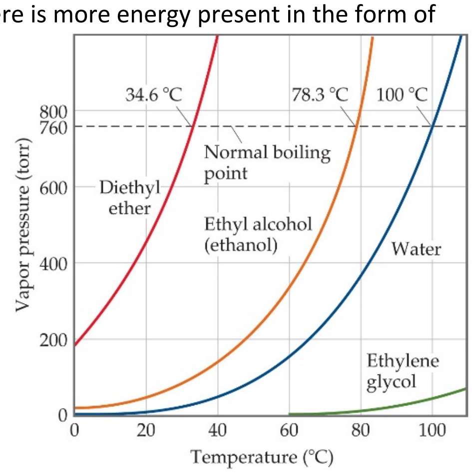
- vapor pressure is a result of molecules escaping from the liquid phase as gas

- vaporization/evaporation is an endothermic process because energy/heat must be added to the system for a molecule to escape the liquid phase

- when the rate of the liquid escaping to the gas is equal to the rate of a gas returning to liquid we have an example of equilibrium

- Volatility, Vapor Pressure & Temperature
  - -- A volatile liquid is one that evaporates and does not readily return to liquid
  - -- hot water will evaporate more quickly than cold because there is more energy present in the form of heat to break the H-bonds between water molecules

- Vapor Pressure & Boiling Point
  - -- As the temperature is increased so is the vapor pressure
  - -- when T increases so do the molecular motions and the ability for a molecule to escape from the liquid and go into the gas phase
  - -- since the pressure of the atmosphere is lower at higher elevations - less temperature is required for water to boil
  - -- One of the way we can use vapor pressure is to calculate the heat of vaporization by plotting the ln of the vapor pressure versus the inverse of the corresponding T:
    - --- This produces a linear equation in the slope encompasses ΔH_{vap}



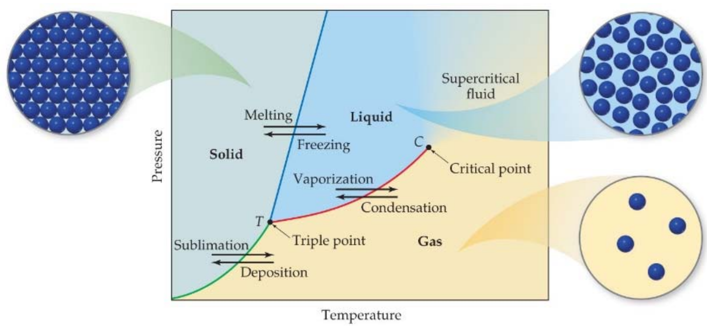
$$\underbrace{\ln P_{vap}}_{y} = \underbrace{-\frac{\Delta H_{vap}}{R}}_{m}\underbrace{\frac{1}{T}}_{x} + \underbrace{C}_{b}$$

--- This is called the Clausius-Clapeyron Equation and you will use this in the Heat of Vap lab

--- We can also ΔH_{vap} get by measuring the vapor pressure at two different temperatures using:

$$\ln\left(\frac{P_{vap,T_1}}{P_{vap,T_2}}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

- **11.6 Phase Diagrams**
  - the strength of intermolecular forces, temperature and pressure contribute to the phase (g, l, or s) of a molecule
  - at lower temperature and pressure gases are preferred whereas solids are more likely at higher temperatures and pressures
  - phase diagrams: graphical representation of the physical states as a function of T&P



-- lines in the diagram:

1) melting point line: the state corresponding to this line is both solid and liquid
2) boiling point line: both gas and liquid present
3) sublimation point line: gas and solid present
   -- note for water this line has a negative slope - due to H-bonds
   -- usually this is positively sloped
   -- the sublimation from ice to gas is what causes ice cubes to get smaller in the freezer

-- triple point: point at which all three phases are present

-- critical point: point at which liquid and gaseous state is indistinguishable

--- the liquid phase is less dense due to high temperature

--- the gas phase is more dense due to high pressure

--- densities of the two states are the same

-- normal points occur at 1 atm of pressure

--- normal bpt for water is 100°C

--- normal fpt for water is 0°C

-- above this critical temperature and pressure we get a supercritical fluid

--- has the physical properties of gas

--- has the ability to dissolve substances like a liquid

--- e.g. supercritical CO_2 to create decaffeinated coffee

- **11.7 Liquid Crystals – Skip it!**