Chem 1045 Lecture Notes | **Chemistry & Chemical Reactivity Kotz/Treichel/Townsend, 8th Ed**

These Notes are to SUPPLEMENT the Text. They do NOT Replace reading the Text Material. Additional material that is in the Text will be on your tests! To get the most information, READ THE CHAPTER prior to the Lecture, bring in these lecture notes and make comments on these notes. These notes alone are NOT enough to pass any test! The author is not responsible for typos in these notes**.**

Chapter 12 Intermolecular Forces and Liquids DRAFT NOTES

With gases, at and around STP, the intermolecular forces are negligible and can be ignored. At high pressure and/or low temperature there are fudge factors that need to be considered and enter into the gas law equations. Here we will look at liquids and their intermolecular forces.

What is the difference between a gas and a liquid. If 300 ml of liquid nitrogen were allowed to evaporate at STP, it would occupy a volume of more than 200 L. This shows the greater amount of space between molecules of a gas vs. a liquid. Going from a liquid to a solid does not have that amount of volume change. Below is a picture of a test tube of liquid benzene (C6H6) vs one of solid or frozen benzene. The volumes are almost the same, so the distances between molecules of a liquid vs. solid are similar.

Liquid benzene Solid benzene

(b)

The Intermolecular Forces between these molecules are:

- Directly related to physical properties such as: melting and boiling points, heat of fusion and vaporization
- Important in determining the solubility of a solid, liquid or gas in various solvents
- Determining the structure of biologically compounds such as DNA

Bonding in Ionic Compounds (700 – 1100 kJ/mole) depends on electrostatic forces. The Intermolecular Forces also depend on electrostatic forces such as **van der Waals** forces which are the attractive and repulsive forces between:

- Molecules with permanent dipoles (dipole - dipole forces)
- Polar molecular and nonpolar ones (dipole – induced dipole forces)
- Nonpolar molecules (induced dipole - induced dipole forces or **London Forces**)

Interactions between Ions and Molecules with a Permanent Dipole

When Ionic Compound (for example NaCl has a Na^+ and Cl^- ions) and a polar molecule (such as water – H_2O or H-O-H where the O is slightly negative and the H slightly positive) are brought together, the positive end of the ionic compound (Na^+) is attracted to the negative side of the polar water molecule (O). This attraction is not as energetic as the bonding of the Na^+ and Cl^- ions. Water has a dipole moment due to the oxygen attracting the electrons. The attractive forces depend on:

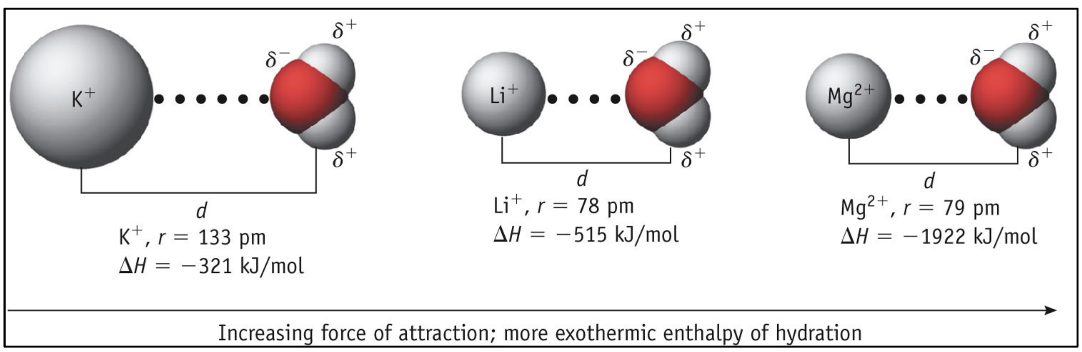
- The distance between the ion and the dipole, the closer they are, the stronger the attraction
- The charge on the ion, the higher the charge the stronger the attraction
- The magnitude of the dipole, the higher the dipole moment, the stronger is the attraction.

Hydration of ions in aqueous solutions is an example of an ion and a polar molecule and the energy released is called the **Enthalpy of Hydration** and is given below for the Alkali Metals and shows as the ion size increases going down the column, the EofH decreases.

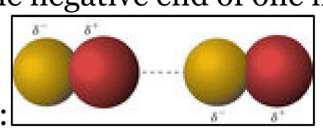
Table 12.1 Radii and Enthalpies of Hydration of Alkali Metal Ions

Cation	Ion Radius (pm)	Enthalpy of Hydration (kJ/mol)
Li^+	78	−515
Na^+	98	−405
K^+	133	−321
Rb^+	149	−296
Cs^+	165	−263

As size decreases going from K^+ to Li^+, the EofH increases from -321 kJ/mole to -515 kJ/mole. Going from a charge of +1 to +2 also increases the EofH from -515 kJ/mole for Li^+ to -1922 kJ/Mole for Mg^{2+}.



Interactions between molecules with dipole-dipole forces.

Molecules with a dipole will line up with the negative end of one molecule facing the positive end of another: 

This dipole-dipole attraction effects the evaporation of a liquid to a vapour, or it's condensation back to a liquid and is called the **Enthalpy of Vaporization**. The greater the attraction force, the greater the EofV and Polar Molecules should have a larger EofV than Non-Polar. In the table below going from non-polar Br_2 to polar ICl raises the BP from 59°C to 97 °C.

Table 12.2 Molar Masses, Boiling Points, and $\Delta_{vap}H°$ of Nonpolar and Polar Substances

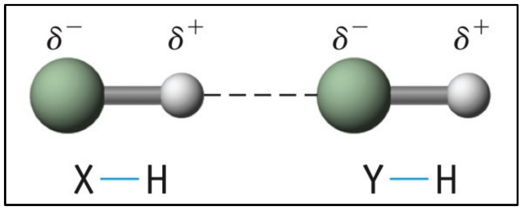
Nonpolar				Polar			
	M (g/mol)	BP (°C)	$\Delta_{vap}H°$ (kJ/mol)		M (g/mol)	BP (°C)	$\Delta_{vap}H°$ (kJ/mol)
N_2	28	−196	5.57	CO	28	−192	6.04
SiH_4	32	−112	12.10	PH_3	34	−88	14.06
GeH_4	77	−90	14.06	AsH_3	78	−62	16.69
Br_2	160	59	29.96	ICl	162	97	—

Solubility is also affected by Intermolecular Forces. Like dissolves Like, Polar Water, H-OH, dissolves in Polar Ethanol, CH_3CH_2-OH. And, Polar Water, H-OH, does not dissolve in Non-Polar Organics such as Octane, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3. The Water / Ethanol Polar

Molecules line up their dipole moments which helps dissolve. Water / Octane does not have a Dipole-Dipole attraction.

Hydrogen Bonding

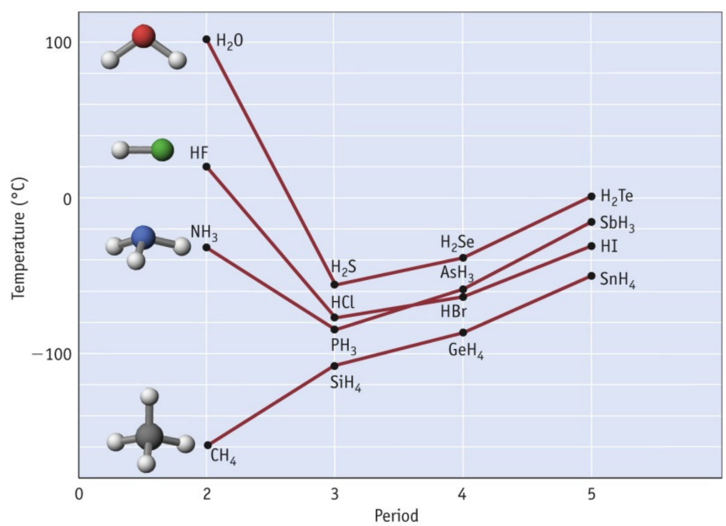
Hydrogen Bonding is a Dipole-Dipole interaction between the Hydrogen of an HX molecule and the X of an adjacent molecule where X is O, N or F.



This occurs due to the high electronegativity of these molecules: O (3.5), N (3.0), F (4.0). The Hydrogen of an HX will line up and is attracted to the lone pair of an adjacent X molecule.

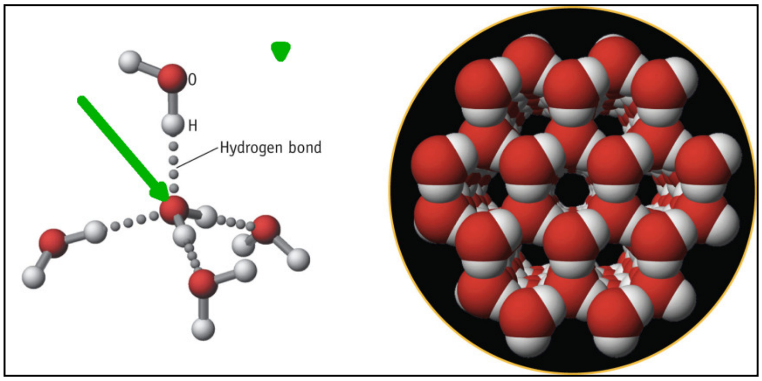
N-H . . . :N-	O-H . . . :N-	F-H . . . :N-
N-H . . . :O-	O-H . . . :O-	F-H . . . :O-
N-H . . . :F-	O-H . . . :F-	F-H . . . :F-

Hydrogen bonding affects the boiling points of these types of molecules, looking at the series below, going up a period (Te -> Se -> S -> O) you would expect Oxygen (H_2O) to have a lower boiling point. But (see chart below), H-O and H-F and H-N have higher than expected boiling points due to hydrogen bonding**. (Student Explain)**



Hydrogen Boding and the Unusual Properties of water

Waters properties are due to Hydrogen Bonding (HB), one water molecule hydrogen bonds to 4 other molecule.



See left image in picture above, the central water molecule. The two hydrogen atoms are HB to the Oxygen lone pair of electrons of two other water molecules. The Oxygen of the central water molecule has it's two electron lone pair HB to two other water molecules.

1. Ice has an open cage structure which results in the density of ice being 10% less than liquid water – ice floats. Most all other liquids have their solid form more dense and it sinks in the liquid form.

2. When ice melts at 0 °C, it increases in density up to 4 °C. This results in the mixing of upper and lower water in lakes as the temperature gets colder. Lakes do not freeze from the bottom up.

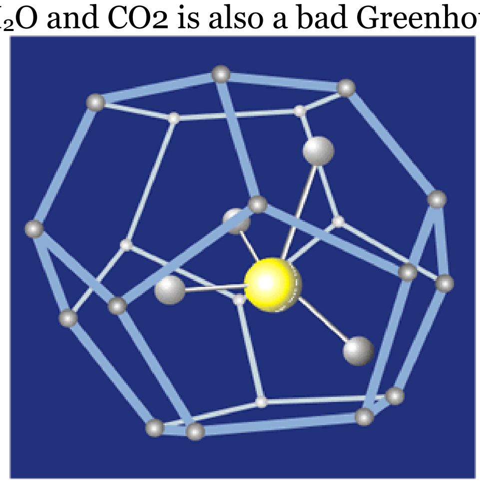
3. Water has a high heat capacity due to hydrogen bonding. For water molecules to heat up, you must first break the hydrogen bonding so the molecules can move about more.

Water	4.186 J/g °C or 1 Cal/ g °C
Aluminum	0.897 J/g °C
Calcium	0.646 J/g °C
Iron	0.449 J/g °C
Ethanol	2.44 J/g °C

Water act's to slow sudden temperature changes. A large body of water (Atlantic Ocean) will keep the temperature of adjacent lands (Florida) from getting cold fast in Nov/Dec and from getting hot fast in Jun/July.

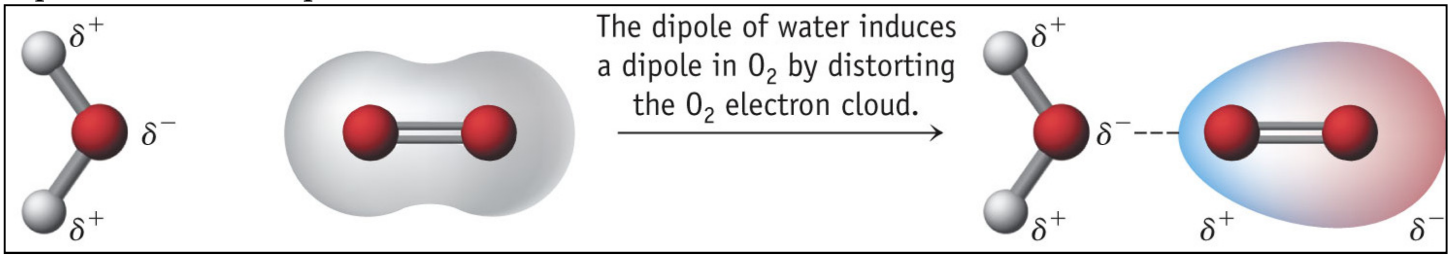
Methane Hydrate is comprised of a sphere (sort of like a soccer ball) of 14 hydrogen bonded water molecules with a molecule of Methane (CH_4) in the center. It exists at very high pressure such as at the bottom of the ocean – greater than 1200 ' below the surface and less than 0 °C. 1 m^3 of Methane Hydrate can release 160 m^3 of Methane (CH_4). Methane is bad for the atmosphere as it is a very potent Greenhouse Gas (Students Explain). But there is enough Methane Hydrate in the local oceans to supply our energy needs for a long time. But, remember – burning Methane still generates CO2:

$CH_4 + 2O_2 \rightarrow CO_2 + 2 H_2O$ and CO2 is also a bad Greenhouse Gas!



Dipole-Induced Dipole Forces

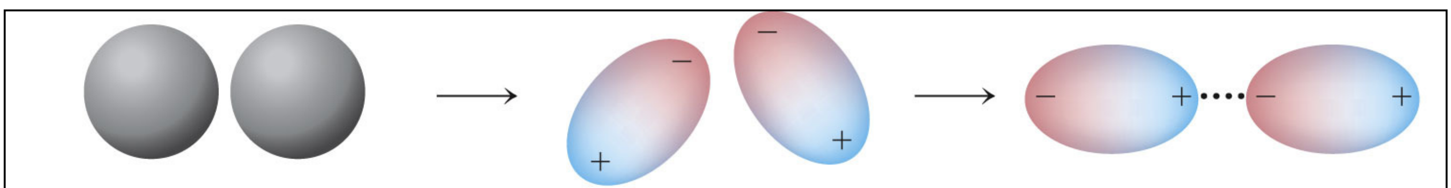
A polar molecule, such as water, as it approaches a non-polar molecule, such as O_2, can attract (positive hydrogen end) the electron cloud around the oxygen molecule or it can repel (negative oxygen end of the water molecule) the oxygen's electron cloud. This results in a Dipole-Induced Dipole interaction or polarization.



The gases (H_2, N_2, and O_2) are slightly soluble in water due to this induced polarization. The larger the non-polar molecule, the more is the induced polarization. Oxygen is larger than Nitrogen is larger than Hydrogen so the solubility's are O_2 2.01 g/mol > N_2 28.0 g/mol > H_2 32.0 g/mol.

London Dispersion Forces

London or Dispersion Forces are the weak attractive forces between molecules resulting from the small, instantaneous dipoles that occur because of the varying positions of the electrons during their motion about nuclei. All covalent bonded molecules exhibit LF. E.g. any alkane. Pentane BP 36°C, 2-Methyl butane BP 28°C, 2,2-Dimethyl propane BP 9.5°C. London Forces increase with Molecular Mass. As one non-polar molecule (such as Pentane $H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$) approaches another molecule of Pentane, there can be an instantaneous shift of electrons from one end of the molecule to the other. This can result in an attraction between the slightly positive end of one molecule to the slightly negative end of another. **London Forces are the only intermolecular forces between non-polar molecules!**

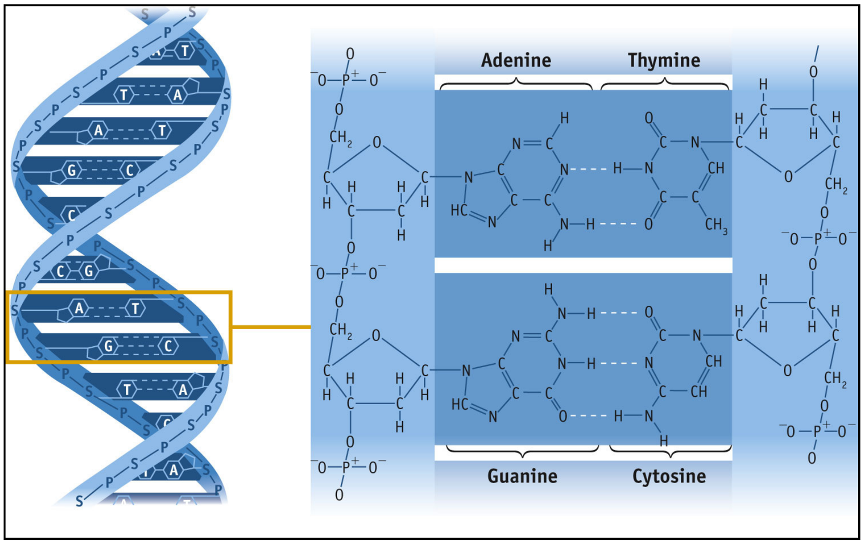


Two nonpolar atoms or molecules (depicted as having an electron cloud that has a time-averaged spherical shape).

Momentary attractions and repulsions between nuclei and electrons in neighboring molecules lead to induced dipoles.

Correlation of the electron motions between the two atoms or molecules (which are now polar) leads to a lower energy and stabilizes the system.

Hydrogen Bonding is responsible for the double helix of DNA and RNA



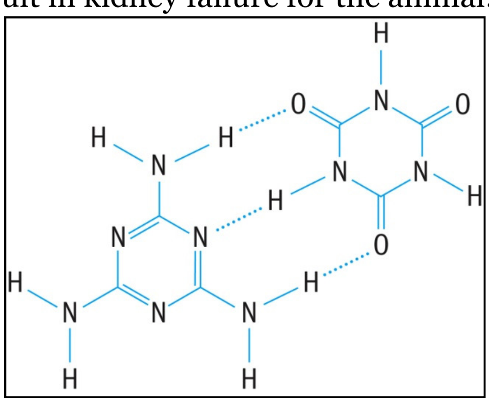
The individual strands are held together by N ··· H-N and N-H ··· O- hydrogen bonding. Take BioChemistry after you take Organic I and II and you'll learn all about this!

Table 12.5 Summary of Intermolecular Forces (in descending order of strength)

Type of Interaction	Factors Responsible for Interaction	Example
Ion–dipole	Ion charge, magnitude of dipole	$Na^+ \ldots H_2O$
Hydrogen bonding, X—H . . . :Y	Very polar X—H bond and atom Y with lone pair of electrons (where X and Y = F, N, O). Typical energy = 20 kJ/mol.	$H_2O \ldots H_2O$
Dipole–dipole . . . $(CH_3)_2O$	Dipole moment (depends on electronegativities and molecular structure). Typical energy = 5–20 kJ/mol.	$(CH_3)_2O \ldots (CH_3)_2O$
Dipole-induced dipole	Dipole moment of polar molecule and polarizability of nonpolar molecule. Typical energy <2 kJ/mol.	$H_2O \ldots I_2$
Induced dipole-induced dipole (London dispersion forces)	Polarizability	$I_2 \ldots I_2$

A China Wheat Gluten supplier killed your dog:

A US pet food manufacturer purchased wheat gluten from China. The Chinese supplier added Melamine and Cyanuric Acid to the wheat gluten to raise the nitrogen level. The "Goodness" of wheat gluten is measured by the amount of nitrogen in it. Melamine and cyanuric acid when mixed, form insoluble crystals of melamine cyanurate, a hydrogen bonded complex. These crystals form in the neutral pH of the kidney's and result in kidney failure for the animal.



Properties of Liquids

Vaporization involves a liquid going to a gas. Molecules of the liquid escape from the surface of the liquid to the gaseous state. Energy is required to do this and is called the Molar Enthalpy of Vaporization, $\Delta_{vap}H^o$.

Liquid + Energy → Vapor $\Delta_{vap}H^o$ = Molar Enthalpy of Vaporization

Condensation involves a liquid loosing energy, comes in contact with the surface of the liquid and enters the liquid phase

Vapor → Liquid + Energy - $\Delta_{vap}H^o$ = Molar Enthalpy of Vaporization

Vaporization is Endothermic, Condensation is Exothermic.

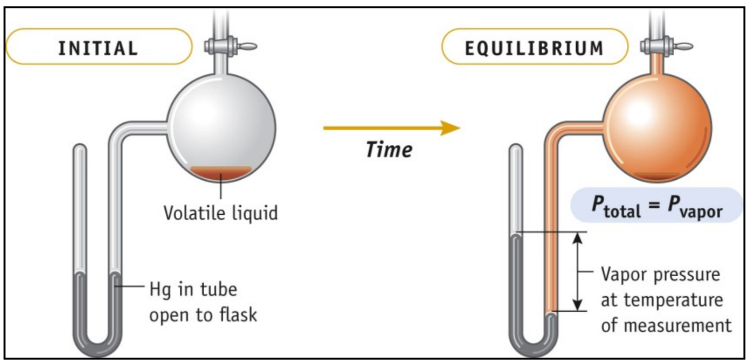
OWL IE 12.5 925 ml of water at 100 oC evaporates. How much energy is transferred and in which direction?

$\Delta_{vap}H^o$ = +40.7 kJ/mol at 100 ^oC Water Density at 100 ^oC = 0.958 g/cm^3 Water $_{mw}$ = 18.02 g/mol

925. ml * 1 ml / cm^3 * 0.958 g/cm^3 * 1 mol / 18.02 g = 49.2 mol H_2O

49.2 mol H_2O * +40.7 kJ/mol at 100 ^oC = 2.00 x 10^3 kJ

Vapor Pressure is the equilibrium vapor pressure resulting from a liquid vapor equilibrium. If you put some water in a sealed flask, after a time period, the amount of liquid remaining is less. The liquid has vaporized to the gaseous state and now exerts a pressure equal to the vapor pressure of the liquid.



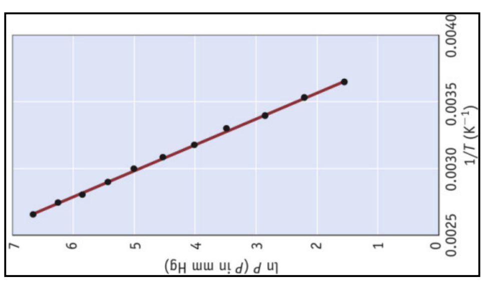
This pressure equilibrates as a **dynamic equilibrium** is established and is called the **equilibrium vapor** pressure. This is due to the tendency of the molecules to escape from the surface of the liquid phase to the vapour phase and is called the **volatility** of the compound. As the temperature increases, the molecules move about more and migrate from the liquid phase to the vapour phase to generate a larger vapour pressure.

The vapour pressure of a compound can be determined from the Clausius-Clapeyron Equation

$$\ln P = - (\Delta_{vap}H^o / RT) + C \qquad \ln = \text{natural log}$$

Where $\Delta_{vap}H^o$ is the Enthalpy of Vaporization of the liquid. Alternatitively:

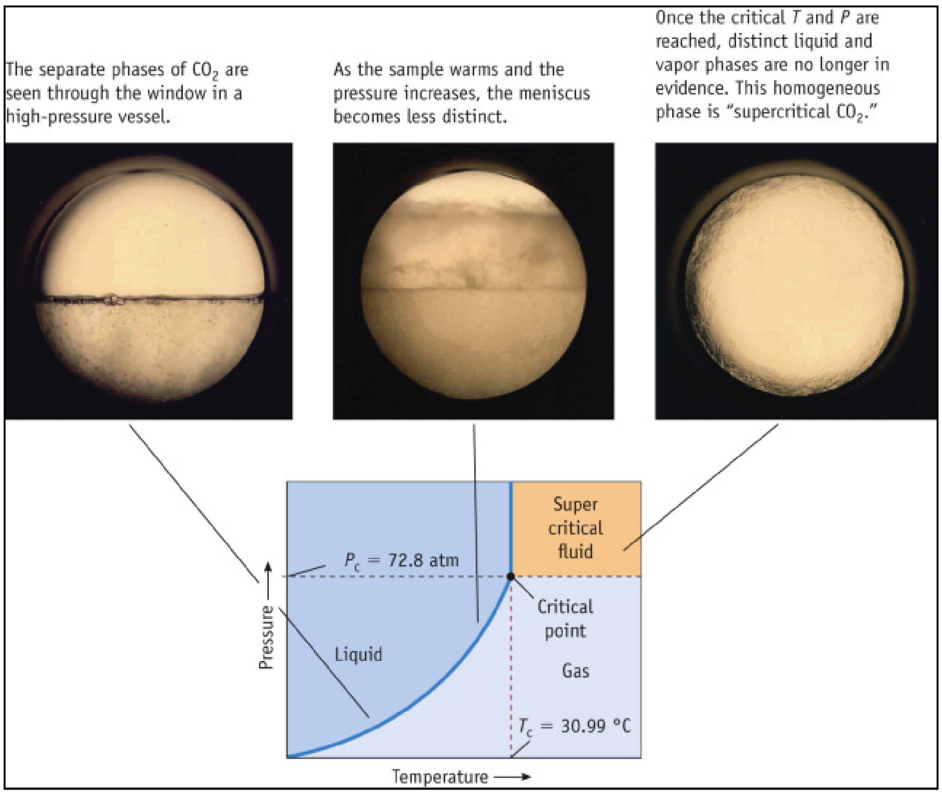
$\ln (P_2/P_1) = (\Delta_{vap}H^o / R) * (1/T_2 - 1/T_1)$ Where R = 0.008315 kJ / K mol



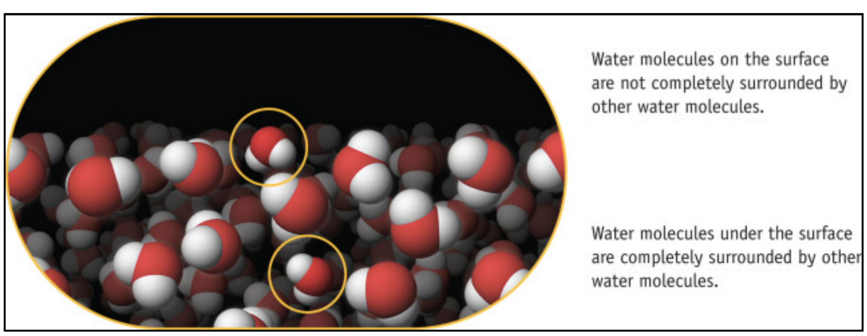
Plotting ln of the vapour pressure vs 1/T (K), see graph above, results in a slope = - $\Delta_{vap}H^o$ / R.

The **Boiling Point** of a liquid is when the vapor pressure of a liquid is equal to the external vapour pressure. (Student explain how long it will take to make a 1 minute hardboiled egg at the top of a mountain (say 15,000 ft above sea level – and WHY?)

Critical Point is the temperature and pressure where the interface between the liquid and vapour disappears. This occurs at the **Critical Temperature, T_c** and the **Critical Pressure, P_c.** A substance at these and higher conditions are referred to a **Supercritical Fluid.** Supercritical CO_2 is used to extract caffeine from coffee beans.



Molecules in at the interior of a liquid (see water in picture below) have equal interactions from all directions. Molecules at the surface of a liquid have equal liquid interactions from the sides and below, but have a different interaction with whatever is above the surface be it air or the wall of a container. The surface molecules then are attracted inwards more than outwards leading to a surface that has a skin. The toughness of this skin is called **surface tension**. Surface tension causes drops to be round.



Related to surface tension is **Capillary Action**. Putting a small diameter tube, or soda straw, into a liquid, the liquid seems to climb up the tube. This is due to the attraction of the tube walls is stronger than the inter-molecular molecule attraction. This also is the cause of a meniscus in your lab burette.

Viscosity is the resistance of a liquid to flow. Oil flows slow, water flows fast. The longer chain molecules have greater intermolecular forces which attract each molecule leading to a more viscous liquid. Honey is viscous due to the hydrogen bonding between the –OH molecules of the sugar it contains.