FORCES, VAPOR PRES, PHASES_______ Ch 16.1-2, 10-11, Petrucci

"[There were] only two fundamental forces to account for all natural phenomena. One was Love, the other was Hate. The first brought things together while the second caused them to part."
Empedocles ~ 450 BC

Z 16.1; P 12-1 Forces

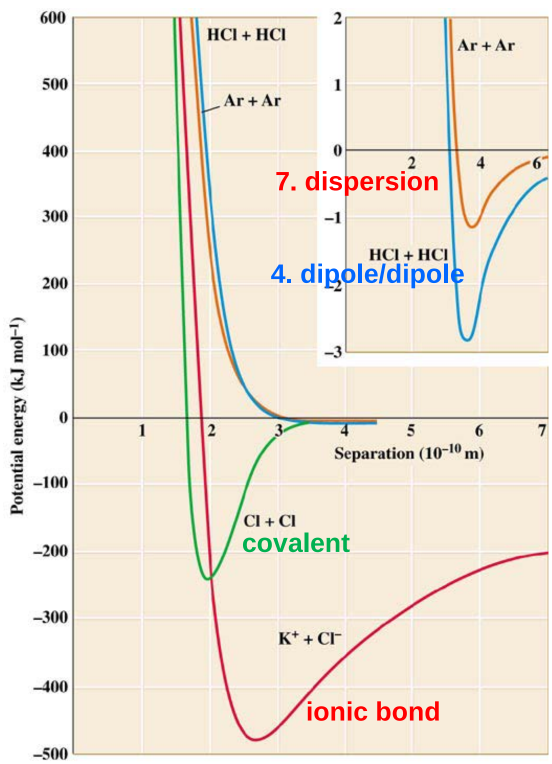
evidence for their existence

condensed states of matter exist (solids, liquids)
real gases do not obey *PV=nRT* under all conditions
nonideal solutions – deviations from Raoult's law (Chapter 17 – Properties of Solutions)

origin of forces

electrostatic (coulombic – between ions, dipoles)
induction or polarization (caused by ions, dipoles)
hydrogen bonding (H bonded to F, N, or O)
dispersion (motion of e^- causes an instantaneous dipole)

FIG I – Potential energy of pairs of atoms, ions, and molecules



types of forces (in ~ decreasing strength)

intramolecular (bonding) – strongest forces:

1. ion/ion- NaCl(s): Na^+, Cl^-
2. covalent bonds
3. metallic

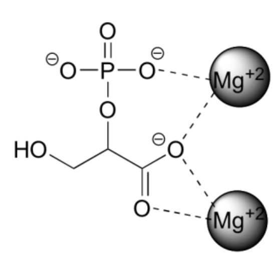
intermolecular (nonbonding):

force	example	energy
1. ion/ion	KF(*s*)	1/r
2. ion/dipole	NaCl(*aq*)	$1/r^2$
3. hydrogen bond	H_2O(*l*)	$1/r^2$
4. dipole/dipole	HCl(*g*)	$1/r^3$
5. ion/induced dipole	He/Li^+	$1/r^4$
6. dipole/induced dipole	H_2O(*l*)/O_2(*g*)	$1/r^6$
7. induced dipole/ induced dipole (dispersion, London)	Ne(*g*)	$1/r^6$

van der Waals forces: dipole/dipole, dipole/induced dipole, dispersion, hydrogen bonding

1. **ion/ion** – Coulomb's Law, potential energy = k $Q_1 \times Q_2$ / r

species	H_2O	NaCl	MgO
melting point (°C)	0	800	2800



2-phosphoglycerate, an intermediate in the breakdown of glucose

2. **ion/dipole**

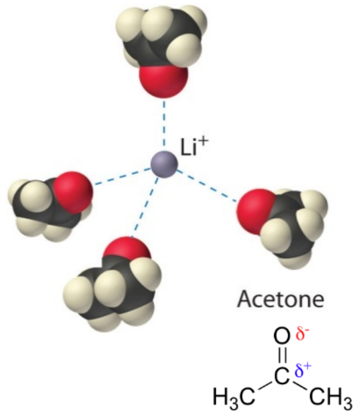
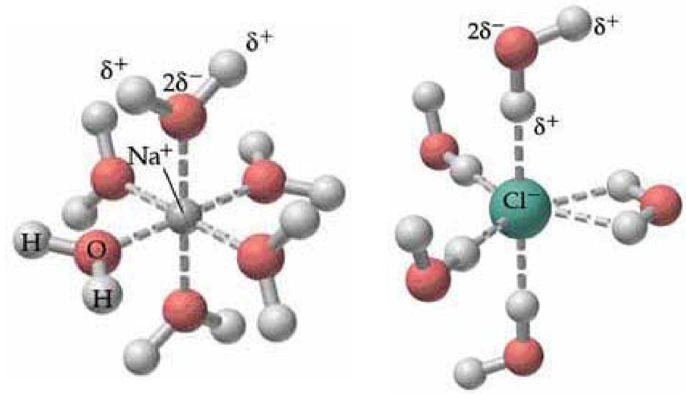


FIG II – Hydration of NaCl

NaCl(s) $\rightarrow$ NaCl(aq) $\equiv$ Na^+(aq) + Cl^-(aq)



3. **hydrogen bond:** H atom bonded to O, N, or F – special case of dipole/dipole but stronger

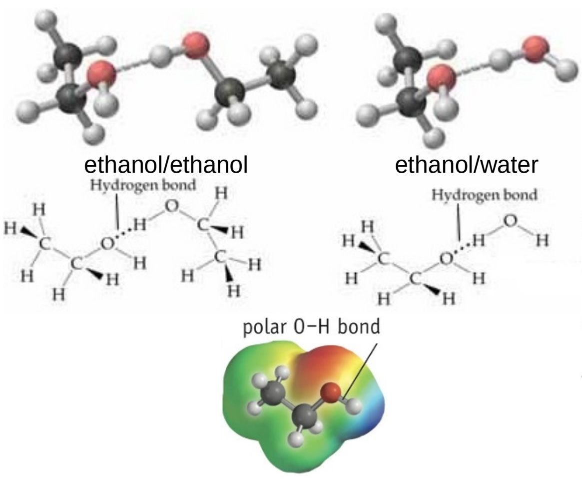
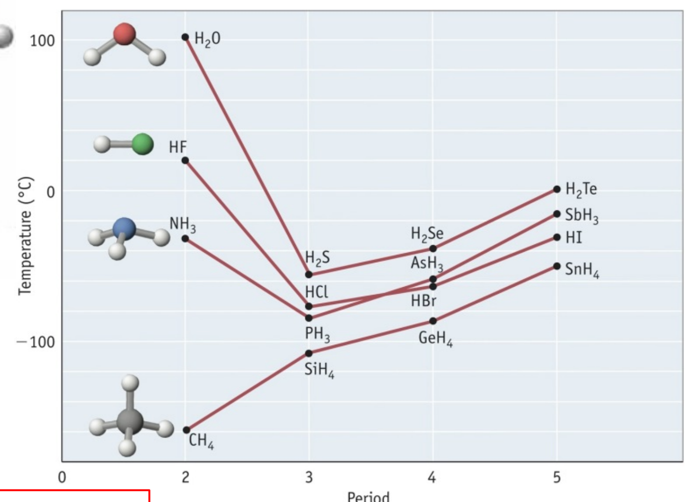
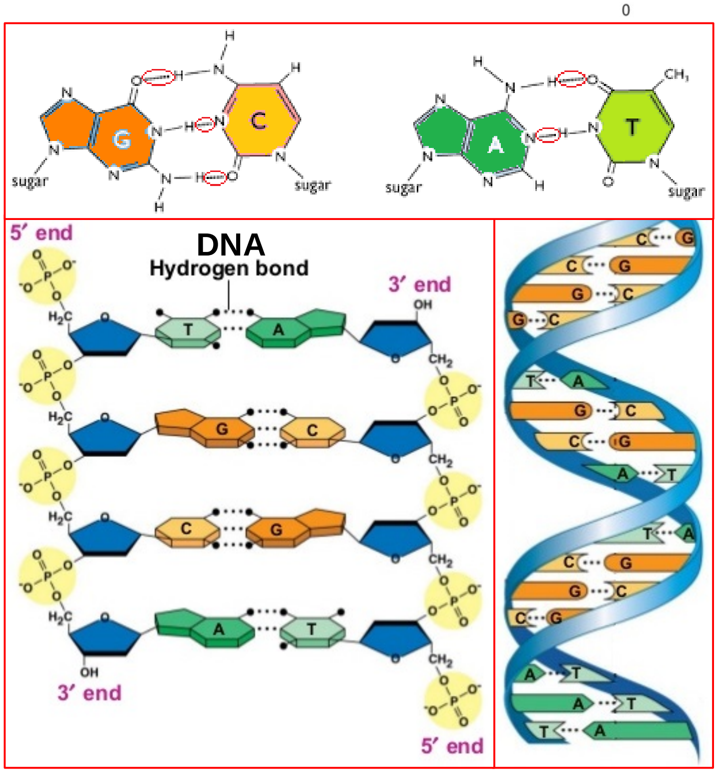
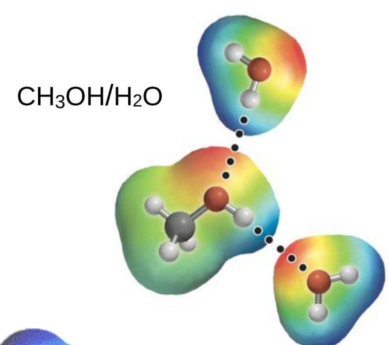
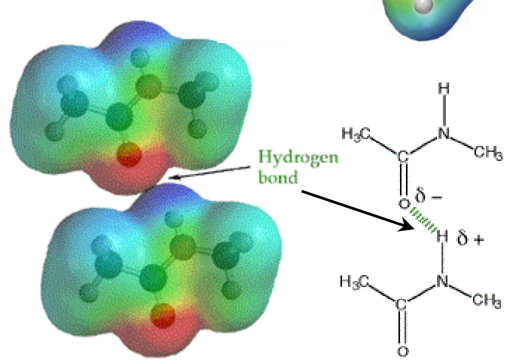


FIG III – Boiling points of hydrides

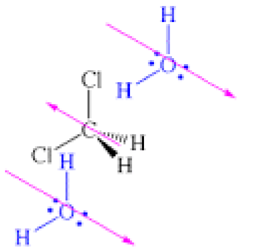




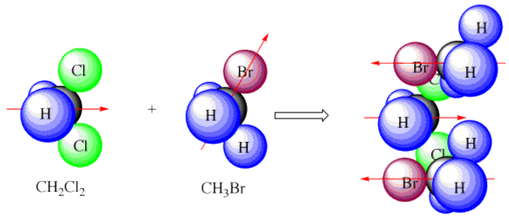


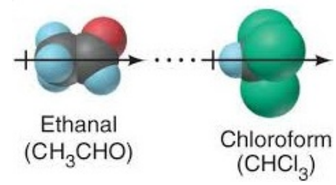


4. **dipole/dipole**



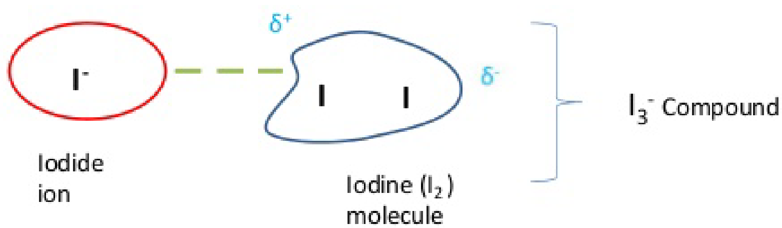
Dipole-dipole interactions

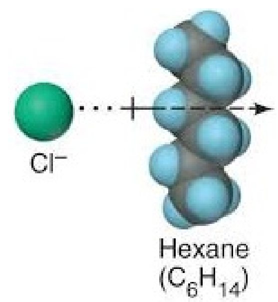




5. **ion/induced dipole**

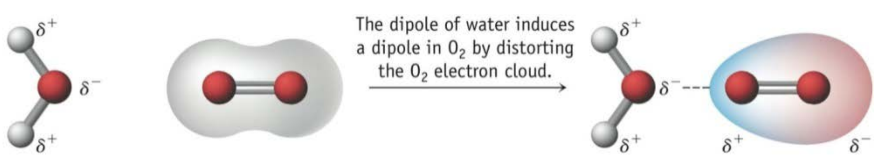
Li^+ ··· He Li^+··· Ne Li^+ ··· Ar

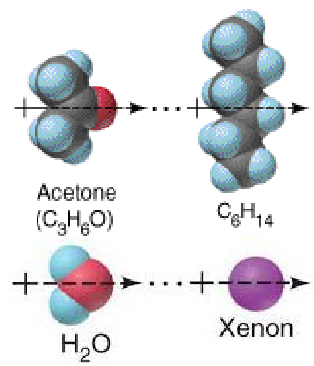




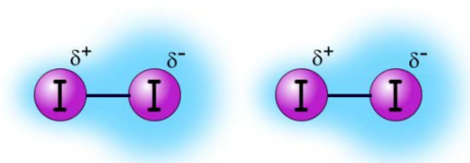
6. **dipole/induced dipole**

FIG IV – Water dipole inducing a dipole on O_2



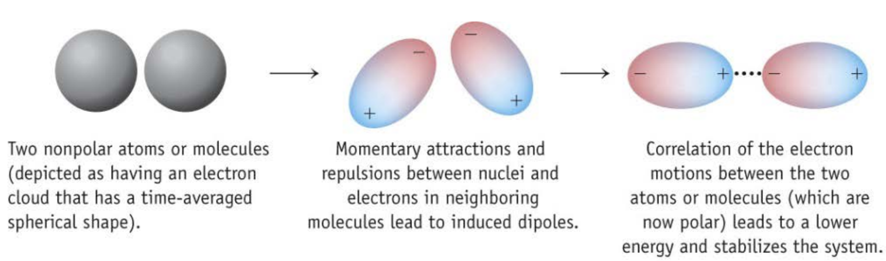


7. **induced dipole/induced dipole (London dispersion forces)**



Dispersion energies are generally small unless one of the molecules is charged.

FIG V – Induced dipole interactions



Br_2(*l*) I_2(*s*)

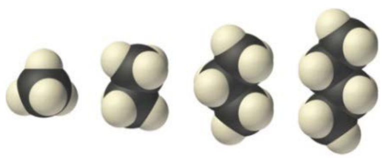
Effect of Dispersion on Boiling Point

halogen	bp (°C)	inert gas	**bp** (°C)
F_2	-188.1	He	-268.6
Cl_2	-34.6	Ne	-245.9
Br_2	58.8	Ar	-185.7
I_2	184.4	Kr	-152.3
		Xe	-107.1
		Rn	-61.8

Table 16.2

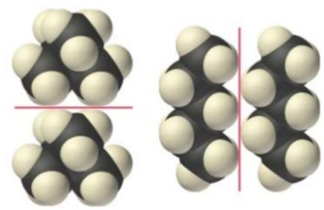
The Freezing Points of the Group 8A Elements

Element	Freezing Point (°C)
Helium	−269.7
Neon	−248.6
Argon	−189.4
Krypton	−157.3
Xenon	−111.9



Methane 16 g/mol −161.5°C | Ethane 30 g/mol −88.6°C | Propane 44 g/mol −42.1°C | *n*-Butane 58 g/mol −0.5°C

Increasing mass and boiling point



2,2-Dimethylpropane (neopentane) 72 g/mol, 9.5°C | *n*-Pentane 72 g/mol, 36.1°C

Increasing surface area and boiling point

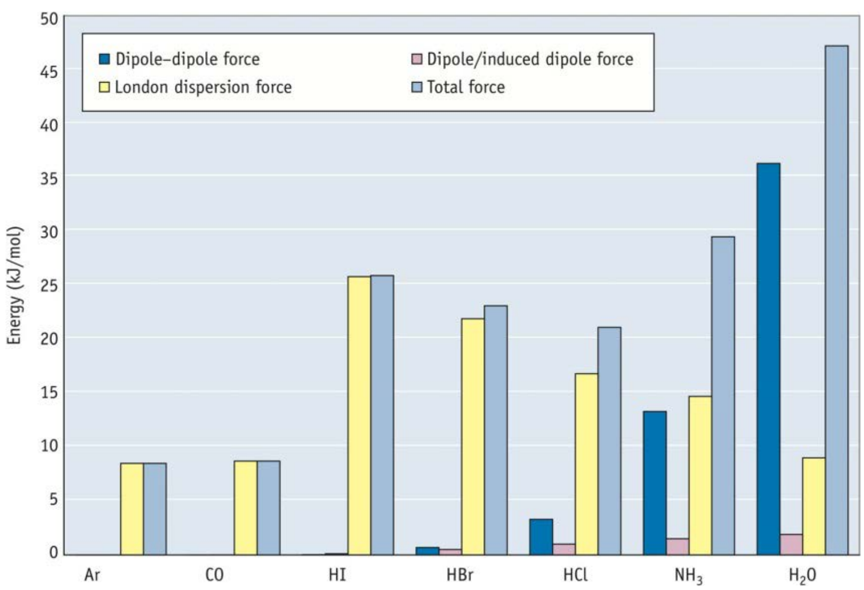


FIG VI – van der Waals forces in some molecules

Aside from small, highly polar molecules such as H_2O, dispersion energies are the largest contribution to intermolecular bonding between uncharged molecules.

Summary of van der Waals Forces

TYPE OF INTERACTION	FACTORS RESPONSIBLE FOR INTERACTION	EXAMPLE
Hydrogen bonding, X—H · · · :Y	Very polar X—H bond and atom Y with lone pair of electrons (where X and Y are often F, N, O).	$H_2O \cdots H_2O$
Dipole–dipole	Dipole moment (depends on electronegativities and molecular structure).	$(CH_3)_2O \cdots (CH_3)_2O$
Dipole-induced dipole	Dipole moment of polar molecule and polarizability of nonpolar molecule.	$H_2O \cdots I_2$
Induced dipole-induced dipole (London dispersion forces)	Polarizability (depends on molar mass)	$I_2 \cdots I_2$

EX 1. Effect of intermolecular forces on some physical properties.

a) What are the dominant intermolecular forces between NaCl (M=58 g/mol) and NaBr (M=103 g/mol)? Which would you expect to have the higher melting point?

b) What are the dominant intermolecular forces between ICl (M=162 g/mol) and Br_2 (M=160 g/mol)? Which would you expect to have the higher boiling point?

c) What are the dominant intermolecular forces between H_2, N_2, and O_2? Which do you expect to be the most soluble in water? the least soluble in water?

Z 16.2; P 12-2 Liquid State

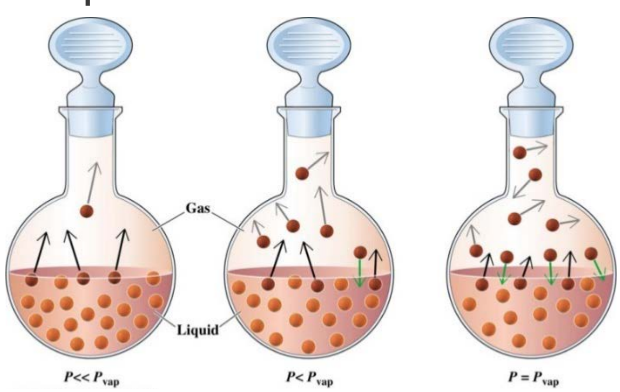
some properties of liquids dependent upon intermolecular forces:

surface tension - resistance to increase in surface area
viscosity - resistance to flow
capillary action - rise of liquid in narrow tube; cohesive/adhesive forces; meniscus

Z 16.10; P 12-2 Changes of State and Phase Equilibria

vapor pressure

liquid in equilibrium with its vapor
determined by IMF's
vapor not an ideal gas!
$P(T)$



The rates of condensation and evaporation over time for a liquid sealed in a closed container. The rate of evaporation remains constant, whereas the rate of condensation increases as the number of molecules in the vapor phase increases, until the two rates become equal. At this point the equilibrium vapor pressure is attained.

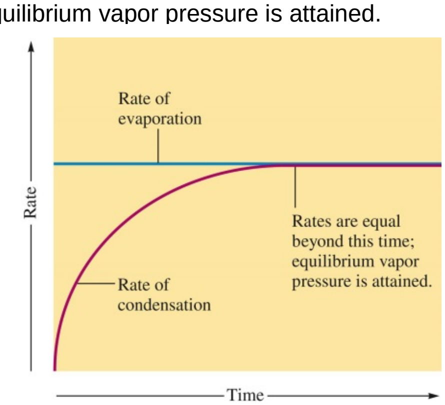
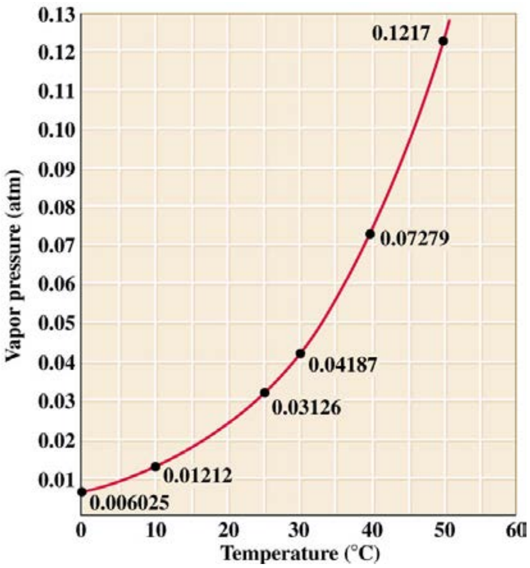


FIG VII – Vapor pressure of water as a function of temperature



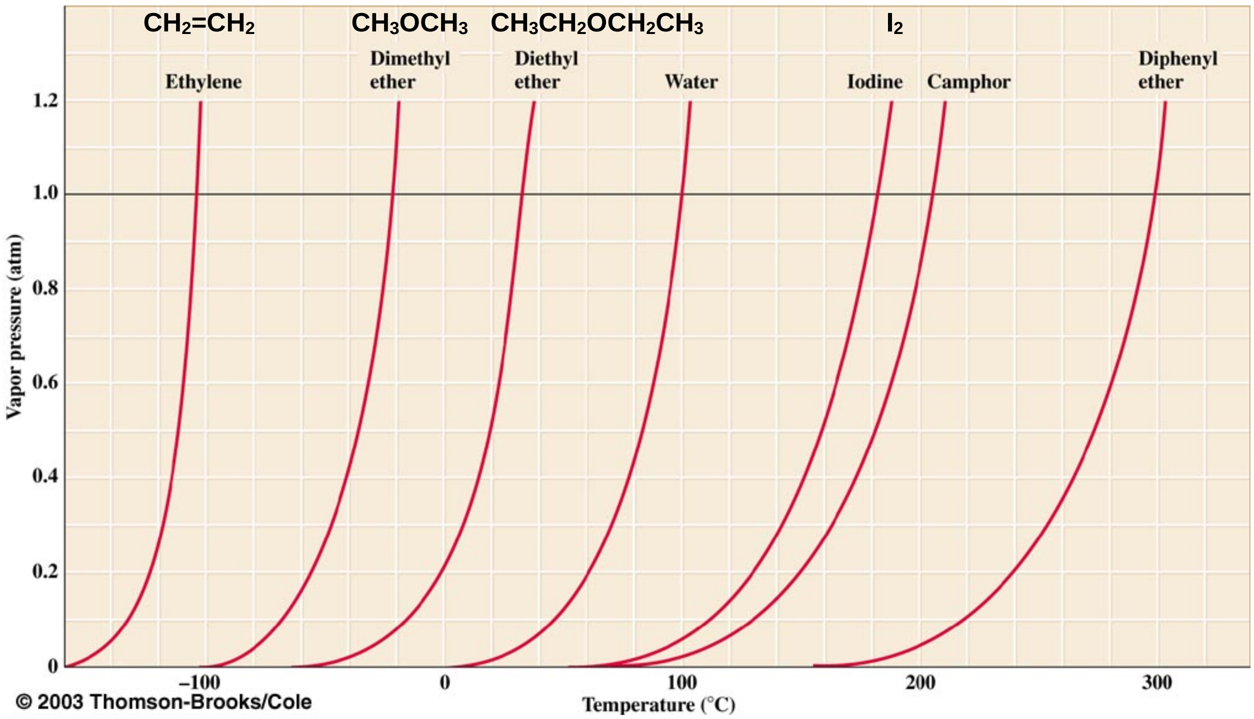
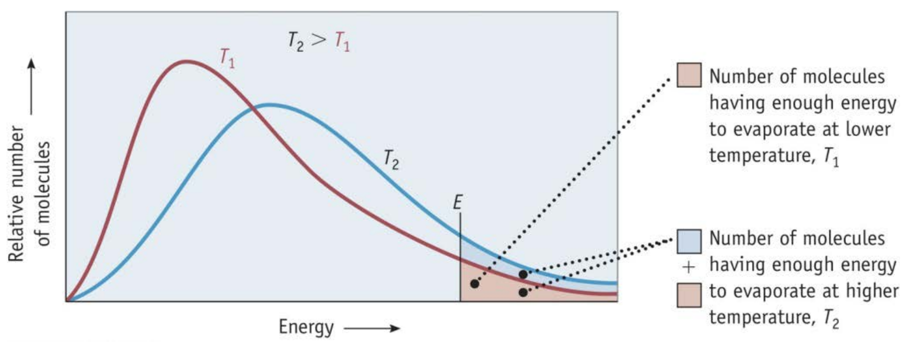


FIG VIII – Distribution of kinetic energies in a liquid



Z 16.10; P12-2,12-3 Phase Transitions

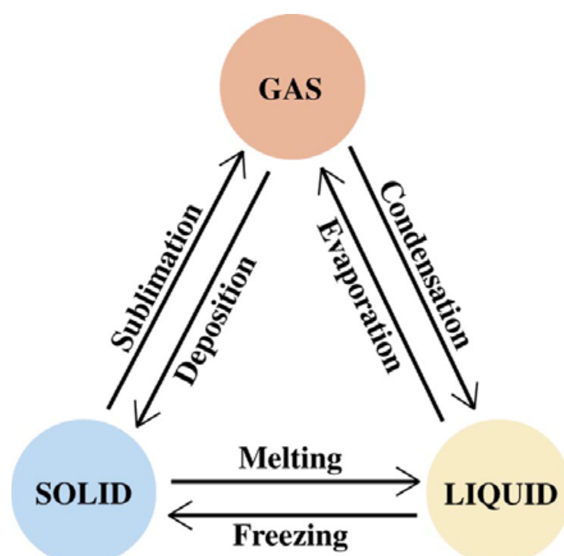
induced by a change in temperature or pressure

boiling point
normal boiling point

melting point
normal melting point

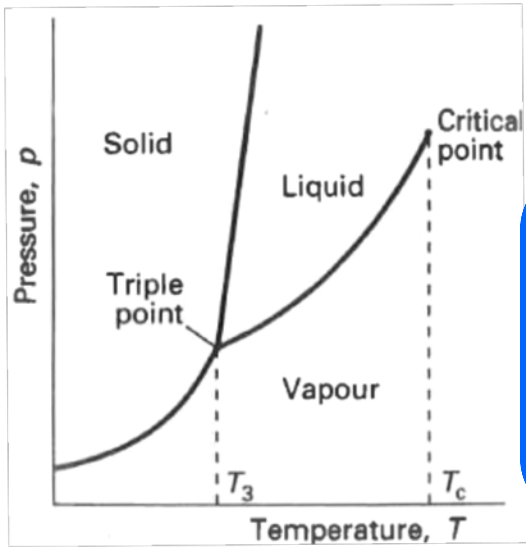
sublimation point
normal sublimation point

melting ≡ fusion



Z 16.11; P 12-4 Phase Diagrams

FIG IX – Simple, phase diagram



phase diagrams *P*(*T*)

shows *P*,*T* behavior of all solid, liquid, gas phases

solid <=> gas
solid <=> liquid
liquid <=> gas

triple point

critical point

The separate phases of CO_2 are seen through the window in a high-pressure vessel.

As the sample warms and the pressure increases, the meniscus becomes less distinct.

Once the critical *T* and *P* are reached, distinct liquid and vapor phases are no longer in evidence. This homogeneous phase is "supercritical CO_2."

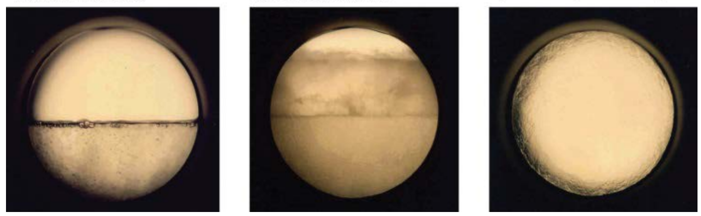
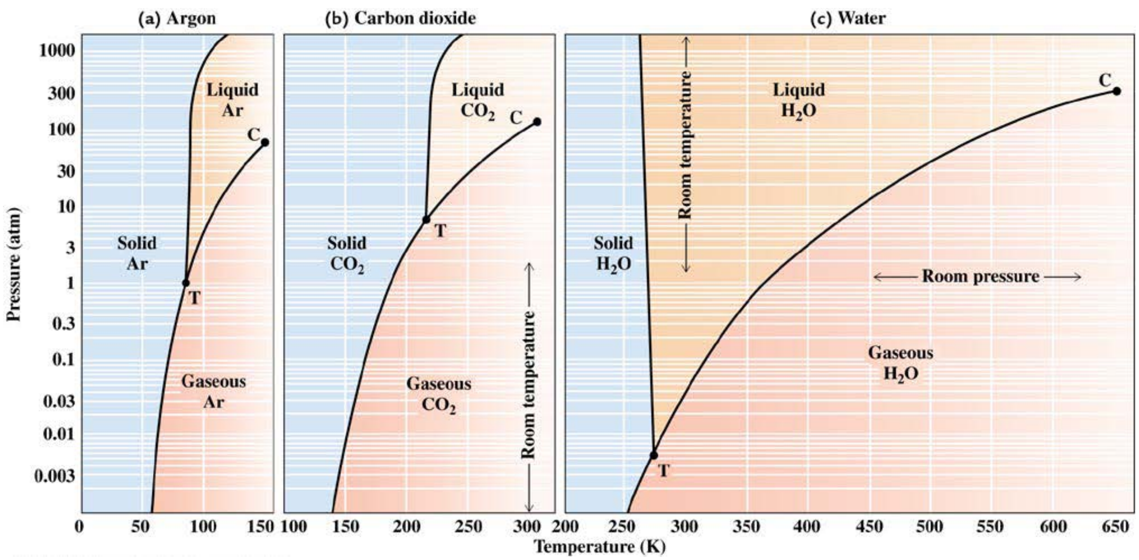


FIG X. Phase diagrams of Ar, CO_2, and water [Note: *y*-axis (pressure) is logarithmic]



EX 2. Consult the phase diagram on the right.

a) What is the phase at room temperature and 1 atm pressure?

b) What is the phase at -114°C and 0.75 atm?

c) If the vapor pressure of a liquid sample is 380 mm Hg, what is the temperature of the liquid phase?

c) What is the vapor pressure of the solid at -122°C?

d) Which is the denser phase, solid or liquid? Explain.