Gases

Z Ch 5

"The particles of the air are in contact with each other, yet they do not fit closely in every part, but void spaces are left between them, as in the sand on the sea shore: the grains of sand must be imagined to correspond to the particles of air, and the air between the grains of sand to the void spaces between the particles of air. Hence, when any force is applied to it, the air is compressed, and, contrary to its nature, falls into the vacant spaces from the pressure exerted on its particles: but when the force is withdrawn, the air returns again to its former position from the elasticity of its particles, as is the ease with horn shavings and sponge, which, when compressed and set free again, return to the same position and exhibit the same bulk."

Hero of Alexandria, ~ AD 60

midterm grades R Oct 21

labs and late lab reports

H_Exp 8 – in-person lab has lab partners;
will need H_Exp 6 data

5.10 Van der Waals gas

Friday quiz emphasis on gases, kinetic theory, no IMF

REVIEW FROM MONDAY

Van der Waals Equation of State (EOS)

$$P = nRT / (V - bn) - a\,(n^2 / V^2)$$

$$PV = nRT$$

$$(P + a\,n^2 / V^2)(V - bn) = nRT$$

$$\left(P + \frac{an^2}{V^2}\right)(V - bn) = nRT$$

Van der Waals Constants of Several Gases

Name	Formula	a (atm L^2 mol^{-2})	b (L mol^{-1})
Ammonia	NH_3	4.170	0.03707
Argon	Ar	1.345	0.03219
Carbon dioxide	CO_2	3.592	0.04267
Hydrogen	H_2	0.2444	0.02661
Hydrogen chloride	HCl	3.667	0.04081
Methane	CH_4	2.253	0.04278
Nitrogen	N_2	1.390	0.03913
Nitrogen dioxide	NO_2	5.284	0.04424
Oxygen	O_2	1.360	0.03183
Sulfur dioxide	SO_2	6.714	0.05636
Water	H_2O	5.464	0.03049

REVIEW FROM MONDAY

Using Van der Waals Equation of State

Example: A 1.98-L vessel contains 215 g of dry ice. After standing at 26ºC, the $CO_2(s)$ turns to $CO_2(g)$. What is the pressure of the gas if it were modelled as a) an ideal or b) a van der Waals gas? M_{CO_2} = 44.0098 g/mol

n = 215/44.0098 = 4.885

a) $P = nRT/V$

= (4.885)(0.082057)(273.15+26)/1.98

= 60.6 atm

b) $P = nRT/(V - \mathbf{b}n) - \mathbf{a}n^2/V^2$

= (4.885)(0.082057)(299.15)/[1.98 - (**0.04267**)(4.885)

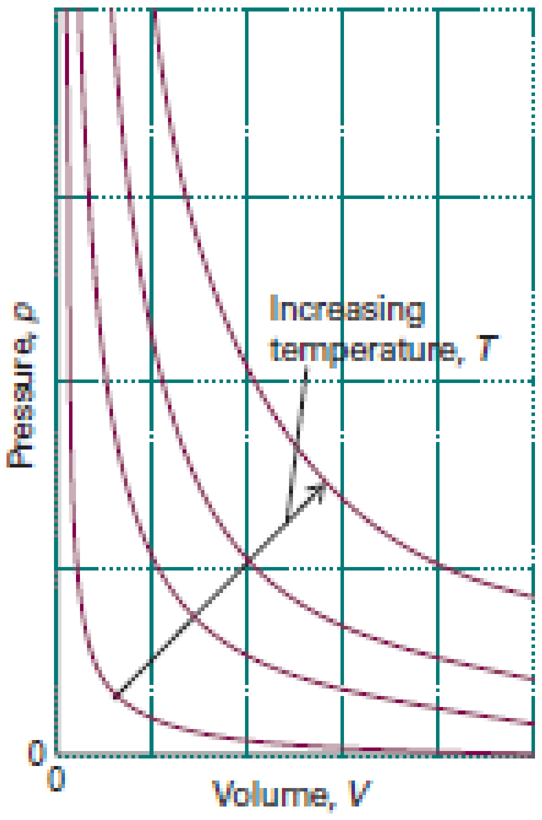
– **3.592**(4.885)^2 / (1.98)

= 45.8 atm

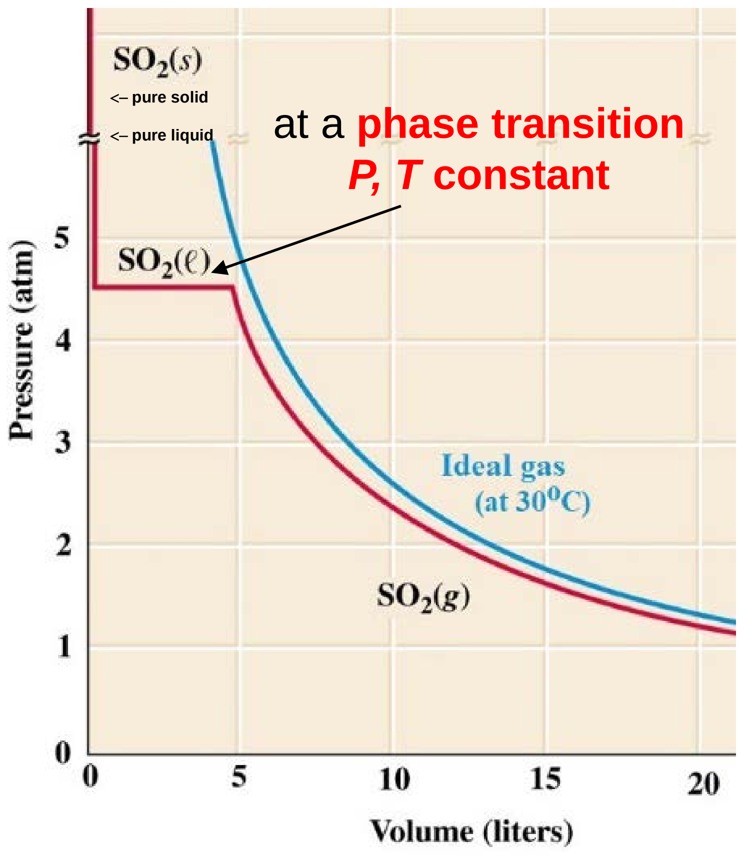
P_{real} = 44.8 atm

Comparing Ideal, Real, and van der Waals Gases

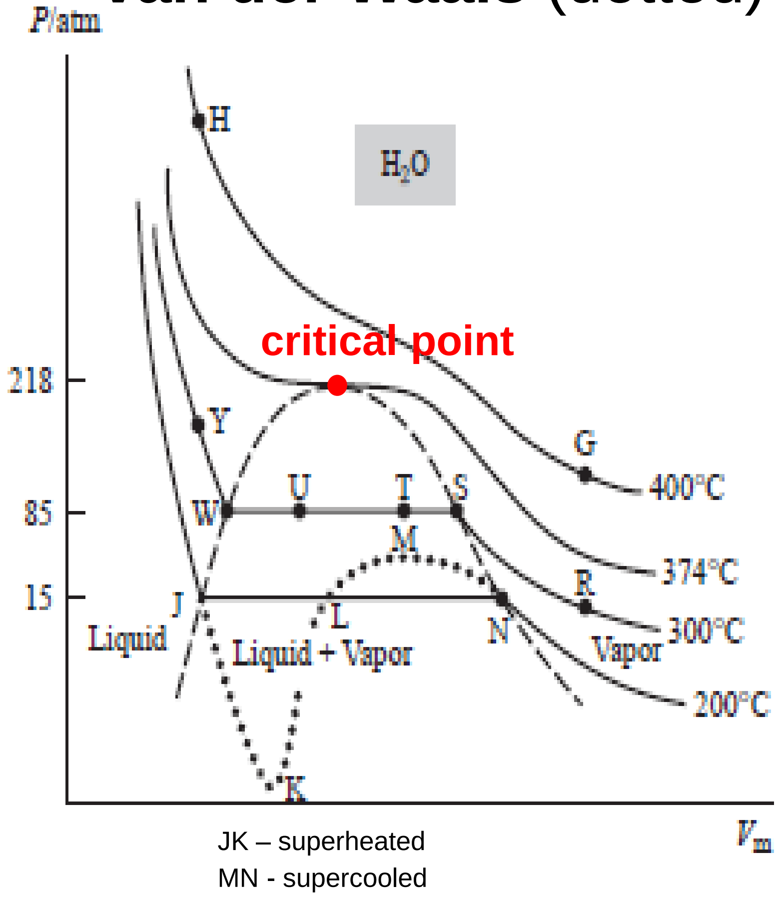
Ideal Gas



Real Gas



Real (solid) and **van der Waals** (dotted)



predicts a phase transition

Forces, Vapor P, Phases__________ Z 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

Evidence for Existence of Forces	Origin of Forces
condensed states of matter exist (solids, liquids)	electrostatic (coulombic – between ions, dipoles)
real gases do not obey $PV = nRT$ under all conditions	induction or polarization (caused by ions, dipoles)
nonideal solutions – deviations from Raoult's law (Chapter 17 – Properties of Solutions)	hydrogen bonding (H bonded to F, N, or O)
	dispersion (motion of e^- causes an instantaneous dipole)

16.1 Intermolecular Forces
16.2 The Liquid State
16.10 Vapor Pressure and Changes of State
16.11 Phase Diagrams

READ SECTION IN PETRUCCI

REVIEW FROM MONDAY

Types of Forces

in decreasing strength

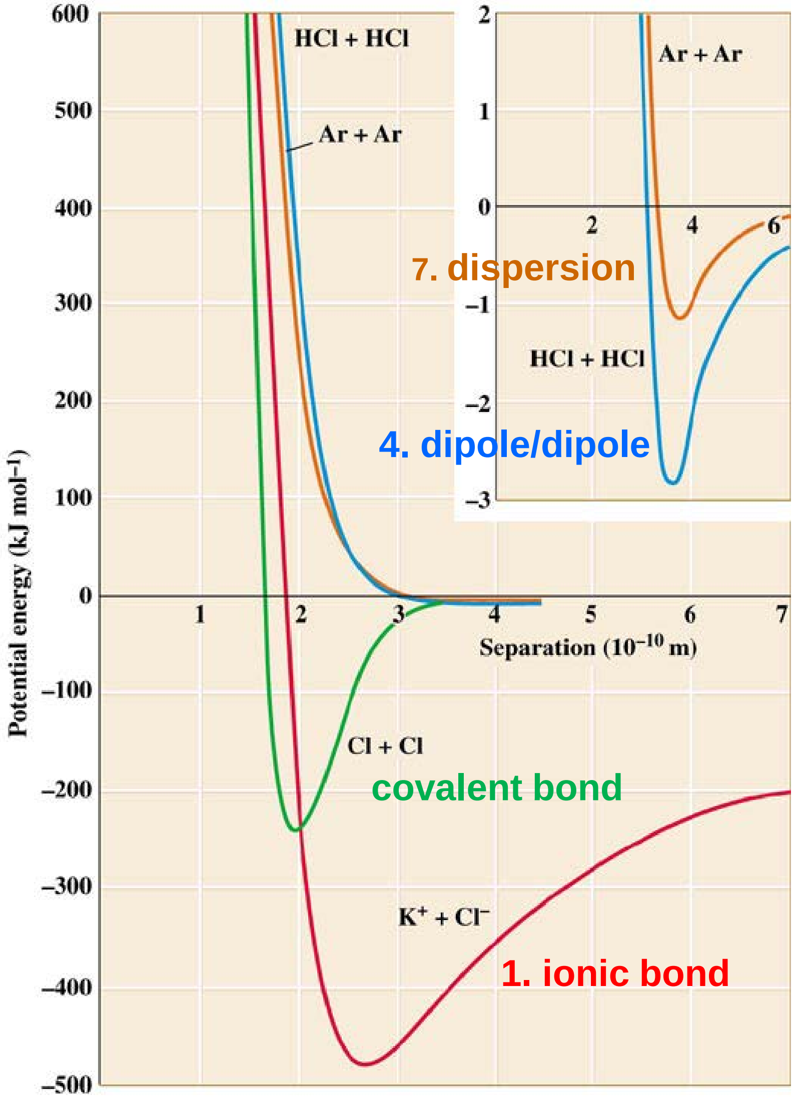
- intramolecular (bonding)
  1. ion/ion
  2. covalent
  3. metallic
- intermolecular (nonbonding)

table of forces
all ways of combining ion, dipole, induced dipole in pairs

van der Waals

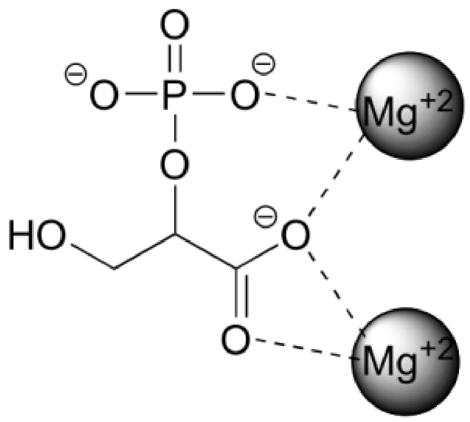
force	example	energy
1. ion/ion	KF(*s*)	1/r
2. ion/dipole	NaCl(*aq*)	$1/r^2$
3. hydrogen bond (strong dipole/dipole)	$H_2O(l)$	$1/r^2$
4. dipole/dipole	HCl(*g*)	$1/r^3$
5. ion/induced dipole	He/Li^+	$1/r^4$
6. dipole/induced dipole	$H_2O(l)$ / $O_2(g)$	$1/r^6$
7. induced dipole/ induced dipole (dispersion,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

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



Ion / Ion

Strongest intermolecular force (IMF) gives us ionic bonding, the bond between a metal and nonmetal. It follows **coulomb's law** where the **potential energy = $k\ Q_1 \times Q_2\ /\ r$.** Salts have extremely high melting points as a result.



2-phosphoglycerate, an intermediate in the breakdown of glucose

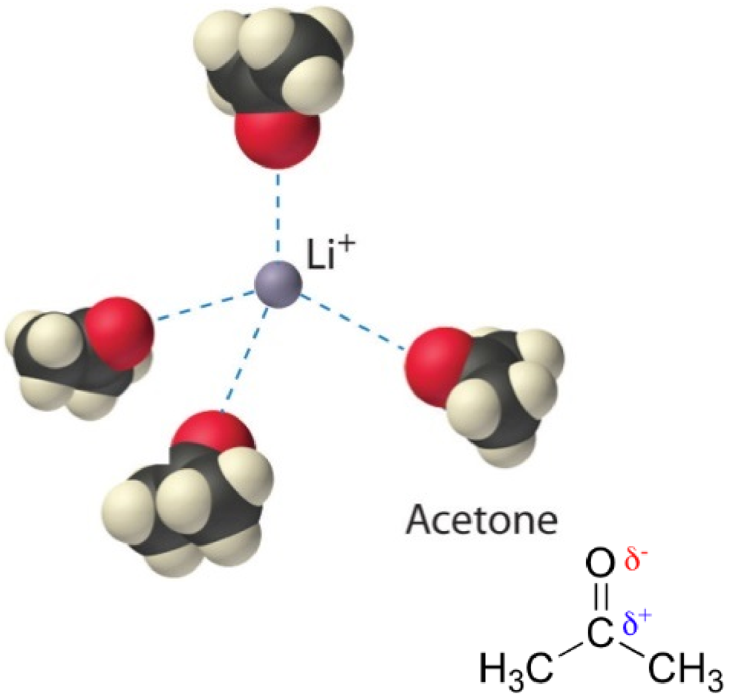
species	H_2O	NaCl	MgO
melting point (ºC)	0	800	2800

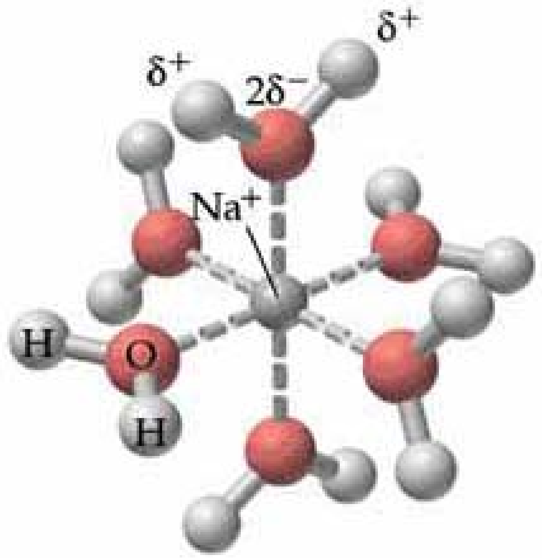
Ion / Dipole

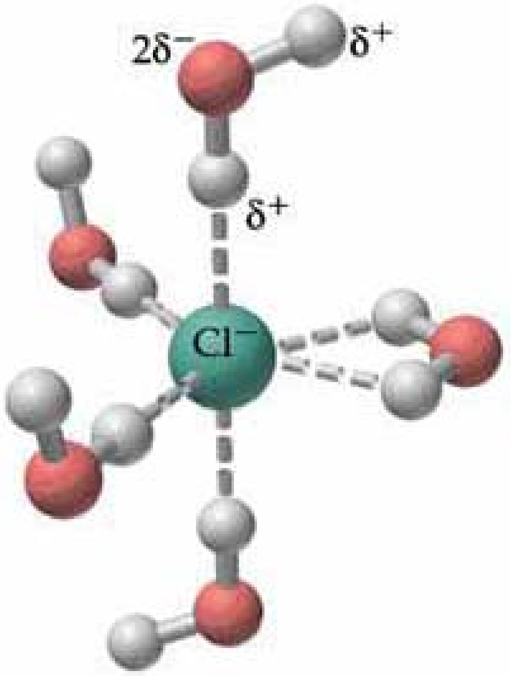
Next strongest IMF are those between a full charge on an ion and the partial charge on a polar compound. Hydration is a good example.

dissolution of solid NaCl in water:

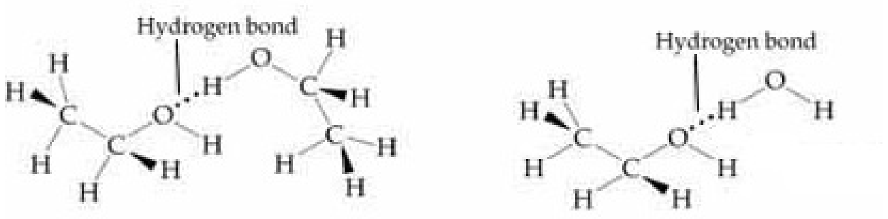
$$NaCl(s) \rightarrow NaCl(aq) \equiv Na^{+}(aq) + Cl^{-}(aq)$$

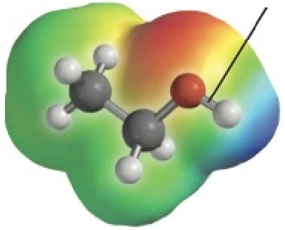






Hydrogen Bond (Dipole / Dipole)





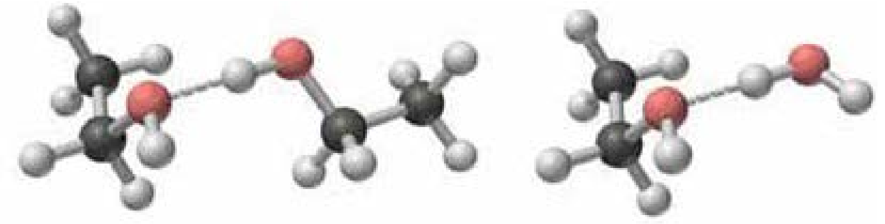
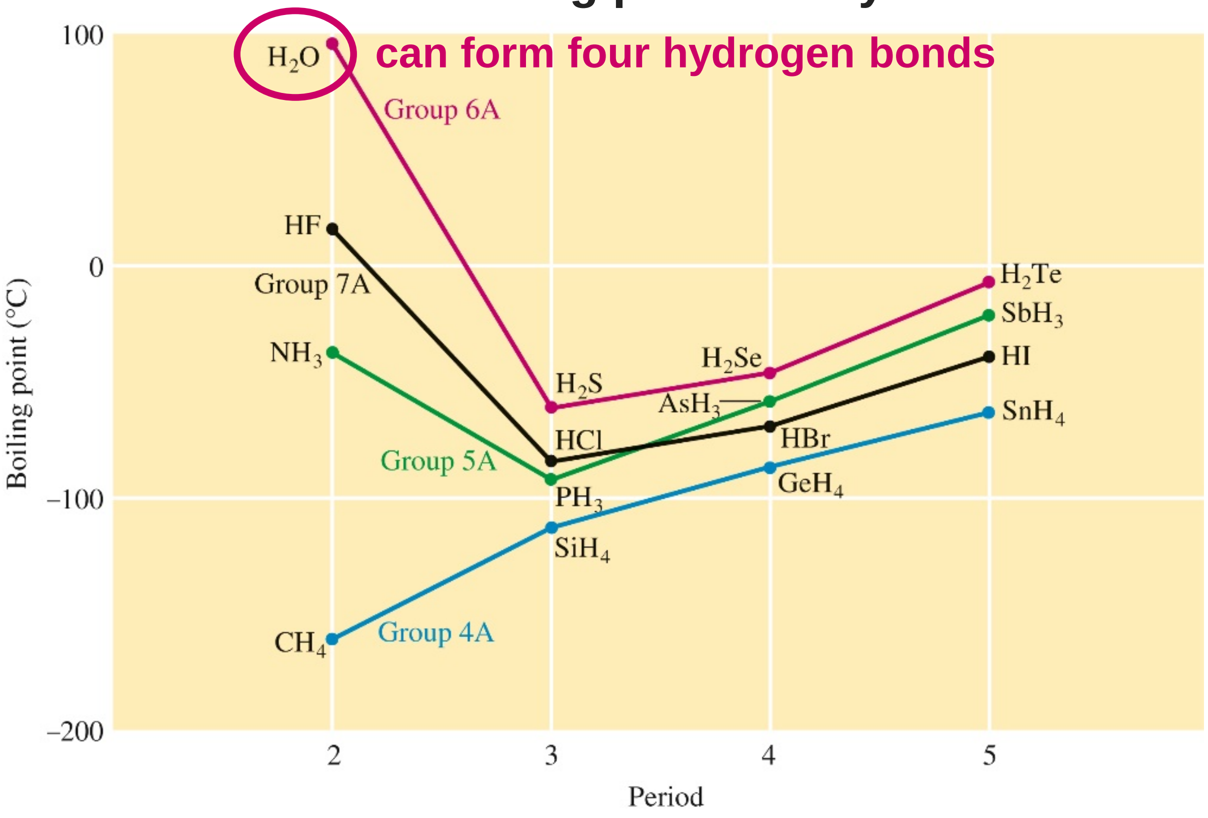
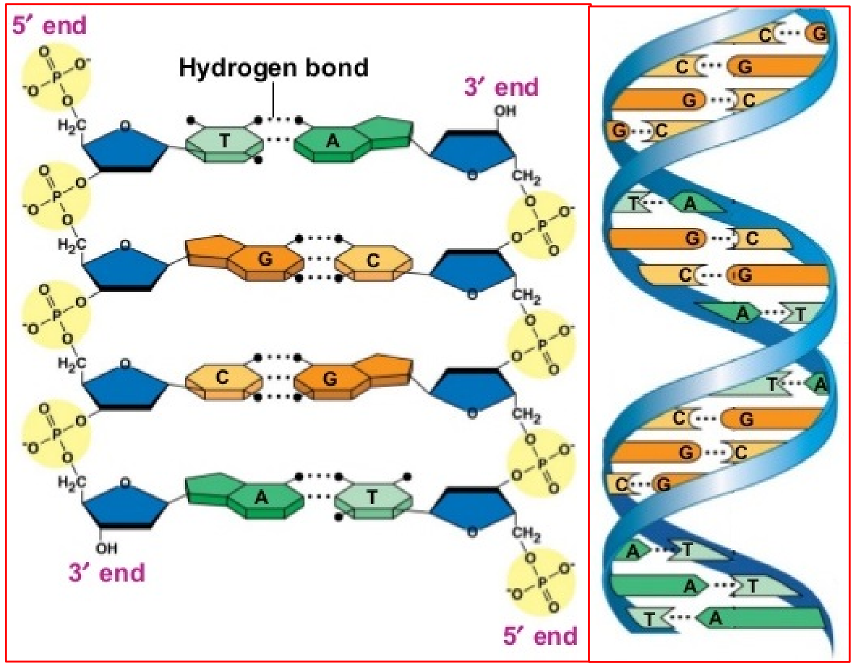


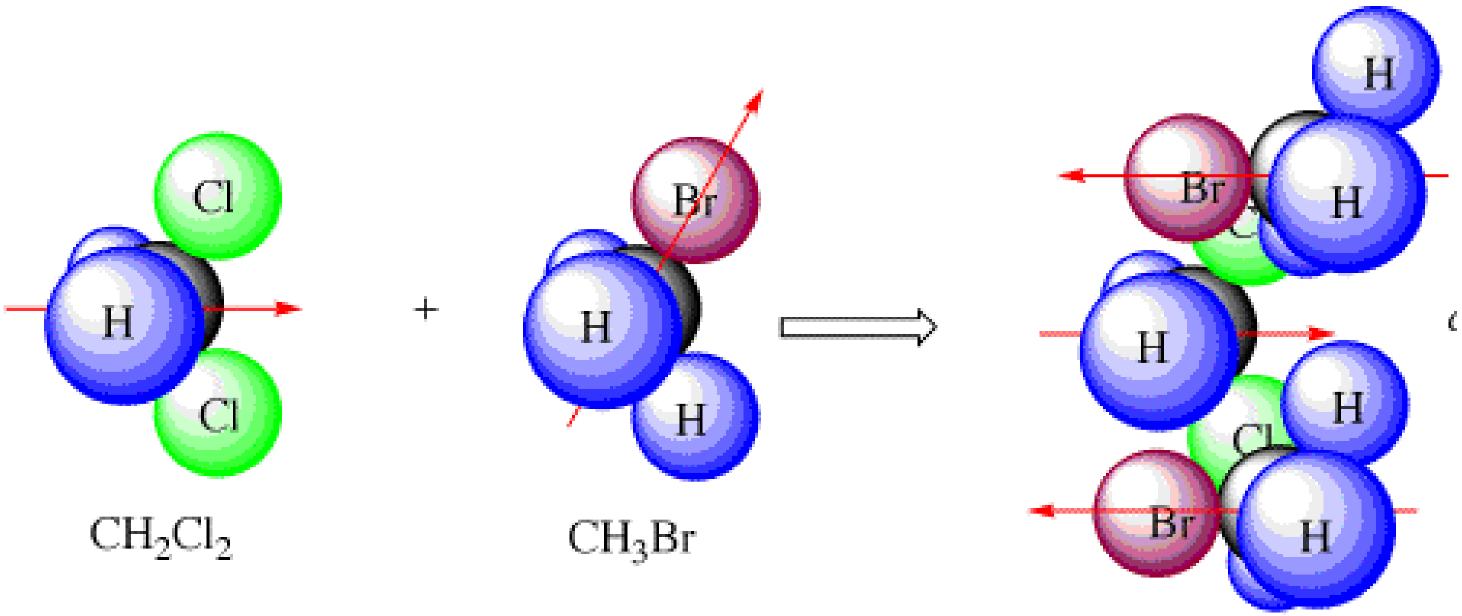
FIG III – Boiling points of hydrides

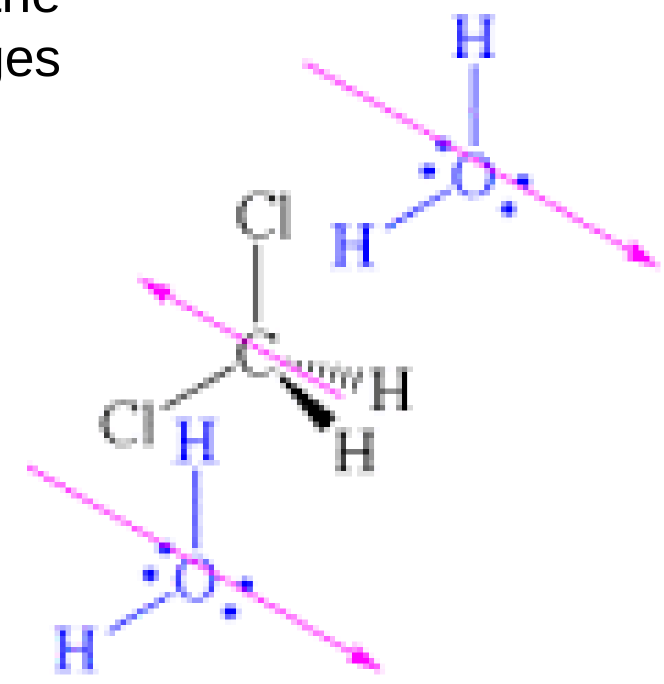




Dipole / Dipole

Interaction between neutral but polar molecules which involve the attraction between the partial positive and partial negative charges that exist in polar compounds.

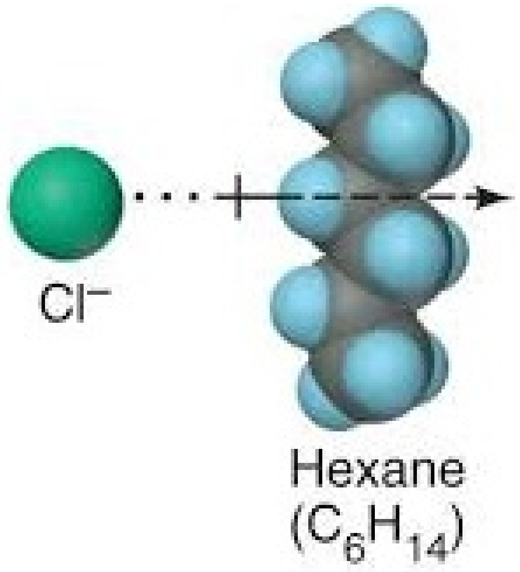




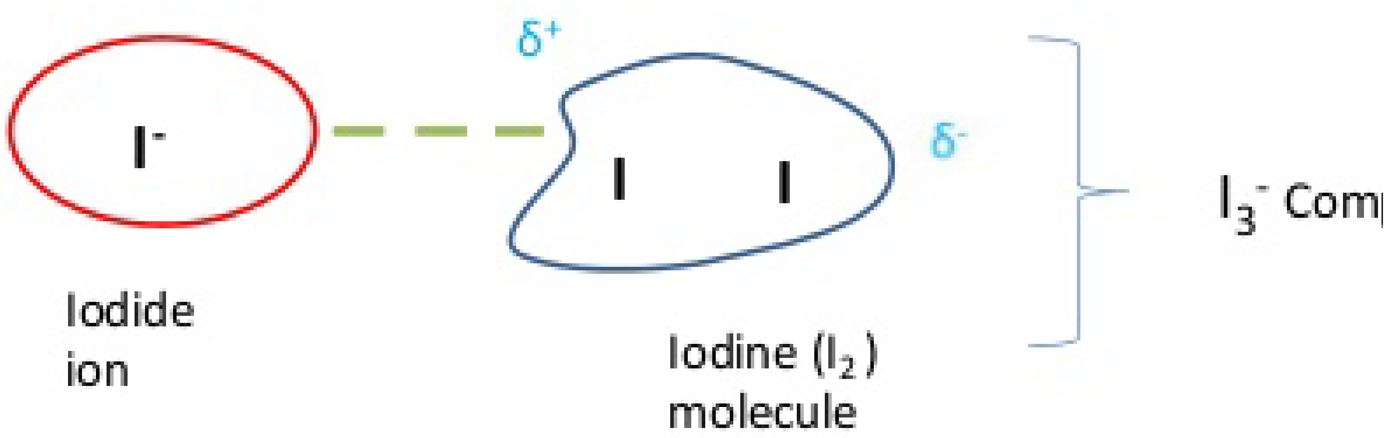
Ion / Induced Dipole

IMF that exists between a full charge on one species and the electron cloud of a nonpolar species which becomes polarized.

$Li^+ \cdots He$ $Li^+ \cdots Ne$ $Li^+ \cdots Ar$



electron cloud is polarized



Dipole / Induced Dipole

An IMF for a polar compound interacting with a nonpolar species. The dipole of the polar compound distorts the electron cloud of the nonpolar species, inducing a dipole moment in it.

solubility of gases in water (N_2, O_2)

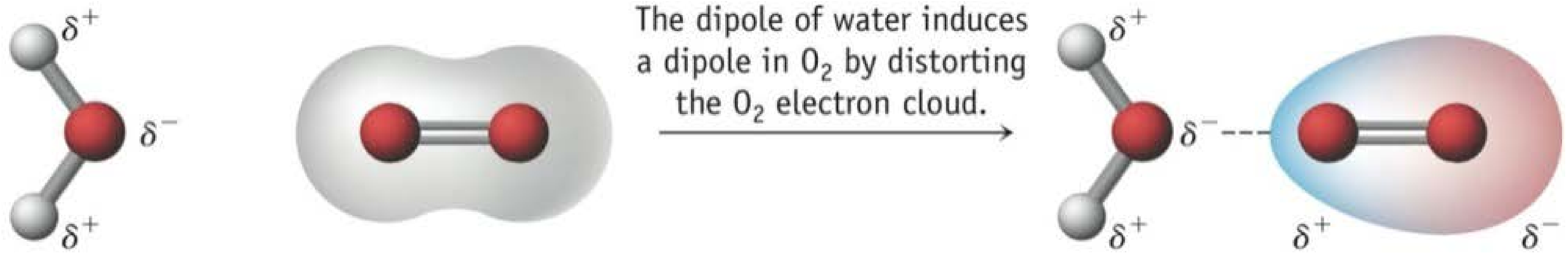
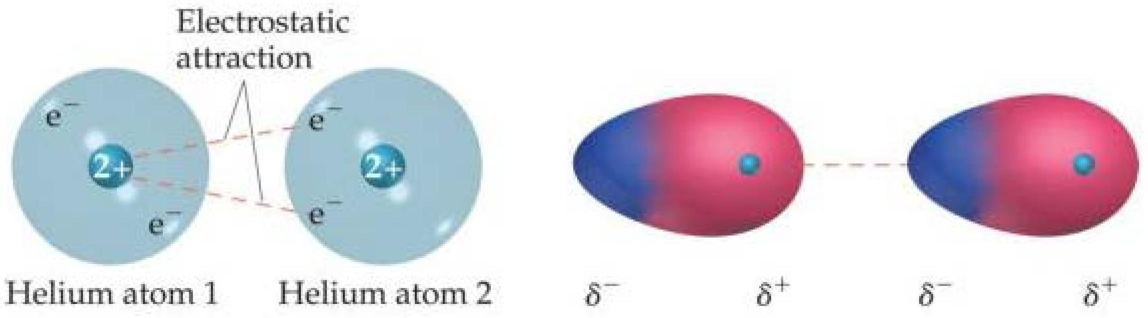


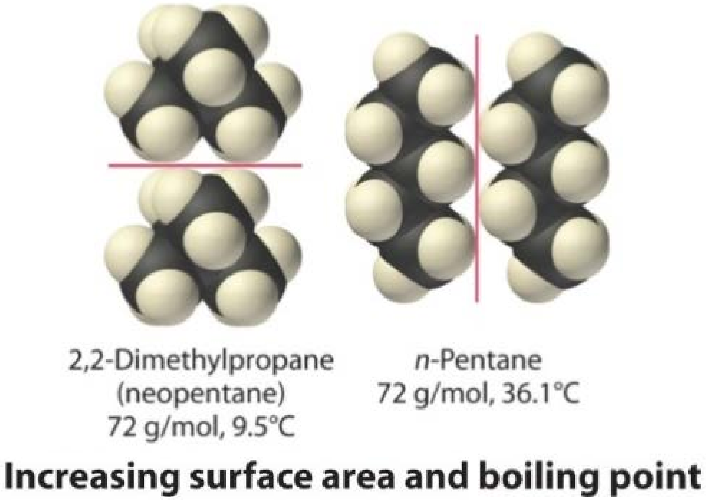
FIG IV – Water dipole inducing a dipole on O_2

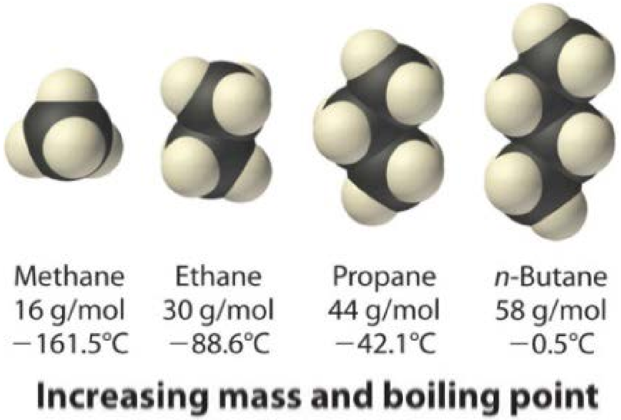
Induced Dipole / Induced Dipole

very short ranged

IMF (London dispersion forces) that exist between nonpolar entities due to attractions between opposite charges which originate in the formation of instantaneous dipole moments induced by the polarization of valence electrons. Occurs for anything that has electrons.







Effect of Dispersion on Boiling, Freezing Point

halogen	bp (°C)	inert gas	bp (°C)	mp (°C)
F_2	-188.1	He	-268.6	-269.7
Cl_2	-34.6	Ne	-245.9	-248.6
Br_2	58.8	Ar	-185.7	-189.4
I_2	184.4	Kr	-152.3	-157.3
		Xe	-107.1	-111.9
		Rn	-61.8	