

# 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contrary to its nature, falls into the vacant spaces from the pressure exerted on its particles: but when the force is withdrawn, the air returns again to its former position from the elasticity of its particles, as is the ease with horn shavings and sponge, which, when compressed and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**

**alternate website:**

**<http://www2.chem.uic.edu/audrey/chem116>**

**Q5 ave 6.5**

**updated grades on BB with %'s**

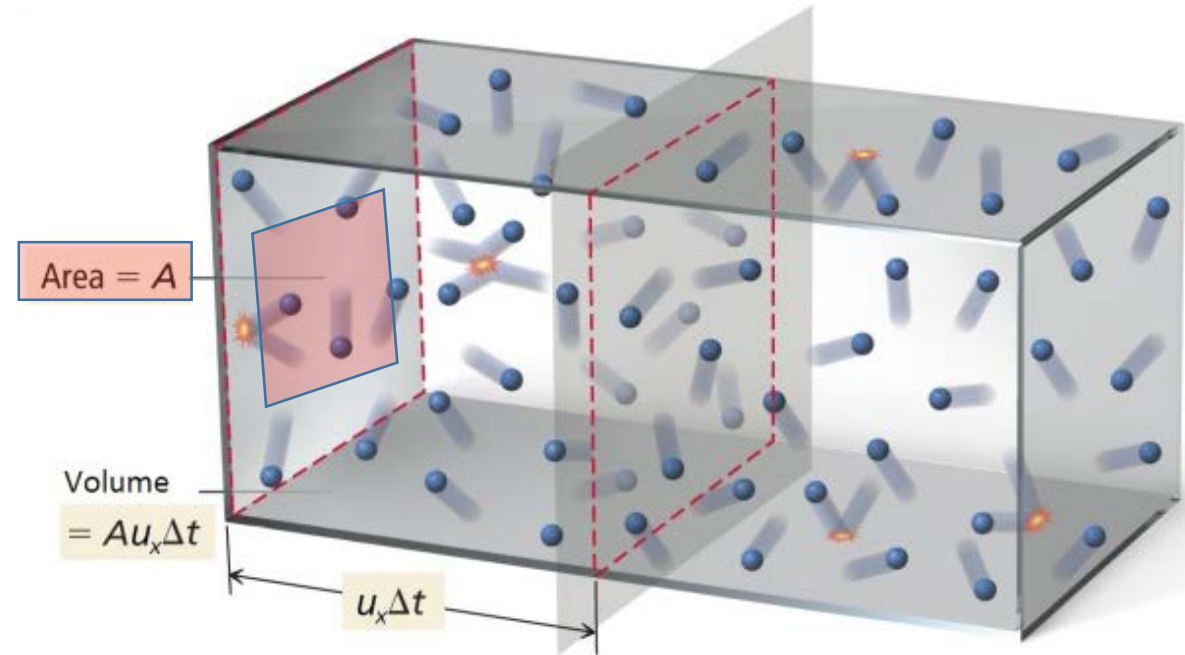
**5.10 Van der Waals gas**

# Collisions of Gaseous Molecules with a Wall

Problem: Consider an area  $A$  of wall  $W$  in contact with a volume  $V$  of gas containing  $N$  molecules. We want to calculate the **frequency of molecular collisions** with the wall, the number of molecules that strike the wall per unit time.

Let  $\Delta N_W$  be the number of molecules that strike the wall  $W$  in the time interval  $\Delta t$ . Then the collision rate ( $Z_W$ ) is  $\Delta N_W / \Delta t$ . What effects this rate? We might expect that  $\Delta N_W / \Delta t$  is proportional to

1. the area of the wall,  $A$
2. number of molecules per unit volume,  $N/V$
3. the average speed (moving towards the wall)



$$\begin{aligned}
 Z_W &= \Delta N_W / \Delta t \\
 &= (N/V) (A) (1/2 \langle u \rangle_{1D}) \\
 &= (N/V) (A) (1/4 \langle u \rangle_{3D}) \quad \langle u \rangle = \sqrt{(8RT / \pi M)}
 \end{aligned}$$

$$\boxed{Z_W = (N/V) A (1/4 \langle u \rangle)}$$

(number density)  $\times$  (area)  $\times$  (relative velocity)

# Collisions Between Gaseous Molecules (Intermolecular)

Collisions of molecules with container walls give us pressure; collisions with light photons, spectroscopy; collisions with one another, chemical reactions.

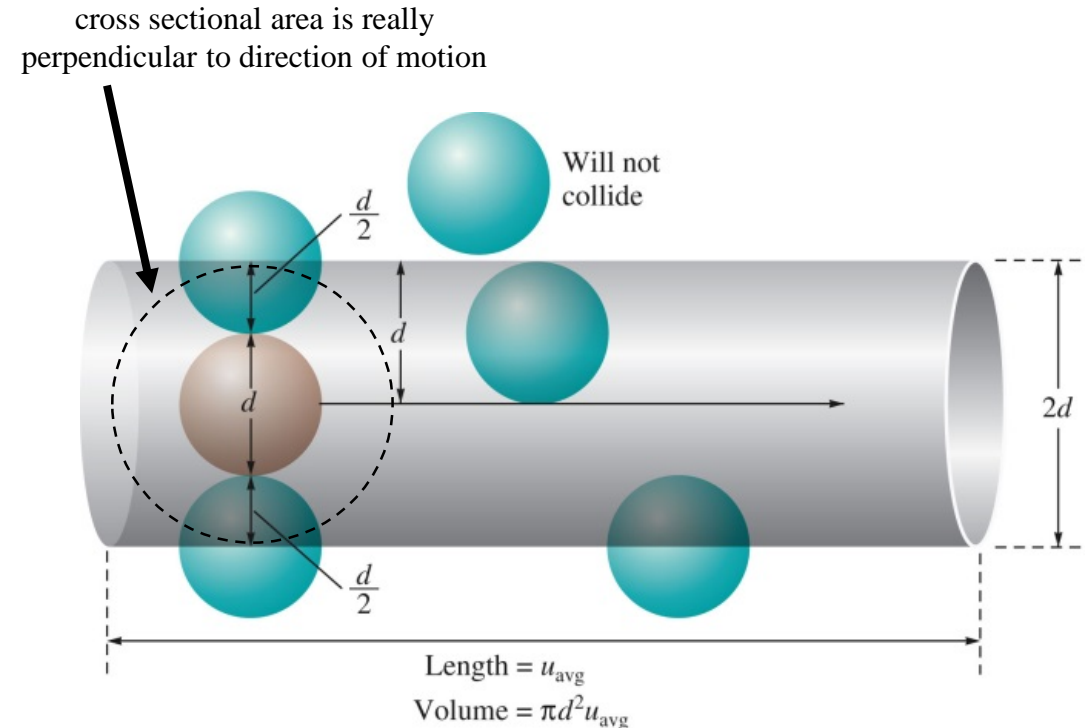
Problem: Calculate the **frequency of collisions of a molecule** with the other molecules of the gas (brown molecule has a cross sectional area centered about it perpendicular to its motion)

Let  $Z$  be the collision rate. What effects this rate? We might expect that  $Z$  is proportional to

1. the cross sectional area,  $\pi d^2$
2. number of molecules per unit volume,  $N/V$
3. the relative velocity of the molecule with respect to the other molecules

$$Z = \sqrt{2} (N/V) \pi d^2 \langle u \rangle$$

(number density)  $\times$  (area)  $\times$  (relative velocity)



since distance = velocity  $\times$  time

mean free path (average distance a molecule travels between successive collisions is

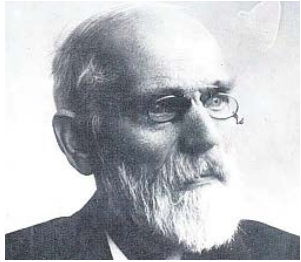
$$\lambda = \langle u \rangle / Z = 1 / \sqrt{2} (N/V) \pi d^2$$

# Real Gases

Ch Z 5.10

"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**



"Thus far we have always considered molecules to be material points, and thus have introduced a simplification in the model which is at once in contradiction with the actual phenomena. Even a molecule in the simplest form, consisting of a single atom, must have a certain extension; the various forces exerted upon it by the other molecules can thus not be considered to act upon a single point."

**Johannes Diderik van der Waals, 1873**

(Nobel Prize in Physics in 1910 "for his work on the equation of state for gases and liquids".)

## 5.10 – Real Gases

interactions (**attractions** and **repulsions**)

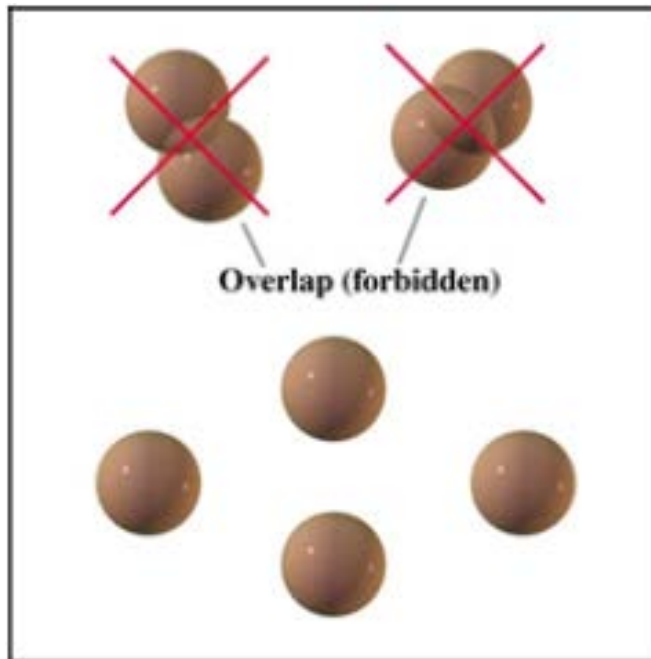
compressibility,  $Z$

van der Waals equation of state (simplest to account for intermolecular forces)

existence of liquid and solid phases

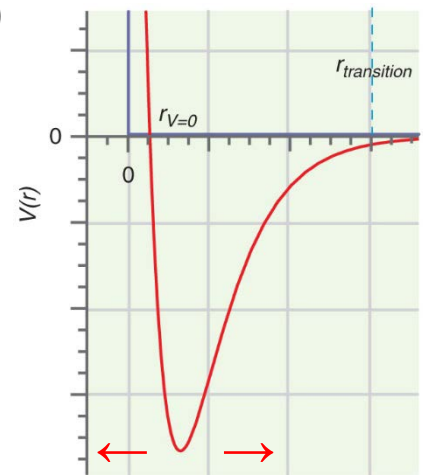
real, ideal, and van der Waals

# Characteristics of a Real Gas

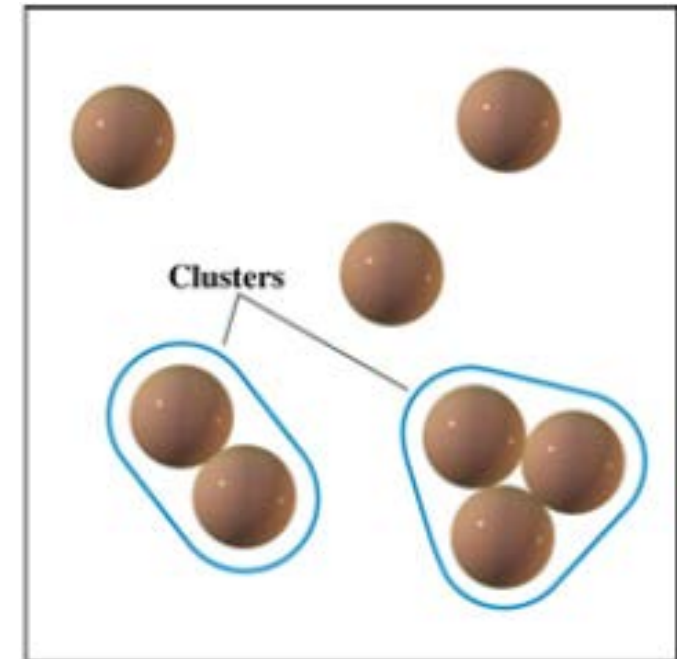


Repulsive forces

Pressure is lowered at attractive distances and raised at very short repulsive distances result: low  $T$ , high  $P$ , get high density  $\rightarrow$  gives a minimum  $V$  for a liquid or solid phase (liquids and solids could not exist were it not for attractive forces)



repulsion | attraction



Attractive forces

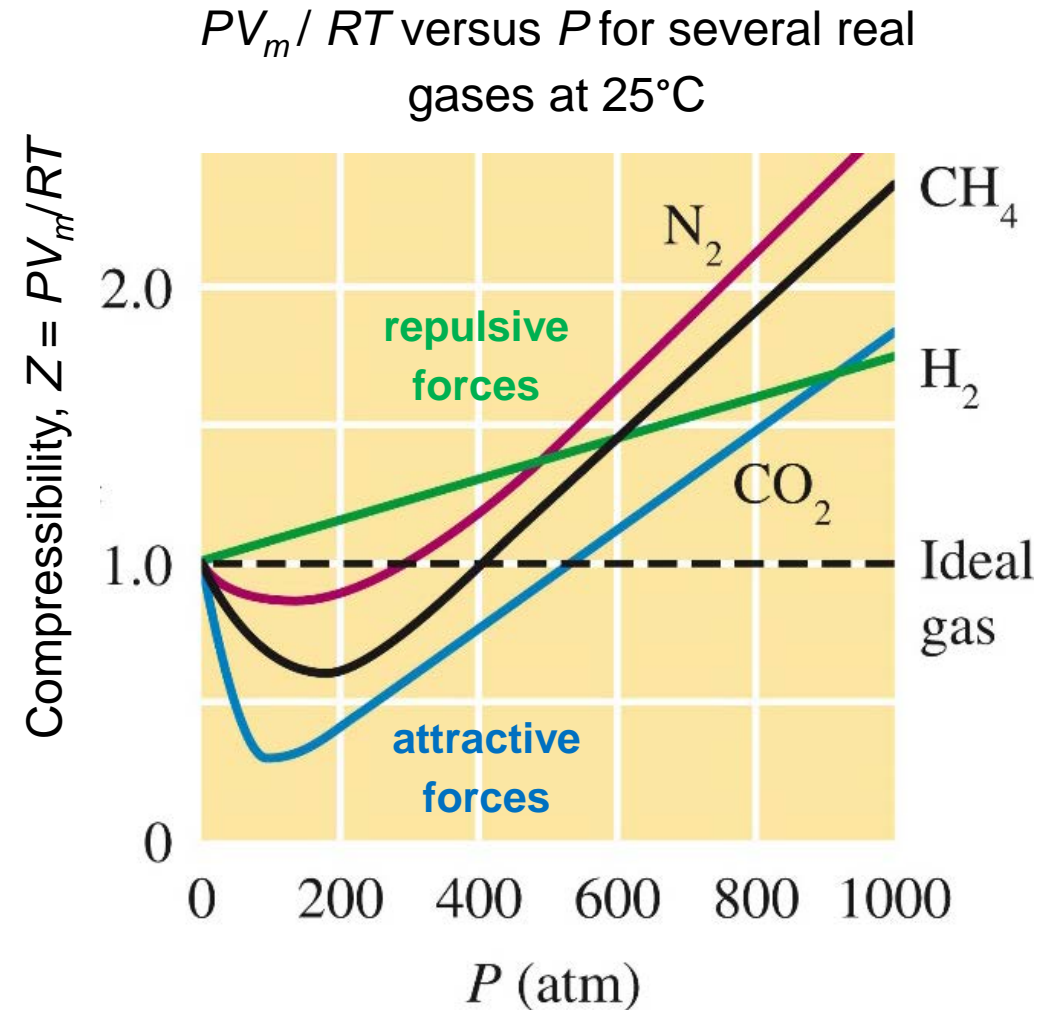
# Compressibility

The effect of **attractive** and **repulsive** forces can be seen in the compressibility,  $Z$  where

$$Z = PV / nRT = PV_m / RT$$

$Z=1$  for an ideal gas and deviations from unity are due to **attractive** and **repulsive** forces between the atoms or molecules.

Pressure is lowered at **attractive** distances (easier to compress) and raised at short (**repulsive**) distances (harder to compress)





# 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 <sup>2</sup> mol <sup>-2</sup> ) | $b$ (L mol <sup>-1</sup> ) |
| Ammonia                                  | NH <sub>3</sub>  | 4.170                                       | 0.03707                    |
| Argon                                    | Ar               | 1.345                                       | 0.03219                    |
| Carbon dioxide                           | CO <sub>2</sub>  | 3.592                                       | 0.04267                    |
| Hydrogen                                 | H <sub>2</sub>   | 0.2444                                      | 0.02661                    |
| Hydrogen chloride                        | HCl              | 3.667                                       | 0.04081                    |
| Methane                                  | CH <sub>4</sub>  | 2.253                                       | 0.04278                    |
| Nitrogen                                 | N <sub>2</sub>   | 1.390                                       | 0.03913                    |
| Nitrogen dioxide                         | NO <sub>2</sub>  | 5.284                                       | 0.04424                    |
| Oxygen                                   | O <sub>2</sub>   | 1.360                                       | 0.03183                    |
| Sulfur dioxide                           | SO <sub>2</sub>  | 6.714                                       | 0.05636                    |
| Water                                    | H <sub>2</sub> O | 5.464                                       | 0.03049                    |

# Using Van der Waals Equation of State

**Example:** A 1.98-L vessel contains 215 g of dry ice. After standing at 26°C, the  $\text{CO}_2(\text{s})$  turns to  $\text{CO}_2(\text{g})$ . What is the pressure of the gas if it were modelled as a) an ideal or b) a van der Waals gas?  $M_{\text{CO}_2} = 44.0098 \text{ g/mol}$

$$n = 215/44.0098 = 4.885$$

$$\text{b) } P = nRT/(V - bn) - an^2/V^2$$

$$\text{a) } P = nRT/V$$

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

$$= 60.6 \text{ atm}$$

$$= (4.885)(0.082057)(299.15)/[1.98 - (0.04267)(4.885)]$$

$$- 3.592(4.885)^2 / (1.98)$$

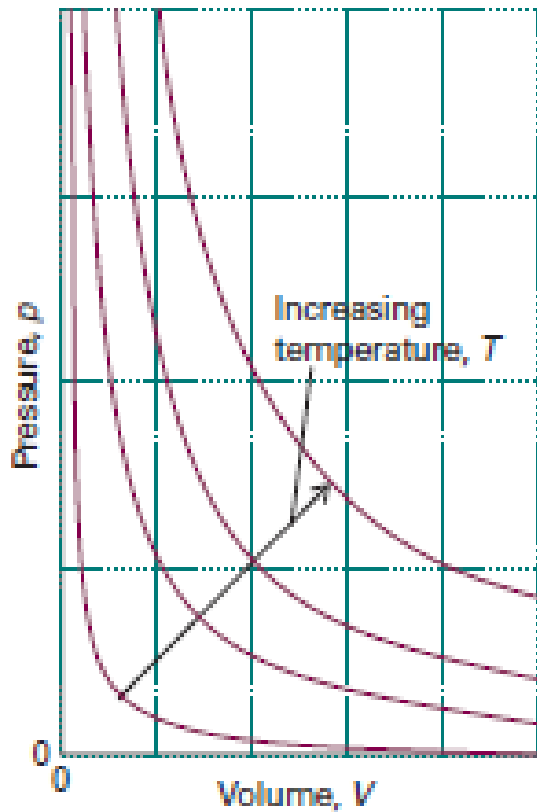
$$= 45.8 \text{ atm}$$

$$P_{\text{real}} = 44.8 \text{ atm}$$

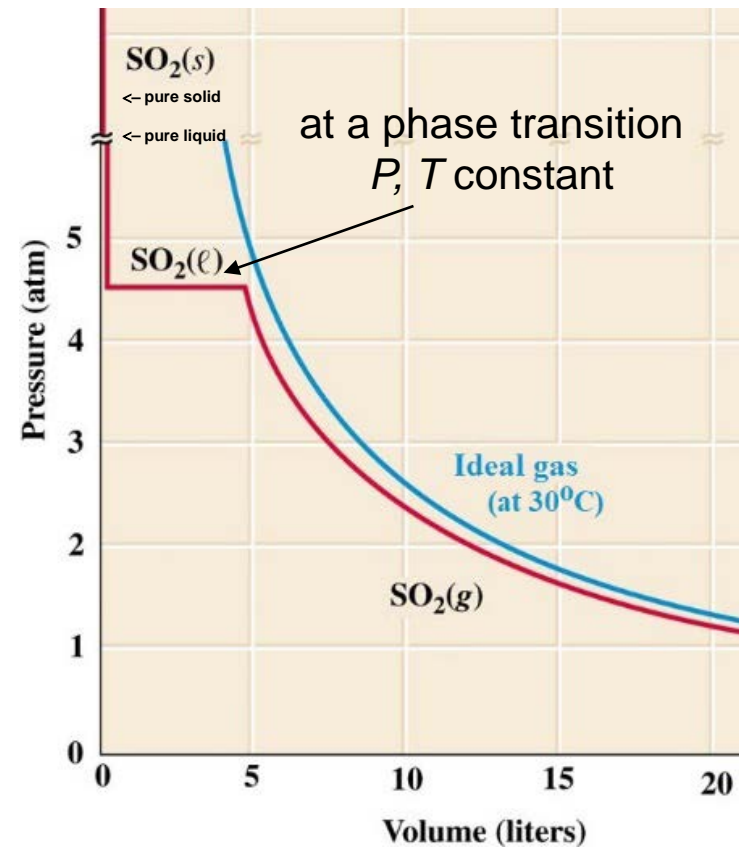


# Comparing Ideal, Real, and van der Waals Gases

## Ideal Gas



## Real Gas



# Predicting $PV$ Plot for a van der Waals Gas

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

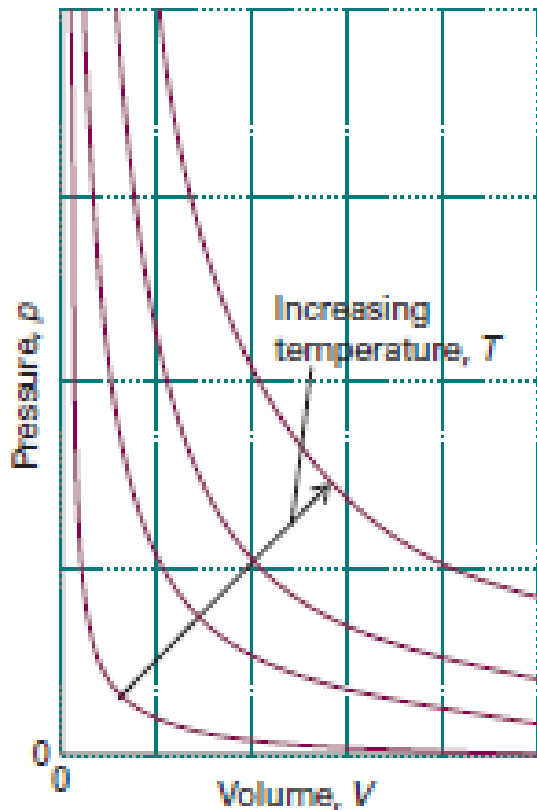
Need  $P$  as a function of  $V$  – What is the functional form?

$$PV^3 + V^2(nRT - Pnb) + an^2V - abn^3 = 0$$

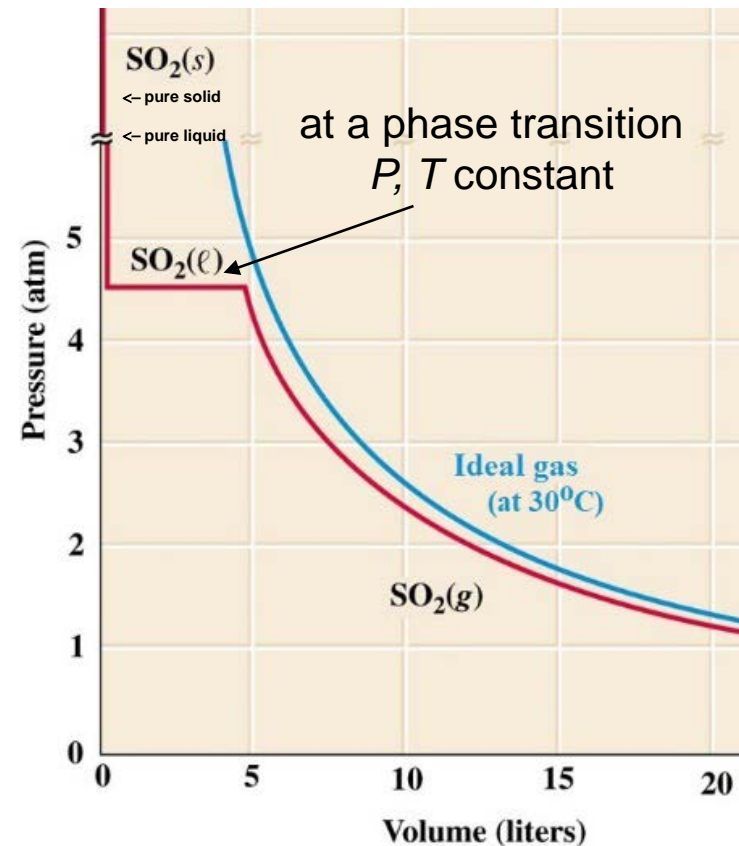
So pressure is a cubic function of volume. How many roots are there? A cubic equation has three roots (there are three values of  $V_m = V/n$  if above equation were solved for  $V_m$  at fixed  $T, P$ ). There is a value of  $T$  (called the critical temperature,  $T_c$ , above which two of the roots are imaginary, below the roots are real and unequal, and at which all three are real and equal. This is the **critical point**.

# Comparing Ideal, Real, and van der Waals Gases

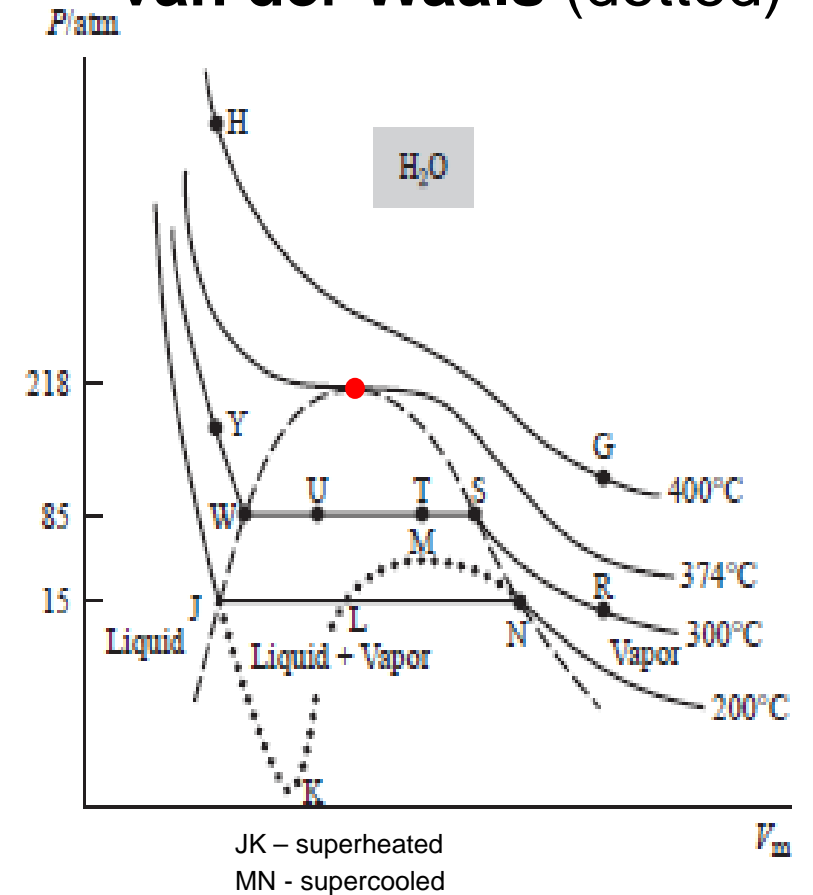
## Ideal Gas



## Real Gas



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



**predicts a phase transition**

# Van der Waals Gases

Open circles data from classic experiment. Below **critical point** smallest vdw molar  $V$  root defines largest  $V_m = V/n$  that system can have with a single phase which is a liquid. Largest molar  $V$  root is smallest  $V_m$  that will support a gaseous phase. Set of these largest and smallest  $V_m$  defines region under the dashed line where system exists in two phases, transitioning between gas and liquid states. Outside this region system is 1) pure **gas**, 2) pure **liquid**, or 3) a "**fluid**" above critical point. For isotherms (constant  $T$ ) below  $T_c$  liquid condenses from gas and is distinguished by a visible surface. For compression at  $T_c$  a surface separating two phases does not appear and  $V$  at each end of horizontal part of isotherm merge to a single point, **critical point** of the gas. At and above  $T_c$ , sample has one phase occupying entire  $V$ . Such a phase is a fluid. Liquid phase does not form above  $T_c$ . It is impossible to form liquid by compression alone if  $T$  is greater than  $T_c$ : to liquefy – obtain a phase that does not occupy entire  $V$  –  $T$  must be lowered below  $T_c$ , then compressed isothermally. Single phase that fills entire  $V$  when  $T > T_c$  may be much denser than normally considered typical of gases, it is denoted a **supercritical fluid**.

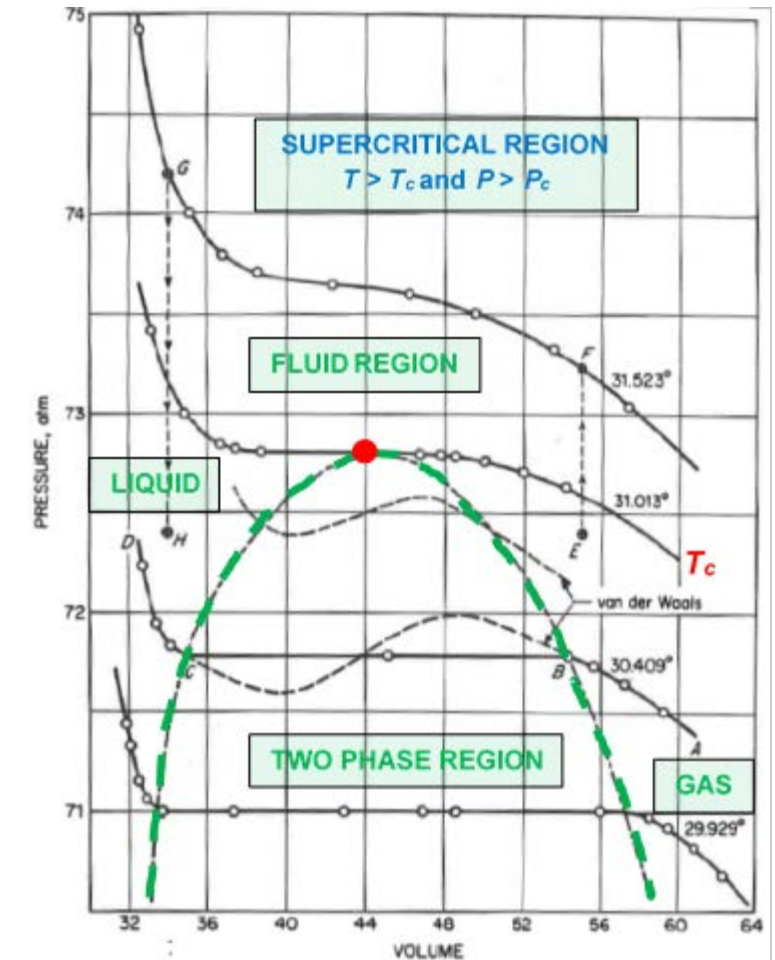


FIG. 1.10 Isotherms of carbon dioxide near the critical point. [Michels, Blaisse, and Michels, *Proc. Roy. Soc. A*, 160, 367 (1937).]

# 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

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)

## 16.1 Intermolecular Forces

## 16.2 The Liquid State

## 16.10 Vapor Pressure and Changes of State

## 16.11 Phase Diagrams

**read Petrucci**

# Types of Forces

in decreasing strength  
intramolecular (bonding)

1. **ion/ion**
2. **covalent**
3. metallic

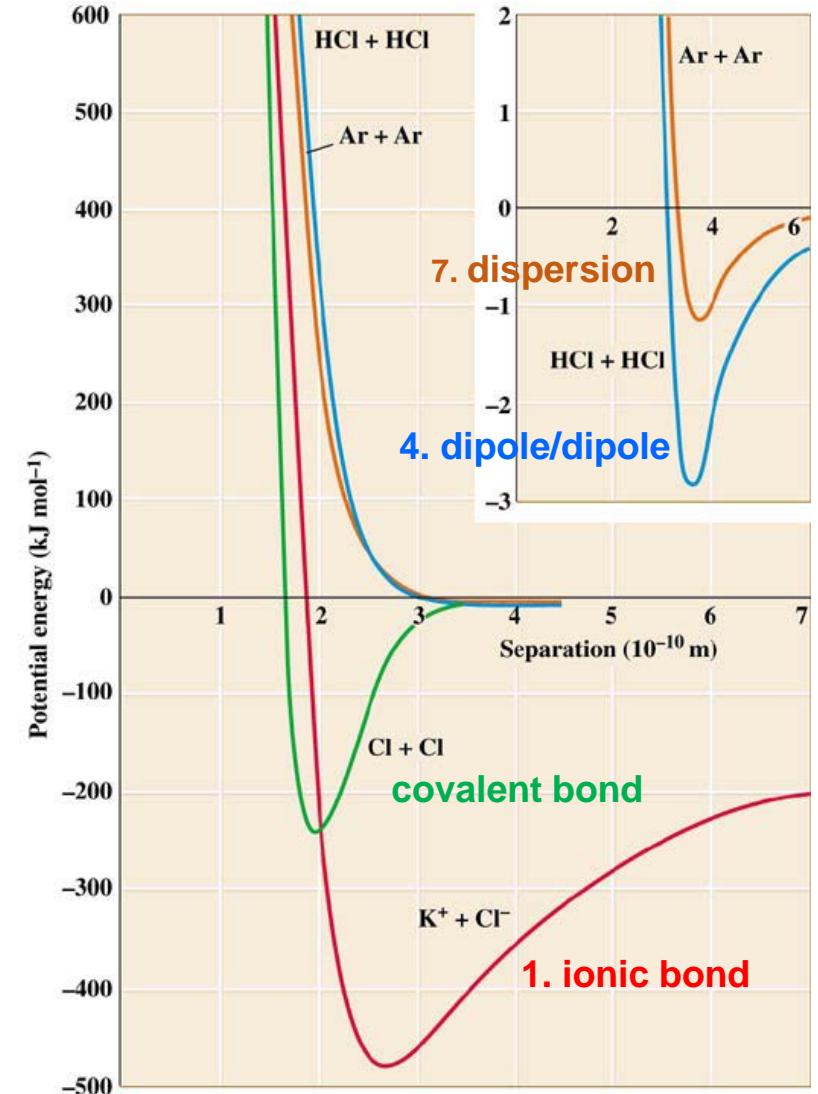
intermolecular (nonbonding)

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

**van der Waals**

| force  | example                                  | energy  |
|--|--|---------|
| 1. <b>ion/ion</b>  | KF(s)                                    | $1/r$   |
| 2. ion/dipole  | NaCl(aq)                                 | $1/r^2$ |
| 3. hydrogen bond<br>(strong dipole/dipole)                       | H <sub>2</sub> O(l)                      | $1/r^2$ |
| 4. <b>dipole/dipole</b>  | HCl(g)                                   | $1/r^3$ |
| 5. ion/induced dipole  | He/Li <sup>+</sup>                       | $1/r^4$ |
| 6. dipole/induced dipole   | H <sub>2</sub> O(l) / O <sub>2</sub> (g) | $1/r^6$ |
| 7. <b>induced dipole/ induced dipole</b><br>(dispersion, London) | Ne(g)                                    | $1/r^6$ |

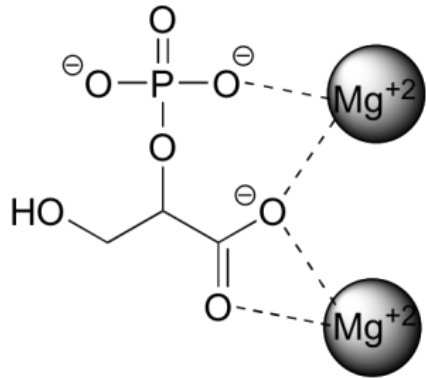
**FIG I – Potential energy of pairs of atoms, ions, and molecules**





# Ion / Ion

Coulomb's Law: potential energy =  
 $k Q_1 \times Q_2 / r$

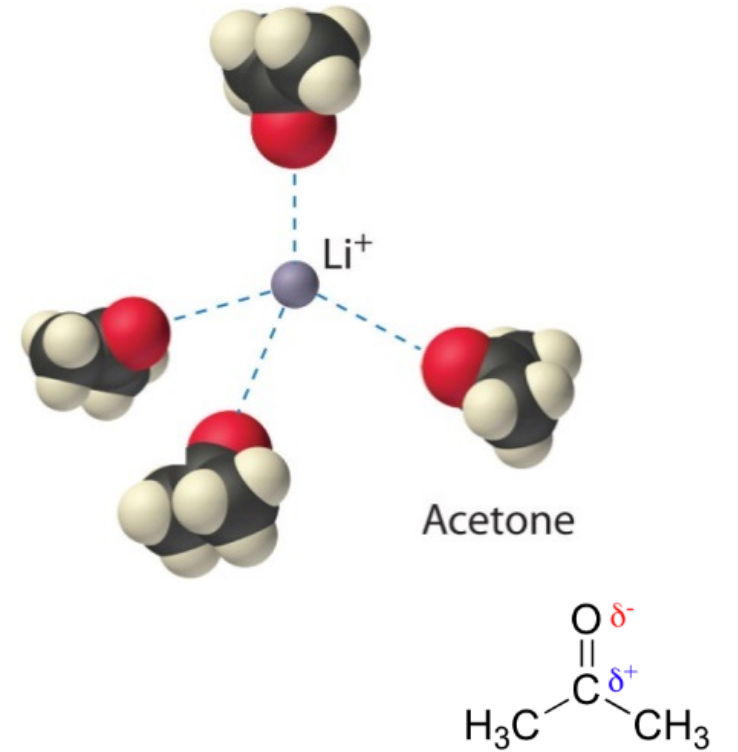
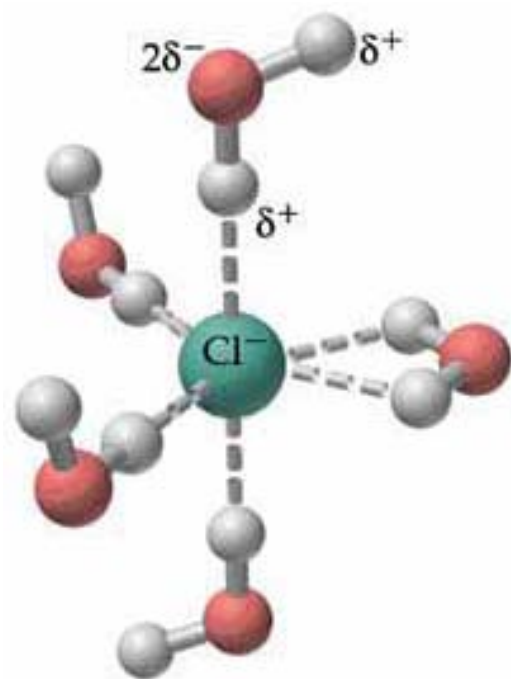
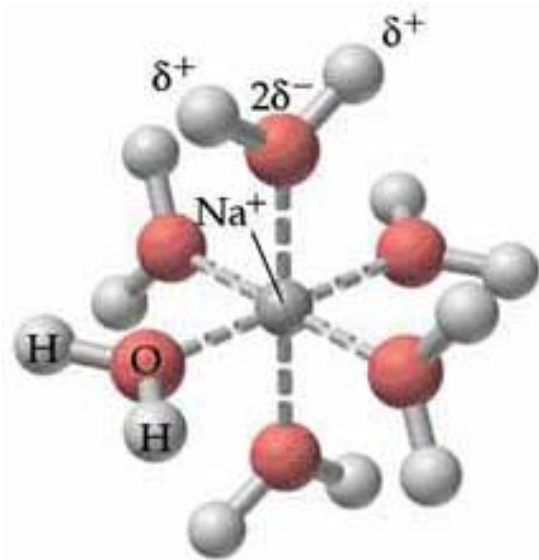
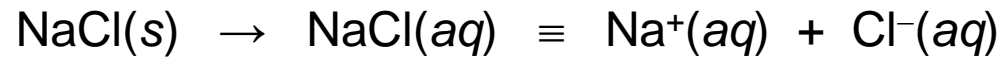


2-phosphoglycerate, an intermediate  
in the breakdown of glucose

| species            | H <sub>2</sub> O | NaCl | MgO  |
|--------------------|------------------|------|------|
| melting point (°C) | 0                | 800  | 2800 |

# Ion / Dipole

dissolution of solid NaCl in water:



# Hydrogen Bond (Dipole / Dipole)

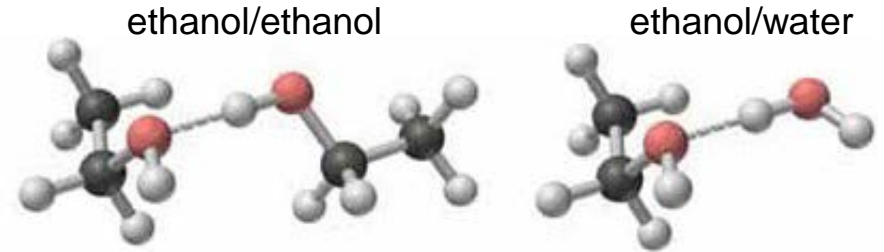
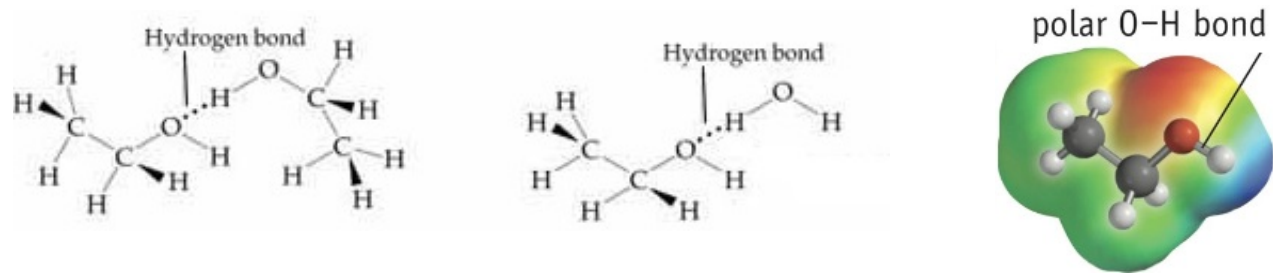
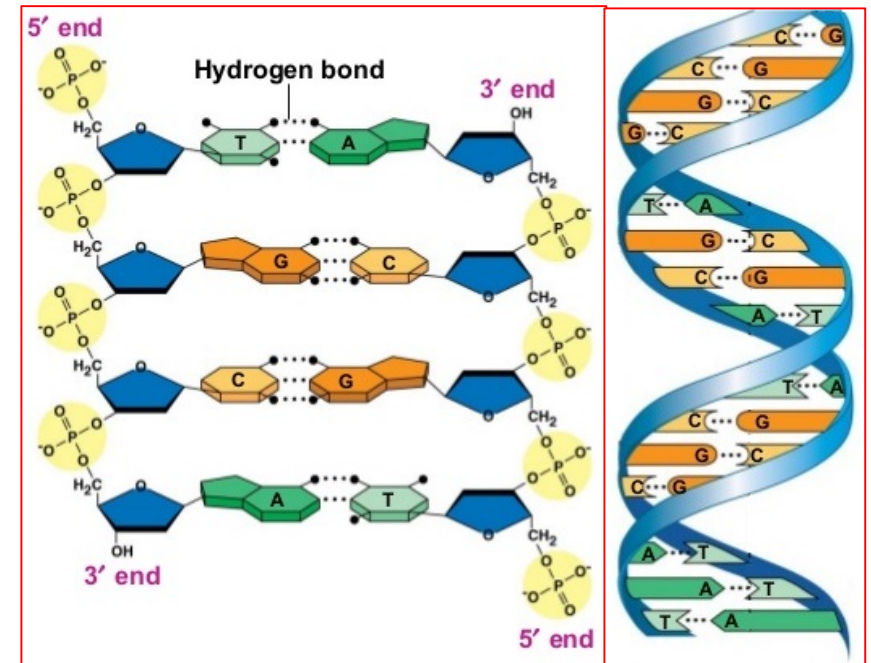
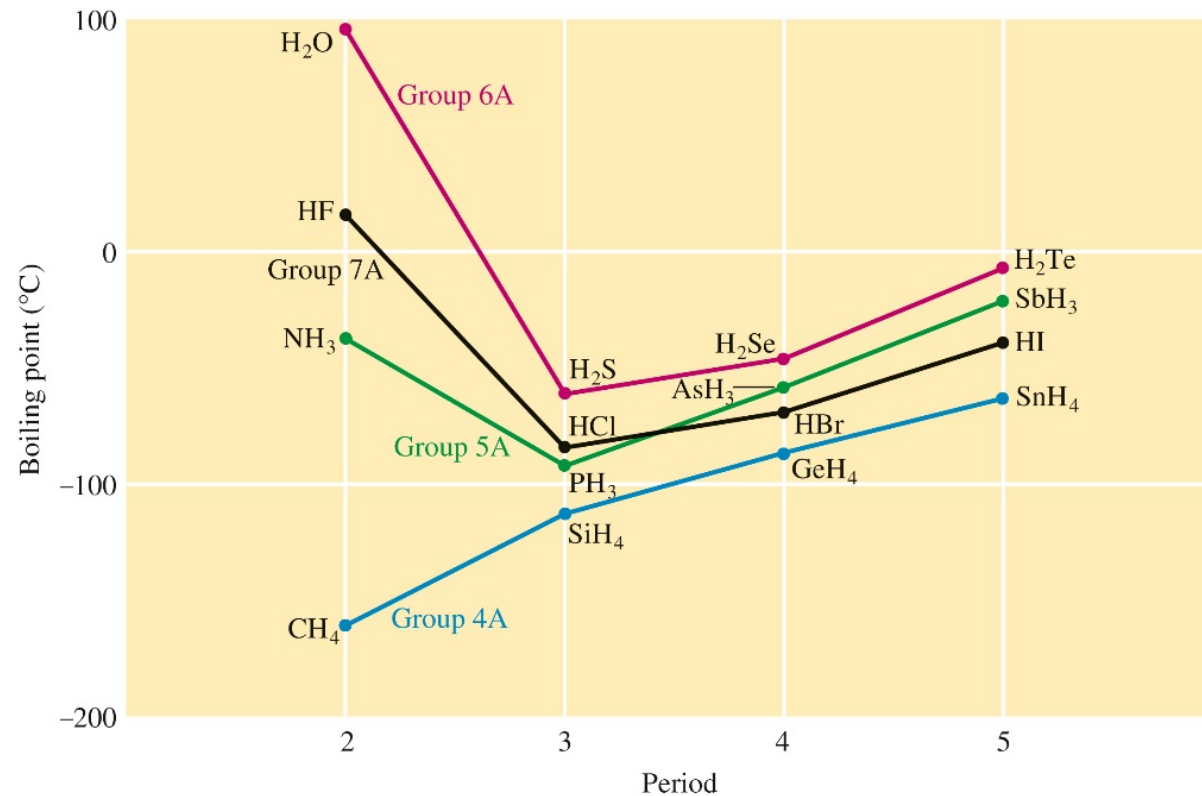
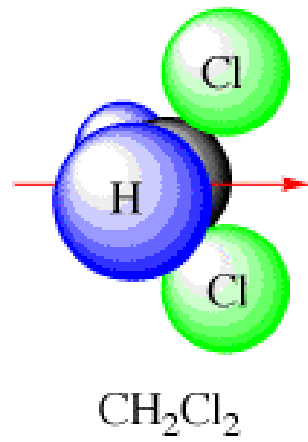
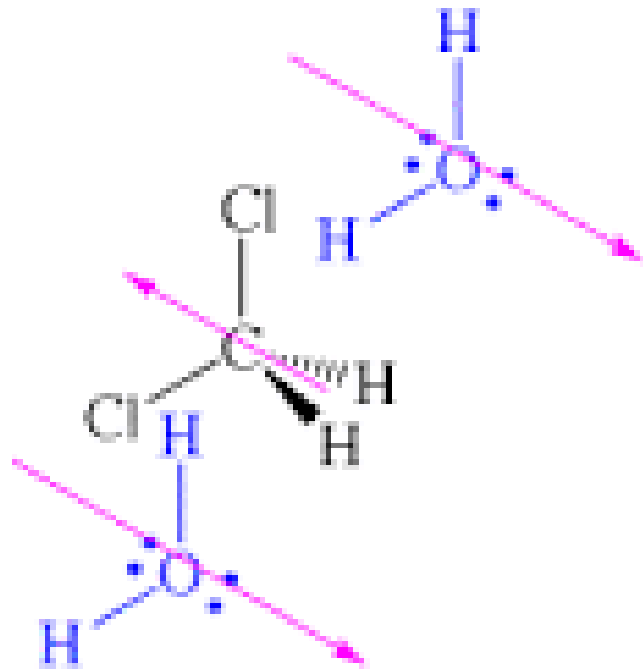


FIG III – Boiling points of hydrides



# Dipole / Dipole



+

