

GASES

→ " Ideally ", gases are gas particles moving freely as an individual atom or molecule in space (container).

4 variables :

- Pressure (P)

- SI unit : Pa (Pascal)

$$\text{Pa} = \frac{\text{kg}}{\text{m}^2 \cdot \text{s}^2} \Rightarrow P = \frac{F}{A} = \frac{\text{mass} \cdot \text{acceleration}}{\text{area}}$$

$$= \frac{\text{kg} \cdot \text{m/s}^2}{\text{m}^2}$$

- Volume (V)

- L

- Moles (n)

- Temperature (T)

- K (Kelvin = Celsius + 273)

Units for pressure

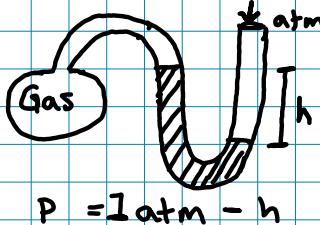
→ 1 atm = 1 standard atmosphere

= 101.3 kPa = 101300 Pa

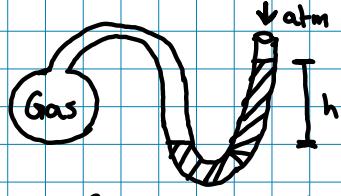
= 14.7 psi (pounds per square inch - 1b/in²)

= 760 torr = 760 mm Hg (exact number)

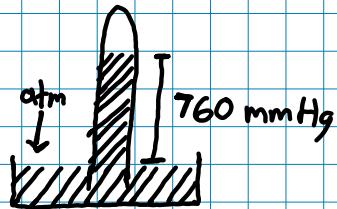
Barometer and manometer



$$P = 1 \text{ atm} - h$$



$$P = 1 \text{ atm} + h$$



Gas Laws

$$\frac{P_1 V_1}{n_1 R T_1} = \frac{P_2 V_2}{n_2 R T_2}$$

Boyle's Law

→ constant moles and temp.

- Pressure and volume are inversely proportional

$$P_1 V_1 = P_2 V_2 \Rightarrow P \propto \frac{1}{V}$$

Charles Law

→ constant pressure and moles

- Volume and temperature are directly proportional

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \Rightarrow V \propto T$$

Absolute zero : 0 Kelvins

→ Molecular motion comes to halt (no motion)

→ Zero volume

Avogadro's Law ($V \propto n$)

→ constant pressure and temp.

- Volume and moles are directly proportional

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \Rightarrow V \propto n$$

IDEAL GAS LAW

$$PV = nRT$$

$$R = 8.314 \frac{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}{\text{mol}} \quad \text{or} \quad R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}$$

(given on exam)

* Ideal gas law isn't always true

Only under ideal gas conditions

- Above 200 K (high temp)

- Below 10 atm (low pressure)

The more one respects these conditions, the better IGL works

* Assume IGL holds true unless told otherwise.

How to find molar mass of a gas, given its density?

$$PV = nRT$$

$$PV = \left(\frac{m}{M_m}\right)RT$$

$$M_m = \frac{(m)}{V} R \cdot T$$

$$\boxed{M_m = \frac{d \cdot R \cdot T}{P}}$$

$$m = \text{mass (g)}$$

$$M.m = \text{molar mass (g/mol)}$$

$$n = \frac{m}{M_m} (\text{mol})$$

$$d = \text{density} = \frac{m}{V} (\text{g/L})$$

Standard Temperature and ~~Pressure~~ (STP)

$$\rightarrow 0^\circ\text{C} (273 \text{ K})$$

$$\rightarrow 1 \text{ atm}$$

Standard molar volume = volume of 1 mol of gas at STP

$$= 22.4 \text{ L/mol}$$

$$\frac{V}{n} = \frac{RT}{P} = \frac{(0.08206)(273 \text{ K})}{1 \text{ atm}}$$

↳ Always the same regardless the identity of the gas.

Gaseous Mixture

Partial pressure = pressure that a gaseous component of a mixture would exert if that gaseous component were present alone in the container.

Dalton's Law of partial pressure:

$$P_A + P_B + P_C + \dots + P_n = P_{TOT}$$

∴ The pressure of a given gas is unaffected by the presence of other gases in the mixture

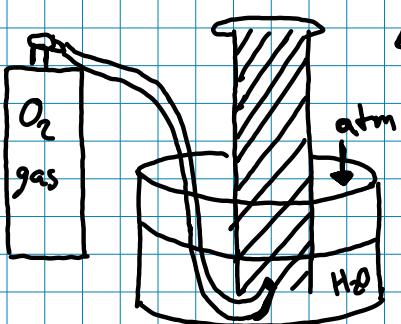
If one has a gas in a container at a given pressure, and one adds a second gas

→ Pressure of gas 1 doesn't change

→ Total pressure of the mixture increases

Gas collected over water

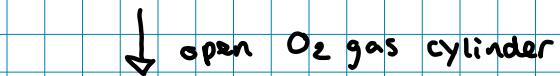
- When gas is collected over water, there is
 - pressure of gas collected
 - pressure of water vapour
- * $P_{TOT} = \text{sum of both partial pressures.}$



upside
down grad
cylinder filled
with H₂O(l)

Closed Gas Cylinder

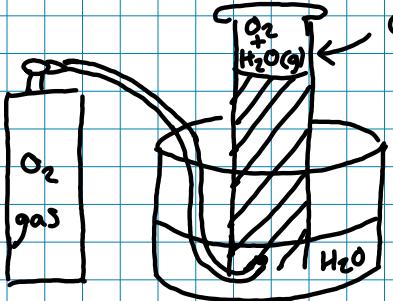
- Atm is strong enough to push down H₂O
- H₂O in cylinder doesn't go down



O₂ and water vap
* Total pressure
of gaseous
mixture is the
same as atmospheric
pressure

Open Gas cylinder

- Air bubbles (gas) go up
- Causes water to get displaced by gas
- Close valve



* Problems where gases are collected over water and then dried \Rightarrow water vapour removed from mixture

ex: He(g) collected over water at 25°C and 1.00 atm
What volume of gas must be collected to obtain
0.586 g He?
The vapour pressure of H₂O is 23.8 torr

$$P_{\text{tot}} = P_{\text{He}} + P_{\text{vap}} = 1.00 \text{ atm}$$

$$0.586 \text{ g He} \cdot \frac{\text{mol He}}{4.003 \text{ g He}} = 0.1464 \text{ mol He}$$

$$P_{\text{tot}} = \left(\underbrace{\frac{P_{\text{He}} \cdot R \cdot T}{V}}_{P_{\text{He}}} \right) + \left(23.8 \text{ torr} \cdot \frac{1 \text{ atm}}{760 \text{ torr}} \right) = 1.00 \text{ atm}$$

$$1.00 = \frac{(0.1464)(0.08206)(298)}{V} + \frac{23.8}{760}$$

$$\boxed{V = 3.7 \text{ L}}$$

Mole fraction / mole percentage

→ 2 gas mixture (gas A + gas B)

Mole fraction (of gas A) :

$$\underline{X}_A = \frac{n_A}{n_{TOT}} \quad \text{or} \quad \begin{matrix} (\text{for mixture of} \\ 2 \text{ gases } A+B) \end{matrix} \quad \underline{X}_A = \frac{n_A}{n_A+n_B}$$

Mole percentage (of gas A) : * For gaseous mixtures
% volume = mole %.

$$\underline{X}_A \times 100$$

Mole fraction and partial pressure

$$\boxed{P_A = \underline{X}_A \times P_{TOT}}$$

Proof:

$$\frac{P_A}{P_{TOT}} = \frac{\frac{n_A \cdot X}{X}}{\frac{n_{TOT} \cdot X}{X}} = \frac{n_A}{n_{TOT}} = \underline{X}_A$$

$$\therefore P_A = \underline{X}_A \cdot P_{TOT}$$

ex. Atmospheric pressure surface of Mars $\cdot 5.92 \times 10^{-3}$ atm
Martian atmosphere 95.3% CO₂ and 2.7% N₂.
Find mole fraction and partial pressure of N₂.

$$\frac{\% \text{ volume}}{100} = \underline{X}_{N_2} = \frac{2.7}{100} = 0.027$$

$$P_{N_2} = \underline{X}_{N_2} \cdot P_{TOT} = 0.027 \cdot (5.92 \times 10^{-3} \text{ atm}) = 1.6 \times 10^{-4}$$

Kinetic Molecular Theory (KMT)

→ explains T , ideal gas laws

Law: Observed

Theory: consistent explanation of law

1. Gas particle volume is negligible
∴ separated by large distance
2. Gas particles are continuously in motion and colliding
 - collisions between particles are elastic
 - collisions with walls creates pressure
3. Average kinetic energy (energy of motion) of gas particles is proportional to the temperature.
→ $T \uparrow$: move faster
 $T \downarrow$: move slower
4. Ideal gas particles exert no force (attract / repel) on other gas particles

example of explanation:

Avogadro's law: $n \propto V$

- constant average kinetic energy at constant temp.
- to maintain constant pressure (collisions with walls) as one increases the number of moles of gas, one must increase the volume of its container

Kinetic Energy (K.E.)

$$\left\{ \frac{1}{2} N_A \cdot m \bar{v}^2 = RT \right.$$

Base equation

Forces

more force → more mass → more particles → more collision
 ↳ more velocity → more frequent collisions

∴ Pressure \propto to Force \propto collisions

$$K.E. = \frac{1}{2} mv^2 \quad (\text{of a single particle})$$

$$\text{Unit : Joule (J)} = \text{kg m}^2/\text{s}^2$$

* For a mol of particles

$$\boxed{(K.E.)_{avg} = \frac{3}{2} (R \cdot T)} \quad [J/mol]$$

$$R = 8.314 \frac{J}{K \cdot \text{mol}} \quad \text{or} \quad \frac{\text{Kg m}^2}{K \cdot \text{mol}}$$

→ $(K.E.)_{avg}$ depends solely on the temperature,
 Not the identity of the gas

Root-mean-square velocity (urms) (extremely close to v_{avg})

$$\boxed{\sqrt{\bar{v}^2} = urms = \sqrt{\frac{R \cdot T \cdot 3}{m \cdot m}}} \quad [m/s]$$

$$R = 8.314 \frac{\text{Kg} \cdot \frac{\text{m}^2}{\text{s}^2}}{\text{K} \cdot \text{mol}}$$

$T \Rightarrow$ in kelvin

$m \cdot m \Rightarrow$ in Kg/mol

$$\rightarrow urms \propto \sqrt{\text{temp}}$$

$$\rightarrow urms \propto \frac{1}{\sqrt{m \cdot m}}$$

* NOT g/mol → Kg/mol

↑ T, speed ↑
 ↑ mass, speed ↓
 Lighter = faster / heavier = slower

Ex: compare urms and $(K.E.)_{avg}$ of H₂ and SF₆

$$urms (\text{of H}_2) = \sqrt{\frac{3RT}{mm}} = \sqrt{\frac{3 \cdot 8.314 \cdot 273}{0.00202 \text{ Kg/mol}}} = 1840 \text{ m/s}$$

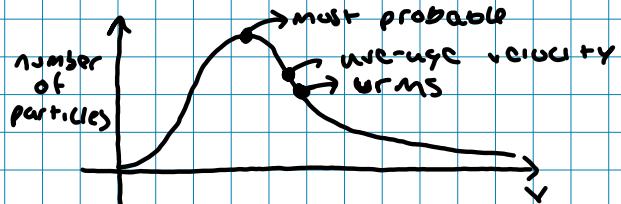
$$urms (\text{of SF}_6) = \sqrt{\frac{3 \cdot 8.314 \cdot 273}{146 \text{ g/mol} \cdot \text{Kg/1000g}}} = 216 \text{ m/s}$$

$(K.E.)_{avg}$ is the same for both. It depend solely on temperature

* Root-mean-square velocity is an average; some particles are going faster and some are going slower.

Root-mean-square velocity vs. mean velocity

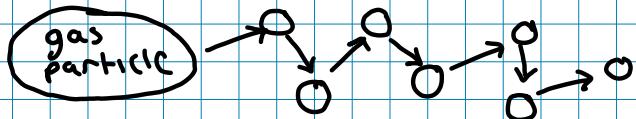
- v_{rms} is slightly higher velocity than mean velocity
- But, it is very close and gives us a good sense of average velocity.



Gas particles travel extremely quickly ($>500 \text{ m/s}$), however it can still take up to 10s for a particle to get from one side to another of a room.

Mean free path - distance a particle travels before colliding with another particle

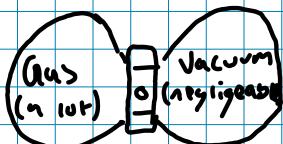
In a room filled with air, the mean free path is very small. The gas will travel in a zig-zag from the back of the front of the room as it hits and collides with different gas particles.



Effusion

Rate of effusion = rate at which a gas travels through a pin-hole into a vacuum

⇒ open stopcock and effusion occurs.



Rate of effusion \propto U_{rms}

Graham's Law

$$\frac{\text{Rate of effusion (gas A)}}{\text{Rate of effusion (gas B)}} = \sqrt{\frac{m.m.(B)}{m.m.(A)}}$$

* Assuming one is comparing same moles of gas.

$$\frac{\text{Rate effusion (A)}}{\text{Rate effusion (B)}} = \frac{\text{Time effusion (B)}}{\text{Time effusion (A)}} = \sqrt{\frac{m.m.(B)}{m.m.(A)}}$$

→ Faster takes less time

→ Lighter particles effuse faster (time ↓, rate ↑)

* units must be the same for numerator/denominator

ex: Sample of argon gas effuses in 147 s. How much time for the same number of moles of SO_2 ?

$$\frac{X \text{ s } (SO_2)}{147 \text{ s } (Ar)} = \sqrt{\frac{m.m.(SO_2)}{m.m.(Ar)}}$$

$$X = 186 \text{ s}$$

check. SO_2 heavier:
takes more time

$$\frac{\text{Rate effusion} \cdot \text{Time}}{(Ar)} \cdot \frac{\text{mol}}{(Ar)} - \frac{\text{mol}}{(SO_2)} = \frac{\text{Rate effusion} \cdot \text{Time}}{(SO_2)} \cdot \frac{\text{mol}}{(SO_2)} - \frac{\text{mol}}{(SO_2)}$$

$$\frac{\text{mol/s}}{\text{s}} - \frac{\text{s}}{\text{s}} = \frac{\text{mol}}{\text{s}} - \frac{\text{mol}}{\text{s}}$$

Real Gases

→ Ideal gases follow ideal gas law: $PV/nRT = 1$
• Only true at low pressure and high temp

* KMT assumes no interparticle forces (attract/repel) and that particles have no volume.

Gas particles don't follow KMT at high pressure:

- High pressure → greater concentration → greater likelihood of particles approaching each other and be ATTRACTED / REPELLED

Gas particles don't follow KMT at low temperature:

- High EK at high temp.
→ move fast, not likely to be affected by attractive or repulsive forces of other particles
- Low EK at low temp.
→ move slow, more likely to be attracted/repelled
ex: beautiful rose: run by → don't pay attention
pass by slowly → attracted

* USE ideal gas law unless told otherwise

At high pressure and low temp. use:

Van der Waals equation

$$\boxed{(P + a(\frac{n}{V})^2)(V - nb) = nRT}$$

a = Van der Waals "a" constant

b = Van der Waals "b" constant

a → in atm $\cdot \frac{L^2}{mol^2}$

b → in $\frac{L}{mol}$

"b" typically increases as the size of gas particle increases
"a" related to strength also increases with the size

* As "a" and "b" constant values increase, we say that the gas deviates more from the $PV = nRT$ value

Theory behind Van der Waals equation :

1. - Particles can't move in the entirety of the container.
 - Only in volume not being occupied by other gas particle(s) (free space)
 - $V - nb$
volume container" - "volume filled with other particles"
 - nb = volume correction factor
 - bigger the volume of a particle = bigger b
2. - Ideal gas \Rightarrow no attraction
 - If there are attractions, the attraction results in the path of a particle towards a wall to be diverted \Rightarrow less collisions
↳ pressure with attraction < ideal gas pressure
 - P = measured pressure
 - $a(n/V)^2$ = correction factor
 - concentration (n/V) \uparrow
 \therefore chance of attraction \uparrow
 \therefore collision with wall \downarrow
 \therefore pressure \downarrow
 - use $(n/V)^2 \Rightarrow$ square because 2 particles required

ex: 8.00 kg N₂(g) fills 100. L flask at 300°C
Calculate pressure.

$$\text{For N}_2 : a = 1.390 \text{ atm } \frac{\text{L}^2}{\text{mol}^2}, b = 0.03913 \text{ L/mol}$$

$$(P + a(n/V)^2)(V - nb) = nRT \quad 8.00 \text{ kg} \cdot \frac{1000 \text{ g}}{\text{kg}} \cdot \frac{\text{mol}}{28.02 \text{ g/mol}} = 286$$

~~$$(P + 1.390 \left(\frac{286}{100} \right)^2)(100 - 286 \cdot 0.03913) = 286 \cdot 0.08206 \cdot 573$$~~

$$(P + 1.390 \left(\frac{286}{100} \right)^2)(100 - 286 \cdot 0.03913) = 286 \cdot 0.08206 \cdot 573$$

$$\frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$$

$$P = 140 \text{ atm}$$

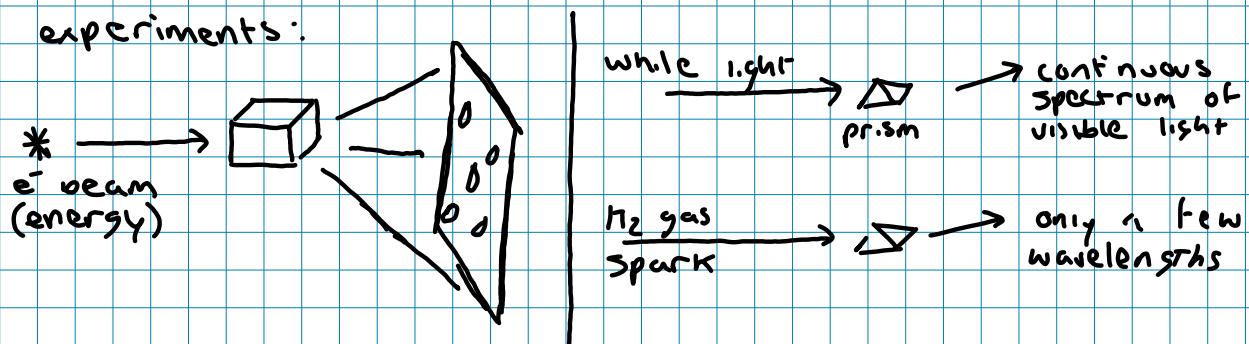
* Note! use $R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$ value

Quantum Numbers

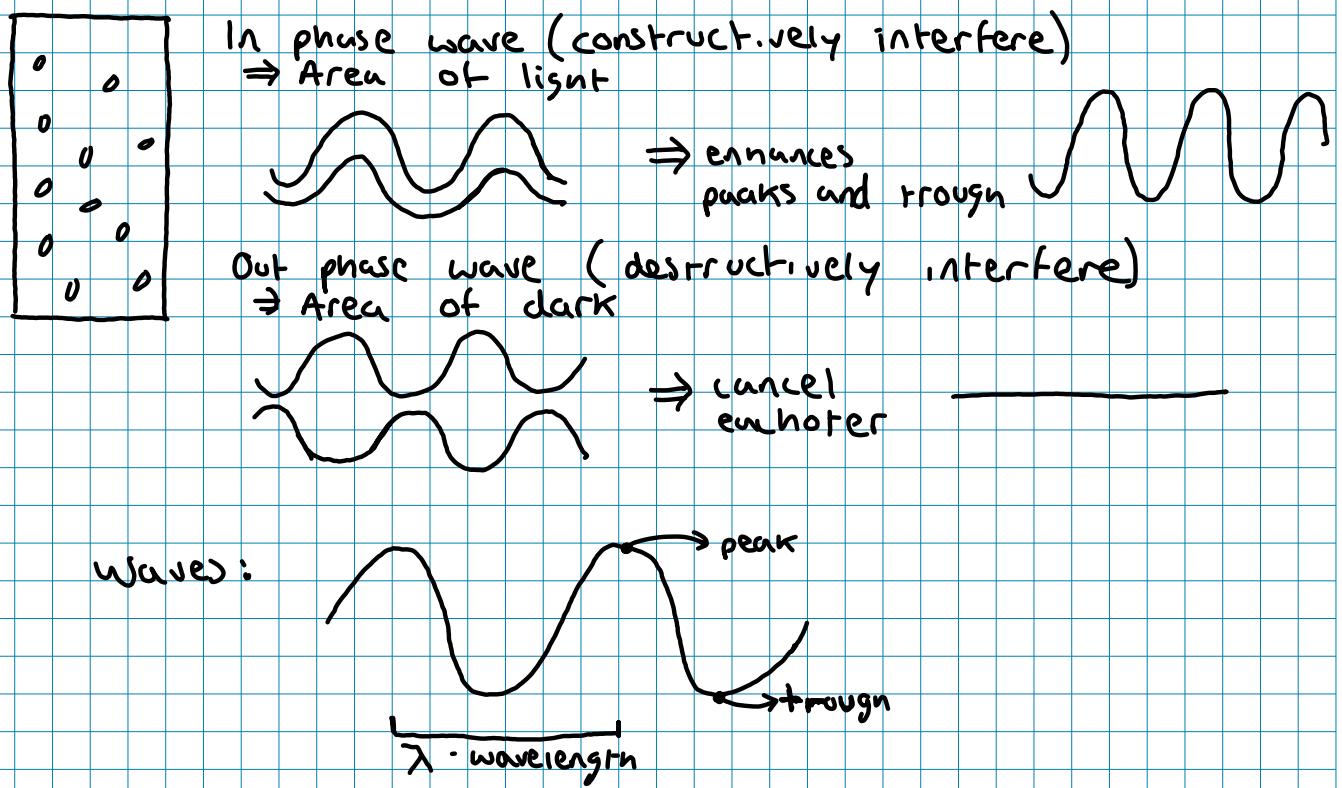
Electrons are the most important subatomic particles in chemical reactivity

One thinks of an electron as a particle and as a wave

experiments:

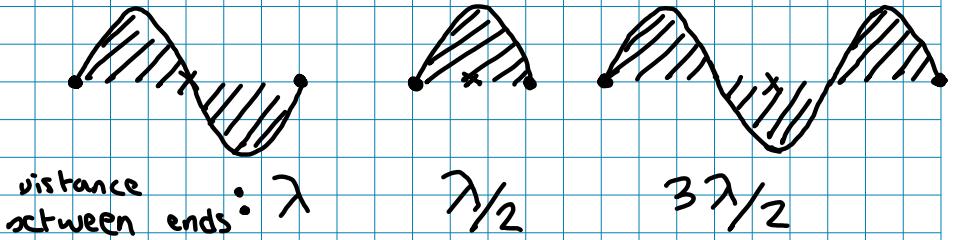


- So only certain wavelengths associated with $H_2(g)$
- Diffraction pattern when electron beam hits crystal



It is theorized that electrons are standing waves (waves with fixed ends). Fixed ends because the nucleus keeps the electrons close.

X - nucleus
● - electron
/// = wave



There are only certain allowed integer values to explain how these electrons live in the electron cloud around the nucleus.

Orbital = (wave function)²
= Area in which electrons have a high probability of existing

Quantum numbers are used to describe orbitals

Quantum numbers:

$\rightarrow n$
 $\rightarrow l$
 $\rightarrow m_l$
 $\rightarrow m_s$

} orbitals
} electrons per orbital

{ * More stable = lower energy }

Quantum numbers \rightarrow quantization of energy
(quantization = only certain allowed values)

1. n = (shell number) = (principal quantum number)

→ size of orbital (larger number = larger size)

* Allowed values : positive integer (1, 2, 3, ...)

ex: which is more stable : $n=1$ or $n=2$?

$n=1$ is smaller orbital than $n=2$

∴ electron in $n=1$ is closer to nucleus

∴ more stable ∴ lower energy

2. ℓ = (subshell number) = (angular momentum qn)

→ shape of orbital

* Allowed values : all integers between 0 to $n-1$

ex: values of ℓ for $n=3$?

$n=3$ ℓ from 0 to $3-1$

0 to 2 ∴ $\ell = 0, 1, 2$

* $\ell = 0, 1, 2, 3$ Sets Poor Daniel Free

Value ℓ	Subshell name	Shape (x = nucleus)
0	S	spherical
1	P	dumbbell 2 lobbed
2	d	4 lobbed
3	f	8 lobbed

Note: $\ell=4$: g and $\ell=5$: h (no known atoms)

Describing orbitals : n (subshell name)

(ex: $n=3, \ell=1 \rightarrow 3p$ orbital)

$n=2, \ell=2 \rightarrow 2d$ orbital

Energy in orbitals:

- For polyelectronic atoms (all atoms but H), if first and second orbital have the same principal quantum number (n)
 - The orbital with the smaller l value has lower energy
- Penetration theory: orbital with lower subshell number (assuming same shell number) penetrates the area near the nucleus more effectively
- Closer to nucleus ∴ more stable ∴ lower energy

Ex: For polyelectronic atom, what is lower energy?

$3s$ or $3p$ orbital?

Both have same shell number, but $3s$ has lower subshell number ∴ $3s$

3. $m_l = (\text{magnetic QN}) = (\text{final QN to describe orbital})$

→ orientation of orbital in 3D

* Allowed values: all integers between $-l$ and l
(including zero)

Ex: If $l = 3$

$$m_l = -3, -2, -1, 0, +1, +2, +3$$

⊗ A combination of these three QN (n, l, m_l) uniquely describes an orbital.

Ex: how many possible orbitals for $n=3$?

$$n = 3$$

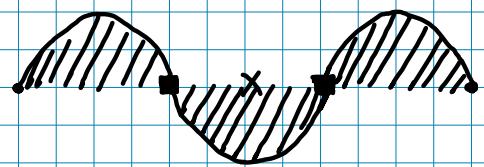
$$l = 0, 1, 2$$

$$m_l = 0 \quad -1, 0, +1 \quad -2, -1, 0, +1, +2$$

↑ ↑ ↑
one $3s$ three $3p$ five $3d$

→ 9 orbitals

Sketching orbitals



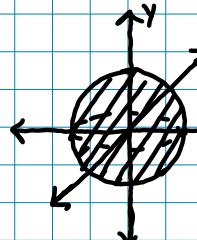
\circ = fixed end
 x = nucleus
 $\diagup \diagdown$ = area where electrons exist
 ■ = node

node of wave = zero amplitude region (there is no wave). zero probability of finding electrons
 → node, nodal surface or nodal plane

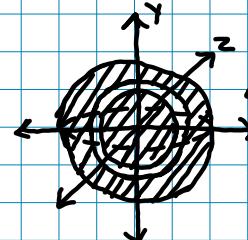
number of nodes = $n-1$ (for s orbital)

S: Draw 1s and 2s orbital: (spherical)

$$1s(n=1) \\ (l=0) \\ (m_l=0) \\ \text{node} = n-1 = 0$$



$$2s(n=2) \\ (l=0) \\ (m_l=0) \\ \text{node} = n-1 = 1$$

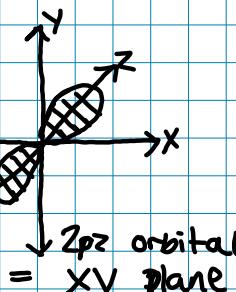
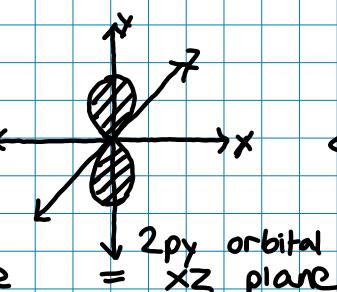
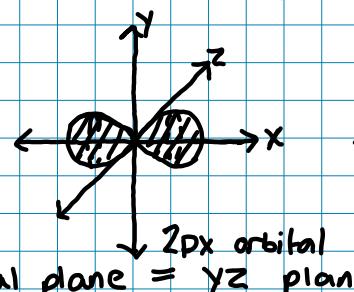


node is unshaded razor thin area

* 3 coordinate axis for each orbital (origin (0,0) is nucleus)

P: Draw 2p orbitals: (dumbbell)

$$3 \left\{ \begin{array}{l} (n=2, l=1, m_l=-1) \\ (n=2, l=1, m_l=0) \\ (n=2, l=1, m_l=+1) \end{array} \right. \\ \text{node} = n-1 = 1 \\ (\text{nodal plane splits in two})$$



nodal plane = yz plane

= xz plane

= xy plane

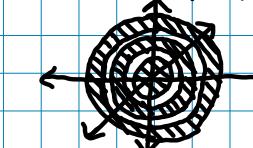
- The 3 orbitals are mutually orthogonal (\perp)
- 3 orbitals for P ($l=1$): p_x, p_y, p_z

d: 3d orbitals:

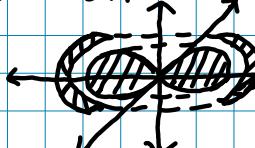
$$\begin{array}{l} n=3 \\ l=2 \\ m_l=-2, -1, 0, +1, +2 \end{array}$$

5 orbitals: $d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}, d_{z^2}$

ex: 3s orbital (2 nodes)



3px orbital (2 nodes)



- between dumbbell
- razor thin layer

2 electrons per orbital

→ each electron differs from the other on how they interact with a magnetic field

$$4. m_s = (\text{electron spin QN}) = (\text{final QN})$$

→ describes electro

* Allowed values : $m_s = +\frac{1}{2}$ (spin up e^-)
 $m_s = -\frac{1}{2}$ (spin down e^-)

electron = \uparrow $\boxed{\uparrow \downarrow}$ is orbital

(*) every e^- can be described by 4 QN (n, l, m_l, m_s)
→ Pauli exclusion principle

ex: What is max number of e^- for ($n=2, m_s = -\frac{1}{2}$)?

$$\begin{array}{l} n=2 \\ l=0 \\ m_l=0 \end{array} \quad \begin{array}{c} 1 \\ -1, 0, +1 \end{array} \quad \left| \begin{array}{l} 4 \text{ orbital} \\ \times 1 e^- \text{ per orbital} \\ (m_s = -\frac{1}{2}) \end{array} \right. = 4 e^- \text{ max.}$$

ex: What is max number of e^- for ($n=4, l=2$)?

$$\begin{array}{l} n=4 \\ l=2 \\ m_l=-2, -1, 0, +1, +2 \end{array} \quad \left| \begin{array}{l} 5 \text{ orbital} \\ \times 2 e^- \text{ per orbital} \\ (m_s = -\frac{1}{2}, +\frac{1}{2}) \end{array} \right. = 10 e^- \text{ max.}$$

ex: What is max number of e^- for ($n=3, m_l=-3$)?

$$\begin{array}{l} n=3 \\ l=0 \\ m_l=0 \end{array} \quad \begin{array}{c} 1 \\ -1, 0, +1 \end{array} \quad \begin{array}{c} 2 \\ -2, -1, 0, +1, +2 \end{array}$$

∴ zero e^-
b/c $m_l \neq -3$

Quantum Numbers and Periodic Table

→ Modern atomic theory shows how electrons are theorized to exist in orbitals

Aufbau Principle = "building up" = states that for each proton in an atom, one places an electron in the lowest energy available orbital
→ lower energy = more stable

Energy:

- Increase in energy as "n" increase
- Increase in energy as "l" increase
- Lower " $n+l$ " = lower energy.

Atomic orbital box / line diagram:

- Arrow designates electron (first pointing up)

Alternative notation:

- Shell number, subshell letter, superscript x $\Rightarrow n l^x$
 $\Rightarrow x$ = number of electrons in subshell

ex: Hydrogen



Helium



Ground State Electron Configuration (GSEC):

- Electrons for an atom go to the most stable (low energy) possible orbital

* If electrons are not written in the most stable possible orbital, it is ~~%~~ an excited state
→ energy must be applied to reach excited state

ex: excited Helium : $\frac{\uparrow}{1s} \quad \frac{\uparrow}{2s}$

* When writing GSEC for elements, one can replace filled orbitals by the previous noble gas

ex: replace $1s^2$ by [He]

Note: relation between shell number and period (row) where element is found.

Hunds Rule: When given the choice to place an electron in 2 degenerate orbitals, one chooses to place the electron in an empty orbital rather than in an orbital with another electron.

- Degenerate = equal in energy
= 2 orbitals that have same "n" and "l"
 - Paired e^- = e^- found in orbital with other e^-
 - unpaired e^- = e^- found in orbital alone
- * Electrons prefer to be unpaired to avoid e^-/e^- repulsion

Valence electrons = electrons found in the highest shell number containing electrons

- Valence shell = shell number containing val. e^-
 - core electrons = non-valence e^- of an atom
- * Valence electrons are found on shell number corresponding to row number

Main group elements, valence e^- correspond to Roman numeral.

- Let n = row number in periodic table

- Valence e^- are:

- gr IA \Rightarrow 1 val $e^- \Rightarrow nS^1$
- gr IIA \Rightarrow 2 val $e^- \Rightarrow nS^2$
- gr IIIA \Rightarrow 3 val $e^- \Rightarrow nS^2 np^1$
- gr IVA \Rightarrow 4 val $e^- \Rightarrow nS^2 np^2$
- gr VA \Rightarrow 5 val $e^- \Rightarrow nS^2 np^3$
- gr VIA \Rightarrow 6 val $e^- \Rightarrow nS^2 np^4$
- gr VIIA \Rightarrow 7 val $e^- \Rightarrow nS^2 np^5$
- gr VIIIA \Rightarrow 8 val $e^- \Rightarrow nS^2 np^6$

Transition metal: last electrons fill d orbital

Lanthanides : last electrons fill 4f orbital
Actinides : last electrons fill 5f orbital

Rule for expected order of filling e^- in orbitals

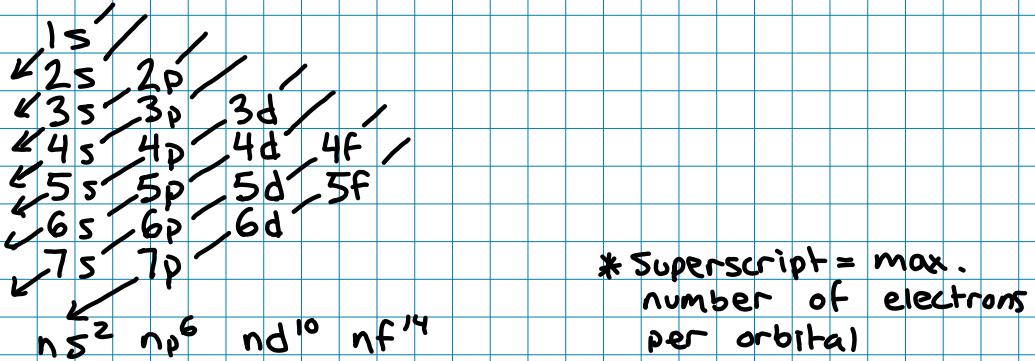
→ Assigned in order of $n+l$ value

→ For 2 orbitals with equal value, assign to lower n

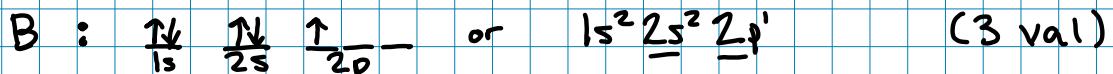
$$\text{ex: } \begin{array}{ccccccccc} 3s & 3p & 3d & & 4s & 4p & 4d \\ n+l = & 3 & 4 & 5 & & 4 & 5 & 6 \end{array} \quad \therefore 3s, 3p, 4s, 3d, 4p$$

(lower "n")

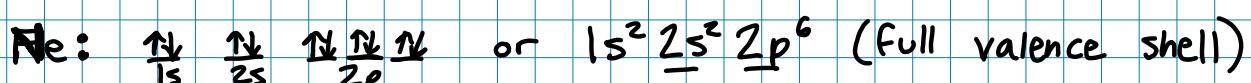
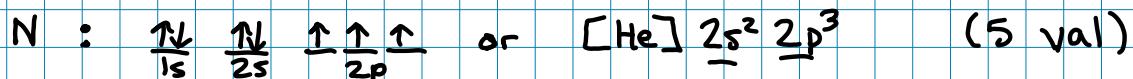
Trick:



GSEC for main group elements: (Row 2)

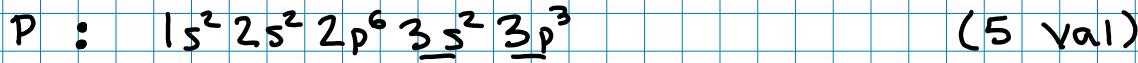


$\frac{\uparrow\downarrow}{1s} \quad \frac{\uparrow\downarrow}{2s} \quad \frac{\uparrow\downarrow}{2p} -$ Wrong b/c paired e^- (Hund's rule)
This is excited state (repulsion)



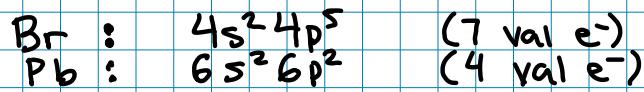
* Note: Valence shell underlined
↳ $n=2$ shell (corresponds to row 2)

GSEC for main group elements: (Row 3)

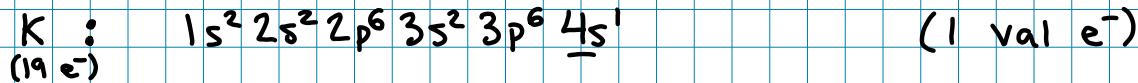


→ same number of val. e^- as N
↳ Both in group VIA

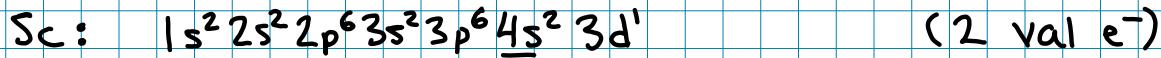
Valence e^- for main gr. elements: (underlined)



GSEC for elements: (Row 4) - main and transition



→ What happened to 3d orbital
↳ follow $n+l$



→ Final e^- went into "d" orbital

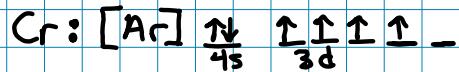
Final e^- go into...

3d	orbital	⇒ Sc - Zn	T metal
4p	orbital	⇒ Ga - Kr	
5s	orbital	⇒ Rb - Sr	
4d	orbital	⇒ Y - Cd	T metal
5p	orbital	⇒ In - Xe	
6s	orbital	⇒ Cs - Ba	
4f	orbital	⇒ Lanthanides	
5f	orbital	⇒ actinides	
5d	orbital	⇒ La - Hg	T metal

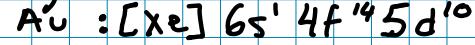
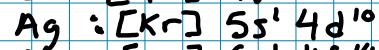
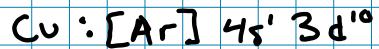
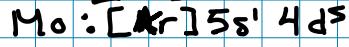
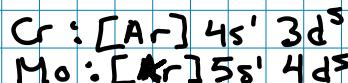
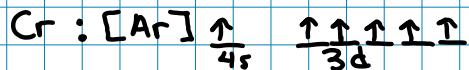
Exceptions to expected order of filling

→ Group VII B : Cr, Mo
 → Group I B : Cu, Ag, Au

Expected GSEC for:



Experimentally:



Theorized: Cr and Mo exception →

To have all electrons unpaired (4s 3d or 5s 4d)
 To avoid unfavourable repulsion.

Cu, Ag and Au →

Having all 5 d orbitals filled provides
 a certain stability

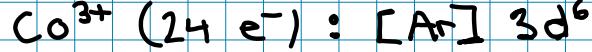
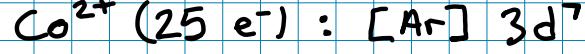
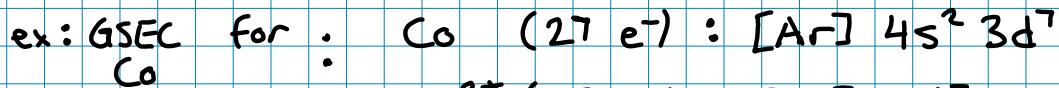
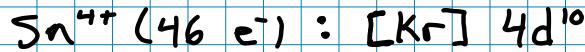
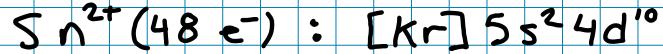
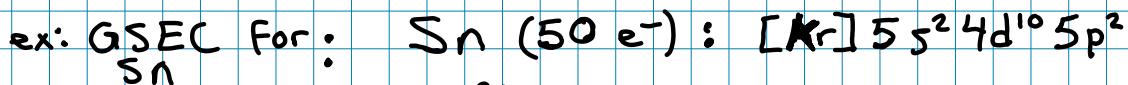
Electron configuration for cations (+)

* Remove e^- from furthest valence shell

- Let $n =$ highest shell number containing e^-

• Main group elements: remove first from np orbitals (if present), then ns

• Transition metals: remove from ns, and only once emptied, remove from $(n-1)d$

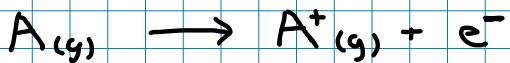


Periodic Trends

- Properties of atoms related to their position in the periodic table
- ex: ionization energy, electron affinity, electronegativity, atomic radius, density, etc.

1. Ionization energy

= energy required to remove a single electron from nucleus, which is attractive (+ and -), of a gaseous atom



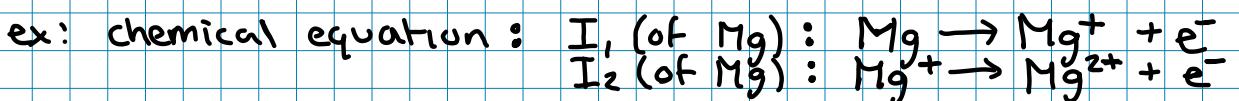
It requires energy to pull electron away from attracting positive nucleus

I_1 = first ionization energy

energy required to remove first e^-

I_2 = second ionization energy

energy to remove second e^-



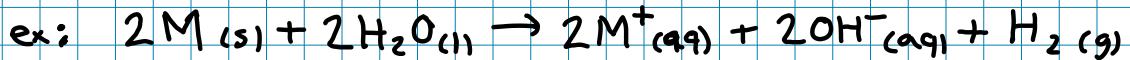
Up → Down trend

- First ionization energy decreases going down a group

Theory: Electrons are removed from furthest valence shell. The higher you are, the ~~higher / up / made~~ closer the valence shell is to the attractive nucleus → the harder it is to pull an e^-

* Same logic, an element will be a better reducing agent when located lower in periodic table (more reactive)

Easier to remove e^- ∴ requires less energy



Which will be better oxidized (=reducing agent)

$M = K$ or $M = Na$?

K b/c valence shell larger than Na ∴ val e^- further from nucleus ∴ better at giving e^-
∴ more reactive

Left \rightarrow Right

~~Biggest to smallest~~ Left trend (general)

I_1 increases going left to right across period

Theory: number of protons increase going left to right

\therefore electrons held more tightly in a given shell
 \therefore harder to remove \therefore requires more energy (more protons = more effective nuclear charge \therefore greater ionization energy)

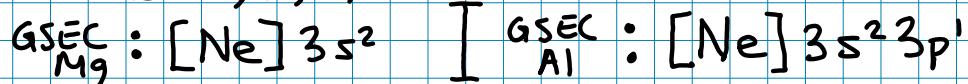
ex: I_1 for row 3:

Na	Mg	Al	Si	P	S	Cl	Ar
495	735	580,	780	1060	1005,	1225	1527

exception

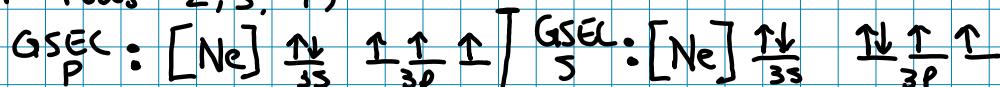
Exceptions:

- Group IIIA element has smaller I_1 than IIA (for rows 2, 3, 4)



The first e^- being removed from Al is from a p orbital, which is less stable than an s orbital \therefore easier to remove

- Group VIA element has smaller I_1 than ~~VIIA~~, VIIA (for rows 2, 3, 4)



It's easier to remove an e^- from sulfur b/c one is relieving an unfavorable e^-/e^- repulsion

- * Exception disappears once we reach row 5 b/c e^-/e^- repulsion is not severe in a very large $5p$ orbital.

Trend in ionization energy in a given atom
ex: Mg \rightarrow GSEC: $1s^2 2s^2 2p^6 3s^2$

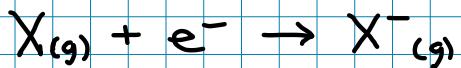
$$I_1 = 735, I_2 = 1440, I_3 = 7730 \text{ kJ/mol}$$

General increase in ionization energy b/c it becomes harder to rip off e^- when proton/electron ratio increases

\rightarrow There is a dramatic jump for I_3 b/c the 3rd e^- is removed from a $n=2$ shell, which is closer to nucleus than $n=3$ shell (valence) from which first 2 e^- were removed.

2. Electron Affinity

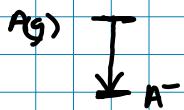
= energy change associated with a gaseous atom or ion accepting a single electron



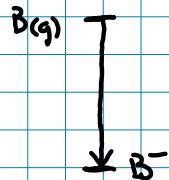
The more negative the value of electron affinity (greater number), the greater the electron affinity
 ∴ the more exothermic the electron affinity
 ∴ the more favourable

The lower the energy, the more stable
 ∴ greater electron affinity means a greater drop in energy
 ∴ more favourable b/c it makes an atom more stable

ex: $A(g)$ e⁻ affinity = -50 kJ



$B(g)$ e⁻ affinity = -100 kJ



B⁻ is more stable (low energy) relative to B(g) than
 A⁻ is relative to A(g)
 ∴ B(g) accepts more favourably.

Left → Right trend

- electron affinity becomes more favourable (greater num.)

Theory: greater number of protons as one moves to the right, so better ability to pick up e⁻

Up → Down trend

- electron affinity becomes less favourable

Theory: as one moves down valence shell is further from nucleus ∴ harder to pick up e⁻.

Exceptions:

- Group VIII A (noble gases) are an exception to increase in electron affinity

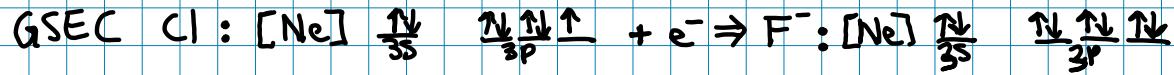
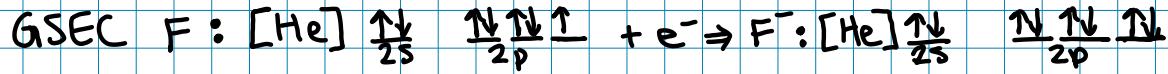
Noble gases have unfavourable electron affinity b/c they have a full valence shell.

ex: Valence e⁻ Ar: $\frac{1N}{3S} \frac{1L}{3P} \frac{1N}{4S} + e^- = \frac{1N}{3S} \frac{1L}{3P} \frac{1N}{4S} \uparrow$

- exception to up \rightarrow down (less favourable) trend

- Cl more favourable than F
- S more favourable than O
- P more favourable than N

N	O	F
P	S	Cl

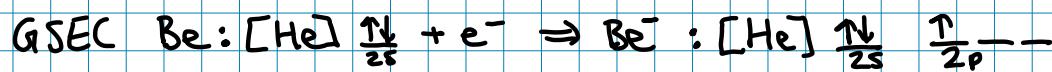
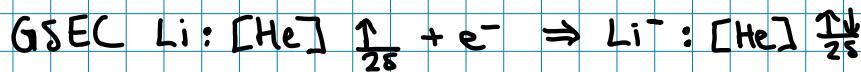


F has a less favourable e^- affinity than Cl b/c it accepts the extra e^- in a $2p$ orbital (smallest p orbital)
 $\therefore e^-/e^-$ repulsion is very strong and unfavourable.

ex: e^- affinity of:	F	- 327.8 KJ/mol
	Cl	- 348.7 KJ/mol
	Br	- 324.5 KJ/mol
	I	- 295.2 KJ/mol

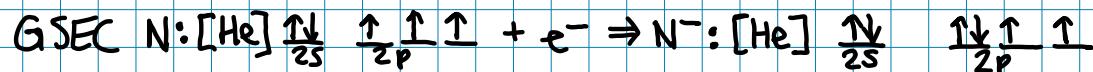
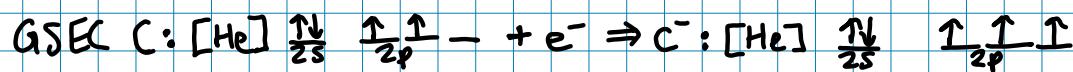
- exception to left \rightarrow right (more favourable) trend

- Group IA has more favourable e^- affinity than IIA (for rows 2, 3, 4)



Li is more favourable e^- affinity than Be
b/c $2p$ orbital is less stable than $2s$, and
Be accepts extra e^- on $2p$, while Li
accepts the extra e^- on $2s$ orbital

- Group IVA has more favourable e^- affinity than VA (for rows 2, 3, 4)



C is more favourable e^- affinity than N
b/c C accepts extra e^- into an empty orbital
but N accepts extra e^- paired with another e^-
creating an unfavourable e^-/e^- repulsion

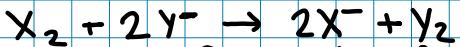
3. Halogen ~~as~~ oxidizing agent

Up \rightarrow Down trend

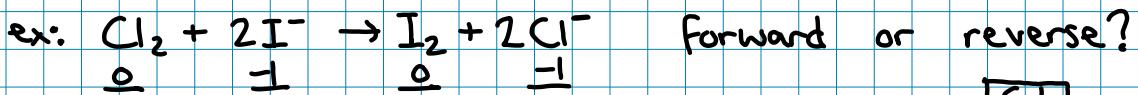
- Going down in the halogen group, halogens become less good oxidizing agents (or less easily reduced)

Theory: valence shell further from attractive force of nucleus as one goes down so less capable of picking up e^-

Note: In reaction between halogen (X_2) and halide (Y^-),



- will go forward if halogen reactant (X_2) is a better oxidizing agent than halogen product (Y_2)
- will go reverse if opposite



Forward b/c Cl_2 is a better oxidizing agent (higher in table) b/c valence shell is closer to attractive force of nucleus

Cl
Br
I

4. Electronegativity

= ability of an atom to draw e^- toward itself within a compound (partial charge)

Left \rightarrow Right trend

- Atom becomes more electronegative

Theory: more protons \therefore better able to pull e^-

Up \rightarrow Down trend

- Atom becomes less electronegative

Theory: as one moves down, valence shell is further away from nucleus \therefore harder to pull e^-

Exceptions:

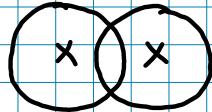
- Group VIII A (noble gases) are exception to left \rightarrow right increase

Noble gases are not very electro negative due to their full valence shell.

5. Atomic Radius

= $\frac{1}{2}$ the distance between the nuclei of 2 identical atoms

Units: $\text{\AA} = 10^{-10} \text{ m}$ (Angstroms)



Right \rightarrow Left trend

- Atomic radius decreases

Theory: more protons \therefore pulls electrons more tightly
 \therefore smaller radius

Up \rightarrow Down trend

- Atomic radius of atoms and ionic radius of identically charged ions increases

Theory: add shells moving down a group \therefore size of atom increases.

Ion sizes

\rightarrow As radius of an ion gets larger, the size gets larger

- Cation (+) always smaller than its parent (atom) (neutral)
- Anion (-) always larger than its parent atom
- \rightarrow with higher proton/electron ratio, electrons held more tightly (smaller size)

Isoelectronic Ions (same number of e^-)

\rightarrow The isoelectronic ion with more protons pulls e^- more tightly \therefore smaller radius.

Ion	# e^-	# protons	
Sn^{2-}	18	16	largest
Cl^-	18	17	
K^+	18	19	
Ca^{2+}	18	20	smallest

These ions have "noble gas configuration" or "complete octet"

$[\text{Ar}] 1s^2 2s^2 2p^6 3s^2 3p^6$ (surrounded by 8 val. e^-)

- Metals don't typically lose e^- beyond noble gas config.
- Non-metals don't typically gain e^- beyond noble gas config.
- * soon try to have e^- config. of noble gas

6. Density (Up \rightarrow Down):

- mass ~~increases~~ increases more rapidly than atomic size going down
 \therefore density increases). ex: Br more dense than Cl

Bonding

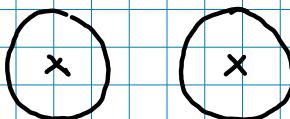
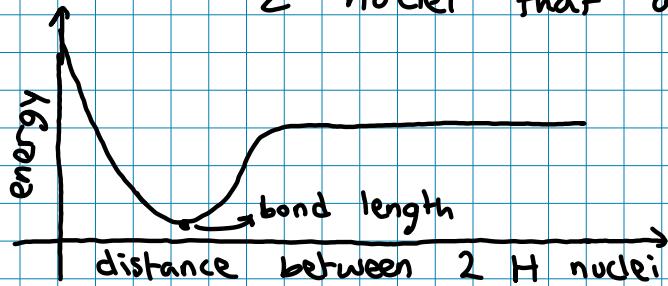
→ Forces that hold atoms in close proximity in compounds or polyatomic ions.

Ionic bond = electrostatic attraction between oppositely charged ions

- Write cation next to anion : $\text{Na}^+ \text{Cl}^-$
- ✗ Do NOT represent ionic bond by a line (line = covalent bond) : ~~Na-Cl~~

Covalent bond = a bond where electrons are shared between 2 nuclei
(holds non-metals together in molecules)

Bond length = most stable (low energy) distance between 2 nuclei that are adjacent in compound.



- energy rises when we approach zero distance b/c nuclei repel each other
- energy rises to the right b/c takes energy to break bond
- ✗ The electrons of one H atom are attracted to the proton of a second H atom ∴ ideal (stable / low energy) distance between 2 nuclei.

Polarity of bonds

- Pauling numbers (Fig 8.3) describe relative electronegativity
→ Greater Pauling number = more electronegative the atom

Note: • F is the most electronegative atom, followed by O.

- Non-metals are more electronegative than metals

Bond Ionic in character:

"Difference between Pauling numbers for 2 atoms" $\gg 2$

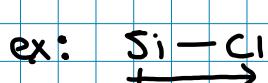
Covalent bond:

"Difference between Pauling numbers for 2 atoms" < 2

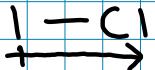
- * Even in covalent bonds between non-identical atoms, there is a difference in electronegativities
- ∴ unequal share of electrons
- ∴ polar covalent bond

The greater the difference in electronegativities (Pauling num.), the greater the polarity

More electronegative atom: δ^-



Less electronegative atom: δ^+



ex: which bond is more polar: C-N or C-O?
(Pauling numbers: C = 2.5, N = 3.0, O = 3.5)

$$\text{C}-\text{N}: 3.0 - 2.5 = 0.5$$

$$\text{C}-\text{O}: 3.5 - 2.5 = 1.0 \quad \therefore \text{C}-\text{O} \text{ is more polar (greater difference)}$$

Not all covalent bonds are polar (if difference = 0)

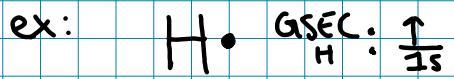
→ Bond between 2 identical atoms

→ Rare 2 atoms with same Paulin number such as P-H (Pauling num.: P = 2.1, H = 2.1)

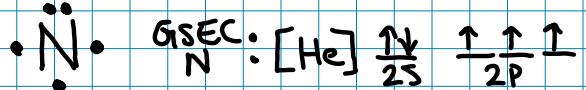
* C-H is thought as non-polar

Lewis dot symbol

→ Nucleus and core electrons = symbol for atom
→ Electrons on valence shell = dot •



* Note: Hydrogen only needs 2 e⁻ to complete its valence shell



- bonding pairs (shared) : pair of e⁻ shared between 2 atoms.
Represent by line: —

- lone pairs (nonbonding) : pair of e⁻ that are attached to only one atom

Duet rule: H follows duet rule to always be surrounded by 2 e⁻ in molecules or ions

Octet rule: Atoms are surrounded by 8 val. e⁻ in molecules

→ Second period non-metals, carbon, nitrogen oxygen, fluorine follow octet

→ Terminal atoms follow octet (atoms that are attached to only 1 other atom)

* Atoms tend to combine to complete their valence shell

ex: Ammonia (NH₃)



Localized Electron theory (L.E): Lewis Structures

- For molecules like HF or NH₃, drawing Lewis structures is pretty easy
- For many simple ions or molecules, one must follow certain steps to be able to draw a structure

① Choose the central atom

- often atom with lowest electronegativity
- never H
- atom that is attached to 2 or more other atoms
note: if only 2 atoms, none are central
- * Some molecules have several central atoms

② Add up total number of electrons

- If ion has negative charge: add val e⁻
- If ion has positive charge: remove val e⁻

③ Place one bonding pair (represented by a line) between each bonded atoms

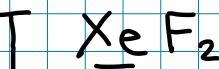
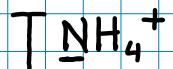
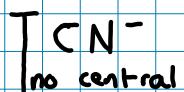
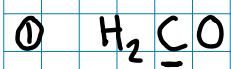
④ Use remaining val e⁻ as lone pairs around each terminal (non-central) atom

- If possible, have 8 val e⁻ around each terminal atom (other than H).

⑤ 3 possibilities:

- A)
 - o All atoms (terminal and central) are surrounded by 8 e⁻
 - o All val e⁻ are used
- B)
 - o All val e⁻ are used up
 - o But not all atoms obey octet rule
 - More lone pair from one atom to bonded pair
 - * Exceptions:
 - B, Be and certain central atoms exceed octet rule
 - Atoms row 3 and heavier can exceed octet b/c they have space in d orbital
- C)
 - o Octet/Duet rule is satisfied
 - o But not all val e⁻ are used
 - Place remaining e⁻ on central atom (lone pairs)

ex: formaldehyde, cyanide, ammonium, xenon difluoride
 underline central atom



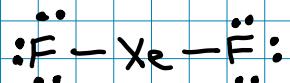
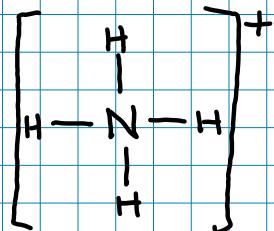
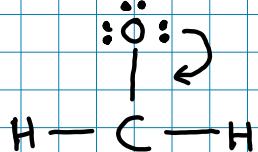
$$\begin{aligned} \textcircled{2} \quad & (\frac{2}{\text{H}} \times 1e^-) + (\frac{1}{\text{C}} \times 4e^-) + (\frac{1}{\text{O}} \times 6e^-) \\ & = 12 \text{ val. } e^- \end{aligned}$$

$$\begin{aligned} & (\frac{1}{\text{C}} \times 4) + (\frac{1}{\text{N}} \times 5) + \underline{\underline{1e^-}} \\ & = 10 \text{ val. } e^- \end{aligned}$$

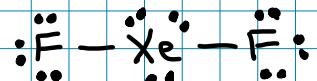
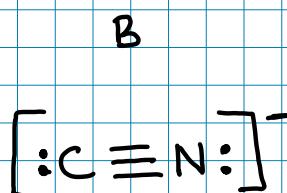
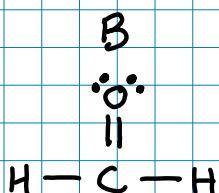
$$\begin{aligned} & (\frac{1}{\text{N}} \times 5) + (\frac{4}{\text{H}} \times 1) - \underline{\underline{1e^-}} \\ & = 8 \text{ val. } e^- \end{aligned}$$

$$\begin{aligned} & (\frac{1}{\text{Xe}} \times 8) + (\frac{2}{\text{F}} \times 7) \\ & = 22 \text{ val. } e^- \end{aligned}$$

③
④

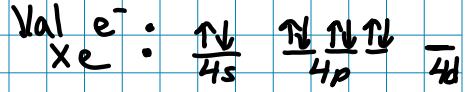


⑤



Notes: - curved arrow

- Xe can use a d orbital to be surrounded by more than 8 val. e^-



Single bond = covalent bond with
 Double bond = covalent bond with
 Triple bond = covalent bond with

$\frac{2}{4} e^-$
 $\frac{4}{4} e^-$
 $\frac{6}{4} e^-$

-
 =
 ≡

* Never exceed triple bond

For larger molecules:

→ When atom X is neutral (zero formal charge)
 → surrounded by Y bonded and Z lone pairs

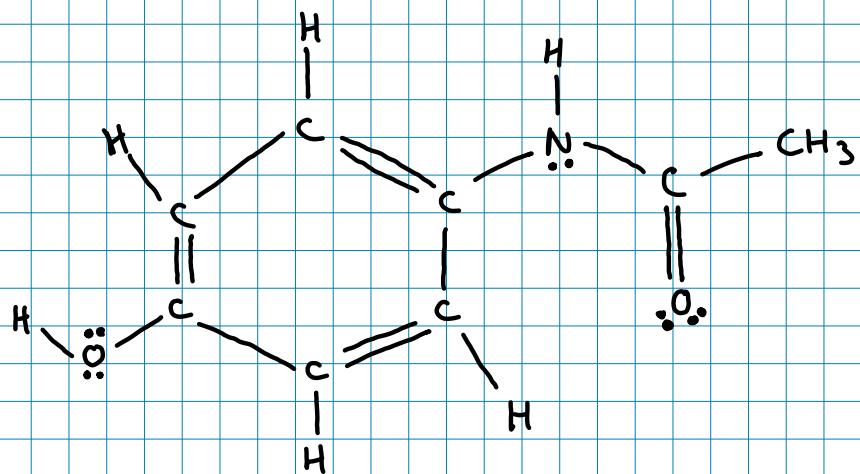
X (obey octet)	Y (bonded)	Z (lone)	
C	4	0	-C- =C= C
N	3	1	-N- :N≡ -N=
O (other VI A)	2	2	:O: :O=
F (other halogen)	1	3	:F: —

Exceptions to octet

- Be neutral (in compounds) surrounded by 4 val. e⁻ H:Be:H
- B neutral (in compounds) surrounded by 6 val e⁻ H:B:H

Note: just because these molecules are neutral, they are still very reactive (space for e⁻)

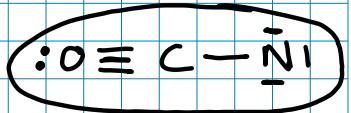
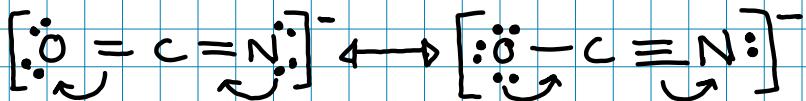
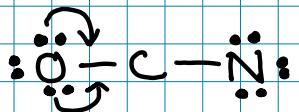
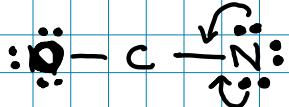
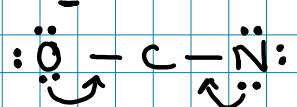
complete skeletal structure:
 - Add lone pairs and bonded pairs
 - Add no new single bonds



Resonance

- sometimes more than one Lewis structure is valid
 - occurs when one has a choice of where to put a multiple bond

ex: OCN^- (16 val. e⁻)



Bad F.C.

* Arrow shows how one goes from one valid Lewis structure to another

→ show how electrons spread to some extent (delocalize)

Resonance = concept explaining how the actual structure of a molecule/ion is a hybrid of all valid Lewis structures

Double headed arrow: placed between valid structures

Hybrid = composite = supercomposition

Each valid Lewis structure (if more than one) is a resonance structure/contributing structure.
→ each of these contribute to the resonance hybrid

Resonance hybrid = composite of all resonance structures.

* The hybrid is the actual structure

Note: single bond ($A-B$) weaker and longer than double bond ($A=B$) weaker and longer than triple bond ($A\equiv B$)

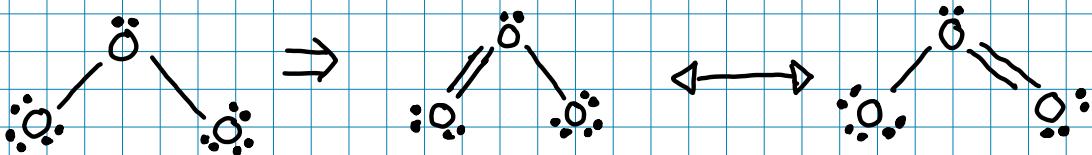
ex: Length and strength of bonds in OCN^-

- C-O bond length and strength is between that of a C=O double bond and C≡O triple bond
- C-N bond length and strength is between that of a C=N double bond and C≡N triple bond

* Electrons are said to be delocalized (curved arrow), which explains how bond is intermediate or hybrid

For valid resonance structures, electrons are located on or between different atoms ON PAPER.

Ex: Draw O_3 resonance structures and describe bond different on paper



\therefore O-O bond length and strength between that of single and double bond.

Formal Charge (F.C.)

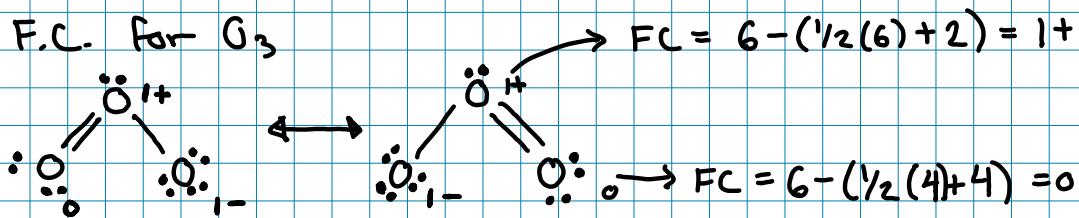
→ comparing number of val e⁻ of an atom in molecule vs as neutral atom on its own

$$F.C. = \frac{\text{number of val } e^- \text{ surrounding atom when neutral}}{-} \left(\frac{1}{2} \left(\begin{array}{l} \text{number of shared } e^- \\ \text{around given atom} \end{array} \right) + \left(\begin{array}{l} \text{number of unshared } e^- \\ \text{around atom} \end{array} \right) \right)$$

b/c shared

- Notes:
- Formal charge of all atoms should add up to overall charge of ion or compound.
 - Formal charge shown near atom

ex. F.C. for O_3



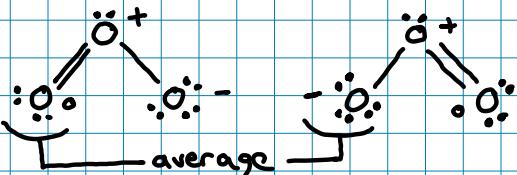
* Equivalent resonance structures:

- every atom X in one resonance structure has a certain F.C. and is surrounded by some bond combo

→ There exist atom X in 2nd resonance structure with same F.C. and bond combo

If one has equivalent resonance structures, the resonance hybrid (actual charge) is an average of all equivalent structures.

ex: F.C. of left oxygen in O_3



$$F.C_{\text{hybrid}} = \frac{O \text{ F.C} + 1^- \text{ F.C}}{2} = \frac{1}{2}^-$$

If structures aren't equivalent, there are:

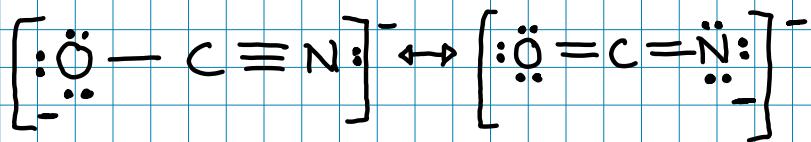
- Major resonance structure: contributing more to hybrid, preferred
- Minor resonance structure: contributes to hybrid but less than the "major"

A structure contributes more if:

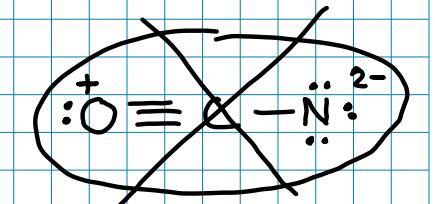
1. Resonance structure minimizes F.C. (close to zero)
2. Negative value for formal charge is on more electronegative atom

Note: If F.C. is not minimized and negative formal charge is on the less electronegative atom (pos. FC on most electro.)
∴ not valid structure.

ex: OCN^-



Major
b/c more electronegative oxygen holds negative F.C. better

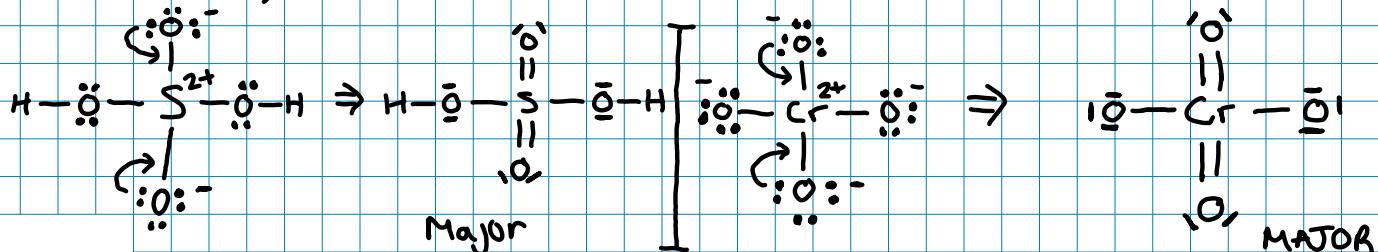


Bad b/c oxygen is more electronegative

Charge N: between O and 1^-
but closer to O

Charge O: between 1^- and 0
but closer to 1^-

Minimizing F.C. (note: S and Cr can exceed octet)



VSEPR Theory / Orbital Hybridization

(Localized electron model)

VSEPR = Valence Shell Electron Pair Repulsion

VSEPR theory and molecular geometry/bond angles:

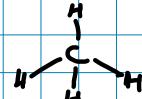
- Minimizing the electron pair repulsion of e^- pairs dictates bond angles and geometry

ex: $\text{BeH}_2 \Rightarrow \text{H}-\text{Be}-\text{H}$ electron pairs want to be as far away from each other

Hybrid orbitals describe where pairs of electrons exist around an atom when part of a molecule.

Remember: Atomic Orbital = area in which e^- have high probability of existing in an ATOM? (NOT in molecule)

ex: valence shell C :



However, we can't say that in a molecule like CH_4 the 8 electrons surrounding C are in $2s, 2px, 2py, 2pz$.

It doesn't make sense b/c $2s$ orbital is lower energy than $2p$. It doesn't make sense that one C-H bond is stronger than another.

Instead, there is another theory to explain how e^- exist around an atom in a molecule.

Hybrid Orbitals

- pairs of e^- that surround an atom in a molecule exist in hybrid orbitals
- hybrid orbitals of the same name \Rightarrow equal energy

- Valence s, p and d orbitals combine to create hybrid orbitals
- The number of orbitals that combine is equal to the number of hybrid orbitals produced

* Each hybrid orbital can hold 2 e^-

Region of electron density : - lone pair
 (effective e^- pair) - single bond
 - multiple bond (1 region)

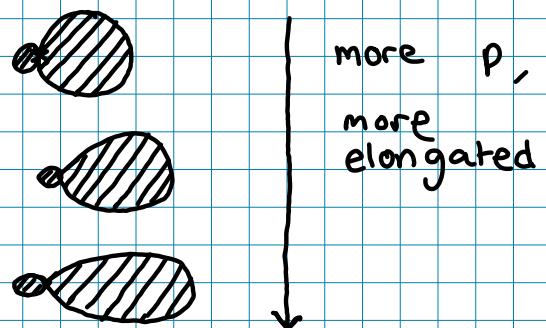
Hybrid orbitals are given names based upon the number of regions of e^- density surrounding a given central atom.

Hybridization of central atom (name of hybrid orbitals)	Number of regions of e^- density	example: A = central atom X = region e^- density
SP	1+1	2
SP^2	1+2	3
SP^3	1+3	4
SP^3d	1+3+1	5
SP^3d^2	1+3+2	6

From theory, Hydrogen, (H), is surrounded by an atomic orbital ('1s') rather than a hybrid orbital when part of a molecule.

Orbital drawing:

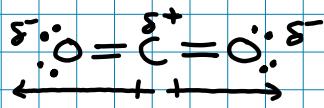
- SP (hybrid of s/p) ∴
- SP^2 (more p like) ∴
- SP^3 (even more p like) ∴



Polarity of molecules

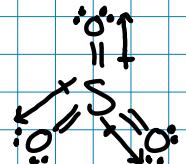
- A bond is polar based on electronegativity (difference in Pauling numbers) of 2 atoms in a bond
- Molecule is polar if e⁻ density is shifted more to one side.
- Molecule is non-polar if dipole moment arrow vectors cancel each other out
 - * If at the end of all hybrid orbitals surrounding the central atom, there's the same atom group

ex: CO₂



non-polar b/c vectors cancel out.

ex: SO₃



non-polar b/c dipole moment arrow vectors cancel out

SP orbitals

$\rightarrow 1 \text{ valence } s + 1 \text{ valence } p \Rightarrow 2 \text{ sp hybrid orbitals}$

Geometry : Linear

ex:	Lewis	Bond pairs	Lone pairs	Arrangement e ⁻ pairs	molecular geometry	3D sketch	Polar
BeCl ₂		2	0	linear	linear		No

Note: Cl +
||
Be 2-

Cl +
||
Cl +

Bad b/c Cl more electronegative

Cl-Be-Cl $\angle = 180^\circ$
(bond angle)

look at e⁻ pairs look at atoms no lone pairs

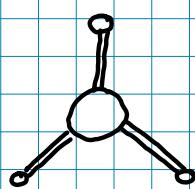
SP² orbitals

$\rightarrow 1 \text{ valence } s + 2 \text{ valence } p \Rightarrow 3 \text{ sp}^2 \text{ hybrid orbitals}$

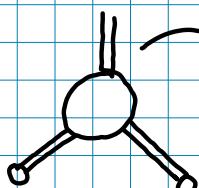
Geometry : Trigonal Planar

ex:	Lewis	Bond pairs	Lone pairs	Arrangement e ⁻ pairs	Molecular geometry	3D sketch	Polar
BF ₃		3	0	trigonal planar	trigonal planar		No
SnCl ₂		2	1		V-shaped bent angular		Yes

BF₃



SnCl₂



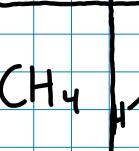
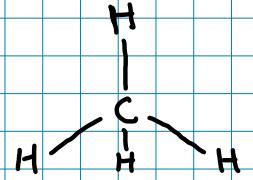
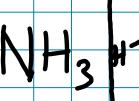
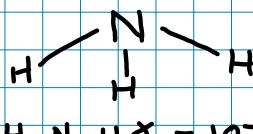
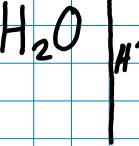
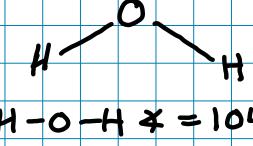
lone pair counts
as a hybrid orbital

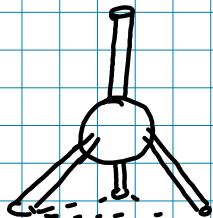
sp^3 orbitals

$\rightarrow 1 \text{ valence } s + 3 \text{ valence } p \Rightarrow 4 \text{ } sp^3 \text{ hybrid orbitals}$

Geometry: Tetrahedral

Note: When a central atom in a molecule is surrounded by lone pairs and bonded pairs, each lone pair causes a bond compression of 2.5° .
 * Lone pairs repel more

ex	Lewis	Bond pairs	Lone pairs	Arrangement e ⁻ pairs	molecular geometry	3D sketch	Polar
CH_4		4	0	Tetrahedral	Tetrahedral	 $H-C-H \approx 109.5^\circ$	No
NH_3		3	1		Trigonal pyramidal	 $H-N-H \approx 107^\circ$	Yes
H_2O		2	2		V-shaped bent angular	 $H-O-H \approx 104.5^\circ$	Yes



sp^3d orbitals

→ 1 valence s + 3 valence p + 1 valence d = 5 hybridized sp^3d orbitals

Geometry: Trigonal Bipyramidal

Note: • equatorial : e⁻ pairs in trigonal bipyramidal that are 120° apart.
("equator" - think circle around earth)

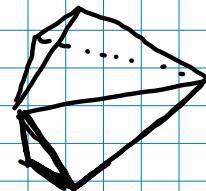
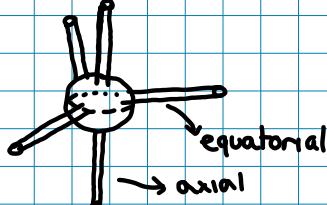
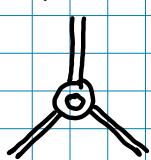
• axial : e⁻ pairs in trigonal bipyramidal that are 180° apart
("axe" - think 180° axis)

* Lone pairs go into an equatorial place to minimize e⁻/e⁻ repulsion (VSEPR)
→ lone pairs repel more

- in axial : 90° relative to 3 e⁻ pairs
- in equatorial : 90° relative to 2 e⁻ pairs

ex:	Lewis	Bond Pairs	Lone Pairs	Arrangement e ⁻ pairs	molecular geometry	3D sketch	Polar
PCl ₅		5	0	Trigonal bipyramidal	Trigonal bipyramidal		No
SF ₄		4	1	See-saw	see-saw		Yes
BrF ₃		3	2	T-shaped	T-shaped		Yes
XeF ₂		2	3	Linear	Linear		No

Top view



2 pyramids superposed

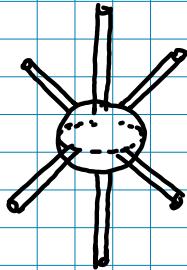
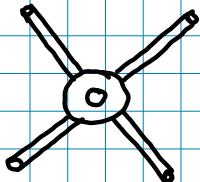
sp^3d^2 orbitals

→ 1 valence s + 3 valence p + 2 valence d = 6 sp^3d^2 hybrid orbitals

Geometry: octahedral

ex:	Lewis	Bond Pairs	Lone Pairs	Arrangement e^- pairs	molecular geometry	3D sketch	Polar...
SF_6		6	0	Octahedral	Octahedral		No
IF_5		5	1		Square pyramid		Yes
XeF_4		4	2		Square planar		Nb

Top View



Number of e ⁻ pair (central atom)	Bond Pairs	Lone Pairs	Arrangement of e ⁻ pairs	Molecular Geometry	\angle
2	2	0	Linear	Linear	180°
3	3	0	Trigonal planar	Trigonal planar	120°
	2	1		V-shaped	
4	4	0	Tetrahedral	Tetrahedral	
	3	1		Trigonal pyramid	
	2	2		V - shaped	109.5°
5	5	0		Trigonal bipyramidal	
	4	1	Trigonal Bipyramidal	see-saw	120°
	3	2		T-shaped	and 90°
	2	3		Linear	
6	6	0		Octahedral	
	5	1	Octahedral	Square pyramid	90°
	4	2		Square planar	

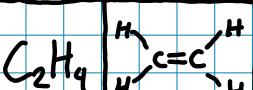
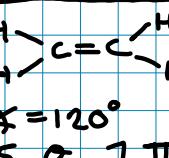
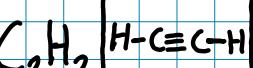
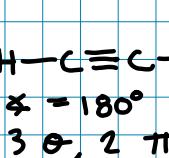
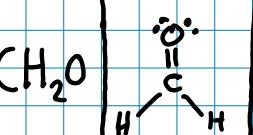
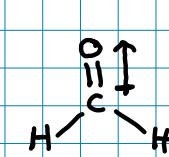
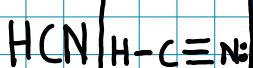
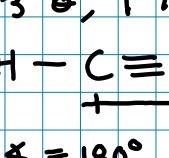
*Note: VSEPR theory is a brilliant theory but it is not infallible.
 For example, experimental data shows that bond angles in PH_3 are closer to 94° than 107°.



However, we are predicting according to theory.

Multiple bonds (VSEPR)

Around 1 central C

ex:	Lewis	Bond Pairs	Lone Pairs	Regions of density	Arrangement/Geometry	3D sketch	Polar
C_2H_4		4	0	$\therefore 3$ SP^2	Trigonal planar		No
C_2H_2		4	0	$\therefore 2$ SP	Linear		No
CH_2O		4	0	$\therefore 3$ SP^2	Trigonal planar		Yes
HCN		4	0	$\therefore 2$ SP	Linear		Yes

* Note:

Every bond has
1 σ bond

In multiple bond, every
bond that isn't
 σ , is a π bond

Bonding in Multiple Bonds

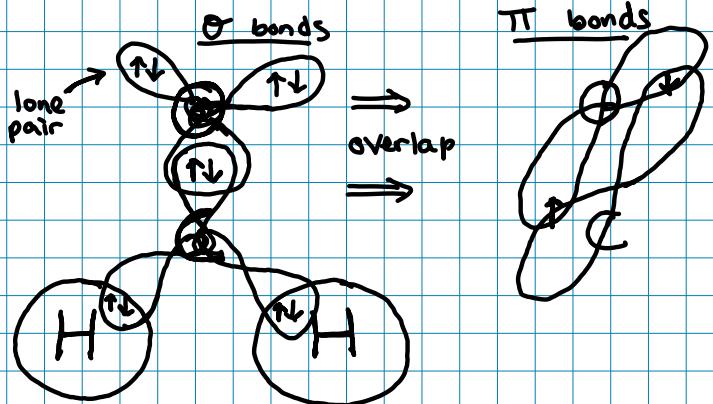
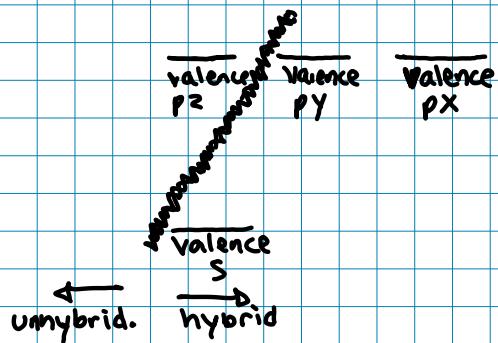
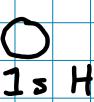
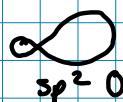
→ For predicting bond angles, assume multiple bonds repel the same as single bonds

- Sigma bond (σ): The overlap of 2 hybrid orbitals (or $1s$ for H)
 - bond located between 2 nuclei
 - The σ bond holds only $2 e^-$
(So other e^- in double or triple bond go in π bond)
- Pi bond (π): The overlap of 2 unhybridized orbitals
 - can hold only $2 e^-$
 - second bond of double bond
 - second/third bond of triple bond

Summary:

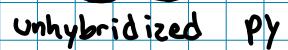
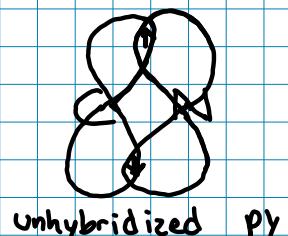
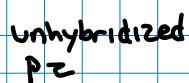
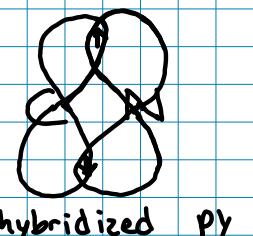
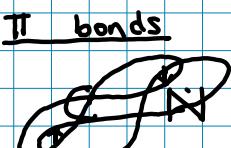
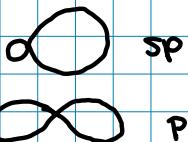
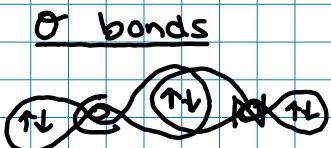
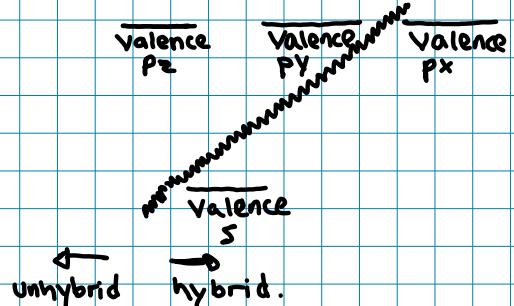
single bond	\Rightarrow	1 σ bond	,	0 π bonds
double bond	\Rightarrow	1 σ bond	,	1 π bond
triple bond	\Rightarrow	1 σ bond	,	2 π bonds

ex: CH_2O



ex: CN^-

$:\text{C}\equiv\text{N}: \rightarrow 2$ regions e^- density : sp

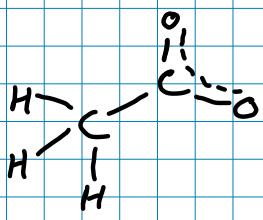
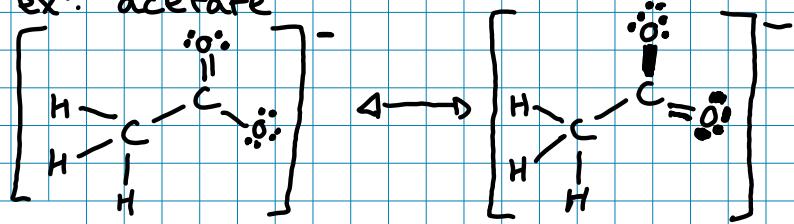


When π bond appears in different places on different valid resonance structures, there is delocalized π bonding. π bond only exists in double bonds or triple bonds.

Delocalize according to dotted curve: , / - \ ,

Delocalized π bonding
Resonance hybrid

ex: acetate



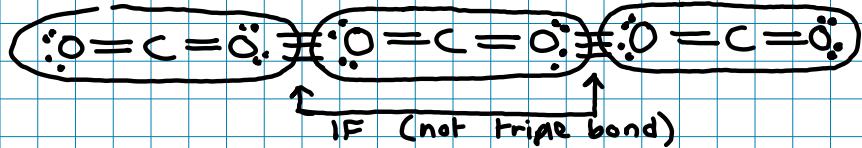
Interparticle Forces (IF)

Condensed states of matter: solid and liquid

Interparticle forces: hold particles together in condensed states of matter

Note: Bond \neq IFs

ex: IFs between CO_2 particles



Liquid vs solid: solid particles have less freedom of motion than liquid particles relative to other particles. Solid particles stay in fixed positions relative to other particles.

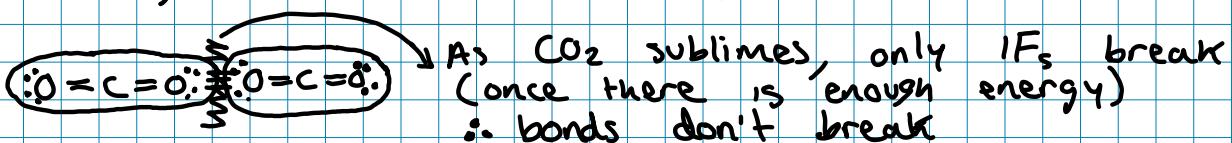
- solid particles: vibrational motion
- liquid particles: translational motion can tumble past other liquid particles

Phase transition

* At 1 atm, we say "normal X point"

Solid \rightarrow Liquid	(melt)	melting point
Solid \rightarrow Gas	(sublime)	sublimation point
Liquid \rightarrow Gas	(evaporation)	boiling point
Gas \rightarrow Liquid	(condensation)	boiling point
Liquid \rightarrow Solid	(freeze)	freezing point (=melting)
Gas \rightarrow Solid	(deposition)	sublimation point

ex: during sublimation of CO_2 , do bonds break?



As CO_2 sublimes, only IFs break
(once there is enough energy)
∴ bonds don't break

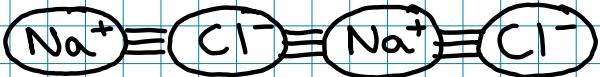
* Can use IFs to predict relative boiling/melting points

① Interionic interaction (ionic bond)

- strongest interparticle force (\therefore demands more energy to break).

- High melting and boiling points

IF = attraction of cation (+) and anion (-)



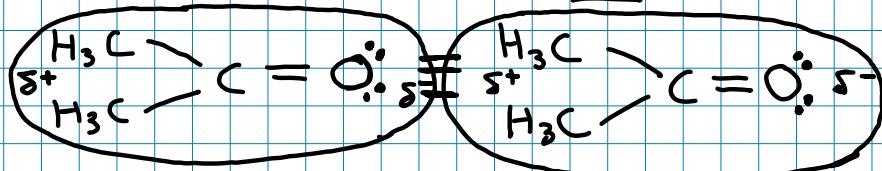
* In this case, break IF \therefore break ionic bond

Following IFs useful for compounds with covalent bonds

② Dipole / Dipole attraction

- Polar molecules are predicted to have higher boiling points as similarly sized nonpolar molecules (think elements of a same row have the same size and it doesn't affect size).

IF = interaction between δ^+ side of a molecule with δ^- side of a second molecule of the same kind. Must be polar.



ex: What has higher boiling point?

① $\text{O}^{\cdot\cdot}$



polar

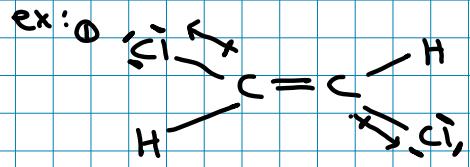
② CH_3



non-polar (only C-C)

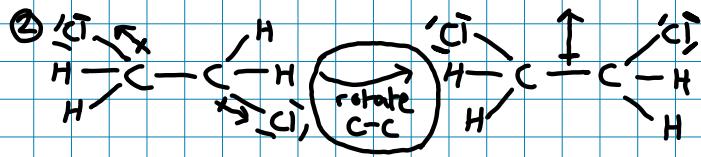
Similar size: 4 second row elements

\therefore ① has a higher boiling point.



non-polar (vectors cancel)

CAN'T rotate double bond (break pi bond)



polar \therefore Higher boiling point

CAN rotate (single bond)

* Stronger IF = higher BP (only if similar size)

③ H-bonding (strongest dipole-dipole)

- HO, HF, HN covalent bonds
- Causes strong dipole/dipole IF

• Normal boiling points of H-containing compounds:

$\boxed{\text{NH}_3 (-33)}$

$\text{PH}_3 (-88)$

$\text{AsH}_3 (-63)$

$\text{SbH}_3 (-17)$

$\boxed{\text{H}_2\text{O} (100)}$

$\text{H}_2\text{S} (-60)$

$\text{H}_2\text{Se} (-42)$

$\text{H}_2\text{Te} (-2)$

$\boxed{\text{HF} (19.5)}$

$\text{HCl} (-85)$

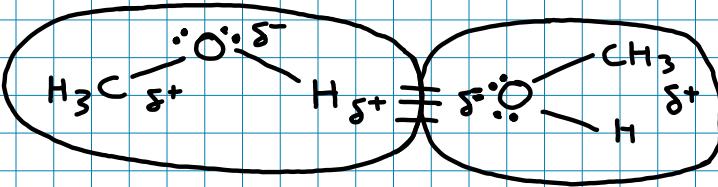
$\text{HBr} (-66)$

$\text{HI} (-35)$

General Pattern: As the non-hydrogen atom size increases, going down a column, the BP also increases.

* Exception: O-H, N-H, F-H bonds (Highest BP)

IF = H-bonding occurs between 2 molecules when H is covalently bonded to O, F or N (small highly electronegative atoms). It is the strongest dipole/dipole interaction (\Rightarrow highest BP)

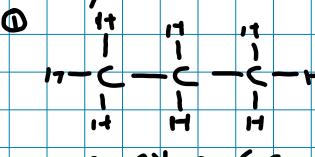


* H becomes only a proton with no e⁻ \Rightarrow extremely \oplus

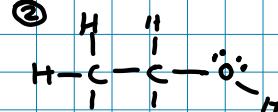
powerful attraction
 \because e⁻ density pulled away from H attached to highly electronegative O, N, F \therefore exposed \oplus charge on H highly attracted to lone-pair.

Note: • H bonding stronger between similarly sized molecules with OH bonds rather than NH or NH₂ (O more electronegative than N \therefore more positive H)
• The more "OH groups" (or NH or NH₂), the more opportunities for H-bonding \therefore stronger IF

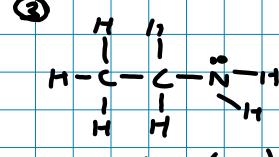
ex: Highest to lowest BP



non-polar (C-H)



H-bonding (OH)



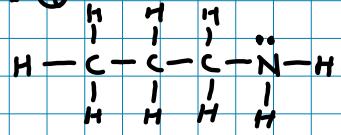
H-bonding (NH)

| similar size

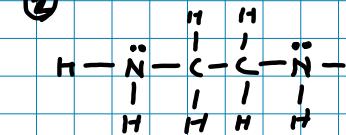
② > ③ > ①

OH stronger than NH

ex: ①



②



② > ①

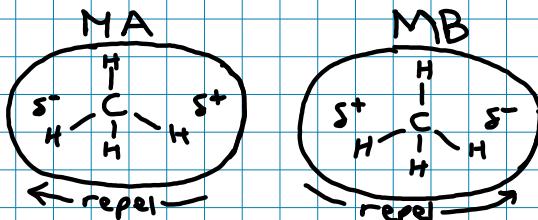
b/c more H-N covalent bonds \therefore more opportunities for H-bonding

④ London Dispersion Forces (LD)

-(Van der Waals, Induced, Instantaneous, Temporary)

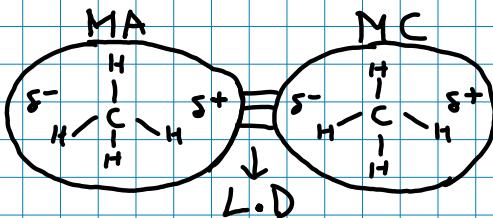
- Explains how noble gases and non-polar molecules can exist in condensed state of matter (but, weaker forces so lower BP \therefore commonly gas)

$IF = 2$ non-polar molecules approach each other \Rightarrow temporary dipole
Sample non-polar molecules



Molecules approaching
 \therefore electrons A repel electrons B
 \therefore Temporary/induced dipole

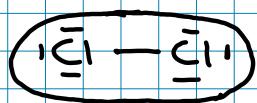
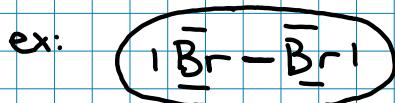
The induced dipole in MA can now be attracted by a MC and create an induced dipole:



* All molecules have $e^- \therefore$ all molecules have LD forces

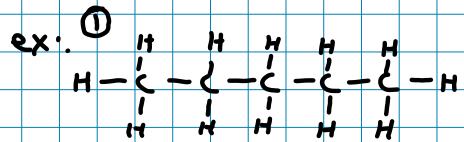
Polar molecules of similar size as non-polar molecules have the same LD. However they also have dipole/dipole.

More shells with e^- s that an atom has ~~XXXX~~
 \therefore greater likelihood of e^-/e^- repulsion (causing LD)
 \Rightarrow Larger atoms within same column, has e^- held less tightly \therefore more polarizable (possibility of creating LD)
 \Rightarrow Presence of larger atom (column \downarrow) \therefore stronger LD.



Cl
Br
I

$\therefore Br_2$ has higher BP b/c larger \therefore more e^- shells



Similar size (same LD forces)
but ② has dipole/dipole b/c polar
 \therefore ② is higher BP

* Reminder: larger VdW "a" constant \Rightarrow stronger forces

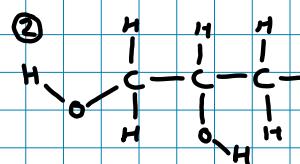
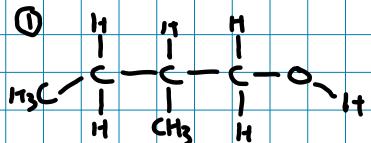
IFs can be used to predict properties:

- Viscosity = resistance of a liquid to flow
(ex: honey is more viscous than water)
- Surface tension = resistance of a liquid to increase surface area
- Volatility = tendency of a liquid / solid to escape to become gas
 - * If liquid A ~~is~~ is more viscous than liquid B, A has higher vapour pressure \Rightarrow b/c more tendency to become gas

A substance \otimes has stronger IFs than \circlearrowleft

- More viscous : \otimes (strong interaction \therefore resist flow)
- Greater surface tension : \otimes
- More volatile : \circlearrowleft (weaker IF \therefore easier to escape)
 \Rightarrow Higher vapour pressure : \circlearrowleft

ex: Which is more viscous

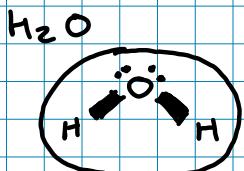


similar size

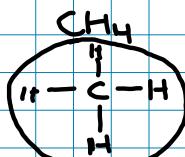
② \Rightarrow more OH bonds \therefore more opportunities H-bonding \therefore stronger IF \therefore More viscous

ex: Which has highest to lowest VdW "a" constant?

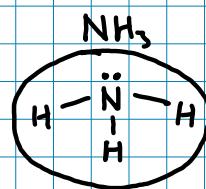
* Reminder: greater "a" constant = greater attraction between particles



most powerful H-bonding (OH)



non-polar (only LD)



H-bonding (NH)

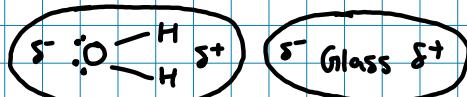
$\therefore \text{H}_2\text{O} > \text{NH}_3 > \text{CH}_4$ in terms of "a" constant

- Capillary Action = spontaneous rising of liquid in narrow tube

Cohesive force: IF between molecules of a liquid

Adhesive force: IF between molecules of a liquid and their container.

Theory: Water meniscus in glass tube is concave
 \Rightarrow considerable attraction between polar H₂O and polar glass (adhesive) causing H₂O to move up the tube



Theory: Mercury's meniscus in glass tube is convex
 \Rightarrow non-polar Hg is not attracted to H₂O

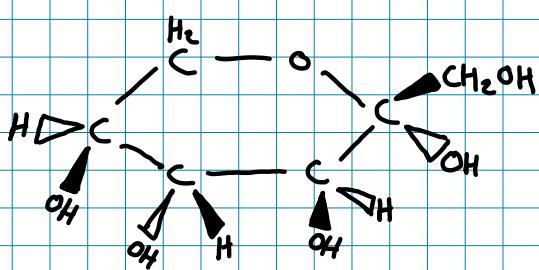
Non-Volatile Substances

\rightarrow substances with very strong IF

- ionic compounds (salts)
- sugars
- very large molecules

Note: - IF you leave these substances out for 5 years, they will still be here and not have become gas
 * Negligible vapour pressure

ex: Fructose



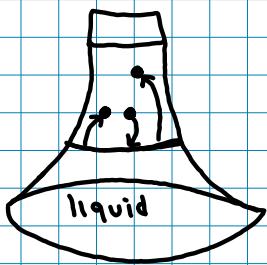
\blacktriangleleft = bond coming out of page

\blacktriangleright = bond pointing away from page

* Many O-H bonds

* Many L.D (many e- shells)
 ∴ prevents fructose from being volatile

Vapour Pressures

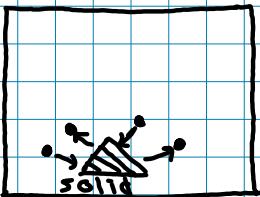


↑ = liquid particle evaporating
↓ = gas particle condensing

- A liquid particle would most likely be at the surface to escape to become a gas b/c at the surface, there are no IF above the liquid (which is what is keeping it condensed)

- Gas particles may hit the liquid surface and be recaptured by IFs \Rightarrow re-condensation

When the "rate of vaporization" = "rate of condensation" a constant equilibrium vapour pressure is exerted above the liquid.



For solids, when rate of deposition = rate of sublimation

\Rightarrow vapour pressure observed above solid

* As temperature increases, the vapour pressure above a solid or liquid increases exponentially.

Boiling point: Temp at which "P_{vap} over liquid" = "external pressure"

Sublimation point: Temp. at which "P_{vap} over solid" = "external pressure"

Melting point: Temp at which "P_{vap} of liquid" = "P_{vap} of solid"
(Note: of the same substance)

\Rightarrow For "normal" point, consider external pressure = 1 atm

Note: At higher altitude \Rightarrow external pressure is lower
 \therefore demands less energy for P_{vap} = external pressure
 \therefore BP is lower

Note: At temp < BP, gas bubble inside liquid gets crushed

Note: Melting point = temp at which the solid and liquid forms of a substance can coexist indefinitely.
 \rightarrow If P_{vap} solid > P_{vap} liquid, eventually all solid converted to liquid
 \rightarrow If P_{vap} solid < P_{vap} liquid, eventually all liquid converted to solid

Heating/Cooling Curves

- Heating curve = temp vs time for a substance being heated at a constant rate.
- Cooling curve = temp vs time for a substance being cooled at a constant rate.



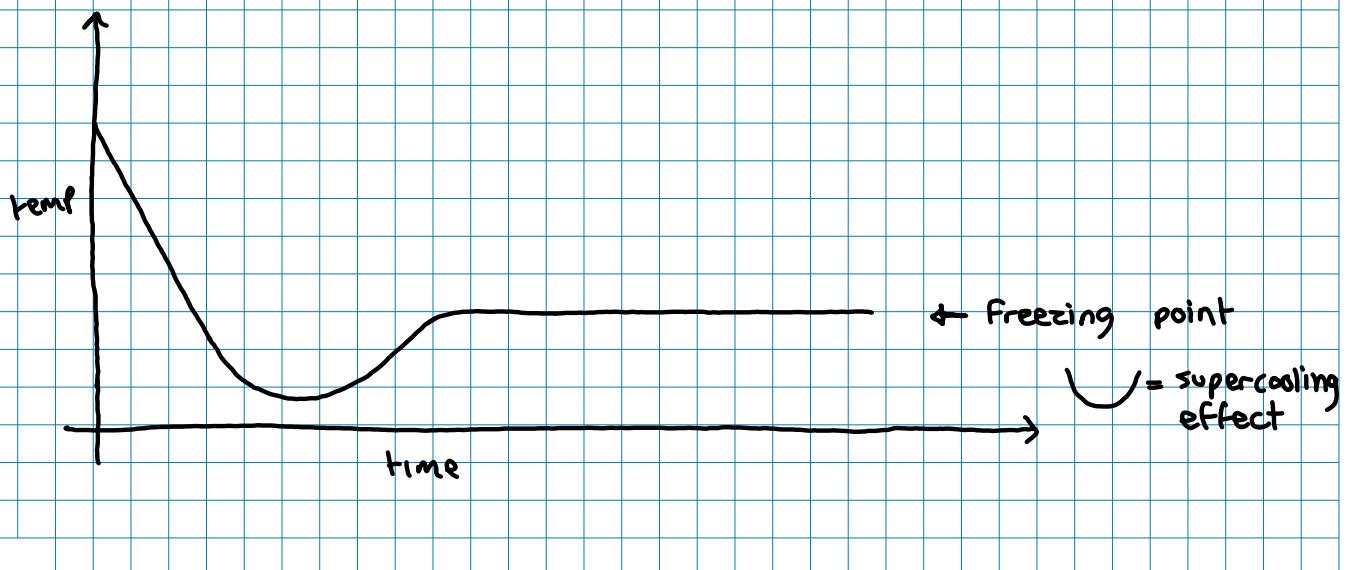
- -10 to 0 \Rightarrow heat going towards raising temp. of ice
- At 0 \Rightarrow energy goes towards breaking enough IFs to allow tumbling of molecules past one another (flow).
- 0 to 100 \Rightarrow heat going towards raising temp. of water
- 100 \Rightarrow remaining IFs are broken (liquid becomes gas)

Note: Flat line at 100°C longer than at 0°C b/c all IFs are broken at 100°C but only some at 0°C.

ΔH_{fus} (heat of fusion) = energy to melt a solid
 ΔH_{vap} (heat of vaporization) = energy to vaporize a liquid.

- * If heated too rapidly, a liquid may achieve temp $>$ BP
 \Rightarrow superheated liquid
- * If cooled rapidly, a liquid may achieve temp $<$ MP
 \Rightarrow super-cooled liquid

Ex: cooling curve for tert-butyl alcohol



Phase Diagram

- phase changes with only temp. and pressure

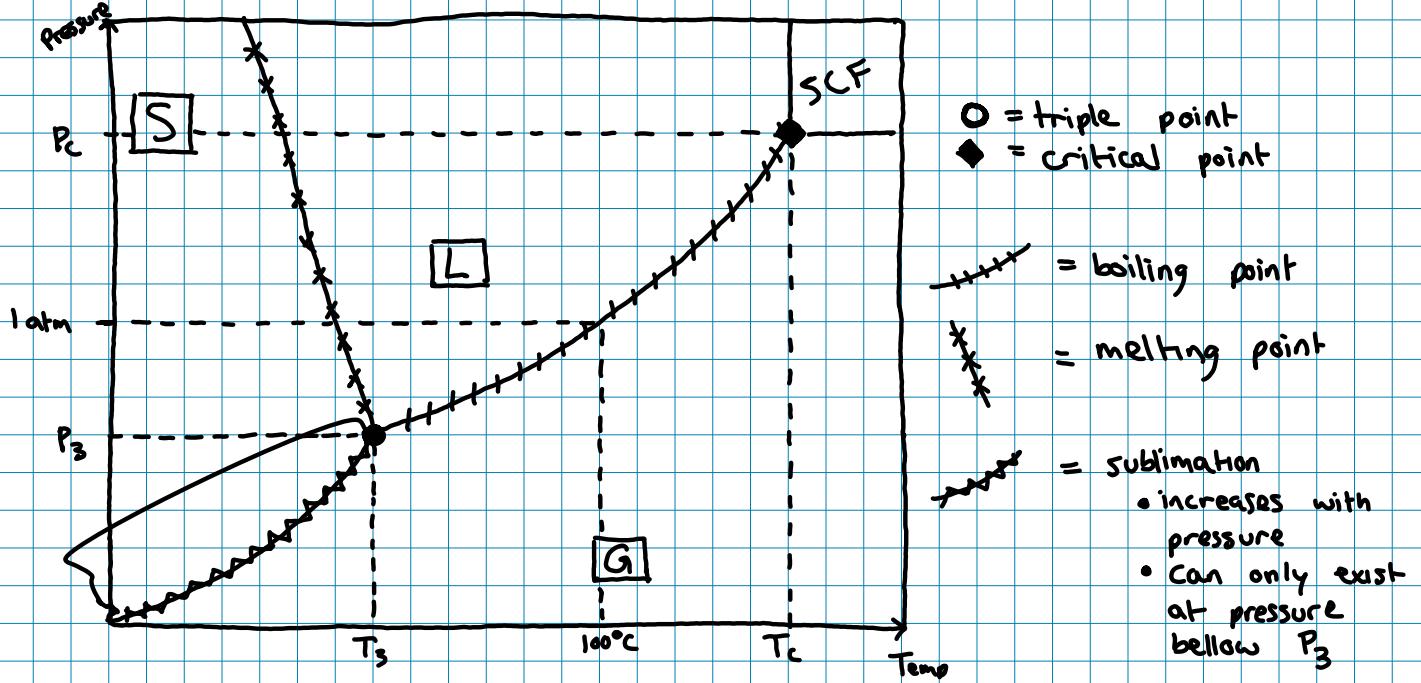
- Solid predominates at low temp, high pressure
- Liquid predominates at ~~high~~ avg. temp. and pressure
- Gas predominates at high temp, low pressure

Solid lines between regions = where 2 phases can coexist

Triple point = at (T_3, P_3) all 3 phases can coexist (S, L, G)
 * can also be where 2 crystal solids and liquid coexist

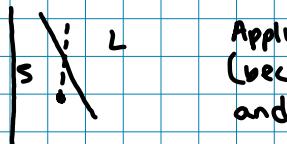
Critical point = Above T_c , no matter how much pressure is applied, one cannot convert the gas to liquid. pt (T_c, P_c)
 * If one applies greater pressure than P_c and greater temp than T_c ∴ the gas is instead converted to supercritical fluid
 ⇒ State of matter that is neither liquid or gas but has properties between the 2 states

ex: Water phase diagram

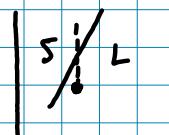


Note: Solid-liquid boundary (MP line):

- Tilt up-right (positive slope) ∵ solid denser than liquid
- Tilt up-left (negative slope) ∵ liquid denser than solid



Apply pressure
(becomes more dense)
and $S \rightarrow L$
(ex: H₂O)



Apply pressure
(becomes more dense)
and $L \rightarrow S$
(ex: CO₂)

Properties of Solutions

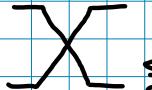
Colligative property = property that depends on the relative number of solvent to solute particles

Reminder: • molarity = $\frac{\text{mol (solute)}}{\text{L (solution)}}$ / mass % = $\frac{\text{mass (solute)}}{\text{mass (solution)}} \times 100$

2 new concentration units are used to describe the 4 colligative properties of solutions:

- Vapour pressure
- Freezing point depression
- Boiling point elevation
- Osmotic pressure

Molality (m) = $\frac{\text{moles (solute)}}{\text{kg (solvent)}}$

Mole fraction (X):  = $\frac{n_{\text{sol'n component}}}{n_{\text{total}}}$

- Sol'n component = solute or solvent
- $n_{\text{total}} = n_{\text{solute}} + n_{\text{solvent}}$

Converting molarity \rightarrow molality

ex: A 4.98 M sol'n of H_2SO_4 has a density of 1.286 g/mL
(mm $\text{H}_2\text{SO}_4 = 98.09 \text{ g/mol}$)

$$\boxed{m = \frac{\text{mol H}_2\text{SO}_4}{\text{kg H}_2\text{O}}}$$

* Assume any volume (1 L)

$$\textcircled{1} \quad 1 \text{ L soln} \cdot \frac{4.98 \text{ mol H}_2\text{SO}_4}{\text{L soln}} = \textcircled{4.98 \text{ mol H}_2\text{SO}_4}$$

$$\textcircled{2} \quad 1 \text{ L soln} \cdot \frac{1.286 \text{ g soln}}{0.001 \text{ L soln}} = \textcircled{1286 \text{ g soln}}$$

$$1286 \text{ g} = 4.98 \text{ mol H}_2\text{SO}_4 \cdot \frac{98.09 \text{ g}}{\text{mol}} + X \text{ g solvent}$$

$$X = 789 \text{ g}$$

$$X = 0.789 \text{ kg solvent}$$

$$m = \frac{4.98 \text{ mol H}_2\text{SO}_4}{0.789 \text{ kg solvent}}$$

$$= \boxed{6.24 \text{ m}}$$

Solution Vapour Pressure

Type 1 (non-volatile solute in solvent)

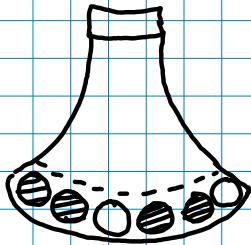
non-volatile solute = sugars or salts

Ideal solution = solution where solute-solvent interactions are the same as solvent-solvent or solute-solute

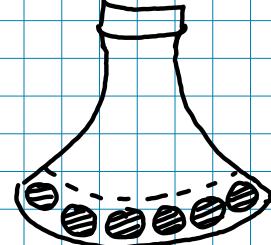
Imagine sol'n: 2/3 solvent, 1/3 solute

$$\chi_{\text{solute}} = 0.33, \quad \chi_{\text{solvent}} = 0.67$$

Solution described above:



Pure solvent:



\circ = x moles of non-volatile solute

\bullet = x moles of solvent

----- = surface

For this sol'n, there is 2/3 the number of solvent molecules at the surface relative to the pure solvent.

$\therefore P_{\text{vap}}$ for the ideal solution is 2/3 of the P_{vap} of the pure solvent

\therefore liquid molecules must be at the surface to escape to gas

Raoult's Law (non volatile solutes)

$$P_{\text{vap}(\text{sol'n})} = \chi_{\text{solvent}} \cdot P^{\circ}$$

$\bullet P_{\text{vap}}$ = vapour pressure above soln

$\bullet \chi_{\text{solvent}}$ = mole fraction of solvent

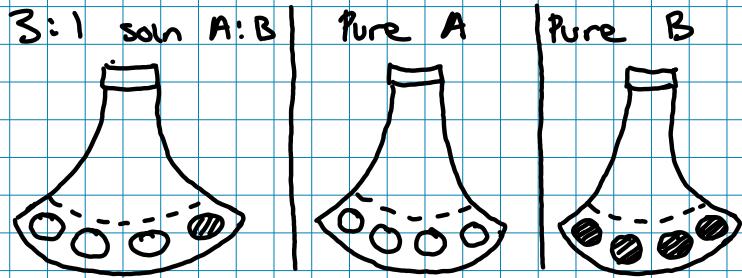
$\bullet P^{\circ}$ = vapour pressure of pure (halo) solvent

* Units of pressure must be the same.

Type 2 (2 volatile solution components)

2 miscible liquids = 2 liquids soluble in one another

Imagine soln with 3:1 molar mixture A to B



$\bigcirc = \frac{x}{\text{moles}}$ of A

$\blacksquare = \frac{x}{\text{moles}}$ of B

Here, in the 3:1 soln

- $P_A = \frac{\text{vapour pressure due to A particles}}{} = \frac{3}{4} P_A^\circ$

- $P_B = \frac{\text{vapour pressure due to B particles}}{} = \frac{1}{4} P_B^\circ$

$$\therefore P_{\text{TOT}} = P_{\text{vap(soln)}} = \frac{3}{4} P_A^\circ + \frac{1}{4} P_B^\circ$$

Modified Raoult's Law (Volatile solvents)

$$P_{\text{vap(soln)}} = \left(X_{\text{solvent}_A} \cdot P_A^\circ \right) + \left(X_{\text{solvent}_B} \cdot P_B^\circ \right)$$

$\underbrace{\phantom{X_{\text{solvent}} \cdot P_A^\circ}}_{P_A}$ $\underbrace{\phantom{X_{\text{solvent}} \cdot P_B^\circ}}_{P_B}$

Note X_{solvent_A} = mole fraction of A in liquid phase

Note:
$$X_A^\bullet = \frac{P_A}{P_{\text{TOT}}} = \text{mol fraction of A in vapour phase}$$

- P_{TOT} = total pressure of gas over soln

- $P_A = X_{\text{solvent}_A} \cdot P_A^\circ$

- $P_B = X_{\text{solvent}_B} \cdot P_B^\circ$

* $X_A + X_B = 1$

ex: H_2O vapour pressure at $80^\circ C$ is 0.4672 atm. What mass of sucrose ($C_{12}H_{22}O_{11}$) must be dissolved in 180.2g of H_2O to lower $P_{\text{vap}}(\text{soln})$ to 0.4640 atm.

Sucrose (non volatile) \rightarrow Raoult's Law	$180.2 \text{ g } H_2O \cdot \frac{\text{mol}}{18 \text{ g}} = 10.00 \text{ mol } H_2O$
$P_{\text{vap}} = X_{\text{solvent}} \cdot P^{\circ}$	
$X_{\text{solvent}} = \frac{0.4640}{0.4672} = 0.9932$	
$X_{\text{solvent}} + X_{\text{solute}} = 1$	
$X_{\text{solute}} = 1 - 0.9932 = 0.0068$	
$0.0068 = \frac{X \text{ mol sucrose}}{10.00 \text{ mol } H_2O + X}$	
$0.068 + 0.0068 X = X$	
$X = 0.068 \text{ mol sucrose}$	

$$0.068 \text{ mol} \cdot \frac{342.30 \text{ g}}{\text{mol}} = \boxed{23 \text{ g sucrose}}$$

ex: 0.300 mol benzene mixed with 0.800 mol toluene ($P_{\text{benzene}}^{\circ} = 1.34 \text{ atm}$, $P_{\text{toluene}}^{\circ} = 0.534 \text{ atm}$). What is mole fraction of toluene in vapour?

Both have P_{vap} \therefore both volatile \rightarrow Modified Raoult's Law

$$\begin{aligned} P_{\text{vap}}(\text{soln}) &= (X_{\text{benzene}} \cdot P_{\text{benzene}}^{\circ}) + (X_{\text{toluene}} \cdot P_{\text{toluene}}^{\circ}) \\ &= \left(\frac{0.300 \text{ mol}}{0.300 + 0.800} \cdot 1.34 \text{ atm} \right) + \left(\frac{0.800}{0.300 + 0.800} \cdot 0.534 \text{ atm} \right) \\ &= (0.365 \text{ atm}) + (0.388 \text{ atm}) \end{aligned}$$

$$P_{\text{vap}}(\text{soln}) = 0.753 \text{ atm}$$

$$X'_{\text{toluene}} = \frac{P_{\text{toluene}}}{P_{\text{tot}}} = \frac{0.388}{0.753} = \boxed{0.515}$$

↑

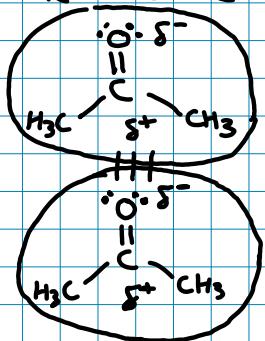
Makes sense:
 - pure toluene has lower P° than benzene
 $\therefore X'$ vapour phase less than X in liquid
 (lower vapour pressure = less liquid becomes vapour)

Non-Ideal Solutions

→ to be ideal solute-solvent interactions = solvent-solvent or solute-solute

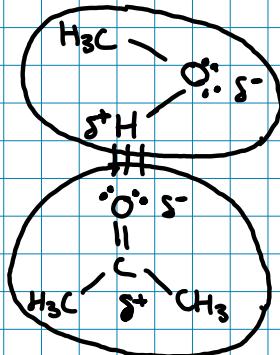
Imagine miscible mixture of acetone and methanol:

Acetone-Acetone interact:



- LD
- dipole-dipole

Acetone-Methanol interact:

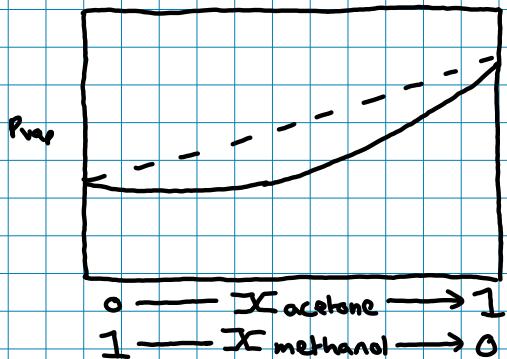


- LD
- H-bonding (strongest)

∴ Stronger interaction

If solute attracts solvent more than solvent-solvent, vapour pressure is less than expected b/c more attraction = less tendency

Negative Deviation from Raoult's Law: solute-solvent interaction stronger than solvent-solvent
⇒ When $P_{\text{app(soln)}}$ is less than expected from Raoult's

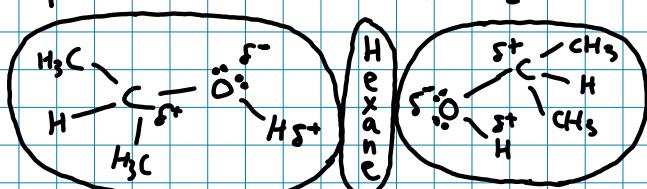


----- = predicted from Raoult's
— = experimentally observed

Note: $\chi_{\text{methanol}} = 0 \rightarrow$ higher pressure b/c less methanol ⇒ less H-bonding
∴ easier to escape

Positive Deviation: solute-solvent interaction weaker than solvent-solvent
⇒ When $P_{\text{app(soln)}}$ is more than expected from Raoult's

This can happen when non-polar liquid (ex: hexane) is mixed with polar solvent (ex: $(\text{CH}_3)_2\text{COH}_3$)



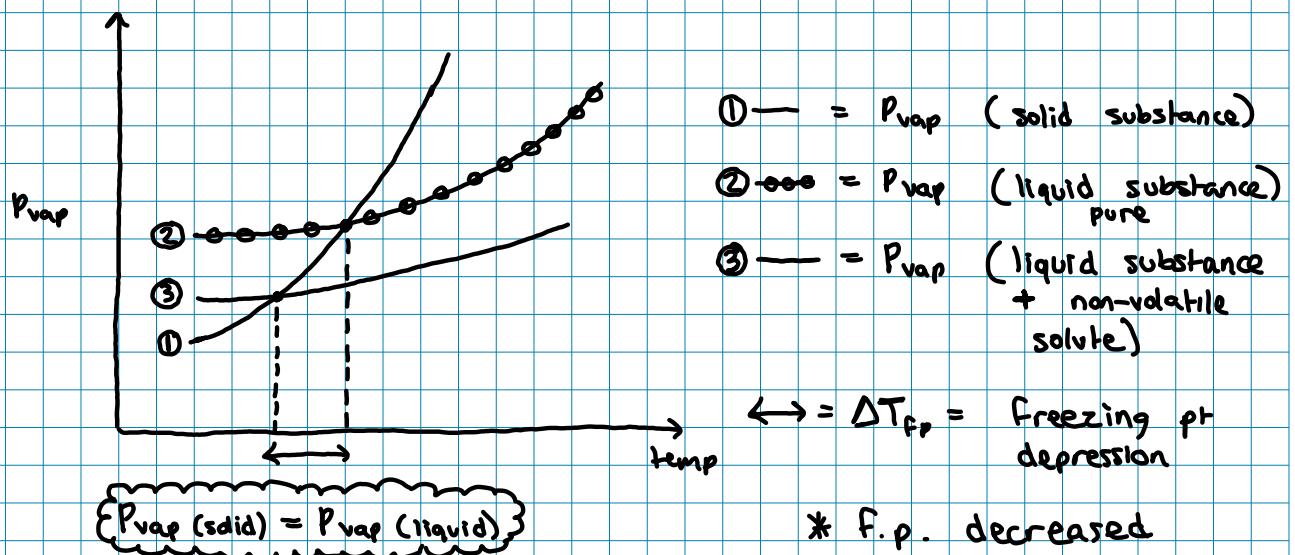
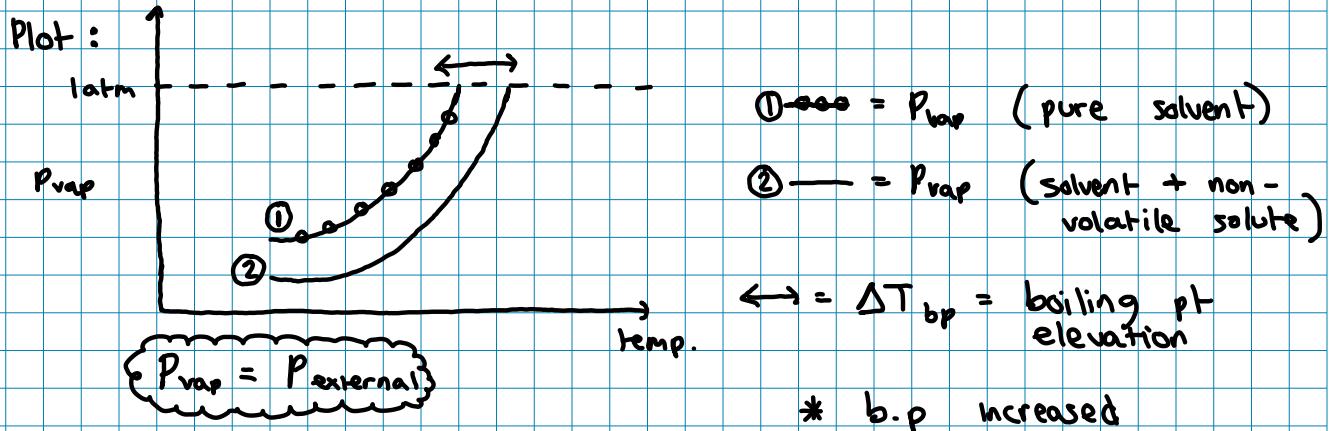
2 isopropane molecules have strong H-bonding. Presence of non-polar disrupts powerful interaction.
Weaker interaction ∴ more particles can escape
∴ higher P_{app} than expected

Freezing-Point Depression and Boiling-Point Elevation

* Occurs when non-volatile solute added to liquid

Reminder:

- Increase temp $\Rightarrow P_{\text{vap}}$ increases exponentially
- Boiling Point $\Rightarrow P_{\text{vap}}(\text{liquid}) = \text{external pressure}$
- Melting Point $\Rightarrow P_{\text{vap}}(\text{solid}) = P_{\text{vap}}(\text{liquid})$
- In presence of a non-volatile solute, P_{vap} of a liquid decreases (Raoult's)



ΔT_{bp} = boiling point elevation = $\frac{\text{temp at which liquid boils with non-volatile solute}}{\text{temp at which pure liquid boils}}$

ΔT_{fp} = freezing point depression = $\frac{\text{temp at which solvent freezes with non-volatile solute}}{\text{temp at which pure solvent freezes}}$

* There is a greater ΔT (bp or fp) if there are more solute particles

$$\boxed{\Delta T_{bp} = K_b \cdot m}$$

$$\boxed{\Delta T_{fp} = K_f \cdot m}$$

$$m = \text{molarity} = \frac{\text{mol solute}}{\text{kg solvent}}$$

K_b = molal bp elevation constant

K_f = molal f.p. depression constant

* K_f and K_b are specific to the solvent

units: $^{\circ}\text{C}/\text{m}$ or K/m ($\frac{\text{change of } 1^{\circ}\text{C}}{\text{change of } 1\text{K}}$)

~~XXXXXX~~

Determining Molar Mass

ex: A 39.8 g sample of non-volatile compound is dissolved in 200.0 g of H_2O and the boiling point is raised by 0.30°C . What is the molar mass of compound?

$$K_b(\text{H}_2\text{O}) = 0.512 \text{ } ^{\circ}\text{C}/\text{mol} = 0.512 \text{ K}/\text{mol}$$

$\left. \begin{matrix} \text{Change of } 1^{\circ}\text{C is} \\ \text{same as } 1\text{K} \end{matrix} \right\}$

$$\Delta T_{bp} = 0.30^{\circ}\text{C}$$

$$\Delta T_{bp} = K_b \cdot m$$

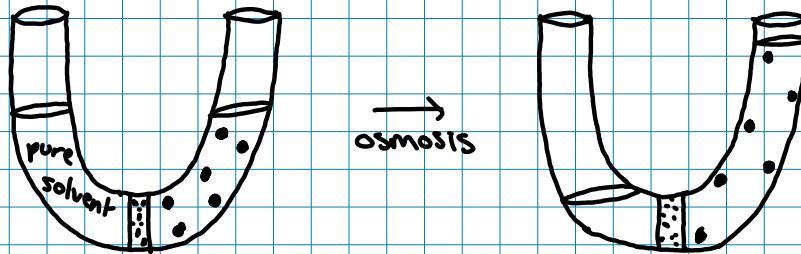
$$0.30^{\circ}\text{C} = 0.512 \cdot m$$

$$\boxed{m = 0.585 \frac{\text{mol}}{\text{kg}}}$$

$$\frac{39.8 \text{ g solute}}{200.0 \text{ g solvent}} \cdot \frac{1000 \text{ g solvent}}{\text{kg solvent}} \cdot \frac{\text{kg solvent}}{0.585 \text{ mol solute}} = \boxed{340 \text{ g/mol}}$$

Osmotic Pressure

Osmosis = net movement of a solvent through a semi-permeable membrane towards the side of the membrane with the greater concentration



Osmosis occurs naturally to attempt to equalize the concentration. Pure solvent moves to dilute the solution.

The pressure due to osmosis = Osmotic Pressure (Π)
 \Rightarrow pressure required to stop the solvent from flowing through the membrane

$$\boxed{\Pi = C R T}$$

$$P = \frac{n}{V} R T$$

$$R = 0.08206 \left(\frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \right)$$

C = concentration of soln pre-osmosis (mol/L)

T = temp. (K)

- * A useful benefit about the 4 colligative properties is that they can be used to find the molar mass.
 \Rightarrow combined with elemental analysis / combustion (find empirical formula), one can find the molecular formula

ex: A dilute aqueous sol'n of non-volatile compound contains 1.19 g compound/L of soln and has $\Pi = 0.0288 \text{ atm}$ at 37°C. Calculate molar mass

$$\Pi = C R T$$

$$0.0288 \text{ atm} = C \cdot (0.08206) (310)$$

$$\boxed{C = 1.13 \times 10^{-3} \text{ mol/L}}$$

$$\frac{1.19 \text{ g}}{\text{L}} \cdot \frac{\text{L}}{1.13 \times 10^{-3} \text{ mol}} = 1.05 \times 10^3 \text{ g/mol}$$

Osmotic pressure is useful b/c even small concentrations produce high osmotic pressures

If we were to calculate the ΔT_{fp} of the same substance as on the previous page:

Assume $0.001 \text{ mol/L} \approx 0.001 \text{ m}$

$$\Delta T_{fp} = K_f \cdot m$$

$$= (1.86)(0.001) = 2 \times 10^{-3} \text{ }^{\circ}\text{C}$$

- Under most lab conditions, one cannot be confident about calculating this change.
- However, using osmotic pressure, one can find better values

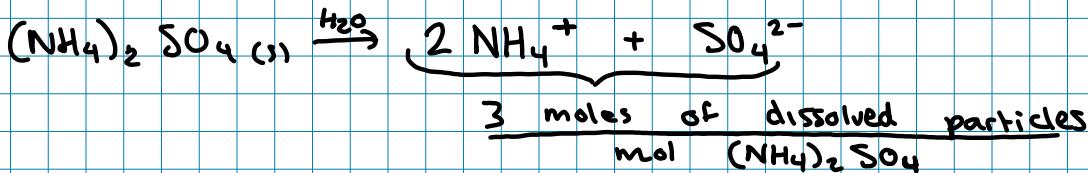
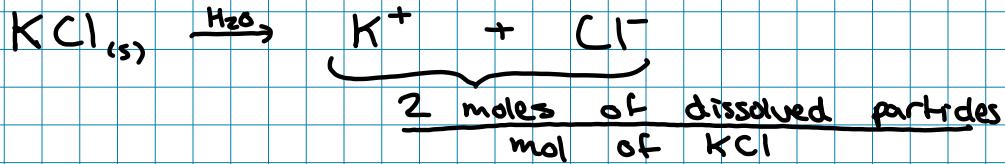
Reverse Osmosis

→ If one applies pressure greater than osmotic pressure to U-shaped tube it is possible to reverse osmosis.

→ Solvent moves to the side where there is lower concentr.
ex: desalination occurs by reverse osmosis
⇒ Does NOT occur naturally

Ionic Compounds as Solutes

- Colligative properties depend on the number of dissolved particles



We must multiply the molarity or molality of ionic compounds by the van't Hoff factor (i)

$$i = 2 \text{ for KCl}$$

$$i = 3 \text{ for } (\text{NH}_4)_2\text{SO}_4$$

With the corrective factor:

$$\bullet \Pi = i \cdot CRT$$

$$\bullet \Delta T_{bp} = i \cdot K_b \cdot m$$

$$\bullet \Delta T_{fp} = i \cdot K_f \cdot m$$

Experimentally, i values may be lower than expected

$$i = \frac{\Pi}{CRT}, \quad i = \frac{\Delta T}{K \cdot m}$$

- Consider $i = 1$ for non dissociating compound (covalent bonds)
- If strong acid or soluble ionic compound, use expected " i "

Ex: 2.00g KCl dissolved in 10.0g H₂O at 30°C. What is vapour pressure of soln? (P_{vp} of pure H₂O = 31.82 torr)

KCl (non-volatile and ionic) → Raoult's Law

$$P_{vp \text{ (soln)}} = \overline{X}_{\text{solvent}} \cdot P_{H_2O}^\circ$$

$$2.00 \text{ g KCl} \cdot \frac{\text{mol KCl}}{74.55 \text{ g}} \cdot \frac{2 \text{ mol particles}}{\text{mol KCl}} = 0.0537 \quad / \quad 10.0 \text{ g H}_2\text{O} \cdot \frac{\text{mol H}_2\text{O}}{18.02 \text{ g}} = 0.555$$

$$\overline{X}_{\text{solvent}} = \frac{0.555}{0.555 + 0.0537} = 0.911$$

$$\therefore P_{vp} = (0.911)(31.82 \text{ torr}) = 29.0 \text{ torr}$$

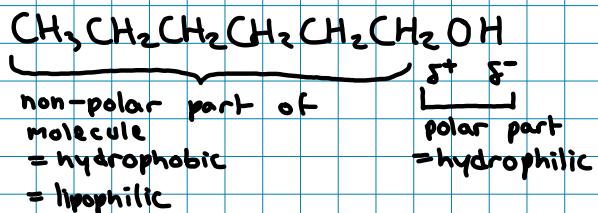
Solubility of Compounds (covalent)

"Like dissolves like"

- Polar compounds dissolve other polar compounds best
- Non-polar compounds dissolve non-polar compounds best

trick: → popular (polar) so attractive hang out together
→ unpopular (non-polar) left out, hang out together

ex.: Between 1-hexanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$) and methanol (CH_3OH), which is more ~~soluble~~ / ~~hydrophilic~~ / ~~hydrophobic~~ soluble in H_2O (polar) and which is in CCl_4 (non-polar)



1-hexanol has a larger hydrophobic area ∴ it is less soluble in H_2O .
However it is more soluble in CCl_4 .

Gas dissolved in solvent

Henry's Law: concentration of gas dissolved in soln is proportional to external partial pressure of that gas.

$$\frac{P_1}{C_1} = \frac{P_2}{C_2} \quad / P \propto C \quad / C = K_H \cdot P$$

- P = partial pressure of gas above soln
- C = concentration of gas dissolved in sol'n
- K_H = Henry's Law constant is specific to gas at a temp.

ex: $N_2(g)$ at 0.78 atm is dissolved in water (K_H of N_2 is 8.42×10^{-7} M/torr). Calculate molarity.

* have same units of pressure

$$\begin{aligned} C &= K_H \cdot P \\ &= (0.82 \text{ M/torr}) (0.78 \text{ atm} \cdot \frac{760 \text{ torr}}{\text{atm}}) \times 10^{-7} \\ &= 5.0 \times 10^{-4} \text{ M} \end{aligned}$$

ex: Fish need O_2 in water at 1.25×10^{-4} M to survive. What partial pressure of O_2 above water is needed to obtain this concentration? (solubility of O_2 at 1 atm is 2.21×10^{-3} M)

$$\frac{P_1}{C_1} = \frac{P_2}{C_2}$$

$$\frac{1 \text{ atm}}{2.21 \times 10^{-3} \text{ M}} = \frac{P_2}{1.25 \times 10^{-4} \text{ M}} \Rightarrow P_2 = 5.66 \times 10^{-2} \text{ atm}$$

ex: To celebrate finishing the course, you pop a bottle of champagne!!

Henry's Law is relevant b/c the drink is stored under high pressure c