Intro to Chemical Principals 8.23.23

[Lecture Notes] Who Cares About Units?

Standard Units of Measurement

Length → Meter
Mass → Kilogram
Time → Second
Temp → Kelvin
Amount of Substance → Mole
Electric Current → Ampere
Luminous Intensity → Candela

} Base Units

Derived Units → m/s

Prefix Multipliers

$1\text{ km} = 1000\text{ m} = 10^3\text{ m}$

$1\text{ mm} = .001\text{ m} = 10^{-3}\text{ m}$

[# Sig Figs Only in LAST #]

Dimensional Analysis: converting units

units given → units needed

$$\text{units given} \times \left(\frac{\text{units needed}}{\text{units given}}\right) = \text{units needed}$$

↑ conversion factor

$1\text{ in} = 25.4\text{ mm}$

$1\text{ kg} = 2.20\text{ lbs}$

ex. Convert 745 nm to m

$1\text{ nm} = 10^{-9}\text{ m}$

$$745\text{ nm} \times \left(\frac{10^{-9}\text{ m}}{1\text{ nm}}\right) = 7.45 \times 10^{-7}\text{ m}$$

↑ scientific notation

__ex.__ Convert 1cup lemonade to mL

$2c = 1pt$

$2pt = 1qt$

$1.057qt = 1L$

$10^{-3}L = 1mL$

$$1cup \times \left(\frac{1pt}{2c}\right) \times \left(\frac{1qt}{2pt}\right) \times \left(\frac{1L}{1.057qt}\right) \times \left(\frac{1mL}{10^{-3}L}\right) = 232\,mL$$

__ex.__ Convert the radius of Na atom (180pm) to Å.

$1Å = 10^{-10}m$

$1pm = 10^{-12}m$

$$180pm \left(\frac{10^{-12}m}{1pm}\right)\left(\frac{1Å}{10^{-10}m}\right) = 1.8Å$$

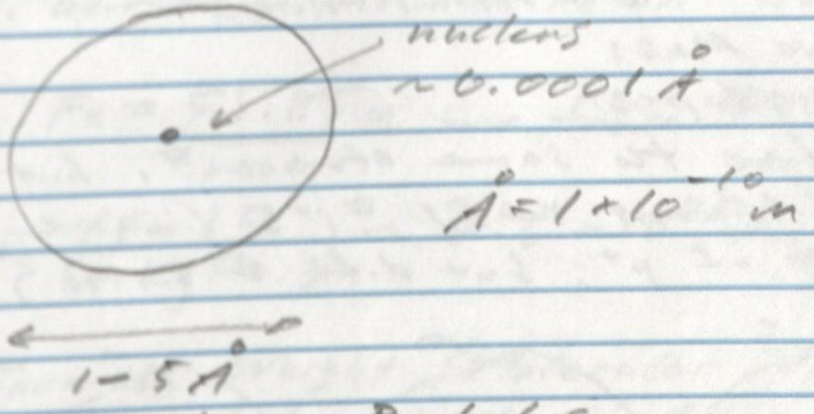
Lecture Notes John Dalton Atom Theory of Matter 8.25.23

I. Atom Composition

A. Dalton's Atomic Theory

1. All matter is composed of atoms
wrong → (isotopes) 2. All atoms of a given element are alike, but they differ from atoms of other elements
3. Compounds form when atoms of different elements combine in fixed proportions
4. A chemical reaction involves the rearrangement of atoms

B. Ernest Rutherford Atomic Model



Å = 1×10^{-10} m

C. Subatomic Particles

		charge	charge unit	mass	atomic mass unit (amu)
electron	e^-	-1.602×10^{-19} C	−1	9.109×10^{-31} kg	0 u
proton	p^+	$+1.602\times10^{-19}$ C	+1	1.672×10^{-27} kg	1 u
neutron	n	0	0	1.674×10^{-27} kg	1 u

1. # protons → defines element
2. # neutrons → defines which isotope
3. # electrons → equal to # protons in a neutral atom/molecule
4. ion – charged atom/molecule w/ different # of p^+ and e^-

ex. Na

$p^+=11$ $e^-=11$ charge $=0$

Na^+

$p^+=11$ $e^-=10$ charge $=+1$

5. atomic # → # of protons (Z)
6. mass # → # of p^+ + n (A)

II. Symbol of Elements

A. Element Annotation

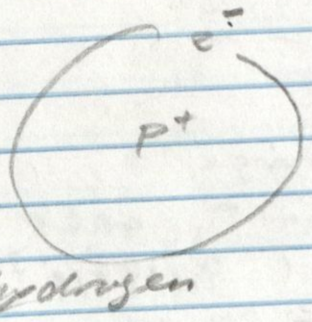
* $^{A}_{Z}X$

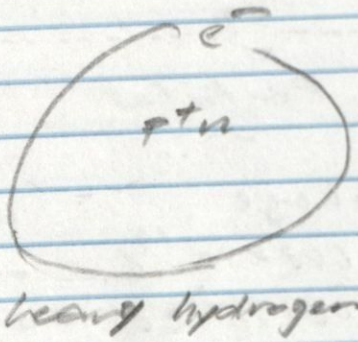
X = Element symbol
A = Mass number
Z = Atomic number

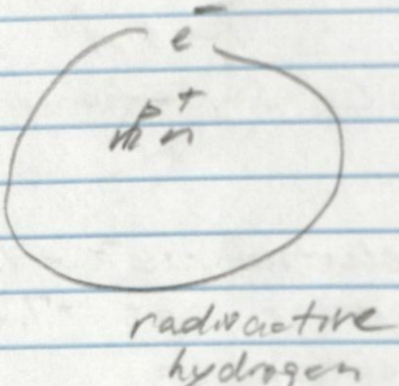
III. Atomic Mass

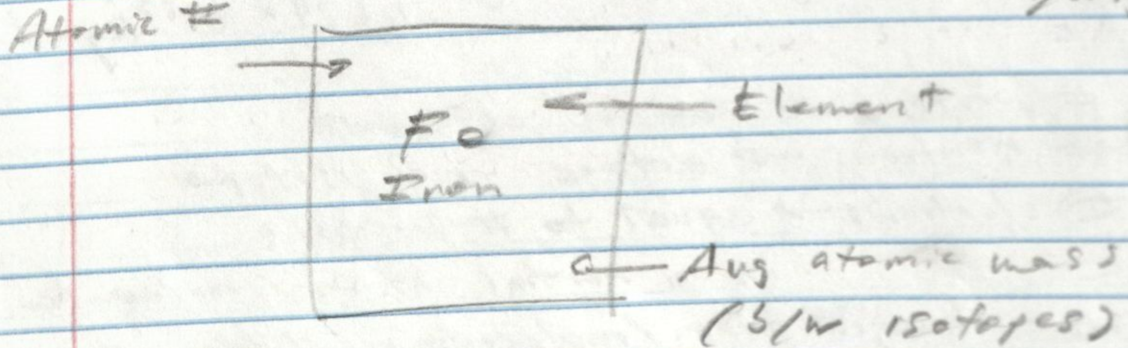
A. Isotopes

have the same atomic #, but have different mass #'s (same # of p^+, but diff # of n)









IV. Counting Atoms and Compounds

A. 1 dozen = 12 mol = n
1 bakers dozen = 13
* 1 mol = 6.022×10^{23}

- for a gas: 22.4L = 1 mol gas @ STP

B. Using mol as conversion factor
ex. How many mols in 1.29×10^{24} atoms?

$$1.29 \times 10^{24} \text{ atoms} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} = 2.14 \text{ mol atoms}$$

ex. how many mols of Fe in 4.8g of Fe

$$Fe = \frac{55.85 \text{ g}}{\text{mol}} \rightarrow \text{from PT}$$

$$4.8\text{g Fe} \left(\frac{1 \text{ mol Fe}}{4.8\text{g Fe}}\right) = 8.6 \times 10^{-2} \text{ mol Fe}$$

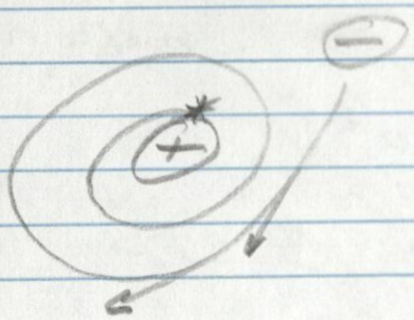
C. Formula Weight (Molecular Weight)
- mass of 1 mol of cmpd. or molec.

ex. mass of H_2O: 2H = (1.01 g/mol)(2) = 2.02 g/mol
1O = (15.99 g/mol)(1) = 15.99 g/mol
18.01 g/mol

ex. how much does $C_{12}H_{22}O_{11}$ weigh?
C = (12.01 g/mol)(12) = 144.12 g/mol
H = (1.01 g/mol)(22) = 22.22 g/mol
O = (15.99 g/mol)(11) = 175.89 g/mol
342.23 g/mol

$$1 \text{ mol} \times \left(\frac{342.23 \text{ g}}{1 \text{ mol}}\right) = 342.23 \text{ g}$$

Lecture Notes Quantum Mechanics of an Atom 8.28.23



In classical mechanics, atoms cannot exist

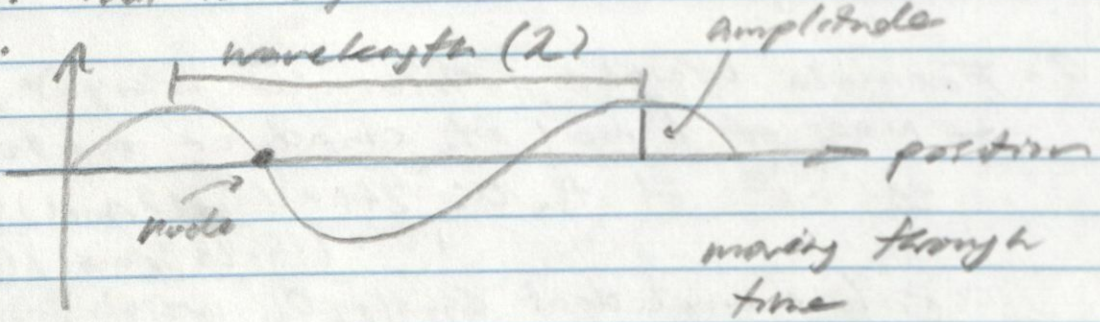
We Use Quantum Mechanics to explain:

1. Wave-particle duality of matter and light
2. The discreet steps in which the energy of an object changes

potential ⟷ kinetic energy

mechanical ⟷ light energy

I. The Wave Nature of Light
  A. What is Light? (video)
  B.



  C. $\underset{m/s}{\text{speed}} = \underset{m}{\lambda}\underset{\text{frequency } (s^{-1} \text{ or Hz})}{\nu}$
  D. speed of light vs. sound

sound:
air → 331.4 m/s
water → 1483 m/s
steel → 4512 m/s

light: air → 3.0×10^8 m/s

II. Electromagnetic Spectrum

A. For light, color is dependent of frequency or wavelength

* $c = \lambda\nu$

B. Energy of a wave

* $E = \underset{\uparrow}{h}\nu$

plank's constant (6.626 × 10^{-34} J·s)

if $c = \lambda\nu$, then $\nu = c/\lambda$

and

* $E = h\nu = h\frac{c}{\lambda}$

if ↑ν, then ↑E

if ↑λ, then ↓E

ex. Given $\lambda = 550\ nm$ & $c = 3.00 \times 10^8\ m/s$

find: ν

use $\nu = \frac{c}{\lambda}$

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8\ m/s}{550\ nm}\left(\frac{1\ nm}{10^{-9}\ m}\right)$$

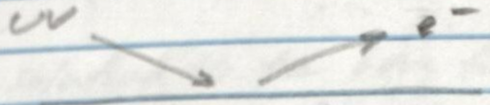
$$= 5.45 \times 10^{14}\ s^{-1}$$

* speed of wavelength is constant as it is all light *

III. Particle Nature of Light

A. The photoelectric effect

1887 Hertz discovered that by shining a UV light on a metal, e^-'s are emitted as sparks



B. Plank - observed

1. ν must be at a certain threshold
2. intensity of light irrelivant
3. the E of e^- was proportional to frequency
4. each metal required a specific frequency

C. Einstein – determined that a light is a beam of particles (photons) whose energy are related to frequency

$* \; E = h\nu$ (of a photon)

ex. $E = h\nu = (6.626 \cdot 10^{-34}\ \text{Js})(5.45 \cdot 10^{14}\ \text{s}^{-})$

$\uparrow$

$= 3.6 \cdot 10^{-19}\ \text{J/photon}$ from prev ex.

$$E_{1\,\text{mol photons}} = \frac{3.6 \cdot 10^{-19}\ \text{J}}{\text{photon}} \left(\frac{6.022 \cdot 10^{23}\ \text{photons}}{1\ \text{mol}} \right)$$

$= 2.18 \cdot 10^{5}\ \text{J/mol photons}$

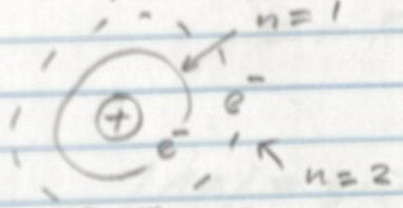
$* \; \text{s}^{-}, \text{s}^{-1} = \frac{1}{\text{s}}$ (per second) *

Lecture Notes Emission Spectra 8.30.23

Atomic Emission Spectrum: identifiable light emissions unique to every element

I. Bohr Model of an Atom (1913)

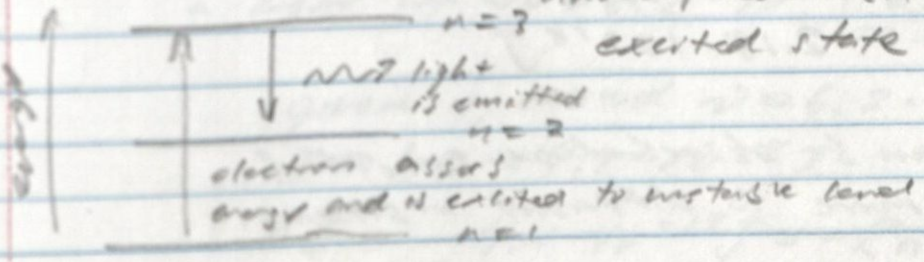
Q. Why do different metals require different frequency to eject an electron (e^-)?



e^- occupy special orbits with constant energy

1st orbit → ground state

unoccupied orbital → excited state

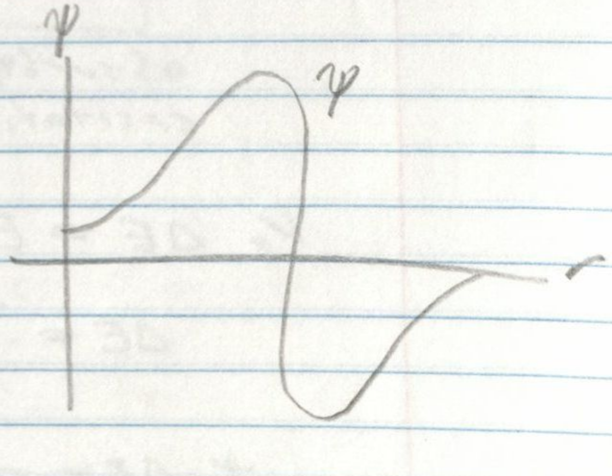


B. e^-'s cannot be b/w states

C. Each element has an emission spectra that is unique to the energy levels of the e^-

II. The Schrödinger Equation

$\psi(r)$ = math equation for the wave nature of e^-



– The solution to the wave functions are called wave functions $\psi(r)$ where r = distance from nucleus to e^-

B. Solving $\Psi(r)$ for a hydrogen atom (H), only discreet energy levels allowed (whole, positive integers)

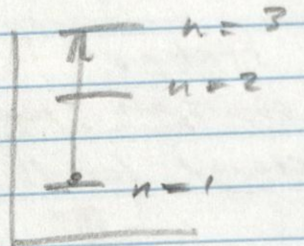
* $E_n = -\frac{Rh}{n^2}$

R = Rydberg's constants
$3.29 \cdot 10^{15}\ s^{-}$
h = Plank's constant
$6.626 \cdot 10^{-34}\ Js$
n = integer ≥ 1

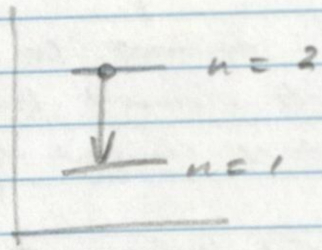
* brings together Plank & Bohr's Models *

Principal Quantum Number:
$R \cdot h = 2.18 \cdot 10^{-18}\ J$

C. Light can be absorbed or emitted as e^- move to different orbitals



absorbtion
excitation



emission
relaxation

D. $\Delta E = E_f - E_i = h\nu$

$$\Delta E = \frac{-Rh}{(n_f)^2} - \frac{-Rh}{(n_i)^2}$$

* $\Delta E = -Rh\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$

[Lecture Notes] 9.1.23

__ex.__ Calculate the wavelength of the $n=3 \rightarrow n=2$ emission line in H atom

given $n_i = 3$, $n_f = 2$ __find__ ΔE, then λ

$$\Delta E = -Rh\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$$= -Rh\left(\frac{1}{4} - \frac{1}{3}\right) = \underset{\nearrow}{-}3.03\cdot10^{-19}J$$

always negative for emission

$$|\Delta E| = h\nu = \frac{hc}{\lambda} \Rightarrow \lambda = 656nm$$

__ex.__ A H atom w/ an electron in $n=4$ emits a light w/ $\nu = 6.2\cdot10^{14}Hz$. What is n_f?

given $n_i = 4$ and $\nu = 6.2\cdot10^{14}s^{-}$ __find__: n_f

$$E = h\nu = 4.1\cdot10^{-18}J$$

$$\Delta E = \underset{\overset{\uparrow}{\text{emission}}}{-}4.1\cdot10^{-19}J = -Rh\left(\frac{1}{n_f^2} - \frac{1}{4^2}\right)$$

$$= -4.1\cdot10^{-19} = -2.18\cdot10^{-18}J\left(\frac{1}{n_f^2} - \frac{1}{16}\right)$$

$$= 0.188 = \frac{1}{n_f^2} - \frac{1}{16}$$

$$4 = n_f^2 \Rightarrow n_f = 2$$

E. Rydberg can be modified for any 1 e^- atom

ex. H, He^+, Li^{2+}, ...

$$E_n = -Z^2 \frac{Rh}{n^2}$$

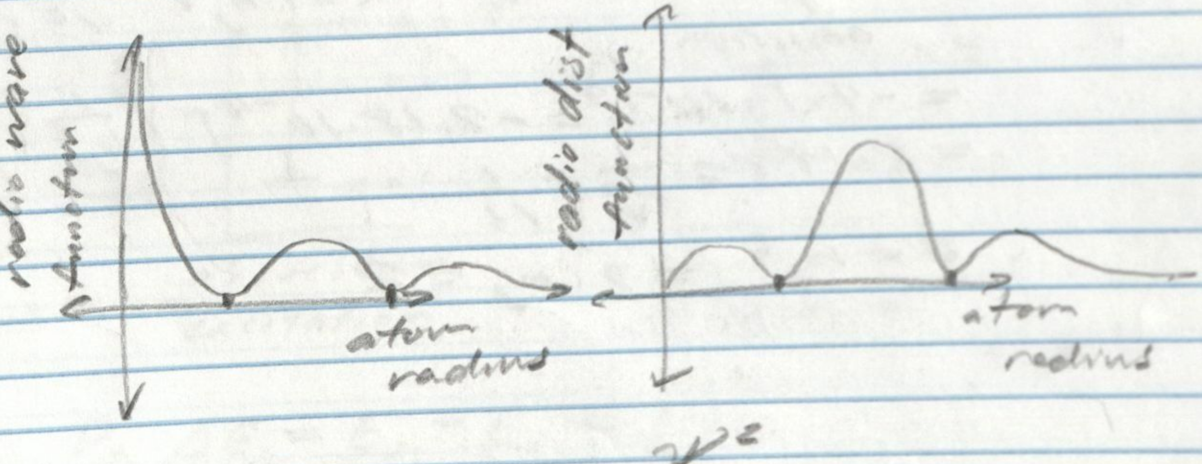
Z = atomic number

I. Born Interpretation

wavefunction → $\Psi(r) = \Psi(x, y, z)$

A. $\Psi^2(x, y, z)$ = prob of finding an e^- at (x, y, z)

B. The Schrödinger Eqn/Born Interpretation give many possible solutions for where an e^- can be.



Probability Density = $\frac{\Psi^2}{V}$

as V↓, $\frac{\Psi^2}{V}$ ↑ to ∞

The radial distribution function:

- probability of finding an e^- at r
- value = 0 at $r = 0$
- increases to a max, then decreases w/ increasing r

II. Quantum Numbers: the short-hand for understanding the likely position of an e^-

- To understand the wavefunction $\Psi(r)$, we need more quantum numbers

A. Definitions and Possible Values

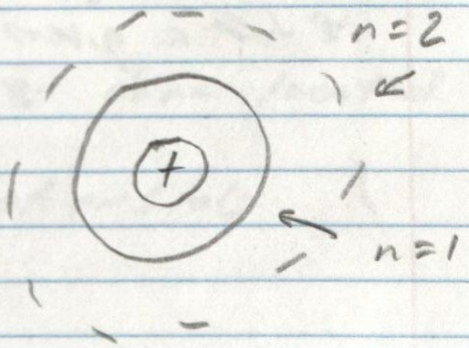
n → principal quantum number → positive integer ≥ 1
(orbital size and energy)

l → orbital (angular momentum) QN → $0 \leq l \leq n-1$ (shape)

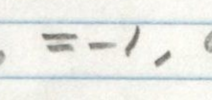
m_l → magnetic QN → $-l \leq m \leq l$ (orientation)

B. Understanding QN

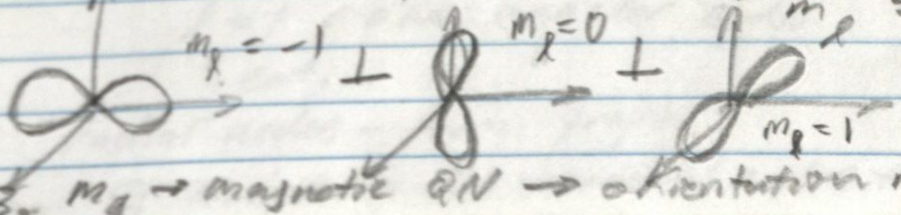
1. n → a. correlates w/ size
b. relates to E of orbital
c. all e^- w/ same 'n' are in same shell



2. l → a. correlates w/ shape and has letter designations
b. $l = 0$, s orbital →



c. $l = 1$, p orbital → $m_l = -1, 0, 1$



(all of these)

3. m_l → magnetic QN → orientation range $-l$ to l

TTQ:

ex. Determine which of the following sets of QN are allowed

$\underline{n=0}$ $l=0$ $m_l=0$ ✗

$n=1$ $\underline{l=1}$ $m_l=0$ ✗

$n=3$ $l=1$ $m_l=-1$ ✓

$n=3$ $l=1$ $\underline{m_l=2}$ ✗

$n=7$ $l=4$ $m_l=4$ ✓

ex. How many possible values are there for m_l if $l=2$?

$m_l = -2, -1, 0, 1, 2$
there are 5 possibilities

* for a given l, there are $2l+1$ orbitals *

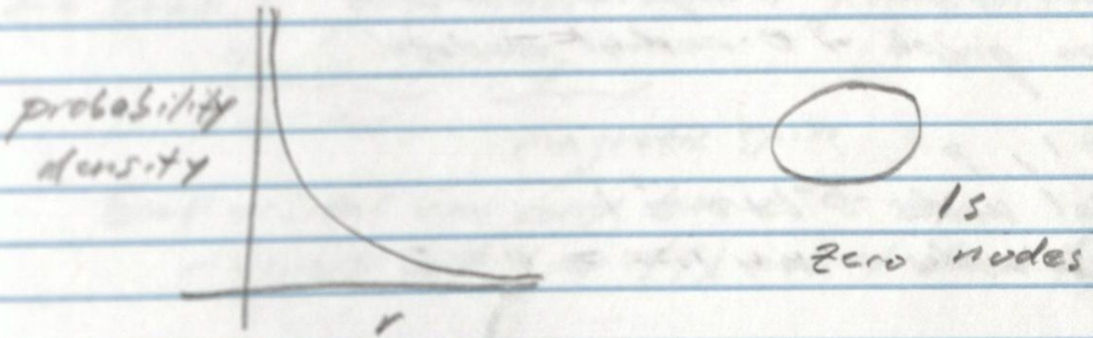
|Lecture Notes| Nodes

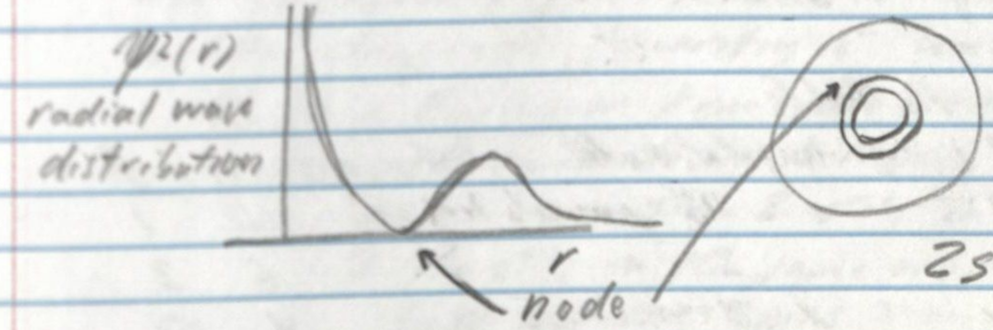
9.4.23

III. **Nodes** - where the probability of finding $e^- = 0$

$\psi(r) = 0$ and $\psi^2(r) = 0$

A. Radial Node





B. Angular Node - a flat plane or cone located at a fixed angle

- determines the shape of orbitals

l = letter → s, p, d, f

l = number → 0, 1, 2, 3

C. Determining the total number of nodes

total nodes = $n-1$

angular nodes - from l

$l=0$, zero angular nodes

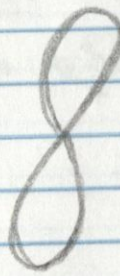
$l=1$, one angular nodes

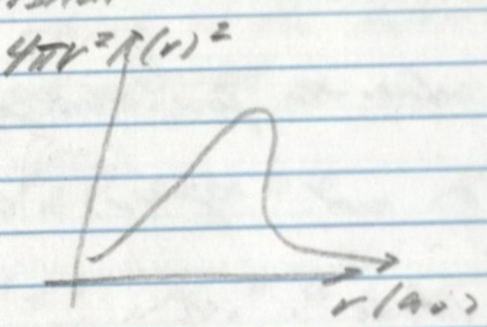
etc...

radial nodes - from graph

or → total nodes = radial nodes + angular nodes

TTQ: Name the Orbital





from shape – 1 angular node
from graph – 0 radial nodes

$l = 1$, p
total nodes $= 1 + 0 = 1$
total nodes $= n - 1 \Rightarrow n = 2$

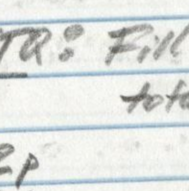
name: 2p orbital

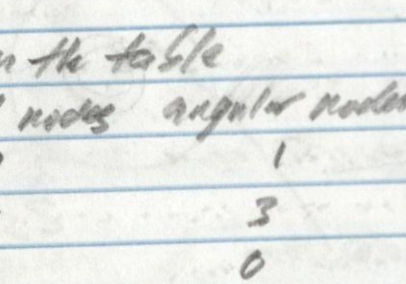
TTQ: Fill in the table

	total nodes	angular nodes	radial nodes	n	l
2p	1	1	0	2	1
6f	5	3	2	6	3
4s	3	0	3	4	0

1. determine n
2. determine l → determine angular
3. determine radial nodes → $n - 1 - l$
4. Sum the nodes

TTQ: Name the Orbital





from shape: 2 angular
$l = 2$ → d
from graph: 1 radial
$n - 1 = \text{total} = 3$,
so $n = 4$
⇒ 4d orbital

IV. Spin – m_s – 4th quantum number

allowed values = $\frac{1}{2}$, $-\frac{1}{2}$
(up) (down)

Lecture Notes / Electron Configurations & Orbital Diagrams 9.6.23

I. Each e^- has a full set of quantum numbers

$\underbrace{n, l, m_l}_{\text{orbital}},\ \underbrace{m_s}_{\text{magnetic spin}}$

Each orbital can carry two e^-'s
– usually w/ 1 up (↿) and 1 down (⇂) ← half arrow indicating 1 e^-

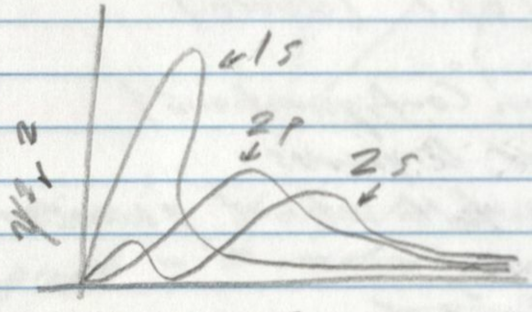
Use the following principles when creating orbital diagrams & writing e^- configurations

A. Paul Exclusion Principle: no 2 e^-'s can have the same four Q.N.'s
1. no more than 2 e^-'s in each orbital
2. the e^-'s in the same orbital must have opposing spins

$\underbrace{\underline{\upharpoonleft}\quad \underline{\downharpoonright}\quad \underline{\upharpoonleft\downharpoonright}}_{\text{allowed}}\qquad \underbrace{\underline{\upharpoonleft\upharpoonleft}\quad \underline{\downharpoonright\downharpoonright}\quad \underline{\upharpoonleft\downharpoonright\upharpoonleft}}_{\text{not allowed}}$

B. Aufbau – "building up": e^-'s are added from the lowest energy orbital to the highest energy orbital
1. For an atom w/ more than one e^-, the e^-'s affect each other
1. repel each other
2. shielding – e^-'s that are farthest from the nucleus are shielded or screened from the full effects of the nuclear charge

2. **Penetration**: an e^- from an outer shell passes through an inner shell and is momentarily less shielded from the nucleus



* So (ℓ) effects orbital energy *
(If you have an orbital w/ only 1 e^-, that is called a **degenerate** orbital)

* Order of adding e^-'s **OR look at PT** *
$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s$

C. Hund's Rule: for a group of degenerate orbitals (orbitals w/ the same energy), add e^-'s w/ parallel spins in each orbital before 'pairing' e^-

ex. N ($7e^-$) $\underset{1s}{\underline{\uparrow\downarrow}}\ \underset{2s}{\underline{\uparrow\downarrow}}\ \underset{2p_x}{\underline{\uparrow}}\ \underset{2p_y}{\underline{\uparrow}}\ \underset{2p_z}{\underline{\uparrow}}$

e^- config: $1s^2 2s^2 2p^3$

* ex. O ($8e^-$)

$\underset{1s}{\underline{\uparrow\downarrow}}\ \underset{2s}{\underline{\uparrow\downarrow}}\ \underset{2p}{\underline{\uparrow\downarrow}}\ \underset{2p}{\underline{\uparrow}}\ \underset{2p}{\underline{\uparrow}}$

* e^- configuration: $1s^2 2s^2 2p^4$

ex. Hg ($Z=80$)

$$\underbrace{[Xe]}_{\text{inner electrons}}\ \underbrace{6s^2 4f^{14} 5d^{10}}_{\text{outer electrons (valence electrons)}}$$

ex. Na ($Z=11$) $1s^2 2s^2 2p^6 3s^1$

$[Ne]3s^1$

Na has 1 unpaired e^-

Na also has 1 valence e^-

F. Ions:

ex. Na^+

if Na is $[Ne]3s^1$ lose e^-

then Na^+ is $[Ne]$ or $1s^2 2s^2 2p^6$

ex. Cl^-

Cl atom → $[Ne]3s^2 3p^5$ gain e^-

Cl^- ion → $[Ne]3s^2 3p^6$

Cl^- is isoelectric with Ar

{ same e^- configuration

Lecture Notes 9.8.23

isoelectric ≠ is. electronic
outer e^- ≠ valence e^-
outer e^- ≠ outer shell e^-
valence e^- = outer shell e^-

- for main group elements (s & p block), v.s.e. are e^- w/ the highest n
- for d & f block elements, v.s.e. include the outer most shell e^- (highest n) *and* the outermost d & f block e^- *IF* the d or f block is *not* full

ex - How many valence shell e^- does Ti have?
$[Ar]\,4s^2 3d^2$ ← not full
$2 + 2 = 4$ v.s.e

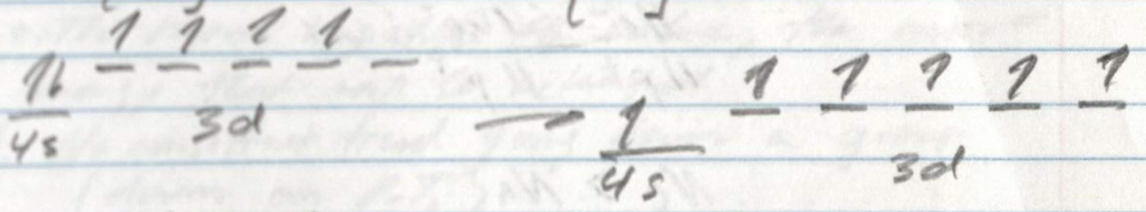
ex. Ge
$[Ar]\,4s^2 3d^{10} 4p^2$
$2 + 2 = 4$ v.s.e.

ex. P?
$[Ne]\,3s^2 3p^3 = 5$ v.s.e.

I. Periodic Trends – Key Factors

1. Nobel gases have the most stable e^- configuration
   ns^2np^6
2. V.s.e. are the most reactive
3. Shielding and Z_{eff} effect periodic trends
4. Filled and half filled shells are stable e^- configurations

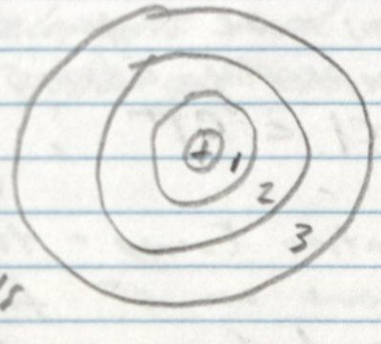
$Cr: [Ar]4s^2 3d^4 \rightarrow [Ar]4s^1 3d^5$



b/c of m_s

Shielding Review:

e^- in $n=3$ are shielded from the (+) charge of the nucleus by e^- in $n=1$ & $n=2$ shells



Z_{eff} - effective nuclear charge

$$Z_{eff} = Z - \# \text{ core } e^- \ (n=1, n=2)$$

A. Atomic Radius – as you move down the P.T., atoms get larger as n increases
– as you go from left to right on the P.T., the atoms get smaller b/c of increased attraction of nucleus & e^- cloud

B. Ionic Radius

1. Cations – are smaller than their corresponding atoms

$Na > Na^+$
$11e^-$ $10e^-$
$11p^+$ $11p^+$

$Ne > Na^+$
$10e^-$ $10e^-$
$10p^+$ $11p^+$ → pulls on e^- more

2. Anions – are larger than their corresponding atoms

$Cl < Cl^-$, also has more e^- repulsion in the cloud

C. Ionization Energy – the energy required to remove an e^- from an atom or an ion to form a cation

1. v.s.e. are the easiest to remove
2. $M(g) + IE_1 \rightarrow M^+(g) + e^-$
(first ionization energy)
$M^+(g) + IE_2 \rightarrow M^{2+}(g) + e^-$
(2nd ionization energy)
3. the larger the Z_{eff} on the e^-, the more energy it takes to remove it
   - 1 IE_1 generally increases as you go left to right across the P.T.
4. the farther the e^- is from the nucleus, the less energy it takes to remove it

OK: 5. Exceptions are due to full and half filled shells

TTQ: Arrange the atoms in increasing order of 1st I.E.

Cl , K, S

K < S < Cl

5. Removal of core e^- requires more energy

D. Electron Affinity (E.A.) – the energy that is released (–) when an atom gains an e^- to become an anion

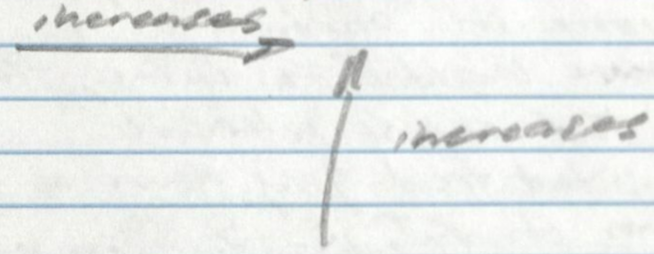
- The more negative the value, the more energy that will be released

1. No consistent trend going down a group (down on P.T.)
2. |E.A.| increases as you go left to right on the P.T.
    - b/c p-block elements tend to gain e^-'s to gain noble gas configurations

Lecture Notes / Exam 2 9.11.23

B. Electronegativity – a relative scale (0–4.0) of e^- pulling power of an atom

1. $E.N. \cong \frac{I.E. + |E.A.|}{2}$ } no calculations
2. 4.0 is the most electronegative
Flourine (F)



3. it is a tool used to help scientists understand different types of bonds

ΔEN = difference in electronegativity b/w two bonded atoms

$1.5 < \Delta EN$	ionic bond	NaCl $3.16 - 0.93 = 2.23$
$0.5 < \Delta EN < 1.5$	polar covalent	H_2O
$\Delta EN < 0.5$	nonpolar covalent	O_2 O–O CH_4

Bonds:

chemical bond – force that holds atoms together

octet rule – atoms are most stable w/
8 v.s.e. (ns^2np^6)

Exceptions:
- * 1. H & He – stable w/ 2 e^-
- 2. B & Al – sometimes stable w/ 6 e^-
- 3. $n \geq 3$ – can have expanded octets

I. Ionic Bonds
1. $\Delta E.N. > 1.5$ (generally)
2. involves a transfer of e^- to form ions
3. strong electrostatic interaction holds the ions together (opposites attract)

ex. $Na^{+1} + Cl^{-1} \rightarrow NaCl$

4. usually between a nonmetal + metal
5. Ionic Compound Formula
   – shows the lowest ratio of atoms present (called an empirical formula)

II. Covalent Bonds – formed between atoms w/ similar electronegativity values
1. $\Delta EN < 1.5$ (generally)
2. e^- are shared between atoms
3. formed when atomic orbitals overlap to form molecular orbitals

ex: H_2 $\quad H\cdot + H\cdot \longrightarrow H{:}H$

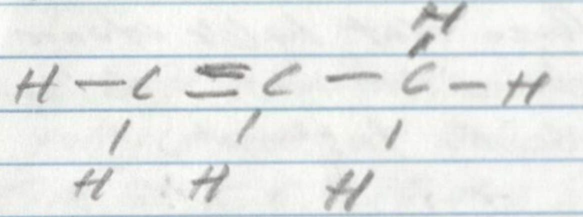
$H - H$

↖ indicates 2 e^-

4. Can use several types of formulas
   - a) empirical formula – lowest ratio of atoms (CH_2)
   - b) molecular formula – actual number of atoms (C_3H_6)

c) Structural formula – show connectivity

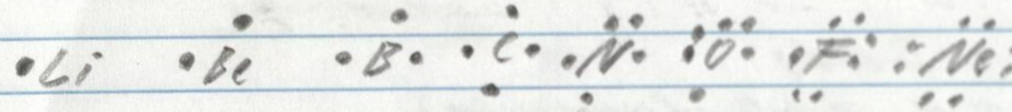
ex.



$$H-\underset{H}{\underset{|}{C}}\equiv\underset{H}{\underset{|}{C}}-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-H$$

d) Ball & Stick or Space Filling Models

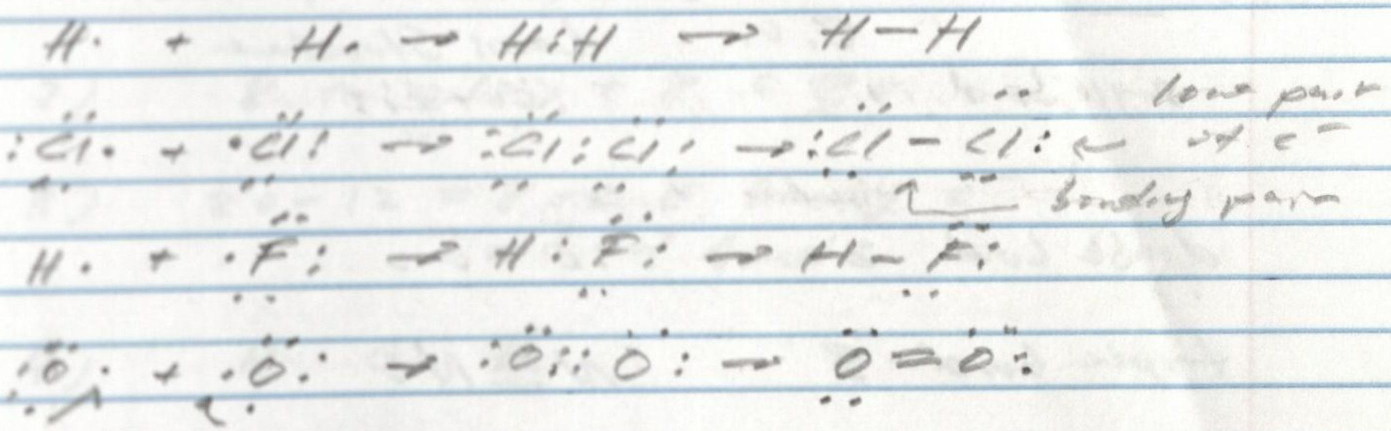
III. Common Bonding Patterns



Lecture Notes

9.13.23

A. Lewis Dots Continued



B. Rules for Drawing Lewis Structures

look on slides

C. Bond Order: the number of bonds that link a specific pair of atoms

ex.

	B.O.	Lewis Structure
single bond	1	:C̈l – C̈l:
double bond	2	:Ö = Ö:
triple bond	3	:N ≡ N:

3. Bond Length and Strength

	C – C	C = C	C ≡ C
B.O.	1	2	3
strength	weak	mid	strong
length	long	mid	strong

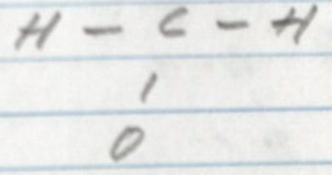
ex. Draw the lewis structure for CH_2O

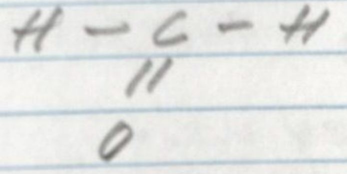
1) C 2H O
v.s.e. 4 + 2(1) + 6 = 12 v.s.e.

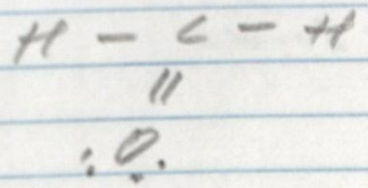
2) 8 + 2(2) + 8 = 20

3) 20 − 12 = 8 → 8 bonding e^-
4 bonds

4) H C H
O

5)

$$\begin{array}{c} H - C - H \\ | \\ O \end{array}$$

6)

$$\begin{array}{c} H - C - H \\ \| \\ O \end{array}$$

7)

$$\begin{array}{c} H - C - H \\ \| \\ :\ddot{\underset{\cdot}{O}}: \end{array}$$

8) count electrons

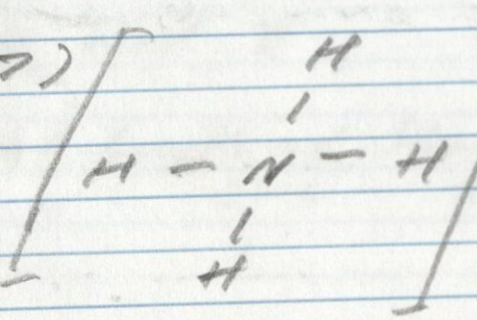
__ex.__ NH_4^+

1) N 4H (+)
5 + 4(1) −1 = 8 v.s.e.

2) 8 4(2) = 16 e^- (for each atom to have octet (duplet)

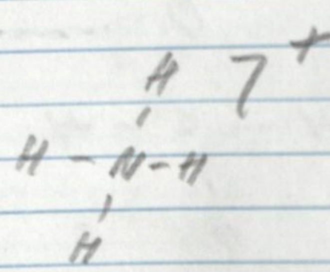
3) 16 − 8 = 8 bonding e^-
② ① 4 bonds.

4-7)



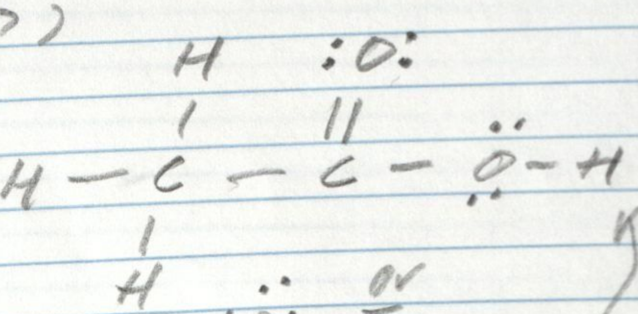
8) count 8 e^-
matches ① 8 v.s.e.

__or__



__ex.__ H_3CCOOH

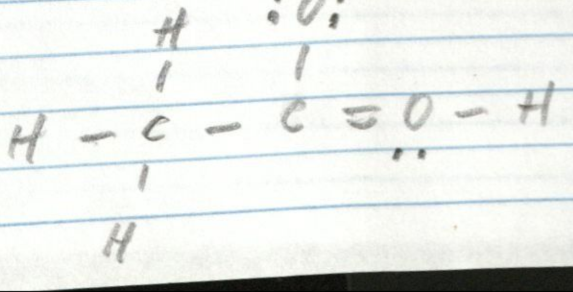
1) C O H
2(4) + 2(6) + 4(1) = 24 v.s.e.
2) 2(8) + 2(8) + 4(2) = 40 e^-
3) 40 − 24 = 16 e^- → 8 bonds
4-7)



__or__

both correct

one is better



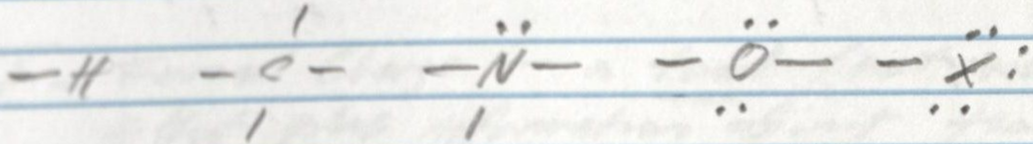
IV. Common Bonding Patterns

E. Functional Groups – characteristic atom or groups of atoms attached to carbon

* Slides *

R – rest of the molecule (most often a C atom attached to other things)

F. Common Formations *Slides*



X = F, Cl, Br, I

Number of bonds + Number of lone pairs = 4 pairs

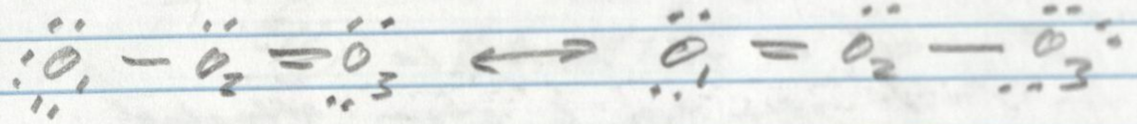
Lecture Notes

9.15.23

IV. Resonance

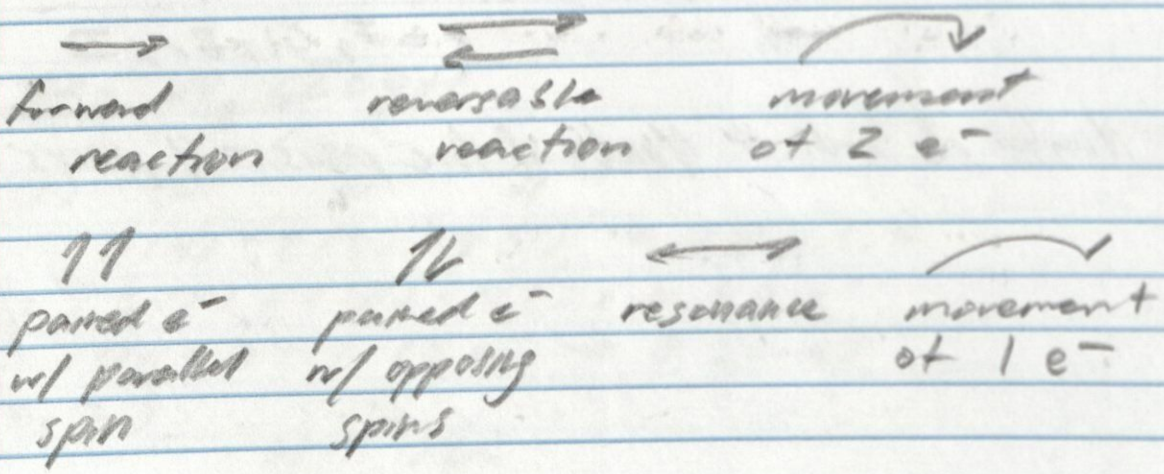
ex. O_3

1) 6(3) = 18 val. e^-
2) 8(3) = 24 e^-
3) 24 - 18 = 6 e^- bonding, 3 bonds



2 equivalent structures
2 resonance structures

Arrows:



TTQ: What is the bond order between O_1 and O_2 of ozone?

$$\text{bond order} = \underset{\substack{\text{2 is \# of}\\ \text{equivalent}\\ \text{structures}}}{\frac{1}{2}}(\underset{\substack{\text{single}\\ \text{bond}}}{1}+\underset{\substack{\text{double}\\ \text{bond}}}{2}) = \frac{3}{2} \leftarrow \text{bond order}$$

Typically O–O s.b. is 148 pm
O=O d.b. is 121 pm

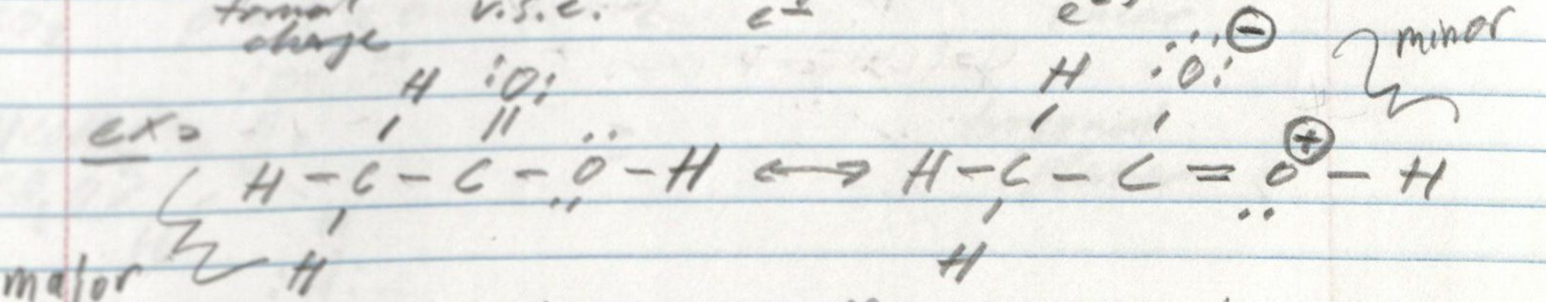
bond length in ozone is 127 pm

VI. Formal Charge — a tool (not measured) that gives information about the most stable and dominant structure

$$\text{A. } \underset{\substack{\text{formal}\\ \text{charge}}}{\text{F.C.}} = \underset{\text{v.s.e.}}{V} - (\underset{\substack{\text{lone pair}\\ e^-}}{L} + \frac{1}{2}\underset{\substack{\text{bonding}\\ e^-}}{B})$$

indicates F.C., not real charge

ex:



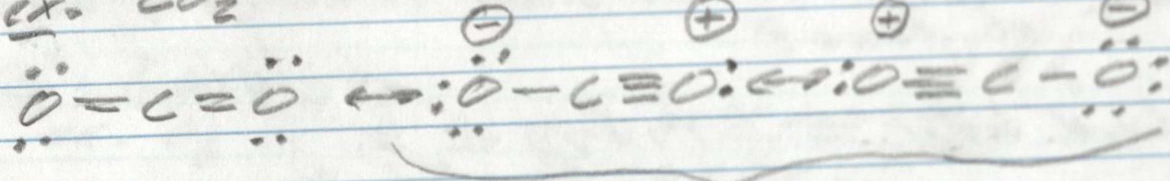
$$=\ddot{O} \rightarrow 6-(4+\tfrac{1}{2}(4))=0 \qquad :\ddot{O}: \rightarrow 6-(6+\tfrac{1}{2}(2))=-1$$

$$-\ddot{O}- \rightarrow 6-(4+\tfrac{1}{2}(4))=0 \qquad =\ddot{O} \rightarrow 6-(2+\tfrac{1}{2}(6))=+1$$

Weighting Resonance Structures:

1. all atoms obey octet rule
2. Formal Charge should be minimized
3. Formal Charges should correlate w/ relative electronegativity

ex. CO_2

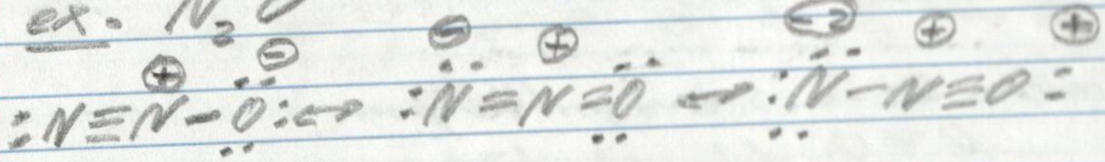


$$\ddot{O}=C=\ddot{O} \leftrightarrow \underbrace{:\overset{\ominus}{\ddot{O}}-C\equiv\overset{\oplus}{O}: \leftrightarrow :\overset{\oplus}{O}\equiv C-\overset{\ominus}{\ddot{O}}:}_{}$$

major

equivalent minor

ex. N_2O



$$:N\equiv\overset{\oplus}{N}-\overset{\ominus}{\ddot{O}}: \leftrightarrow :\overset{\ominus}{\ddot{N}}=\overset{\oplus}{N}=\ddot{O} \leftrightarrow :\overset{-2}{\ddot{N}}-\overset{\oplus}{N}\equiv\overset{\oplus}{O}:$$

major

minor

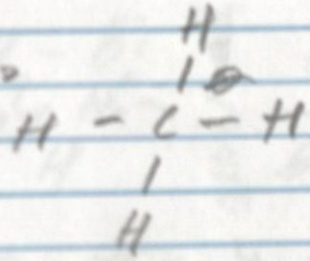
not significant

TTQ. What is the bond order between the nitrogens?

answer: qualitative: between 2 & 3, closer to 3

Lecture Notes 9.18.23

ex.



predict: 90° H-C-H angle

find: 109.5° H-C-H angle

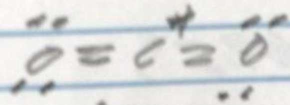
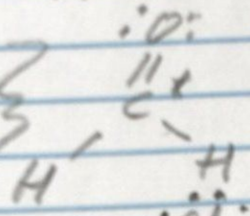
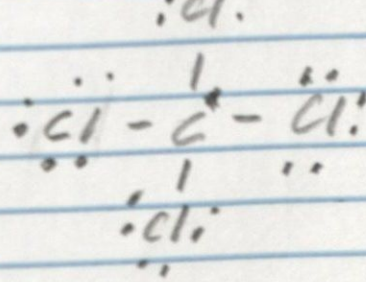
I. Valence Shell Electron Pair Repulsion - VSEPR

A. electron groups - repel each other in 3D space groups are quantified by using a steric number

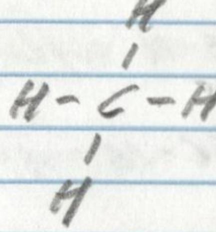
$$\text{steric number} = \Sigma \left\{ \begin{array}{l} \text{single bonds,} \\ \text{double bonds,} \\ \text{and/or triple bonds} \end{array} \right. + \begin{array}{c} \text{lone pair} \\ e^- \end{array}$$

steric number for CH_4 = 4 + 0 = 4

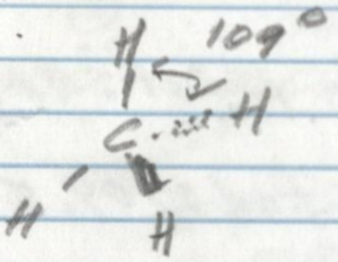
B. 1. With the steric number you can predict the shape

		steric # on C	e^- geometry
CO_2		2	linear
$HCOH$ / CH_2O		3	trigonal planar
CCl_4		4	tetrahedral

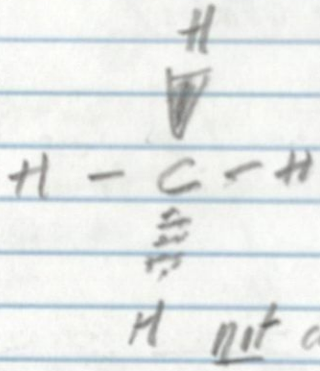
2. Drawing Tetrahedral

CH_4


Lewis Structure



correct



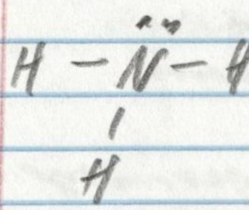
not correct!

dash and wedge must be adjacent (next to) each other

In Chem 4, more shapes will be covered

C. The Effects of Lone Pair Electrons

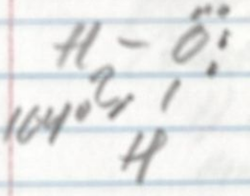
ex. NH_3 steric #: 3+1 = 4



electron geometry: tetrahedral

expect H-N-H bond to be 109.5°, but it is ~107°

the lone pair e^-'s on the N repel the N-H bonds ex: H_2O



steric number = 2+2 = 4

e^- geometry – tetrahedral

bond angle H-O-H ~ 104°

D: Electron Geometry vs. Molecular Geometry (Shape)

e^- geometry – describes the e^- arrangement around a central atom

molecular shape – describes the shape of the atoms around a central atom

ex: H_2O — e^- geometry: tetrahedral — molecular shape: bent

* memorize table 5.5 in slides *
(on electron geometry and molecular shape)

E. Molecular Shape and Polarity

1. $+\!\!\!\longrightarrow$ shows a difference in electronegativity

δ^+ δ^-

δ^+ - slightly positive
δ^- - slightly negative

* dipole moment *

2. Bond Polarity

$\underset{\cdot\cdot}{\ddot{O}} = \underset{\cdot\cdot}{\ddot{O}}$ not polar
$H - C$ not polar

} $\Delta E.N.$
$\Delta E.N. < 0.5$

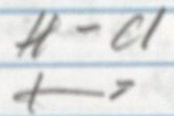
$O - C$
$\longleftarrow\!\!\!+$ polar

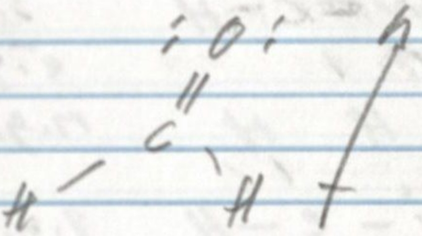
$H - Cl$ polar
$+\!\!\!\longrightarrow$

} $\Delta\ 0.5 < \Delta E.N. < 1.5$

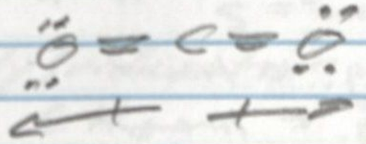
3 - Molecular Polarity — for a molecule to be polar, it must meet certain conditions (must have polar bonds)

1) if there is only <u>one</u> polar bond, the molecule is polar

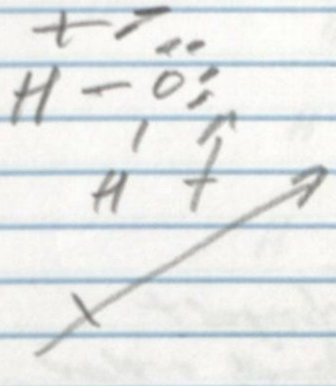




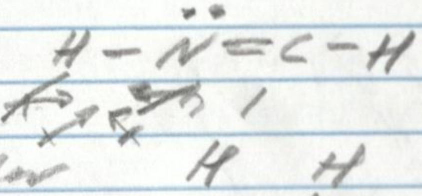
2) if there are multiple polar bonds, you have to determine if there is a net dipole moment (so, must determine molecular shape)

ex.  linear — no net dipole — dipoles are pulling in equal and opposite directions

$O=C=O$

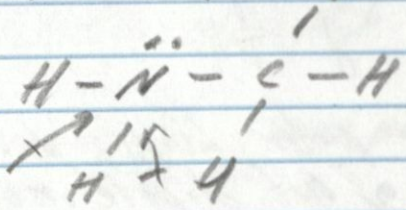
ex.  bent — has a net dipole and is polar ex: Draw the Lewis Structures for

1) $NHCH_2$
2) NH_2CH_3
3) HCN

1)


polar

s.n = 3
e^-g = trig. planar
m.g. = bent

2)


polar

s.n. = 4
e^-g = tetrahedral
m.g. = pyramidal

3. $\underrightarrow{H-C\equiv N:}$

polar

s.n. = 2
e^-.g. = linear
m.g. = linear

- What molecule has the strongest C–N bond? (3) → bond order of 3

- What are the molecular shapes around N in each molecule?

- Which molecule is not polar?

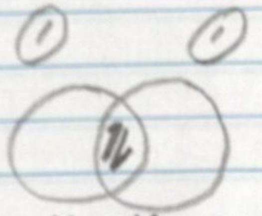
Lecture Notes 9.20.23

I. Valence Bond Theory

A. Definition – a chemical bond is the overlap between two half filled atomic orbitals

ex: H_2 H $\underset{1s}{\underline{\uparrow}}$

H $\underset{1s}{\underline{\uparrow}}$



} 2 1s orbitals overlap

H–H , H_2

B. Hybridization – sp^3, sp^2, sp

① ex. CH_4 H $\underline{\uparrow}_{1s}$

H $\underline{\uparrow}_{1s}$

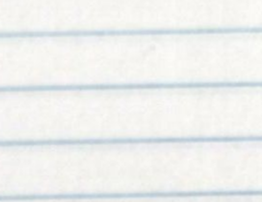
H $\underline{\uparrow}_{1s}$

H $\underline{\uparrow}_{1s}$

C $\underset{2s}{\underline{\uparrow\downarrow}}$ $\underset{2p}{\underline{\uparrow}\ \underline{\uparrow}\ \underline{\ \ }}$ $\rightarrow$ $\underset{sp^3}{\underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}}$

hybridize "mix"
s+p+p+p

a) Lewis Structure



$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array}$$

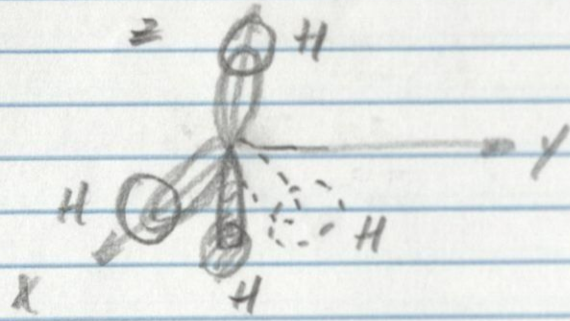
#groups (domain) – 4

steric # – 4

4 atomic orbitals are required on the central atom (C)

* but C only has 2 half filled orbitals *

C. Shape of sp^3 orbital



Shape is tetrahedral

* Hybridization makes V.B.T. consistant w/ experimental data*

ex. NH_3

H – N̈ – H
      |
      H

$H\ \underline{\uparrow}_{1s}$

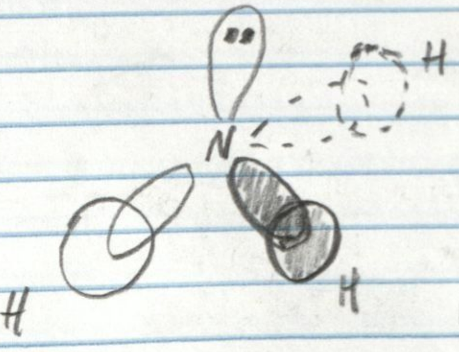
$H\ \underline{\uparrow}_{1s}$

$H\ \underline{\uparrow}_{1s}$

$N\ \underline{\uparrow\downarrow}_{2s}\ \ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}_{2p}$

steric #: 4
so, need 4 orbitals

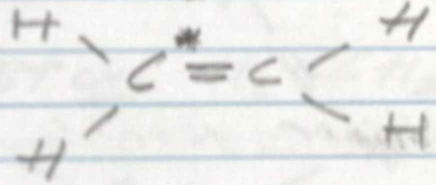
$$\underset{2s}{\underline{\uparrow\downarrow}}\ \ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}_{2p}\ \ N \xrightarrow{\text{mix}} \underbrace{\underset{sp^3}{\underline{\uparrow\downarrow}}}_{\text{lone pair } e^-}\ \underbrace{\underset{sp^3}{\underline{\uparrow}}\ \underset{sp^3}{\underline{\uparrow}}\ \underset{sp^3}{\underline{\uparrow}}}_{\text{bonding } e^-}$$



e^- geometry is tetrahedral

molecular geometry is trigonal pyramidal

② ex. C_2H_4



H $\underline{\uparrow}$

H $\underline{\uparrow}$

C $\underset{2s}{\underline{\uparrow\downarrow}}$ $\underline{\uparrow}$ $\underset{2p}{\underline{\uparrow}}$ $\underline{\ \ }$

b) hybridization
stene # : 3
need 3 orbitals

$\underset{2s}{\underline{\uparrow\downarrow}}$ $\underline{\uparrow}$ $\underset{2p}{\underline{\uparrow}}$ $\underline{\ \ }$ $\xrightarrow[\text{mix}]{}$ $\underset{sp^2}{\underline{\uparrow}}$ $\underset{sp^2}{\underline{\uparrow}}$ $\underset{sp^2}{\underline{\uparrow}}$ $\underset{2p}{\underline{\uparrow}}$

s + p + p
have p left over

↑
"pure" p

c) shape of sp^2 is trigonal planar

* "pure" p orbital is for double bonds *

ex. C_2H_2

$H - \overset{*}{C} \equiv C - H$

H $\underline{\uparrow}$

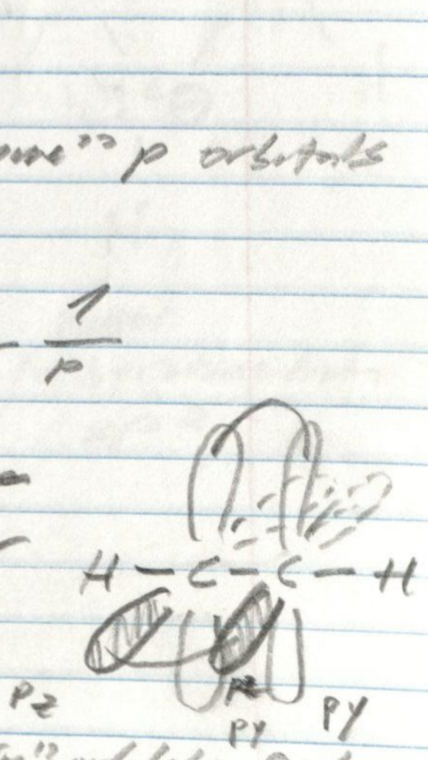
C $\underline{\uparrow\downarrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$ $\underline{\ \ }$

a) stere # is 2
need 2 orbitals s+p w/ 2 leftover "pure" p orbitals

b) hybridize

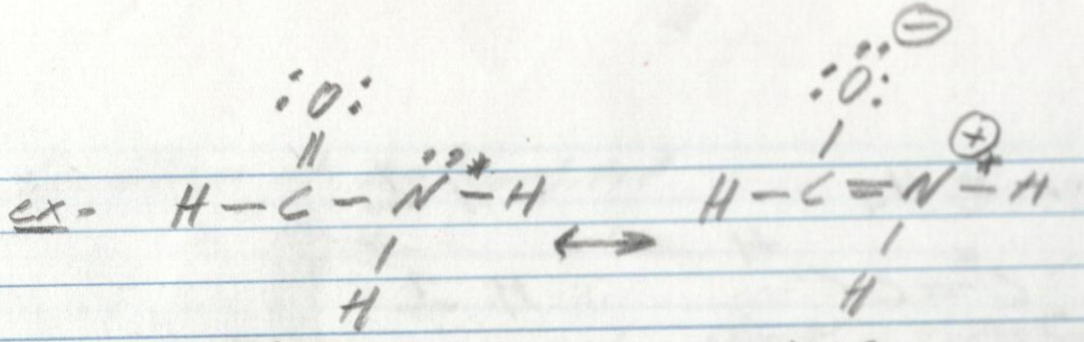
$\underset{s}{\underline{\uparrow\downarrow}}$ $\underline{\uparrow}$ $\underline{\uparrow}$ $\underline{\ \ }$ $\xrightarrow[\text{mix}]{}$ $\underset{sp}{\underline{\uparrow}}$ $\underset{sp}{\underline{\uparrow}}$ $\underset{p}{\underline{\uparrow}}$ $\underset{p}{\underline{\uparrow}}$

shape = sp is used for linear shape
& left over "p" orbitals are used for
the double and triple bonds



c. single bond — σ bond, formed from
pure or hybridized orbitals
double & triple — π bonds, formed from pure "p" orbitals only

ex-

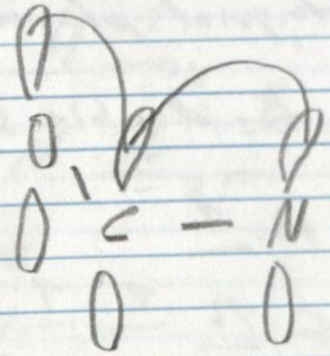


$$\mathrm{H{-}\overset{\overset{:\ddot{O}:}{\|}}{C}{-}\underset{\underset{H}{|}}{\ddot{N}^{*}}{-}H \longleftrightarrow H{-}\overset{\overset{:\ddot{O}:^{\ominus}}{|}}{C}{=}\underset{\underset{H}{|}}{N^{\oplus *}}{-}H}$$

major	minor
N steric # = 4	N steric # = 3
sp^3	sp^2

N must be sp^2 hybridized b/c N must have a pure p orbital to create the double bond

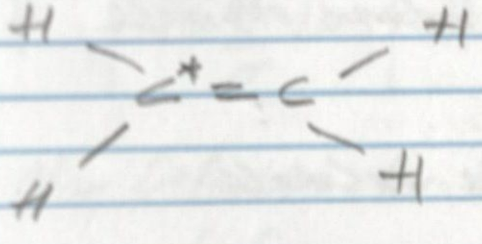
so, molecule is planar and e- are delocalized



Lecture Notes

1.22.23

VBT ex. H_2CCH_2

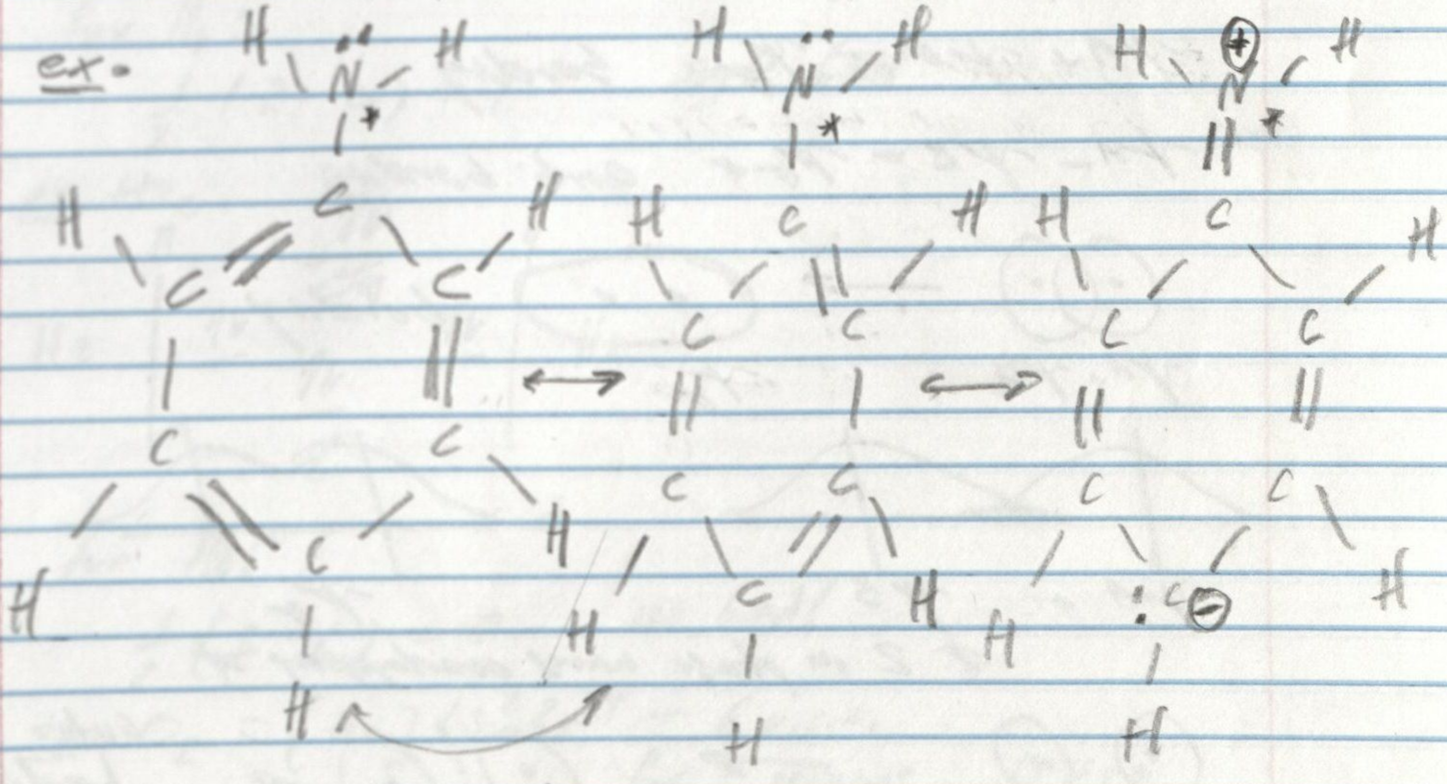


π: pi bonds

σ: sigma bond

steric #:	e^- geometry:	molec. geo:	hybridization
3	trig. planar	trig planar	$s+p+p \Rightarrow sp^2$

ex.



equivalent

minor

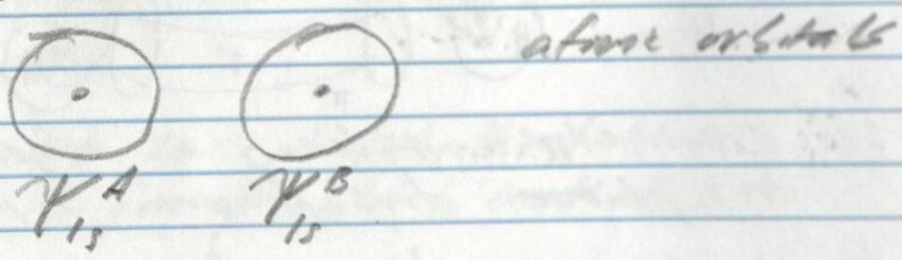
steric #:	e^- geo:	molec. geo:	hybridization
4 or <u>3</u> ↗	trig planar	trig. planar	sp^2

III. Molecular Orbital Theory: e^-'s are

A. delocalized over an orbital

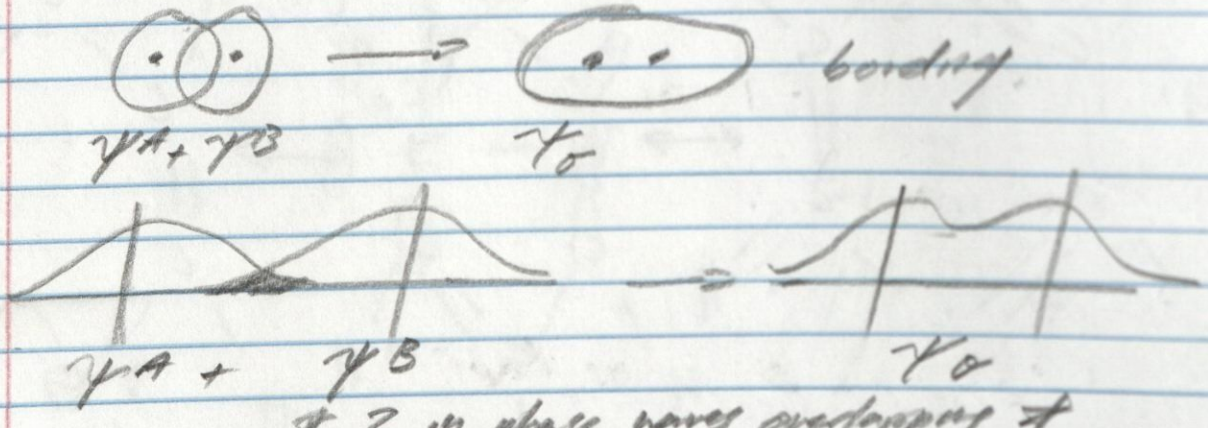
- mathematically, this arises from a linear combination of atomic orbitals

B.

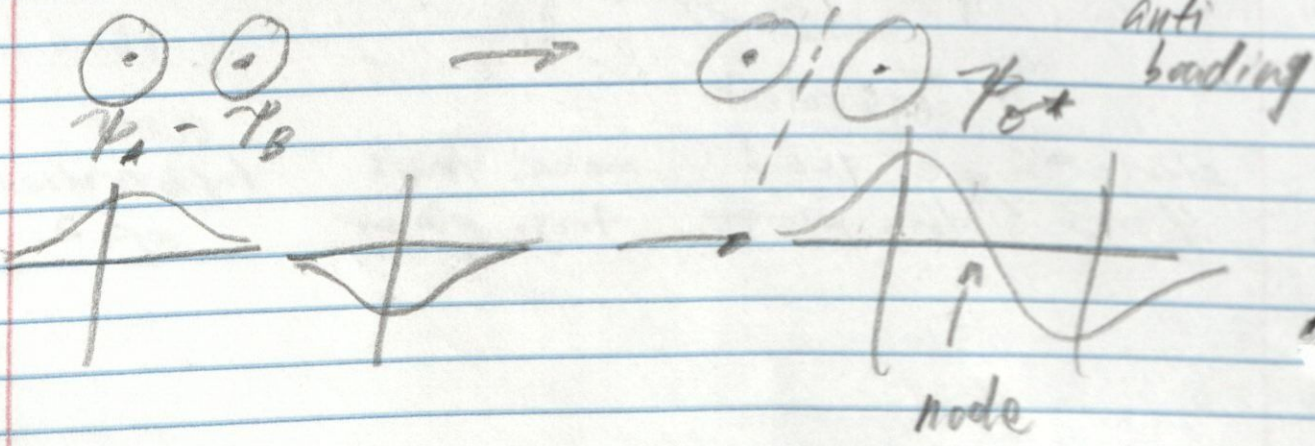


$\psi^A + \psi^B = \psi_\sigma$ bonding

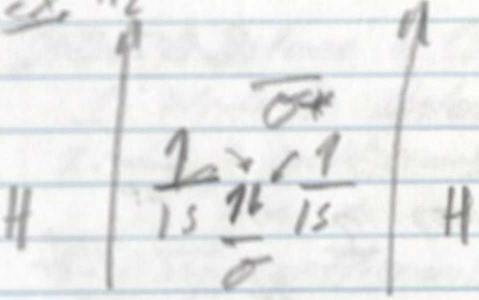
$\psi^A - \psi^B = \psi_{\sigma^*}$ anti bonding



* 2 in phase waves overlapping *



ex. H_2



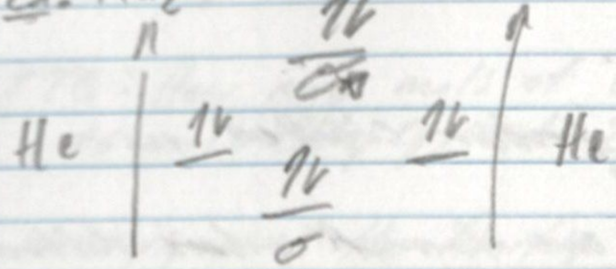
New Definition for Bond Order:

$$\frac{1}{2}(N_{bond} - N_{antibonding})$$

for H_2:

$\frac{1}{2}(2-0) = 1$ single bond

ex. He_2

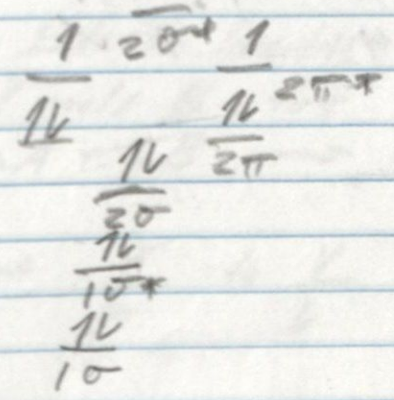


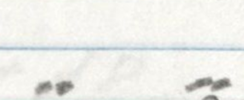
for He_2:

$\frac{1}{2}(2-2) = 0$ no bond!

ex. $O_2 = [He] 1s^2 2p^4$ – 6 v.s.e.

for 2 oxygens, 12 v.s.e.



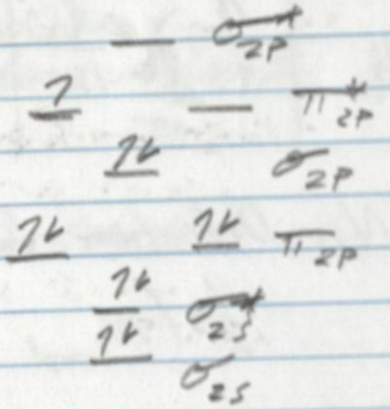


bond order: $\frac{1}{2}(8-4) = 2$

Lecture Notes

9.25.23

ex.
B.O. $N_2 = \frac{1}{2}(8-2) = 3$
triple bond



B.O. $N_2^{-1} = \frac{1}{2}(8-3) = 2.5$
between a double
& triple bond

I. Symbols
reactants → products
(g) gas (l) liquid (s) solid (aq) aqueous
Δ - heat

II. Lavosier - matter is neither created nor destroyed
Dalton - compounds are formed when different elements combine in fixed proportions

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

C	1	1	✓
H	4	~~2~~ 4	x ✓
O	~~2~~ 4	~~3~~ 4	x ✓

Steps to Balance a Chemical Equation:

1. Write the skeletal equation
2. Using coefficients, balance the atoms that are in complex compounds
3. Using coefficients, balance the atoms that occur as free elements last
4. Clear any fractions & use the smallest set of whole numbers
5. Varify

III. Reaction Stoichiometry

$$CH_4 (g) + 2O_2 (g) \rightarrow CO_2 (g) + 2H_2O (g)$$

1 mol CH_4 : 2 mols O_2 : 1 mol CO_2 : 2 mols H_2O

TTQ: How many mols of CO_2 are produced from 10 mols $CH_4 (g)$ and 2 mols $O_2 (g)$?

oxygen is the <u>limiting reagent</u>

given: 2 mols O_2, 10 mols CH_4

find: mols $CO_2 (g)$ produced

$$2 \text{ mols } O_2 (g) \times \frac{1 \text{ mols } CO_2}{\underset{\text{coefficients}}{2 \text{ mols } O_2}} = 1 \text{ mol } CO_2 \text{ produced}$$

How to find the limiting reagent given x mol A and y mols B for

$$aA + bB \longrightarrow cC + dD$$

compare $\frac{x}{a}$ to $\frac{y}{b}$, the smaller ratio being the limiting reagent ex. How many grams of $NH_3(g)$ can be produced from 86.3g $NO(g)$ and 25.6g $H_2(g)$?

$2NO(g) + 5H_2(g) \rightarrow 2NH_3(g) + 2H_2O(g)$

given: 86.3g NO, 25.6g $H_2(g)$

find: g $NH_3(g)$

1) Is the chemical equation balanced? YES!

2) Find the limiting reagant

$$86.3g\ NO(g) \cdot \frac{1mol\ NO(g)}{30.01g\ NO(g)} = 2.88 mol\ NO$$

$$25.6g\ H_2(g) \cdot \frac{1mol\ H_2(g)}{2.02g\ H_2(g)} = 12.7 mol\ H_2$$

$$\frac{2.88}{2} < \frac{12.7}{5}$$

$$\Rightarrow 1.44 < 2.54$$

NO is the limiting reagant

* Theoretical Yield

$$\underset{\text{coefficients}}{2.88 mol\ NO \cdot \frac{2mol\ NH_3}{2mol\ NO}} \cdot \underset{\text{molecular weight}}{\frac{17.03g\ NH_3}{1mol\ NH_3}} = 49.05g\ NH_3$$

Calculate how much H_2 is left.

$$2.88\text{ mol } NO_2 \cdot \frac{5\text{ mol } H_2}{2\text{ mol } NO_2} \cdot \frac{2.02\text{g } H_2}{1\text{ mol } H_2} = 14.5\text{ g } H_2$$ is consumed

$25.6\text{g } H_2 - 14.5\text{g } H_2 = 11.1\text{g } H_2$ gas in excess

Someone does the reaction and the
<u>actual yield</u> is 40.2g

$$\frac{40.2\text{g}}{49.05\text{g}} \times 100\% = 81.96\%$$

percent yield

Lecture Notes 9.27.23

I. Definitions

Solutions - ions or molecules that are mixed and have the same composition throughout the substance

Solvent - major component of a solution

Solute - minor component of a solution

$$\text{Concentration} = \frac{\text{amount of solute}}{\text{amount of solvent}}$$

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{liters (L) of solvent}} = (M)$$

II. Molarity Calculations (M)

TTQ. what is the molarity of a solution that contains 3.0 g of NaCl in 100 mL of water?

given: 3.0 g NaCl, 100 mL H_2O

find: ____ mol NaCl / L H_2O

$$3.0\,g\,NaCl \cdot \frac{1\,mol\,NaCl}{58.44\,g\,NaCl} \cdot \frac{1}{100\,mL\,H_2O} \cdot \frac{10^3\,mL\,H_2O}{L\,H_2O}$$

$= 0.513M$ ↑ M.W. conv. factor ↑

III - Dilutions

Stock solution - concentrated form of a solution

$$M_1 V_1 = M_2 V_2$$

concentration of initial soln

volume of initial soln

concentration and volume of diluted soln

$$\left(\frac{mol\,A}{\cancel{L}}\right)\left(\cancel{L}\right) = \left(\frac{mol\,A}{\cancel{L}}\right)\left(\cancel{L}\right)$$

$$mol_A = mol_A$$

TTQ. How many mols of sucrose are in 250 mL of 0.750 M solution of sucrose in water?

given: 0.250 L soln, 0.750 mol sucrose / L soln

$\frac{0.750 \text{ mol sucrose}}{}$

II. Stoichiometry of Solutions

TTQ. How many moles of Cl^- ions are in 2.00 L of a 2.5 M solution of $MgCl_2$

given: 2.00 L soln, 2.5 M $MgCl_2$

$$MgCl_2(aq) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$$

find: mols Cl^-

$$\frac{2.5 \text{ mol } MgCl_2}{1 \text{ L soln}} \cdot 2 \text{ L soln} \cdot \frac{2 \text{ mol } Cl^-}{1 \text{ mol } MgCl_2} = 10 \text{ mol } Cl^-$$

TTQ. A sample of 20.5 mg K_3PO_4 is added to 15.0 mL of 0.050 M $AgNO_3(aq)$ to form $Ag_3PO_4(s)$. What is the theoretical yield of $Ag_3PO_4(s)$ in mg? given: 70.5 mg KPO_4

0.050 M $AgNO_3(aq)$ in 15.0 mL

reactants

find: ___ mol $Ag_3PO_4(s)$ produced

all (aq) except (s)

known: $K_3PO_4(s) \rightarrow 3K^+(aq) + PO_4^{3-}(aq)$

$AgNO_3(aq) \rightarrow Ag^+(aq) + NO_3^-(aq)$

$\hookrightarrow 3K^+ + PO_4^{3-} + Ag^+ + NO_3^- \longrightarrow AgPO_4(s) + 3K^+ + NO_3^-$

① $3Ag^+(aq) + PO_4^{3-}(aq) \rightarrow Ag_3PO_4(s) \leftarrow$ net ionic eqn

② Determine the limiting reagent

$70.5\,mg\,K_3PO_4 \cdot \frac{1g\,K_3PO_4}{10^3 mg\,K_3PO_4} \cdot \frac{1mol\,K_3PO_4}{212.27g\,K_3PO_4} \cdot \frac{1mol\,PO_4^{3-}}{1mol\,K_3PO_4}$

$= 0.000332\ mol\ PO_4^{3-}$
$= 0.332\ mmol\ PO_4^{3-}$

$\frac{0.050\,mol\,AgNO_3}{1\,L\,soln} \cdot 0.015L\,soln \cdot \frac{1mol\,Ag^+}{1mol\,AgNO_3}$

$= 0.75\,mmol\,Ag^+$

$\frac{0.332\,mmol\,PO_4^{3-}}{1} > \frac{0.75\,mmol\,Ag^+}{3}$

$0.332 > 0.25 \rightarrow Ag^-$ is the L.R. 1)

$0.75\,mmol\,Ag^+ \cdot \frac{1mmol\,Ag_3PO_4}{3\,mmol\,Ag^+} = 0.25\,mmol\,Ag_3PO_4$

$0.25\,mmol\,Ag_3PO_4 \cdot \frac{418.58\,mg\,Ag_3PO_4}{1\,mmol\,Ag_3PO_4} = 104.645\ mg\ Ag_3PO_4\,(s)$

Review TTQ: What are the major and minor structures of NO_3^-

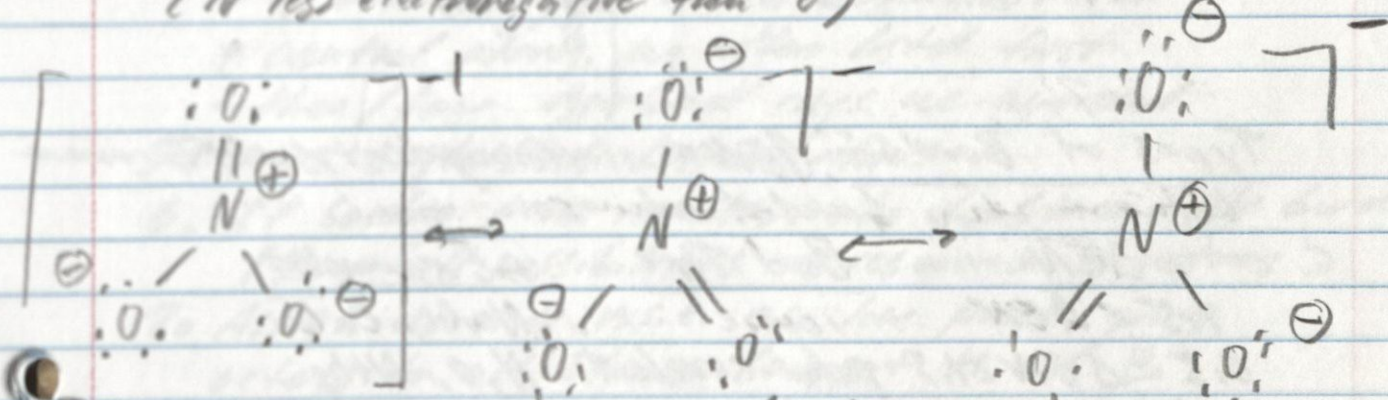
1) v.s.e. $5(1) + 6(3) + 1 = 24$ v.s.e

2) octet $8(1) + 8(3) = 32$

3) $32 - 24 = 8$ bonding e^-, 4 bonds

$24 - 8 = 16$ bonding e^-, 8 lone pairs

(N less electronegative than O)



3 equivalent structures, so quantitative bond order

What is N−O bond order?

$BO = \frac{1}{3}(2+1+1) = \frac{4}{3}$ or $1\frac{1}{3}$

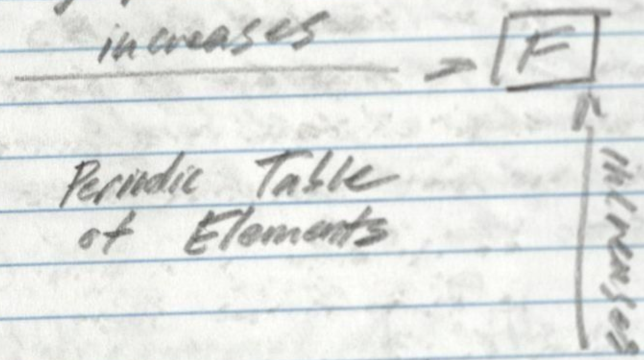
What is the hybridization? $s+p+p = sp^2$

What is molecular shape? trig. planar

nonpolar

Independent Notes / Exam 2 9.28.23

Electronegativity: a scale 0.0–4.0 of e^- pulling power of an atom



Types of Bonds: ΔEN = electronegativity difference between two bonded atoms

ΔEN	Bond Type	Examples
$1.5 < \Delta EN$	ionic	NaCl, CaO
$0.5 < \Delta EN < 1.5$	polar covalent	H_2O, NH_3
$\Delta EN < 0.5$	nonpolar covalent	CH_4, C_6H_6

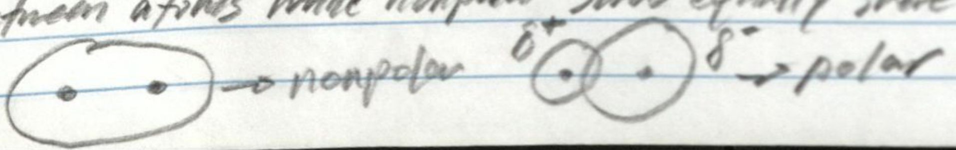
Ionic Bonds: $\Delta EN > 1.5$

- involves a transfer of electrons
- * – usually between a nonmetal and metal
- formulas show lowest ratio of atoms present
- * – sum of charges must be zero overall
  - NaCl, Li_2O, BaI_2, Al_2O_3

Covalent Bonds: $\Delta EN < 1.5$

- involves a sharing of electrons
- atomic orbitals overlap to form molecular orbitals
- usually between nonmetals
- can use many types of formulas
  - empirical: lowest ratio, CH_2
  - molecular: actual number, C_3H_6
  - structural: shows connectivity

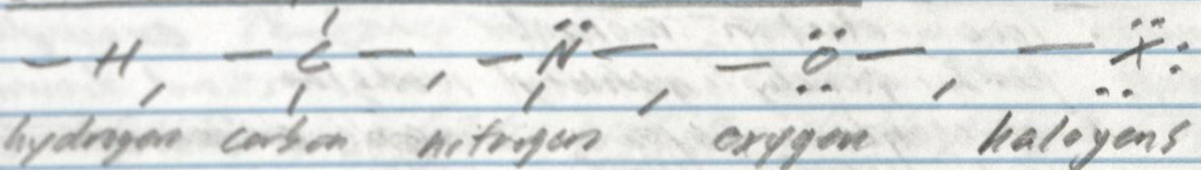
* polar bonds result when e^-'s are unequally shared between atoms while nonpolar bonds equally share e^-'s *



How to Draw Lewis Structures:

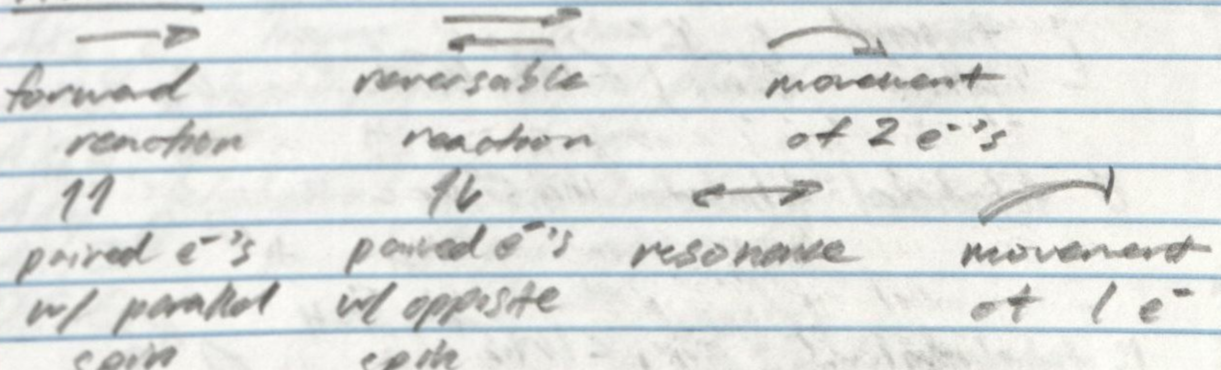
1. Determine number of v.s.e. (± for ions)
2. calculate number of e^-'s needed for octet
   (or duplet for H or hextet for B)
3. subtract 1. from 2. → number of bonding e^-'s
4. Write down most likely skeletal arrangement:
   - central atoms are least electronegative
   - H and halogens are usually terminal
   - central atoms are often listed first
   - three/four membered rings are avoided
5. Place single bonds between atoms
6. If bonding pairs remain, make double or triple bonds
   (keep all possibilities → resonance structures)
7. Assign remaining v.s.e. as lone pairs, giving
   octets to all atoms (except H and B)

Covalent Compound Common Formations:



* Remember Common Functional Groups on
Formula Sheet *

Arrows:



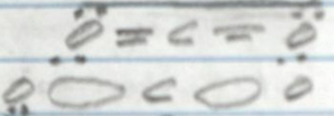
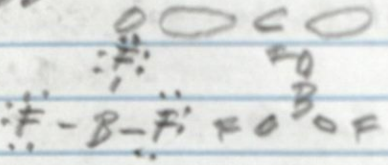
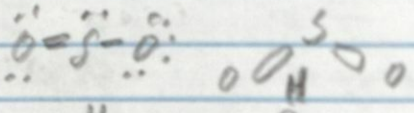
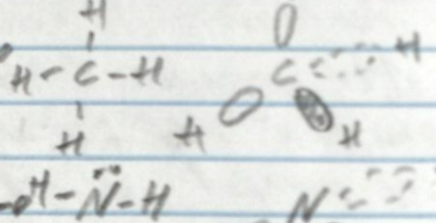
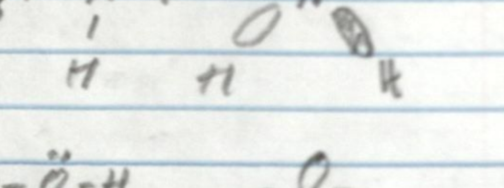
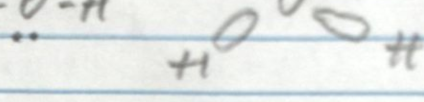
Bond Order: depends on whether there is a single (1), double (2), or triple (3) bond between 2 atoms, and is the weighted average of all resonance structures
— described quantitatively ad qualitatively

Formal Charge: gives information on the most stable resonance structure (major structure)
formula in formula sheet
1. All atoms obey octet rule
2. Formal charges should be minimized
3. Formal charges should correlate with relative electronegativity

Steric Number: helps predict molecular shape

$$\text{steric number} = \sum \text{bonding groups} + \text{lone pairs}$$

Electron ad Molecular Geometry:

electron groups	bonding groups	lone pairs	electron geometry	molecular geometry	~ bond angles	example ad drawing
2 [sp]	2	0	linear	linear	180°	
3 [sp^2]	3	0	trigonal planar	trigonal planar	120°	
3	2	1	trigonal planar	bent	<120°	
4 [sp^3]	4	0	tetrahedral	tetrahedral	109.5°	
4	3	1	tetrahedral	trigonal pyramidal	<109.5	
4	2	2	tetrahedral	bent	<109.5°	

electron geometry: e^- arrangement around a central atom
molecular geometry: atom arrangement around a central atom
dipole moment: shows a difference in electronegativity

$\underset{\delta^+ \qquad \delta^-}{+\!\!\!\longrightarrow}$

δ^+ : slightly positive
δ^- : slightly negative

Molecular Polarity: for a molecule to be polar, it must have a net dipole moment

Valence Bond Theory: considers the overlap between two half filled atomic orbitals as a chemical bond

Hybridization: "mixes" half filled atomic orbitals (s, p, d, f) & creates new orbitals (sp, sp^2, sp^3) that can be completely filled. ex.

$$\underset{2s}{\underline{\uparrow\downarrow}}\ \underset{2p}{\underline{\ \uparrow\ }}\ \underset{2p}{\underline{\ \uparrow\ }}\ \underset{2p}{\underline{\quad}} \longrightarrow \underset{sp^3}{\underline{\ \uparrow\ }}\ \underset{sp^3}{\underline{\ \uparrow\ }}\ \underset{sp^3}{\underline{\ \uparrow\ }}\ \underset{sp^3}{\underline{\ \uparrow\ }}$$

* makes VBT consistent w/ experimental data *

$$\underset{2s}{\underline{\uparrow\downarrow}}\ \underset{2p}{\underline{\ \uparrow\ }}\ \underset{2p}{\underline{\ \uparrow\ }}\ \underset{2p}{\underline{\quad}} \longrightarrow \underset{sp}{\underline{\ \uparrow\ }}\ \underset{sp}{\underline{\ \uparrow\ }}\ \underset{p}{\underline{\ \uparrow\ }}\ \underset{p}{\underline{\ \uparrow\ }}$$

* leftover p orbitals used for double & triple bonds *

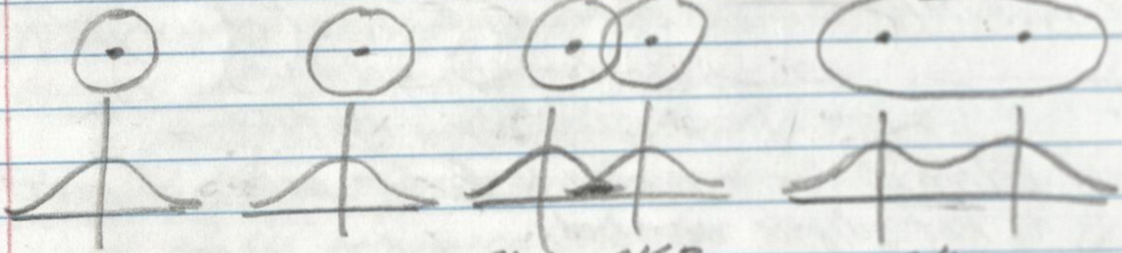
Summary of Shapes:

General Formula	Electron Geometry	Molecular Shape	Hybridizations
AX_2	linear	linear	sp
AX_3	trigonal planar	trigonal planer	sp^2
AX_2E		bent	
AX_4	tetrahedral	tetrahedral	sp^3
AX_3E		trigonal pyramidal	
AX_2E_2		bent	

sp^x hybridization:

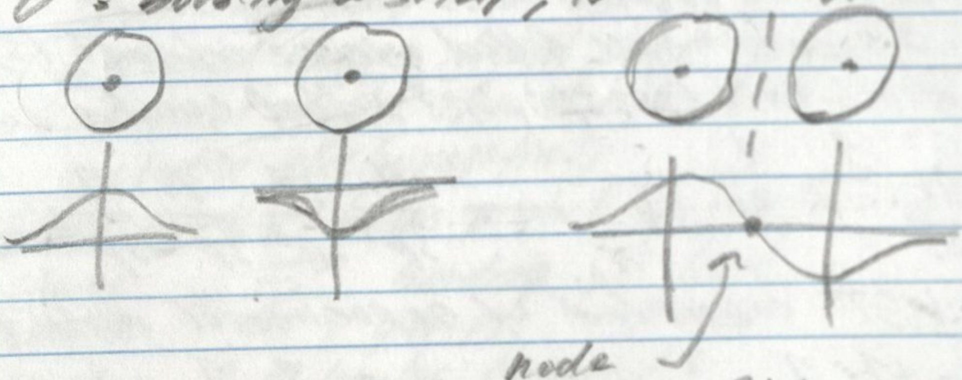
A – central atom
X – bonded atoms
E – lone pair electrons

<u>Molecular Orbit Theory</u>: e^-'s are delocalized over an atom, resulting in molecular orbitals



$\psi_A + \psi_B = \psi_A + \psi_B = \psi_\sigma$

σ: bonding orbital, lower energy



$\psi_A - \psi_B \longrightarrow \psi_{\sigma^*}$

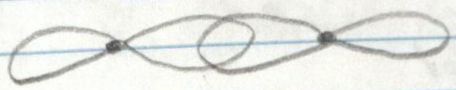
σ^*: antibonding orbital, higher energy

* same concept for π and π^* bonds *

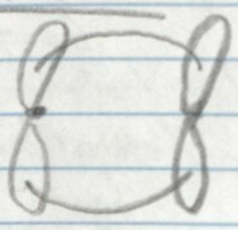
* Sigma bonds formed through head-to-head overlap between pure or hybridized orbitals *

* pi bonds are formed by side-to-side overlap between pure p orbitals <u>only</u> *

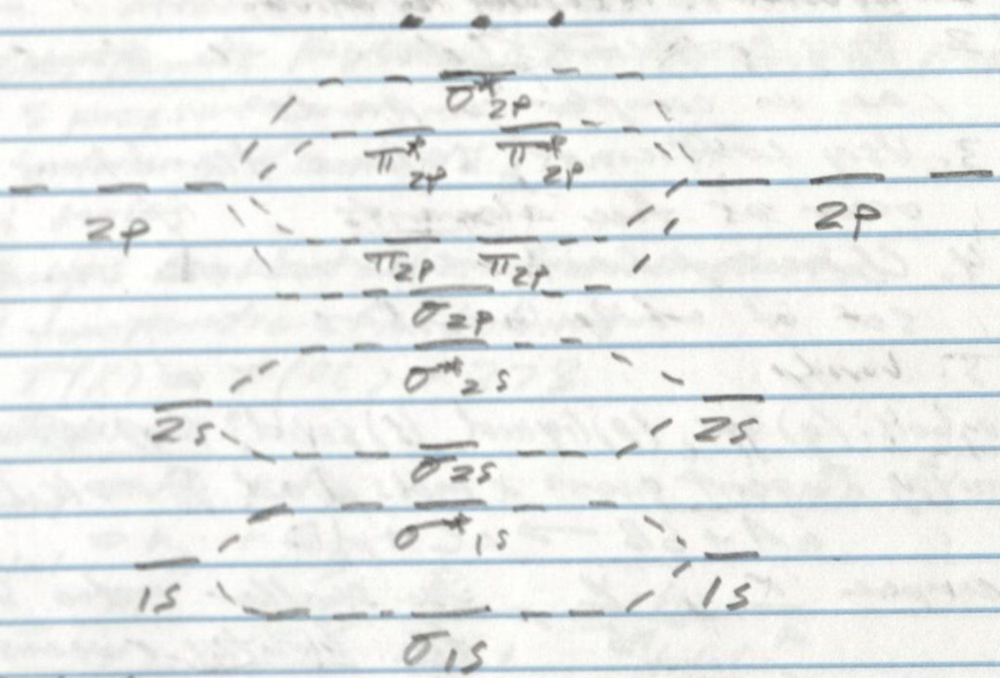
<u>Sigma Bonds</u>:



<u>Pi Bonds</u>:



Molecular Orbital Diagrams:

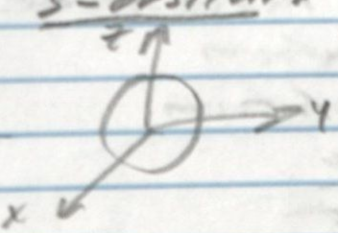


Bond Order:

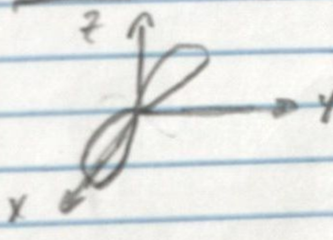
$$BO = \frac{1}{2}\left(N_{\text{bonding } e^-\text{'s}} - N_{\text{antibonding } e^-\text{'s}}\right)$$

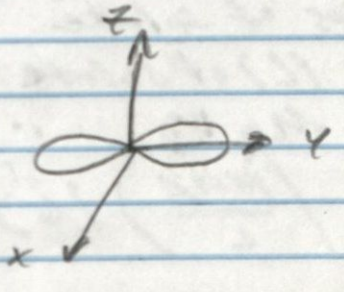
Atomic Orbitals:

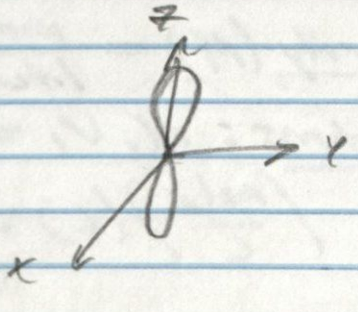
s-orbitals:



p-orbitals:







Steps to Balancing a Chemical Equation:

1. Write the skeletal equation
2. Using coefficients, balance the atoms that are in complex compounds
3. Using coefficients, balance the atoms that occur as free elements
4. Clear any fractions and use the smallest set of whole numbers
5. Verify

Symbols: (g) gas, (l) liquid, (s) solid, (aq) aqueous, (Δ) heat

Limiting Reagent given x mols A and y mols B for

$$aA + bB \rightarrow cC + dD$$

compare $\frac{x}{a}$ to $\frac{y}{b}$, the smaller ratio being the **limiting reagent**

Theoretical Yield is given from chemical equations

Actual Yield is found experimentally

$$\text{Percent Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \cdot 100\%$$

Solutions: ions or molecules that are mixed and have the same composition throughout the substance

Solvent: major component of a solution

Solute: minor component of a solution

$$\text{Concentration} = \frac{\text{amount of solute}}{\text{amount of solvent}}$$

$$\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{liters (L) of solute}}$$

Dilutions: $M_1V_1 = M_2V_2$

$$\left(\frac{\text{mol A}}{L}\right)(L) = \left(\frac{\text{mol A}}{L}\right)(L)$$

Pressure $= \frac{\text{Force}}{\text{Area}}$ → atm (atmospheric units)

Ideal Gas Law: $PV = nRT$ (on formula sheet)

P: pressure
V: volume (in liters)
n: moles
R: gas constant (on formula sheet)
T: temperature (in Kelvin)

$$T(K) = T(^\circ C) + 273$$

Partial Pressures:

$$P_{total} = P_A + P_B$$

$$n_{total} = n_A + n_B$$

$$X_i = \frac{n_i}{n_{total}} \Rightarrow \frac{P_i}{P_{total}} = \frac{n_i}{n_{total}}$$

1 atm = 760 mm Hg
1 atm = 101.3 kPa

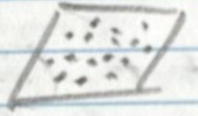
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Independent Notes / Missed Lecture 10.2.23

I. Pressure $= \frac{\text{Force}}{\text{Area}}$

- results from the collisions of gases on the surface of a box


low p


high p

II. Gas Laws

A. Variables: P — pressure
V — volume
n — moles
R — gas constant
T — temperature (K)

B. Gas Constant: $R = 0.0821 \frac{L \cdot atm}{mol \cdot K}$

C. Many units for pressure (conversions provided)

D. Discoveries:
- Charles $V \propto T$
- Avogadro $n \propto V$
- Boyle $V \propto 1/P$
- Gay-Lussac $T \propto P$

Ideal Gas Law → $PV = nRT$

For Gases w/ Ideal Behaviors:
- Gas particles have negligible volume
- Gas particles are equally sized
- There are no intermolecular forces
(sufficiently low pressure and high temperature)
- Gas particles move randomly

TTQ: $2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$. If a 36L airbag must reach a pressure of 1.15 atm at 23°C, how many grams of NaN_3 are needed?

given: $V = 36L$, $P = 1.15\,atm$, $T = 23 + 273 = 296K$

find: ___ g NaN_3

$$PV = nRT \implies n = \frac{PV}{RT}$$

$$n = \frac{(1.15\,atm)(36L)}{(0.0821\,L\cdot atm/mol\cdot K)(296K)} = 1.70\,mol\ gas$$

$$2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$$

$$1.70\,mol\ N_2(g) \cdot \frac{2\,mol\ NaN_3(s)}{3\,mol\ N_2(g)} \cdot \frac{65.01\,g\ NaN_3}{1\,mol\ NaN_3} = 73.678\,g\ NaN_3$$

III. Partial Pressure: in a mixture of gases, each gas exerts its own pressure that is independent of other gases

$$P_{total} = P_A + P_B$$

just as $n_{total} = n_A + n_B$

so, you can calculate the mol ratio as:

$$x_i = \frac{n_i}{n_{total}}$$

then use the mol ratio to calculate the pressure ratio:

$$\frac{P_i}{P_{total}} = \frac{n_i}{n_{total}}$$

TTQ. There is a mixture of 4 moles of $H_2(g)$, 8 moles of $O_2(g)$, 12 moles of He(g), and 6 moles of $N_2(g)$ in a closed container. What is the total number of moles of gas in that system?

$$\overset{H_2}{4} + \overset{O_2}{8} + \overset{He}{12} + \overset{N_2}{6} = 30 \text{ moles of gas total}$$

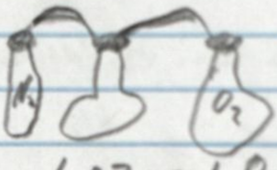
TTQ. If there is a mixture of H_2 and O_2 gas in a container w/ 10 moles total and the mole ratio of hydrogen is .67 mol H_2 to 1 mol total gas, how many moles of each gas are there?

$$\frac{0.67 \text{ mol } H_2}{1 \text{ mol total}} \cdot 10 \text{ mol total} = 6.7 \text{ mol } H_2$$

$$10 \text{ mol total} - 6.7 \text{ mol } H_2 = 3.3 \text{ mol } O_2$$

TTQ. 24.0L of $N_2(g)$ at 2 atm and 12.0L of $O_2(g)$ at 2 atm are added to a 10L container at 273K. Find the partial pressures of $N_2(g)$, $O_2(g)$, and the total pressure of gas.

given: 24.0L N_2, 2 atm , T = 273K
12.0L O_2, 2 atm
(final) V = 10L
find: P_{O_2} & P_{N_2} & P_{total}



$$n_{O_2} = \frac{PV}{RT} = \frac{(2.0 \text{ atm})(12.0 L)}{(.082 \, L \cdot atm/mol \cdot K)(273 K)} = 1.07 \text{ mol } O_2$$

$$n_{N_2} = \frac{PV}{RT} = \frac{(2.0 \text{ atm})(24.0 L)}{.082 \, L \cdot atm/mol \cdot K)(273 K)} = 2.14 \text{ mol } N_2$$

$$n_{total} = 1.07 \text{ mol} + 2.14 \text{ mol} = 3.21 \text{ mols}$$

$$P_{total} = \frac{nRT}{V} = \frac{(3.21 \text{ mol})(.082 \, L \cdot atm/mol \cdot K)(273 K)}{10.0 L} = 7.22 \text{ atm}$$

$$P_{O_2} = (7.22 \text{ atm})\left(\frac{1.07 \text{ mol}}{3.21 \text{ mol}}\right) = 2.41 \text{ atm}$$

$$P_{N_2} = 7.22 \text{ atm} - 2.41 \text{ atm} = 4.81 \text{ atm}$$

Independent Notes / Missed Lecture 10.3.23

I. Reactions are reversible

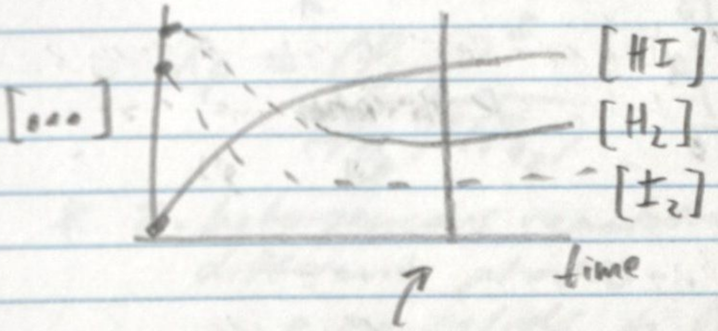
ex. Hemoglobin binding w/ oxygen

$$Hb + O_2(g) \underset{tissues}{\overset{lungs}{\rightleftharpoons}} HbO_2$$

* dynamic equilibrium: rate of forward reaction = rate of reverse reaction

* At equilibrium, the concentrations of all species are stable, but the forward & reverse reactions are happening *

ex. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$



* when the reaction reached equilibrium

* II. Equilibrium Constant (K) = quantifies
the relative amounts of reactants and products

A. About K
1. K has same value regardless of initial concentrations
2. K has no units
3. K is also written as K_{eq}, K_c, K_p

for a gaseous reactions:

$$aA(g) + bB(g) \rightarrow cC(g) + dD(g)$$

* $K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ $[\ldots]$ in $\frac{M}{*}$

* $K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$ P in $\frac{atm}{*}$

* $K_c \neq K_p$

* 4. $K = \frac{\text{products}}{\text{reactants}}$

- if $K >> 1$ forward reaction is favored
products are favored

- if $K << 1$ reverse reaction is favored
reactants are favored

- if $K = 1$ neither direction is favored

Lecture Notes 10.4.23

III. Writing and Using Equilibrium Constants

A. Homogeneous vs. heterogeneous reaction

* 1. Homogeneous reactions — all reactants and products in the same phase (state)

* • all reagents appear in K

ex: $CH_3CO_2CH_2CH_3(l) + H_2O(l) \rightleftharpoons CH_3CO_2H(l) + CH_3CH_2OH(l)$

$$K = \frac{[CH_3CO_2H][CH_3CH_2OH]}{[CH_3CO_2CH_2CH_3][H_2O]}$$

ex: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$K_p = \frac{(P_{SO_3})^2}{(P_{SO_2})^2(P_{O_2})}$$

* 2. heterogeneous reactions — reagents in different phases

- no solids in K
- * • pure water is <u>not</u> in K (in liquid phase)
- no spectator ions

ex: $H_2O(g) + C(s) \rightleftharpoons H_2(g) + CO(g)$

$$K_p = \frac{(P_{H_2})(P_{CO})}{P_{H_2O}}$$

ex. $Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$

$$K_c = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$$

ex. $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$

$$K_p = \frac{(P_{NOCl})^2}{(P_{NO})^2(P_{Cl_2})}$$

ex. $H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)$

$$K_c = \frac{1}{[OH^-][H_3O^+]}$$

← could be H^+

ex. $SnO_2(s) + 2CO(g) \rightleftharpoons Sn(s) + 2CO_2(g)$

$$K_p = \frac{(P_{CO_2})^2}{(P_{CO})^2}$$

TTQ. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (on slides)

$$K_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3} = \frac{(1.66)^2}{(2.46)(7.38)^3} = 7.59 \cdot 10^{-5}$$

$K_p << 1$ reverse is favored
reactants are favored

I. Manipulating Keq

* A. K depends on a balanced equation

$A \rightleftarrows B$ $\qquad K_1 = \frac{[B]}{[A]}$

if $A \rightleftarrows 2B$ $\qquad K_2 = \frac{[B]^2}{[A]}$

notice $K_1 \neq K_2$

B. Multiplied by a factor

$A + B \rightleftarrows C + D$ $\qquad K_1 = \frac{[C][D]}{[A][B]}$

$nA + nB \rightleftarrows nC + nD$ $\qquad K_2 = \frac{[C]^n[D]^n}{[A]^n[B]^n}$

C. Reverse the reactions $\qquad$ * $K_2 = (K_1)^n$

$A + B \rightleftarrows C + D$ $\qquad K_1 = \frac{[C][D]}{[A][B]}$

$C + D \rightleftarrows A + B$ * $K_2 = \frac{[A][B]}{[C][D]} = \frac{1}{K_1}$

D. Sequential Reactions

$\cancel{A} + B \rightleftarrows \cancel{C} + D$ $\qquad K_1$

$\cancel{C} + F \rightleftarrows G + \cancel{A}$ $\qquad K_2$

=> $B + F \rightleftarrows D + G$ $\qquad$ * $K_3 = (K_1)(K_2)$

* II. Reaction Quotient (Q) — used at any point in the reaction to gauge the progress of a reaction relative to equilibrium

$aA + bB \rightleftharpoons cC + dD$

* $Q = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

ex. Studying the following reaction at 3 conditions. $K_c = 50$ (given)

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

condition 1: $[H_2]_i = 0.50M$, $[HI]_i = 0M$
$[I_2]_i = 0.50M$

$Q = \dfrac{0}{(0.5)(0.5)} = 0$ * $Q << K$
rxn favors products
rxn goes right
forward reaction favored

condition 2: $[H_2]_i = [I_2]_i = 0$ $[HI]_i = 0.50$

$Q = \dfrac{(0.50)^2}{0} \rightarrow \infty$ * $Q >> K$
rxn favors the reactants
rxn goes left
rxn goes to reactants

condition 3: $[H_2]_i = [I_2]_i = [HI]_i = 0.5$

$Q = \dfrac{(0.5)^2}{(0.5)(0.5)} = 1$ * $Q << K$
rxn goes right

* If $Q = K$, rxn is at equilibrium

VI - Using ICE Tables

given: $2CH_4(g) \rightleftharpoons C_2H_2(g) + 3H_2(g)$

given: $[CH_4]_i = 0.115M$, $[C_2H_2]_i = [H_2]_i = 0M$

$[C_2H_2]_{eq} = 0.035M$

find K:

	$2CH_4(g)$	$\rightleftharpoons C_2H_2(g)$	$+ 3H_2(g)$
Initial:	0.115M	0	0
Change:	$-2(0.035M)$	$+0.035M$	$+3(0.035M)$
Equilibrium:	0.045M	0.035M	0.105M

STEP 1: realize 0.035M C_2H_2 is the change

STEP 2: determine the other changes

STEP 3: determine the equilibrium concentrations

STEP 4: plug into K expression

$$K = \frac{(0.035)(0.105)^3}{(0.045)^2} = 0.02$$

Lecture Notes 10.6.23

HW 18 Q 8/9

$I_2(g) + Cl_2(g) \rightleftharpoons 2ICl(g)$, $K_p = 81.9$

given: $P(I_2)_i = P(Cl_2)_i = 0.130$ atm

find: P_{eq} of all reagents

	$I_2(g)$ +	$Cl_2(g)$	$\rightleftharpoons 2ICl(g)$
I	0.130	0.130	0
C	$-x$	$-x$	$+2x$
E	$(0.130-x)+$	$(0.130-x)$	$2x$

$$K_p = \frac{(2x)^2}{(0.130-x)(0.130-x)} = \frac{(P_{ICl})^2}{(P_{I_2})(P_{Cl_2})}$$

$$K_p = \frac{(2x)^2}{(0.130-x)^2} \Rightarrow \sqrt{K_p} = \sqrt{\frac{(2x)^2}{(0.130-x)^2}}$$

solve for x b/c we know K_p

$$(9.05)(0.130-x) = 2x$$

$$1.176 - 9.05x = 2x$$

$$1.176 = 11.05x$$

$$0.106 = x$$

$P_{I_2} = P_{Cl_2} = (0.130 - x) = 0.024$

$P_{ICl} = 2x = 0.213$

14a: Given: $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$

$K_c = 1.67 \cdot 10^{-7}$ @ 800 °C

note K_c is very small

$[H_2S]_i = 0.025M$, $[H_2] = [S_2] = 0$

find the concentrations at equilibrium

	$2H_2S(g)$	$\rightleftharpoons$ $2H_2(g)$	+ $S_2(g)$
I	0.025	0	0
C	$-2x$	$+2x$	$+x$
E	$(0.025-2x)$	$2x$ +	x

$$K = \frac{(2x)^2(x)}{(0.025-2x)^2} = \frac{4x^3}{(0.025-2x)^2}$$

* Since K_c is probably << 0.025 (in denominator) we can disregard the x in denominator

if $2x$ is very small

$$\Rightarrow K_c = \frac{(2x)^2 x}{(0.025)^2} \rightarrow x = 2.97 \cdot 10^{-4}$$

to check if approximation is good

$$\frac{x}{0.025} = \frac{2.97 \cdot 10^{-4}}{0.025} \cdot 100\% = 1.9\%$$

* if % ERROR < 5%, approximation is good

$[H_2S]_{eq} = 0.025 - 2(2.97 \cdot 10^{-4}) = 2.44 \cdot 10^{-2} M$

$[H_2]_{eq} = 2(2.97 \cdot 10^{-4}) = 5.94 \cdot 10^{-4} M$

$[S_2]_{eq} = 2.97 \cdot 10^{-4} M$

$$K_c = \frac{(5.94 \cdot 10^{-4})^2 (2.97 \cdot 10^{-4})}{(2.44 \cdot 10^{-2})^2} = 1.67 \cdot 10^{-7}$$ ✓

TTQ: Given: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

brown ↑ ↖ colorless

$[NO_2]_i = 0.1M$, $K_c = 0.36$ @ 100°C

Find: $[N_2O_4]_{eq}$ and $[NO_2]_{eq}$

$N_2O_4 \rightleftharpoons 2NO_2$

	N_2O_4	$2NO_2$
I	0	0.1
C	+x	-2x
E	x	0.1-2x

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.1-2x)^2}{x}$$

if approx & ignored 2x:

$$0.36 = \frac{(0.1)^2}{x} \Rightarrow x = 0.027$$

check approx:

$$\frac{0.027}{0.1} \times 100\% = 27\% > 5\%$$

$$K_c = \frac{(0.1-2x)^2}{x} = 0.36$$

$$4x^2 - 0.7x + 0.01 = 0$$

$$x = 0.176 \text{ or } 0.014$$

↑

* this would result in a negative concentration

$x = 0.014$

$[N_2O_4]_{eq} = 0.014$

$[NO_2]_{eq} = 0.1 - 2(0.014) = 0.072M$

Lecture Notes / Le Châtelier's Principle 10.9.23

Le Châtelier's Principle: when a chemical system at equilibrium is disturbed, the reaction shifts in the direction that minimizes the disturbance

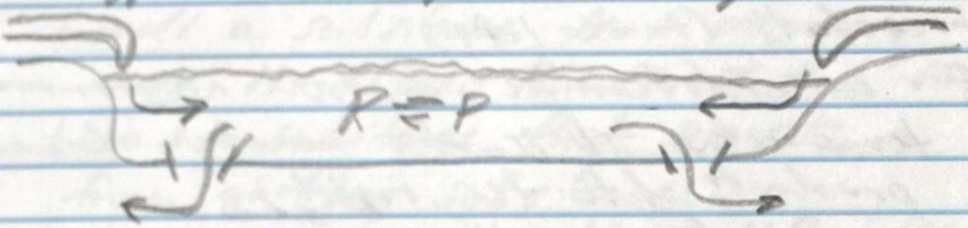
I. Changes in concentrations

$R \rightleftharpoons P$

A. adding reactants or removing products shifts the rxn towards the products (right)

B. adding products or removing reactants shifts the rxn towards the reactants (left)

An analogy: a tub w/ 2 faucets & 2 drains



II. Changing Pressure on Gaseous Reactions

$$\underbrace{N_2(g) + 3H_2(g)}_{4\text{mols}} \rightleftharpoons \underbrace{2NH_3(g)}_{2\text{mols}}$$

1) As you increase the pressure, the reaction shifts towards the side with the lower number of moles of gas

2) As you decrease the pressure, the reaction shifts towards the side with the larger number of moles of gas

3) If the number of moles is equal on both sides, changing pressure does not shift the reaction

4) Adding an inert gas does not shift the equilibrium

III. Changing the temperature of a reaction

exothermic: produces heat

$$R \rightleftharpoons P + \text{heat}$$

endothermic: consumes heat

$$\text{heat} + R \rightleftharpoons P$$

1) For an exothermic reaction, an increase in temperature shifts the reaction towards the reactants (to the left)
2) For an exothermic reaction, a decrease in temperature shifts the reaction towards the products (to the right)
3) For an endothermic reaction, a decrease in temperature shifts the reaction towards the reactants (to the left)
4) For an endothermic reaction an increase in temperature shifts the reaction towards the products (to the right)

II Demo: $\text{heat} + \underset{\substack{\nearrow \\ \text{color-less}}}{N_2O_4(g)} \rightleftharpoons 2\underset{\substack{\uparrow \\ \text{brown}}}{NO_2(g)}$

cold solution: light brown

hot solution: dark brown

Acids and Bases Definitions:

I. Arrhenious Definition

acid: a substance that when dissolved in H_2O increase the $[H^+]$ ($[H_3O^+]$)

ex. $H{-}Cl(g) \xrightarrow[H_2O]{} H^+(aq) + Cl^-(aq)$

$\uparrow$

covalent bond is broken

base: a substance that when dissolved in H_2O increases the $[OH^-]$

ex. $NaOH(s) \xrightarrow[H_2O]{} Na^+(aq) + OH^-(aq)$

* this does not explain $NH_3(g)$ *

II. Brønsted-Lowry Definition

acid: a substance that donates a proton

ex. $H{-}Cl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

base: a substance that accepts a proton (H^+) from another substance

ex. $NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$\uparrow$

proton acceptor base

III. Amphoteric and amphiprotic

amphoteric: a substance that can act as an acid or a base

ex. H_2O, HCO_3^-, HSO_4^-, Lewis acids

amphiprotic: a substance which can donate or accept a proton

ex. H_2O, HCO_3^-, HSO_4^-

Lecture Notes 10.11.23

IV. Conjugate Acid-Base Pair: two substances related to each other by the transfer of one proton (H^+)

acid + base $\rightleftharpoons$ conj base + conj acid

ex. $HCl(aq) + NH_3(aq) \rightleftharpoons Cl^- \quad NH_4^+$

acid (loses H^+) base (gains H^+)

* conjugate acid base pairs are HCl/Cl^- and NH_3/NH_4^+

ex. $H_2SO_4(aq) + H_2O(l) \rightleftharpoons HSO_4^-(aq) + H_3O^+(aq)$

acid base C.B. C.A.

ex. $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$

base acid C.A. C.B.

HCO_3^-/H_2CO_3 and H_2O/OH^-

Molecular Structure and Acid Strength

I. The Effects of molecular structure on acidity
- Why is H_2S acidic and CH_4 not acidic?
- Why is HF a weak acid, and HCl is a strong acid

A. Bond Polarity

$A - A$ nonpolar covalent bond, e^- shared equally
$A - B$ polar covalent bond
(could be nonpolar, depending on ΔE.N.)

* compare C−H to F−H:
C−H → $\Delta EN = 0.4$ nonpolar
F−H → $\Delta EN = 1.9$ polar
⟵+

* in order for a compound to be acidic, the bond must be polarized w/ an H^+

H − Li	H − C	H − F	* H^+ must come off
⟵+	nonpolar	+⟶	
not acidic	not acidic	acidic	

B. Bond Strength: the strength of the bond affects the acidity of the molecule

	bond strength	acid strength
H − F	↑ strongest	weakest acid
H − Cl		
H − Br	weakest	↓ strongest acid

- When considering the acidity of a molecule you must first determine which H is acidic
- When comparing the acidity of H's to other H's, there can be more than one factor

ex. HCl & HF, HF bond is short and strong, and
[illegible] electronegative, but

ex: HCl & HF, HF bond is short & strong, and F is very electronegative. HCl's bond length is longer & weaker than HF, and Cl is more electronegative, so ....

C. Oxoacids: $H-\underset{\cdot\cdot}{\ddot{O}}-Y$

Y can be terminal atoms or it can bond to other atoms

1) The more electronegative Y is, the more it weakens the O-H bond

acidity

$H-O-Cl$ $\uparrow$ strongest
$H-O-Br$
$H-O-I$ weakest

2) The more oxygens bound to Y, the more acidic it is.

acidity

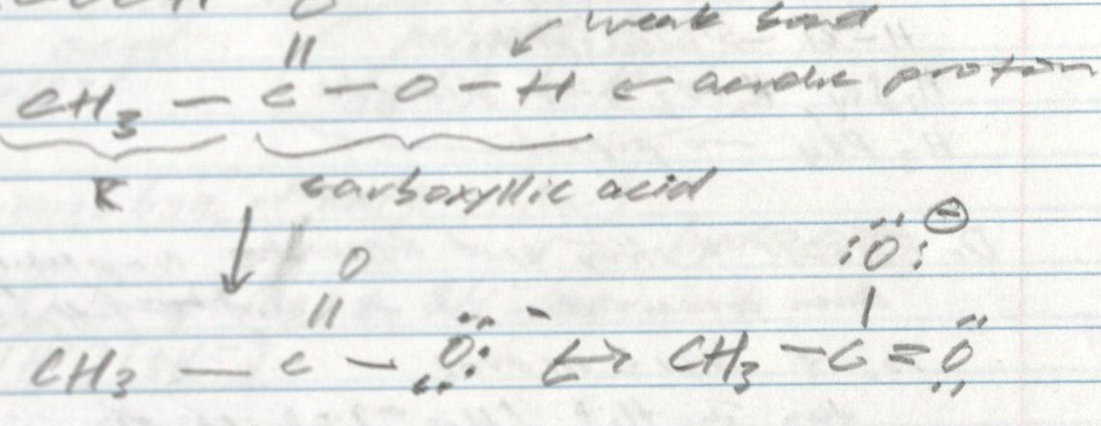
$H-O-ClO_3$ $\uparrow$ strongest
$H-O-ClO_2$
$H-O-Cl$ weakest

ex: compare $H_2SO_4 > H_2SO_3$

$HNO_3 > HNO_2$

D. A common functional group:

CH_3COOH



$$\underbrace{CH_3}_{R}-\underbrace{\overset{O}{\overset{\|}{C}}-O-H}_{\text{carboxyllic acid}}$$

$$\downarrow$$

$$CH_3-\overset{O}{\overset{\|}{C}}-\ddot{O}:^- \leftrightarrow CH_3-\overset{:\ddot{O}:^{\ominus}}{\overset{|}{C}}=\ddot{O}$$

conj base is resonance stabilized

II. Strong Acids: H^+ dissociates completely in H_2O

A. $HA + H_2O \longrightarrow A^- + H_3O^+$

B. There are 7 strong acids:
HCl, HBr, HI, HNO_3, $HClO_4$, H_2SO_4, $HClO_3$
(on the equation sheet)

C. Note: H_2SO_4 is polyprotic as is H_2CO_3
$H-Cl$ → monoprotic
H_2SO_4, H_2CO_3 → diprotic
H_3PO_4 → triprotic

D. Because a strong acid dissociates completely:
given concentration of the acid = $[H_3O^+]$
so, if $HCl = 0.100\,M$, then in H_2O,
$[H_3O^+] = 0.100\,M$

Lecture Notes 10.19.23

C. Note: H_2SO_4 is polyprotic as is H_2CO_3

$H-Cl$ → monoprotic

H_2SO_4, H_2CO_3 → diprotic

H_3PO_4 → piprotic

D. Because a strong acid dissociates completely
Given concentration of the acid = $[H_3O^+]$

so, if $HCl = 0.100M$
then in H_2O, $[H_3O^+] = 0.100M$
H
...

* ~~III~~. Acid Ionization Constant (K_a) — "how acidic"

↙ hydronium

$$Ha\,(aq) + H_2O\,(l) \rightleftarrows A^-(aq) + H_3O^+(aq)$$

$$K_a = \frac{[P]}{[R]} = \frac{[A^-][H_3O^+]}{[HA]}$$

also written as:

$$HA\,(aq) \rightleftarrows H^+(aq) + A^-(aq)$$

$$\ast\ K_a = \frac{[P]}{[R]} = \frac{[A^-][H^+]}{[HA]}$$

- HA/A^- are a conjugate acid base pair
- The larger the K_a, the stronger the acid
- The stronger the acid, the weaker the conjugate base

TTQ. Circle the stronger acid

carbonic acid [✓ nitrous acid]
$K_a: 4.5 \times 10^{-7}$ [✓ $K_a: 5.1 \times 10^{-4}$]

* IV. Autoionization of water (K_w)

hydroxide

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

$$K_w = \frac{[H^+][OH^-]}{1}$$

* @ 25°C, $K_w = 1.0 \cdot 10^{-14}$

* In pure water, $[H^+] = [OH^-]$ at a neutral pH

$$K_w = [H^+][OH^-] = (x)(x) = x^2 = 1.0 \cdot 10^{-14}$$
$$[H^+] = 1.0 \cdot 10^{-7} M \text{ @ } 25°C$$

TTQ. What is $[OH^-]$ in water at 25°C if
$[H_3O^+] = 1.0 \cdot 10^{-3} M$

given: $1.0 \cdot 10^{-3} M = [H_3O^+]$
know: $K_w = 1.0 \times 10^{-14}$ @ 25°C
$K_w = [H_3O^+][OH^-]$

$$1.0 \times 10^{-14} = (1.0 \times 10^{-3})([OH^-])$$
$$1.0 \times 10^{-11} = [OH^-]$$

- in an acidic solution $[H_3O^+] > [OH^-]$
- in a basic solution $[H_3O^+] < [OH^-]$

V. Acid Base - relative to CA/CB pair

$SA + B \rightarrow WCB + CA$

* The stronger the acid, the weaker the conjugate base

A. $HCl + H_2O \rightarrow Cl^- + H_3O^+$
HCl is S.A.
so, Cl^- must be a very weak base

B. $\underbrace{HCN + H_2O \rightleftharpoons CN^-} + H_3O^+$

HCN is a weak acid
CN^- is also weak (base), but is a stronger base than Cl^-
so, the reversible reaction is possible

I. A. pH – a convenient way to specify the acidity of a solution

* p(anything) = -log (anything)
* $p(H) = -\log(H_3O^+) = -\log(H^+)$

p – "power of 10"

ex. if $[H_3O^+] = 1.0 \times 10^{-3}$ M
$pH = -\log(1.0 \times 10^{-3}\,M) = 3$

* pH > 7, soln is basic
* pH = 7, soln is neutral
* pH < 7, soln is acidic

C. A soln with pH=3 is <u>10</u> times more acidic than a solutiom w/ a pH=4

D. A negative pH is possible
if $[H_3O^+] = 2.0M$
$-\log(2.0) = -0.30$

Lecture Notes 10.23.23

* ex. Calculate the K_a of formic acid (HCO_2H) if 0.10M solution has a pH of 2.38 at 25°C?

$$\underbrace{HCOOH(aq)}_{acid} + \underbrace{H_2O(l)}_{base} \rightleftharpoons \underbrace{HCOO^-(aq)}_{conj\ base} + \underbrace{H_3O^+(aq)}_{conj\ acid}$$

$$K_a = \frac{[HCOO^-][H_3O^+]}{[HCOOH]}$$

	HCO_2H	+ H_2O ⇌	HCO_2^-	+ H_3O^+
I	0.10	X	0	0
C	−x		+x	+x
E	0.10 − x		x	+ x

$pH = -\log[H_3O^+]_{eq}$
$2.38 = -\log(H_3O^+)$
$10^{-2.38} = [H_3O^+] = 4.2 \cdot 10^{-3}$
x ↗

$HCO_2H = 0.10 - 4.2 \cdot 10^{-3} =$
$HCO_2^- = 4.2 \cdot 10^{-3}$
$H_3O^+ = 4.2 \cdot 10^{-3}$

$$K_a = \frac{x^2}{(0.10 - x)} = \frac{(4.2 \cdot 10^{-3})^2}{0.10 - 4.2 \cdot 10^{-3}} = 1.8 \cdot 10^{-4}$$

* II. $pK_a = -\log K_a$

<u>ex.</u> Based on the pKa's provided, which is
a stronger acid?

Tosic Acid　　　Acetonitrile
-1 ← stronger　　　25

* if a large K_a is a strong acid, then a
small pK_a is a strong acid

* $pOH = -\log[OH^-]$

<u>ex.</u> What is the pOH of a 0.05M solution
of $Sr(OH)_2$ (aq)?
← strong base

$$Sr(OH)_2 \rightarrow Sr^{2+} + 2OH^-$$

$[Sr(OH)_2] = 0.05M$

$[OH^-] = 0.1M$

$pOH = -\log(0.1) = 1$

* IV. $pH + pOH = 14$ @ 25°C in (aq)

<u>TTQ.</u> What is the $[OH^-]$ in a solution with
a pH of 8.5 at 25°C?

$pOH = 14 - pH$

$pOH = 14 - 8.5$

$pOH = 5.5 = -\log[OH^-]$

$10^{-5.5} = [OH^-]$

$3.16 \cdot 10^{-6} M = [OH^-]$

* V. Strong Bases : completely dissolve in a solution in one step

$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

$Ca(OH)_2(aq) \rightarrow Ca^{2+}(aq) + 2OH^-(aq)$

* Common Strong Bases *memorize*

$LiOH$

$NaOH$

KOH

$Sr(OH)_2$

$Ca(OH)_2$

$Ba(OH)_2$

VI. Base Ionization Constant (K_b)

* Weak Bases : most of the common weak bases produce OH^- by accepting a proton from water

$$\underbrace{\underset{\text{base}}{B(aq)} + H_2O(l) \rightleftharpoons \underset{\text{conj acid}}{BH^+(aq)}} + OH^-(aq)$$

$$K_b = \frac{[P]}{[R]} = \frac{[BH^+][OH^-]}{[B]}$$

ex: $NH_3(aq)$

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

ex: What is the pH of a 0.20M solution of $NH_3(aq)$ at 25°C? $K_b(NH_3) = 1.8 \cdot 10^{-5}$ ← weak base

	$NH_3(aq)$	$+ H_2O(l)$	$\rightleftharpoons NH_4^+(aq)$	$+ OH^-(aq)$
I	0.20	X	0	0
C	$-x$		$+x$	$+x$
E	$0.20-x$		x	x

$$K_b = \frac{x^2}{0.20-x}$$

← ignore

$K_b = 1.8 \cdot 10^{-5} = \frac{x^2}{0.2}$

$\Rightarrow x = 1.9 \cdot 10^{-3}$

check $\frac{1.9 \cdot 10^{-3}}{0.20} \cdot 100\% = 0.9\% < 5\%$ ✓

$x = [OH^-] = 1.9 \cdot 10^{-3}$

$pOH = -\log(1.9 \cdot 10^{-3})$

$pOH = 2.7$

$pH = 14 - pOH$

$pH = 14 - 2.7 = 11.3$

VIII. Relate Ka & K_b

a $\cancel{NH_4^+(aq)} \rightleftharpoons \cancel{NH_3(aq)} + H^+(aq)$

b $\cancel{NH_3(aq)} + H_2O(l) \rightleftharpoons \cancel{NH_4^+} + OH^-(aq)$

$\cancel{NH_4^+(aq)} + H_2O(l) + \cancel{NH_3(aq)} \rightleftharpoons \cancel{NH_3(aq)} + H^+(aq) + \cancel{NH_4^+(aq)} + OH^-(aq)$

$\Rightarrow K_a = \frac{[NH_3][H^+]}{[NH_4^+]} \quad \Rightarrow K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$

combine these reactions

$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

recall: $K_w = [H^+][OH^-] = 1.0 \cdot 10^{-14}$ @ 25°C

so, for a conjugate acid/base pair

* $K_a \cdot K_b = K_w$

also

* $pK_a + pK_b = pK_w = 14.0$

Lecture Notes 10.25.23

TTQ. Calculate the K_b for the fluoride ion (F^-), given that K_a of HF @25°C is $6.8\cdot10^{-4}$

given $K_a(HF) = 6.8\cdot10^{-4}$

find: $K_b(F^-) = ?$

$$K_w = K_a \cdot K_b \Rightarrow K_b = \frac{K_w}{K_a} = \frac{1.0\cdot10^{-14}}{6.8\cdot10^{-4}}$$

$K_b = 1.47\cdot10^{-4}$

II. Polyprotic Acids: acids with more than one ionizable proton

$$H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^-(aq)$$
$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$

* acids deprotonate sequentially

$$K_a(H_2SO_4) > K_a(HSO_4^-)$$
$$pK_a(H_2SO_4) < pK_a(HSO_4^-)$$

TTQ. What species would you expect to find in $H_2SO_4(aq)$?

H_2O, HSO_4^-, H_3O^+, SO_4^{2-}, OH^-

* if it was a weak acid, like HF, then some of the weak acid would also be present

Exam 4 Material: Salt Solutions

I. How do salts affect the pH of a solution? ①

A. Cations: if a cation is a conj. acid of a weak base, then the solution will be acidic

ex. NH_4^+

$$\underset{\text{conj acid}}{NH_4^+(aq)} + H_2O(l) \rightleftharpoons \underbrace{\underset{\text{weak base}}{NH_3(aq)} + H_3O^+(aq)}_{\text{Soln has } H_3O^+ \text{ and is acidic}}$$

② Group 1, 2, or other +1 cations (transition metals) have negligible effect on pH. These ions in water result in a neutral solution

ex. Na^+, Ca^{2+}, Mg^{2+}

③ The addition of cations to pure water will not result in a basic solution

B. Anions

$\boxed{1}$ if the anion is the conjugate base of a weak acid, then the soln will be basic

$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + \underset{\text{basic soln}}{\underset{\uparrow}{OH^-(aq)}}$

② if the anion is the conjugate base of a strong acid, the anion has negligable effect

$Cl^-(aq) + H_2O(l) \not\rightleftharpoons \underset{\text{strong acid}}{\underset{\uparrow}{HCl}} + OH^-$

ex. Br^-, I^-

$\boxed{3}$ very few anions contain hydrogens that could be acidic (polyprotic)

$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$

$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$

TTQ. The salts below are each dissolved in water. Predict if the resulting solution is acidic, basic, or neutral? $NaCH_3CO_2$, NH_4Cl, $MgBr_2$

$NaCH_3CO_2 \rightarrow Na^+ + \underset{\text{B. 1.}}{\underset{\uparrow}{CH_3CO_2^-}}$

soln is basic

$NH_4Cl \rightarrow \underset{\text{A. 1.}}{\underset{\uparrow}{NH_4^+}} + Cl^-$

solution is acidic

$\underbrace{MgBr_2 \rightarrow Mg^{2+} + 2Br^-}$ solution is neutral

Lecture Notes

8.27.23

I. Buffer Definition: a solution that resists change of pH upon addition of a strong acid or strong base.

ex. blood (7.4, HCO_3^-), seawater (pH = 8.2)

A. Buffers resist change because they contain:
- acid to neutralize added OH^-
- base to neutralize added H^+

B. Buffers are created by combining
- a weak acid (or a weak base) with it's conjugate, so both are in the solution

Recall: Strong Acids / Bases

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

- Ka is very large
- essentially no HCl is left in solutions

Recall: weak acids / bases

$$CH_3CO_2H(aq) \rightleftharpoons H^+(aq) + CH_3CO_2^-(aq)$$

- partially ionized
- most of CH_3CO_2H is still in solution

II. Making a Buffer

1. Mix your weak acid (or base) with its conjugate

ex. $CH_3CO_2H + NaCH_3CO_2$

acetic acid ↗ ↑ sodium acetate

ex. $NH_3 + NH_4NO_3$

2. Add a strong base to a weak acid

$CH_3CO_2H + NaOH \rightarrow CH_3CO_2^-(aq) + H_2O(l) + Na^+(aq)$

Add a strong acid to a weak base

ex. $NH_3(aq) + HCl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq) + H_2O(l)$

note: must add less of your SA or SB so that some of your original reactant is present in solution (think limiting reagents)

*3. pH of a solution is near the pKa of the acid chosen

TTQ: Which base would be a good buffer with a pH near 9.2?

a) convert pK_b to pK_a

$14 = pK_a + pK_b$

	pK_b
Aniline	9.37
Hydrazine	5.77
Ammonia	4.75
triethylamine	2.99

ammonia

TTQ 23 ex. benzoic acid

17Q. How many grams of NH_4Cl must be added to 2.0L of 0.10M NH_3 ($K_b = 1.8 \cdot 10^{-5}$) aqueous solution to form a buffer with a pH of 9.00?

given: $V_{NH_3} = 2.0L$, $M_{NH_3} = 0.10$, $pH = 9$

$K_b(NH_3) = 1.8 \cdot 10^{-5}$

find: g NH_4Cl

strategy: use K_b and stoichiometry

1. K_b $NH_4Cl \xrightarrow{H_2O} NH_4^+(aq) + Cl^-(aq)$

$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

recall: $pH + pOH = 14$

given $pH = 9 \Rightarrow pOH = 5$

$\therefore [OH^-] = 1.0 \cdot 10^{-5} M$

Solve for $[NH_4^+]$

$$K_b \frac{[NH_3]}{[OH^-]} = [NH_4^+] = 0.18M$$

$$\frac{0.18 \text{ mol } NH_4^+}{1L} \cdot 2.0L \text{ sol} \cdot \frac{1 \text{mol } NH_4Cl}{1 \text{mol } NH_4^+} \cdot \frac{53.491 g\ NH_4Cl}{1 \text{mol } NH_4Cl}$$

$= 19.26 g\ NH_4Cl$

III. Henderson-Hasselbach

(a buffer calculation shortcut)

- if $HA \rightleftharpoons H^+ + A^-$

$$K_a = \frac{[H^+][A^-]}{[HA]} \Rightarrow [H^+] = K_a \frac{[HA]}{[A^-]}$$

and

$$pH = pKa - \log\left(\frac{[HA]}{[A^-]}\right)$$

or

$$pH = pKa + \log\left(\frac{[A^-]}{[HA]}\right)$$

1) If you have a lot of HA & A^- compared to the amount of H^+ & OH^- then the buffer works & pH does not change much

2) Maximum buffer capacity is when $[A^-] = [HA]$

TTQ. Find the pH of a 0.050M solution of benzoic acid and 0.150M sodium benzoate, $K_a = 6.5 \cdot 10^{-5}$

$$\text{benz. acid} \rightleftharpoons H^+(aq) + \text{benzoate}$$

I	0.050	0.00	0.150
C	$-x$	$+x$	$+x$
E	$0.050 - x$	x	$0.150 + x$

$$K_a = \frac{[H^+][\text{benz}^-]}{[B.A]} = \frac{x(0.150 + x)}{0.050 - x} = 6.5 \cdot 10^{-5}$$

approx & solve for x

$$x = 2.2 \cdot 10^{-5} = [H^+]$$

check approximations

$$\frac{2.2 \cdot 10^{-5}}{0.05} \cdot 100\% = 0.044\% < 5\% \checkmark$$

$$pH = -\log(2.2 \cdot 10^{-5}) = 4.66$$

Independent Notes | Exam 3 10.27.23

Equilibrium Constant (K): quantifies relative amounts of reactants and products

- $aA + bB \rightarrow cC + dD$
- $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$, $K_p \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$ $K_c \neq K_p$
- K and Keq have no units
- K_c is in M, K_p is in atm
- $K > 1$, products are favored
- $K < 1$, reactants are favored
- $K = 1$, neither direction is favored

- $K = \frac{P}{R}$

Homogeneous Reactions: all reactants and products exist in the same phase

- all reagents appear in K

Heterogeneous Reactions: reagents in different phases

- no solids, liquid water, or spectator ions in K

Reaction Quotient (Q): used similarly to K in any point of a reaction to gauge its properties relative to equilibrium

- $Q < K$, products are favored
- $Q > K$, reactants are favored
- $Q = K$, reaction is at equilibrium

Ice tables:

	aA	+	bB	$\rightleftharpoons$	cC	+	dD
I	n		n		n		n
C	$-ax$		$-bx$		$+cx$		$+dx$
E	$n-ax$	+	$n-bx$		$n+cx$	+	$n+dx$

- plug equilibrium values into K expressions
- approximations: % ERROR < 5% ✓

Le Châtelier's Principle: when a chemical system at equilibrium is disturbed, the reaction shifts in the direction that minimizes the disturbance

- adding reactants or removing products shifts the reaction towards the products
- adding products or removing reactants shifts the reaction towards the reactants

For a gaseous reaction:

- increasing the pressure shifts the reaction towards the side with the lower number of moles of gas
- decreasing the pressure shifts the reaction towards the side with the higher number of moles of gas
- if the number of moles of gas are equal on both sides or an inert gas is added, the reaction equilibrium is unchanged

For an exothermic reaction: producing heat ($R \rightleftharpoons P + \Delta H$)

- an increase in temperature shifts the reaction towards the reactants
- a decrease in temperature shifts the reaction towards the products

For an endothermic reaction: consuming heat ($R + \Delta H \rightleftharpoons P$)

- an increase in temperature shifts the reaction towards the products
- a decrease in temperature shifts the reaction towards the reactants

Bronsted-Lowry Definition of Acid/Base:

- Acid: a substance that donates a proton (H^+, H_3O^+)
- Base: a substance that accepts a proton

Amphoteric: a substance that can act as an acid or a base (H_2O, HCO_3^-, HSO_4^-, Lewis acids)

Amphiprotic: a substance that can donate or accept a proton (H_2O, HCO_3^-, HSO_4^-)

Conjugate Acid/Base Pair: two substances related to each other by the transfer of one proton

acid + base $\rightleftharpoons$ conj base + conj acid

ex: $HCl(aq) + NH_3(aq) \rightleftharpoons Cl^-(aq) + NH_4^+(aq)$

CA/CB Pairs: HCl/Cl^-, NH_3/NH_4^+

Molecular Structure and Acid Strength

A. Bond Polarity: in order for a compound to be acidic, the bond must be polarized w/ a proton

H–Li	H–C	H–F
$\longleftarrow\!\!\!+$	not polar	$+\!\!\!\longrightarrow$
not acidic	not acidic	not acidic

B. Bond strength: the weaker the bond the stronger the acid

H–F ↑ strongest bond | weakest acid
H–Cl
H–Br | weakest bond ↓ strongest acid

C. Oxoacids: $H-\ddot{\underset{..}{O}}-Y$ ← can be terminal or bound to other atoms

1) the more electronegative Y is, the more it weakens the OH bond and strengthens the acid

H–O–Cl ↑ strongest acid (most EN)
H–O–Br
H–O–I | weakest acid (least EN)

2) The more oxygens bonded to Y, the stronger the acid

$H-O-ClO_3$ ↑ strongest acid
$H-O-ClO_2$
$H-O-ClO$ | weakest acid

Strong Acids: proton dissociates completely in H_2O
- $HA + H_2O \rightarrow A^- + H_3O^+$
- there are 7 strong acids:
  $HCl, HBr, HI, HNO_3, HClO_4, H_2SO_4, HClO_3$

Polyprotic Acids: acids that can donate multiple protons
- $H-Cl$ → monoprotic
- H_2SO_4, H_2CO_3 → diprotic
- H_3PO_4 → triprotic

* because a strong acid dissolves completely in water, $[SA] = [H_3O^+]$ *

Acid Ionization Constant (K_a): measures strength of acid
- $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$
- $K_a = \frac{[P]}{[R]} = \frac{[A^-][H^+]}{[HA]}$ * the stronger the acid, the weaker the conjugate base *

Autoionization of Water (K_w)
- $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$
- $K_w = \frac{[H^+][OH^-]}{1} = 1.0 \cdot 10^{-14}$ @ 25°C
- in pure water $[H^+] = [OH^-]$ at $pH = 7$ (neutral)
- in an acidic solution $[H_3O^+] > [OH^-]$
- in a basic solution $[H_3O^+] < [OH^-]$

pH: a compact way to measure the acidity of a solution
- $p(x) = -\log(x) \Rightarrow pH = -\log(H^+) = -\log(H_3O^+)$
- $pH > 7$, solution is basic
- $pH = 7$, solution is neutral
- $pH < 7$, solution is acidic

Return of ICE Tables:

	acid	+	H_2O	⇌	conj base	+	conj acid (H_3O^+)
I	n		✗		n(0)		n(0)
C	−x		✗		+x		+x
E	n−x				n+x	+	n+x

$K_a = \frac{[CB][CA]}{[A]}$

$pH = -\log(H_3O^+)$

$pK_a = -\log K_a$

- if larger K_a is a stronger acid, then a smaller pK_a is a stronger acid

$pOH = -\log[OH^-]$

* $pH + pOH = 14$ @ 25°C in (aq)

Strong Bases: completely dissolve in solution in one step

- $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$
- common strong bases:
  - $LiOH$ $Sr(OH)_2$
  - $NaOH$ $Ca(OH)_2$
  - KOH $Ba(OH)_2$

Weak Bases: produce OH^- by accepting a proton from water

- $B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$

Base Ionization Constant (K_b):

- $K_b = \frac{[BH^+][OH^-]}{[B]}$ * ICE tables used the same as with K_a *

Relate K_a & K_b:

- $K_a \cdot K_b = K_w = 1.0 \cdot 10^{-14}$ @ 25°C
- $pK_a + pK_b = pK_w = 14.0$ @ 25°C

* polyprotic acids deprotonate sequentially *

- $K_a(H_2SO_4) > K_a(HSO_4^-)$
- $pK_a(H_2SO_4) < pK_a(HSO_4^-)$

Lecture Notes 10.30.23

ex (from last lecture):

$$pH = -\log K_a - \log \frac{[HA]}{[A^-]}$$

$$\overset{}{} \quad [A^-] \downarrow \quad [HA] \downarrow$$

$$pH = -\log(6.5 \cdot 10^{-5}) + \log(0.150/0.05)$$

$$pH = 4.66$$

* if $[HA] = [A^-]$ then $\log(1) = 0$
so $pKa = pH$ *

ex. what is the pH of a solution containing
0.10M $C_2H_3O_2$ ad 0.10M $C_2H_2O_2^-$?
$K_a = 1.8 \cdot 10^{-5}$

$$pH = pKa + \log\left(\frac{0.10}{0.10}\right) = pka + \log(1)$$

$$pH = pK_a = 4.74$$

What is the pH after adding 0.01M NaOH?

$$HA + OH^- \Longleftarrow A^-$$

	HA	OH^-	A^-
initial	0.10	0.01	0.10
addition	-0.01	-0.01	+0.01
after	0.09		0.11

$$pH = pKa + \log\left(\frac{0.11}{0.09}\right)$$

$$pH = 4.77 + 0.087 = 4.83$$

Compare to 0.01M NaOH in H_2O

$$\underset{0.01}{NaOH} \rightarrow \underset{0.01}{Na^+} + \underset{0.01}{OH^-}$$

pH or pOH $= -\log(0.01) = 2$
so $pH = 14 - 2 = 12$

26. given: 0.150M morphine w/ pH = 10.5
find: K_b

pOH = 14 − 10.5 = 3.5
$[OH^-] = 3.16 \cdot 10^{-4}$ M

	morphine + H_2O	⇌	morphineH$^+$	+ OH^-
I	0.150			
C	−x		+x	+x
E				$3.16 \cdot 10^{-4}$

$x = 3.16 \cdot 10^{-4}$

$$K_b = \frac{x^2}{(0.150 - x)} = 6.67 \cdot 10^{-7}$$

Q20. given 0.10M of WA @25°C

$HA \rightleftharpoons H^+ + A^-$

0.10 <0.10

a. $[H^+] < 0.10$ true
b. $[H^+] = [A^-]$
c. $[HA] > [H^+]$ true
d. pH = 1.0 false

Q21. $KOH \rightarrow K^+ + OH^-$

0.0045M 0.0045M

$[OH^-] = 0.0045$ M

pOH = −log(0.0045) = 2.346

pH = 14 − 2.346 = 11.654

Lecture Notes 11.1.23

TYQ - Calculate the pH of a soln by mixing 200 mL of 0.300M HClO with 100 mL of 0.200 M KClO.

$\downarrow$

$K^+ + ClO^-$

$K_a(HClO) = 2.9 \cdot 10^{-8}$

$pH = pka + \log\left(\frac{B}{A}\right)$

* for $\left(\frac{B}{A}\right)$ can use mols instead of of M if the final volume is the same in numerator & denominator ex: in the same flask *

mols of B = KClO = $(0.200 \frac{mol}{L})(0.1L) = 0.02$ mol B

mols of A = HClO = $(0.300 \frac{mol}{L})(0.2L) = 0.06$ mol A

$pH = -\log(2.9 \cdot 10^{-8}) + \log\left(\frac{0.02}{0.06}\right)$

$pH = 7.5376 + (-0.477)$

$pH = 7.06$

IV. Buffer Capacity

- $(\pm) 1 + pKa$
- best when [A] = [B]

ex: NH_4^+ / NH_3

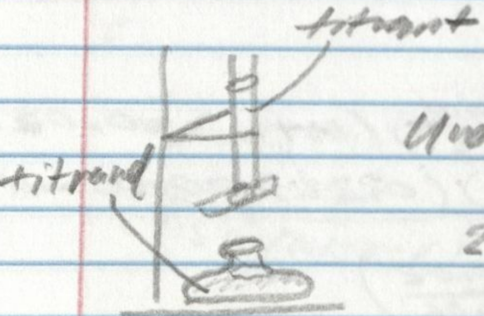
$NH_4^+ \rightleftharpoons NH_3$

- if add OH^-, what will happen?
  shift right toward products, pH goes up
- if add H^+, what will happen?
  shift left towards reactants, pH goes down

I. Titrations: allows us to obtain information about a solution
(pKa, charge, concentration)

In this class → acid / base
In other classes → charge

Goal: to understand how a pH changes as a function of adding titrant

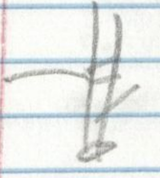


Understand titrants requires:
1) Stoichiometry
2) A/B equilibria

II. Strong Acid - Strong Base
TTQ. For the titration of 0.1 M HCl with 0.1 M NaOH:

$NaOH(aq) + HCl(aq) \rightleftharpoons NaCl(aq) + H_2O(l)$

$OH^-(aq) + H^+(aq) \rightleftharpoons H_2O(l)$



what's in the flask?
initially: $\underbrace{H_2O, H^+, OH^-}_{1.0 \cdot 10^{-7} M}, \underbrace{H^+, Cl^-}_{0.1 M}$

a) before any titrant is added
$pH = -\log[H^+] = -\log(0.1) = 1$

b) After 5 mL of titrant is added what's in the flask?
$H_2O, H^+, Cl^-, Na^+, OH^-$
$HCl + NaOH \rightarrow H_2O + NaCl$
$H^+ + OH^- \rightarrow H_2O$

	H^+ +	OH^- →	H_2O
I	0.0025 mol	0.0005 mol	
A	−0.0005	−0.0005	
A	0.002	–	

now: H_2O, H^+

$pH = -\log\left(\frac{0.002 \text{ mol}}{0.03 \text{ L}}\right) = 1.17$

c) at the equivalence point?

n = mols

$\underset{\downarrow \text{ in titrand}}{n_{solute}} = n_{titrant}$

all solute is converted to its conjugate

– in this case, add $H^+ \rightarrow H_2O$ in rxn

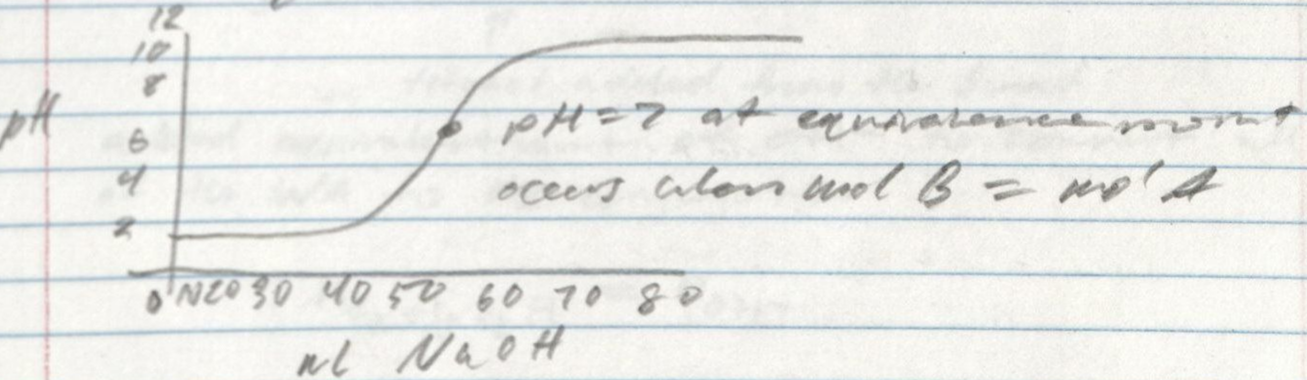
$H^+ + OH^- \rightarrow H_2O$

in pure water, know $[H^+] = 1.0 \cdot 10^{-7}$ M

Flask: H_2O, Na^+, Cl^-, $\underbrace{H^+, OH^-}_{1.0 \cdot 10^{-7}}$

so $pH = -\log(1.0 \cdot 10^{-7}) = 7$

* So for all SA/SB titrations, pH = 7 at equivalence point



pH = 7 at equivalence point occurs when mol B = mol A

TTQ: What volume of NaOH should be added to reach equivalence point?

strategies available:

- ICE tables — too complicated
- $M_1 V_1 = M_2 V_2$ — not the same soln (not diluting
- Stoichiometry — Yes!

$$0.025\ \text{L HCl} \cdot \underset{\text{M HCl}}{\frac{0.1\ \text{m HCl}}{1\ \text{L HCl}}} \cdot \underset{\text{rxn/eqn}}{\frac{1\ \text{m NaOH}}{1\ \text{m HCl}}} \cdot \underset{\text{M NaOH}}{\frac{1\ \text{L NaOH}}{0.1\ \text{m NaOH}}} = 0.025\ \text{L NaOH}$$

add 25 mL of NaOH solution

Lecture Notes 11.3.23

II. Weak Acid / Strong Base Titrations

TTQ. $HCHO_2 + NaOH \rightleftharpoons CHO_2^- + H_2O$

a) before titrant is added

b) at the equivalence point

c) at the 1/2 equivalence point (30mL NaOH)

d) after the equivalence point (30mL NaOH)

a) this is C_2H_3OH in H_2O

$H_2O + C_2H_3O_2H \rightleftharpoons$

I

C

E

... Ka = ... =

$x = 4.24 \cdot 10^{-5} = [H_3O]^+$

$pH = -\log(4.24 \cdot 10^{-5}) = 2.37$

b) at equivalence point

$C_2H_3O_2H + OH^- \rightleftharpoons C_2H_3O_2H^- + H_2O$

titrant added from the buret

added equivalent amt of OH^- to convert all of the WA to its conjugate

$n_{C_2H_3O_2H} = n_{OH^-}$

so in the flask, just $C_2H_3O_2^-$ & H_2O

$C_2H_3O_2^- + H_2O \rightleftharpoons C_2H_3OH + OH^-$

use Kb! Must find new $[C_2H_3O_2^-]$

$n_{C_2H_3O_2} = 0.0025\,mol$

$$M = \frac{0.0025}{\underset{\substack{\downarrow \\ V_i}}{0.025L} + \underset{\substack{\downarrow \\ V_{added}}}{0.025L}} = \frac{0.0025\,mol}{0.05L} = 0.05M$$

$$C_2H_3O_2^- \rightleftharpoons C_2H_3OH + OH^-$$

	$C_2H_3O_2^-$	C_2H_3OH	OH^-
I	0.05	0	0
C	$-x$	$+x$	$+x$
E	$0.05-x$	x	x

$$K_b = \frac{K_w}{K_a} = \frac{1.0\cdot10^{-14}}{1.8\cdot10^{-5}} = 5.6\cdot10^{-10}$$

$$K_b = \frac{x^2}{0.5-x} \Rightarrow x = 5.27\cdot10^{-6} = [OH^-]$$

$pOH = -\log[OH^-] = 5.77$

$pH = 14 - pOH = 8.23$

\# for a WA, if equivalence point > 7, then it must be a WA #

c) at ½ equivalence point

$WA + OH \rightarrow CB + H_2O$

if ½ of WA is converted to CB, then

$[WA] = [CB]$

$$pH = pK_a + \overset{0}{\cancel{\log(B/A)}}$$

$$pH = pK_a$$

$$pH = pK_a = -\log(1.8\cdot10^{-5}) = 4.74$$

Titrations Overview

SA + SB or SB + SA:

1. Treat as limiting reagent and excess reagent
2. Determine $[H_3O^+]$ or $[OH^-]$ then pH

WA + SB:

Before Base is Added:

— use ICE and K_a or H.H.

At 1/2 at the equivalence point

— pH = pK_a

At equivalence point:

— use K_b

After equivalence point

— determine the excess $[OH^-]$ and use pOH ⇒ pH

In Between Stages:

- [WA] + [CB] in solution
- use Hendeson Hasselbach (H.H.)

WB + SA is opposite:

- $K_b \rightarrow K_a$
- $[OH^-] \rightarrow [H^+]$

d) @ 30mL (after equivalence point)
25mL + 5mL
equiv. pt. + excess

$[OH^-] = 5.27\cdot10^{-6} M$

$n_{OH^-} = \frac{5.27\cdot10^{-6} M}{L} \cdot 0.050L = 2.64\cdot10^{-7}$ mol OH^-

how many moles in flask @ equiv. pt.

V_{total} @ equiv. pt.

XS = excess

$n_{XS\,OH^-} = 0.005L \cdot \frac{0.10\,mol}{L} = 0.0005$ mol OH^-

total moles of OH^- in flask:

$(2.64\cdot10^{-7}) + 0.0005 = 0.0005\underbrace{00264}_{\text{insignificant}}$

$M_{OH} = \frac{0.0005\,mol\,OH}{0.05L + 0.005L} = 9.09\cdot10^{-3}$

pOH = 2.04

pH = 11.96

Lecture Notes 11.6.23

I. Ionic Compounds Review

$$NaCl(s) \xrightarrow[H_2O]{} Na^+(aq) + Cl^-(aq)$$

*The salt of a metal & nonmetal dissolves into ions

$$NaHCO_3(s) \xrightarrow[H_2O]{} Na^+(aq) + HCO_3^-(aq)$$
$$CaCO_3(s) \xrightarrow[H_2O]{} Ca^{2+}(aq) + CO_3^-(aq)$$

II. K_{sp} – solubility product equilibrium

A. K_{sp} can be used to quantitatively describe "how much" salt will be dissolved

$$AB(s) \rightleftharpoons aA^+(aq) + bB^-(aq)$$
$$K_{sp} = [A^+]^a[B^-]^b$$

B. A large K_{sp} indicates a high concentration of ions – high solubility (strong electrolyte)

A small K_{sp} indicates a low concentration of ions – low solubility (weak electrolyte)

Demo. $NaCl$ $K_{sp} \sim 36$

$NaHCO_3$ $K_{sp} \sim 1.3$

chalk ($CaCO_3$) $K_{sp} \sim 3.8 \cdot 10^{-9}$

in class $CaSO_4 \cdot H_2SO_4$ $K_{sp} \sim 2.4 \cdot 10^{-5}$

* C. Molar Solubility (S): the concentrations in mol/L of a salt that dissolves under specific conditions

TTQ. Calculate the molar solubility of $PbCl_2$. $K_{sp} = 1.17 \cdot 10^{-5}$. What are $[Pb^{2+}]$ and $[Cl^-]$?

$$PbCl_2\,(s) \rightleftharpoons Pb^{2+}\,(aq) + Cl^-\,(aq)$$

given: $K_{sp}\,(PbCl_2) = 1.17 \cdot 10^{-5}$ @ 25°C

find: (S)

	(S) ⇌	Pb^{2+} +	$2Cl^-$
I		0	0
C		+S	+2S
E		S	2S

$K_{sp} = [Pb^{2+}][Cl^-] = (S)(2S)^2$

$1.17 \cdot 10^{-5} = 4S^3$

$S = 1.43 \cdot 10^{-2}\,M$

$[Pb^{2+}] = S = 1.43 \cdot 10^{-2}\,M$

$[Cl^-] = 2S = 2.86 \cdot 10^{-2}\,M$

* So, $1.43 \cdot 10^{-2}\,M$ of $PbCl_2$ will dissolve in 1L of $H_2O\,(l)$

III. Common Ion Effect

Concepts:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

* If NaCl(aq) is in the water, more Cl^- ions are in the water. Due to Le Châtlier's Principle the reaction shifts left. Less $PbCl_2$ will dissolve

17.9: Calculate the molar solubility of CaF_2 in a solution containing 0.100 M NaF.
$K_{sp} = 1.46 \cdot 10^{-10}$

NaF is a strong electrolyte & will dissolve completely

$$NaF \rightarrow Na^+ + F^-$$
0.1M 0.1M 0.1M

	$CaF_2(s) \rightleftharpoons$	$Ca^{2+}(aq) +$	$F^-(aq)$
I		0	0.1M
C		+S	+2S
E		(S)	(0.1+2S)

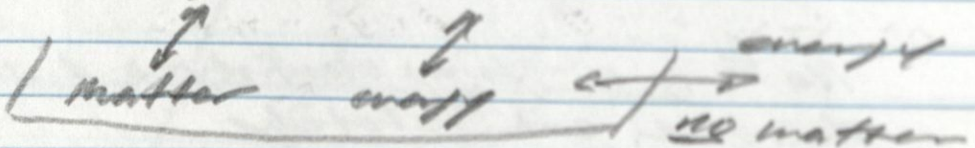
$K_{sp} = 1.46 \cdot 10^{-10} = (S)(0.1+2S)^2$
$1.46 \cdot 10^{-10} = (0.1)^2(S)$ ← approximate
$1.46 \cdot 10^{-8}$ M $= S$ ← CaF_2 in F^-

$CaF_2(s)$ in pure water: $S = 3.32 \cdot 10^{-4}$ M

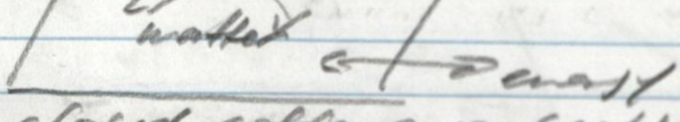
I. Introduction to Thermodynamics
Where does heat go?
Does a system do work?

A. Systems
System: what you are studying
surroundings: everything else
universe: system + surroundings

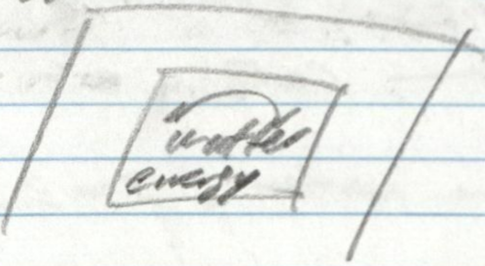
3 Types:
1) Open system: can exchange matter and energy w/ surroundings



ex: coffee cup
2) Closed System: exchanges energy with the surroundings



ex: closed coffee cup (coffee mug??)
3) Isolated System: no matter or energy can be exchanged



ex. perfect thermos (Yeti)

Independent Notes | Missed lecture 11.9.23

I. Work: achieving motion against an opposing force

Energy: capacity to do work

Energy (E(u)): internal energy (total energy of a system)

Types: kinetic, potential, chemical energy

1) Kinetic: energy due to motion

2) Potential: energy due to position or composition

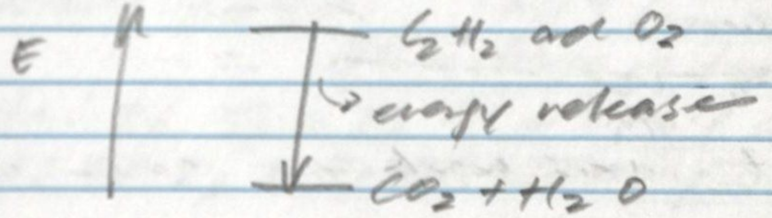
3) Chemical: bonds are a form of potential energy

$H-C\equiv C-H$ (acetylene)

ΔE: change in internal energy of a system (or surroundings)

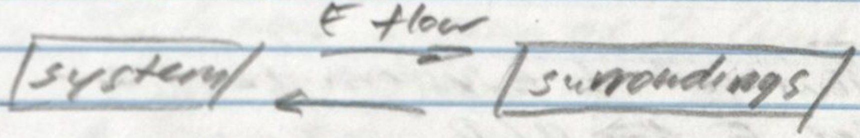
$\Delta E = E_f - E_i$

ex. $C_2H_2 + \frac{5}{2}O_2 \rightarrow CO_2 + H_2O$



if $\Delta E < 0$, exothermic

if $\Delta E > 0$, endothermic



if E flows from system to surroundings,

$\Delta E_{sys} < 0$ (loss of E for the system)

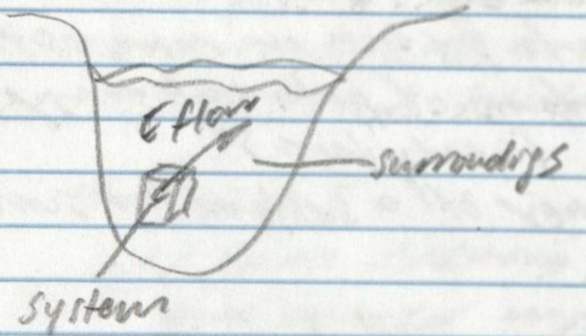
(but also a gain of E for the surroundings)

II. The First law of Thermodynamics

* A. E_{total} ($E_{universe}$) is constant

$\Delta E_{total} = \Delta E_{sys} + E_{surr} = 0$

$\Delta E_{sys} = -\Delta E_{surr}$



* case study the surroundings to learn about the system *

B. There are 2 ways to change the Esys and/or Esurr

$\Delta E = \underset{\uparrow}{q} + \underset{\uparrow}{w}$

q is heat   w is work

* if heat flows into a system then the system gains energy ⟺ $q > 0$ is sys gains E

* if heat flows out of a system then the system loses E ⟺ $q < 0$

* If work is done on the system then $w > 0$

* If work is done by the system then $w < 0$

C. Definitions:

exothermic: heat flows out of a sys
endothermic: heat flows into a sys
adiabatic: no heat flows ($q = 0$)

D. Calculating heat associated with matter

$\Delta q = m C_s \Delta T$ $\quad m$ = mass
or $\quad C_s$ = specific heat capacity
$\Delta q = n C_m \Delta T$ $\quad \left(\frac{J}{g \cdot {}^\circ C}\right)$ or $\left(\frac{J}{g \cdot K}\right)$

*the quantity of heat $\quad n$ = mols
required to raise the $\quad C_m$ = molar heat capacity
temperature of 1g of $\quad \left(\frac{J}{mol \, {}^\circ C}\right)$ or $\left(\frac{J}{mol \cdot K}\right)$
substance by 1°C*
ΔT = change in temp (°C or K)

note: If $T_f > T_i \Leftrightarrow \Delta T > 0$ & $\Delta q > 0 \Leftrightarrow$ endothermic
__and__: If $T_f < T_i \Leftrightarrow \Delta T < 0$ & $\Delta q < 0 \Leftrightarrow$ exothermic

TTQ: Slideshow
find: T_f (water)
T_f (water) is same as T_f (block)
$q_{sys} = -q_{surr}$
$q_{Al} = -q_{H_2O}$

$$m_{Al} C_s^{Al}(T_f^{Al} - T_i^{Al}) = \overset{\overset{*}{\downarrow}}{-} m_{H_2O} C_s^{H_2O}(T_f^{H_2O} - T_i^{H_2O})$$

solve for T_f

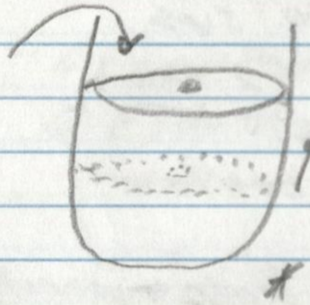
$(32,5g)(0.903 J/(g \cdot k))(T_f - 318.95K) =$
$-(105.8g)(4.18J(g \cdot k))(T_f - 288.55K)$

$\Rightarrow T_f = 290.45K \approx 17.3°C$

Lecture Notes 11.10.23

E. Calculating Pressure-Volume Work

constant external pressure



$\Delta V > 0$ expansion

$*w = -P_{ext}\Delta V$

* negative because $\Delta V > 0$ and work is being done by the system (pushing against the surroundings) (opposite of work being done on a system)

TYQ. How much work is required to inflate a balloon from 0.1 L to 1.85 L against an external pressure of 1.00 atm?

$w = -P_{ext}\Delta V = -(1.00\,atm)(1.85\,L - 0.10\,L)$

$= -1.75\,L\cdot atm$

convert given equation sheet

$1\,L\cdot atm = 101.3\,J$

$-1.75\,L\cdot atm \cdot \frac{101.3\,J}{1\,L\cdot atm} = -177\,J$

F. State Function – a property whose value does <u>not</u> depend on the path taken to reach that value * independent of path *

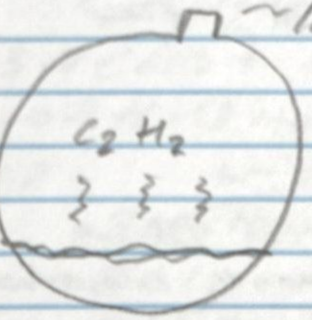
ΔV or ΔE is a state functions
(ΔV – potential energy of a system)

I. Enthalpy – heat of a reaction (ΔH)
- is a state function
- is an extrinsic property (depends on the amount)

$\Delta H = \Delta E + P_{ext} \Delta V$

$Ca(1s) + H_2O(l) \rightleftharpoons CaO(aq) + C_2H_2(g)$

$H-C \equiv C-H$



heat is evolved and pressure builds up, working against the atmosphere

- if the process occurs at a constant external pressure, (like a chemical reaction in an open container), then $\Delta H = \Delta q$.

$\Delta H > 0$, endothermic
$\Delta H < 0$, exothermic

II. 3 ways to calculate/estimate ΔH

1) Relate ΔH_{rxn} to known reactions

<u>TTQ</u>: How much heat is evolved when 13.2g of propane is burned?

$\Delta H_{rxn} = -2044\ kJ/mol$

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

start w/ measured value ↗ $13.2g\ C_3H_8 \cdot \frac{1mol\ C_3H_8}{44.09g\ C_3H_8} \cdot \frac{1\ rxn}{1mol\ C_3H_8} \cdot \frac{2044kJ}{1rxn}$

$= 612\ kJ$ are released/evolved

- If a reaction is multiplied by a factor, then ΔH is multiplied by that factor

  if $A + 2B \rightarrow C$; $\Delta H_{rxn} = x$

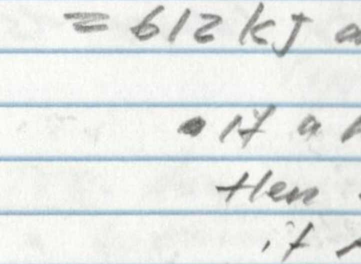
  then $2A + 4B \rightarrow 2C$; $\Delta H'_{rxn} = 2x$

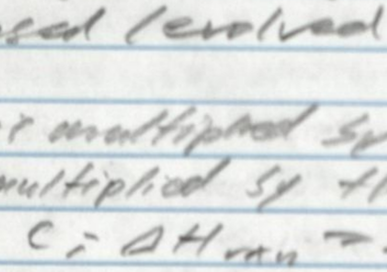
- if a chemical reaction is reversed, the sign (±) changes

  if $A + 2B \rightarrow C$; $\Delta H = x$

  then $C \rightarrow A + 2B$; $\Delta H = -x$

Hess's Law ↗
- If a reaction can be expressed as a sum of steps, ΔH for the overall reaction is the sum of ΔH's for each step





$\Delta H = \Delta H_{R\rightarrow I} + \Delta H_{I\rightarrow P}$

ex.

$A + 2B \rightarrow C$ $\quad \Delta H = x$

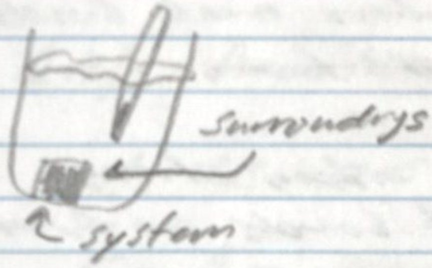
$+ \quad C \rightarrow D$ $\quad \Delta H = y$

$A + 2B \rightarrow D$ $\quad \Delta H_{rxn} = x + y$

Lecture Notes 11.13.23

* Exam 4: 5% salt, ~16% Buffers, ~22% titrations, 11% Ksp, Elec ~19 ~11-16%, Enthalpy ~22%.

To best calculate ΔH_{rxn} - use a calorimeter



$q_{sys} = -q_{surr}$

TTQ: Using Hess's Law, find ΔH_{rxn} for the following reaction: $3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$

Known reactions:

ΔH_{rxn} (kJ)

flip rxn (x -1)

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$ -2044

x by 3 $C(s) + O_2(g) \rightarrow CO_2(g)$ -393.5

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ -483.6

x by 2

do on both sides

$\cancel{3CO_2}(g) + \cancel{4H_2O}(g) \rightarrow C_3H_8(g) + \cancel{5O_2}(g)$ 2044

$3C(s) + \cancel{3O_2}(g) \rightarrow \cancel{3CO_2}(g)$ -1180.5

$4H_2(g) + \cancel{2O_2}(g) \rightarrow \cancel{4H_2O}(g)$ -967.6

$3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$ -104.1 kJ

* reactions given on exam

(2) Use bond energies (on equation sheet)

$$* \ \Delta H_{rxn} = \sum \Delta H_{\substack{\text{bonds}\\ \text{broken}}} + \sum \Delta H_{\substack{\text{bonds}\\ \text{formed}}}$$

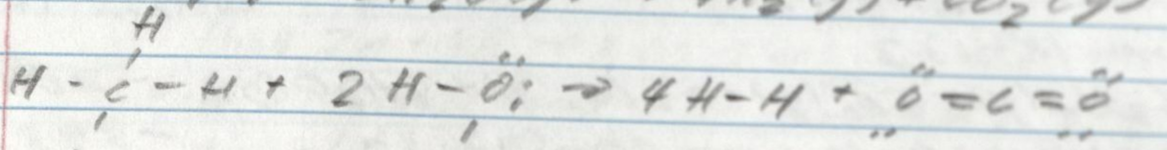
endothermic (+)   exothermic (−)

Note: A reaction is exothermic when weak bonds are broken and strong bonds form

A reaction is endothermic when strong bonds are broken and weak bonds are formed

TTA: Using bond enthalpies, find ΔH_{rxn} for the following reaction:

$CH_4(g) + 2H_2O(g) \rightarrow 4H_2(g) + CO_2(g)$



$$H-\underset{H}{\overset{H}{C}}-H + 2\,H-\underset{H}{\ddot{O}}: \rightarrow 4\,H-H + \ddot{O}=C=\ddot{O}$$

		ΔH (kJ/mol)
break	4 C−H bonds	4(413) = 1652
	4 O−H	4(463) = 1852
form	4 H−H bonds	−4(436) = −1744
	2 C=O	−2(745) = −1490

$$\Delta H_{rxn} = [4(413) + 4(463)] + [4(-436) + 2(-745)]$$
$$= 3508 - 3234$$
$$= 270 \text{ kJ/rxn}$$

(3) from ΔH_f° ΔH - enthalpy
f - from formation (from nature)
° - standard state

(°) - stadad state
- 1atm, 25°C, 1M (for a solution)

ΔH_f° - formation of a single product
quantity of 1 mol

$A + 2B \rightarrow \underline{C}$ one product, one mol

$E + \frac{1}{2}F \rightarrow \underline{G}$ one mole of one product

* A & B, or E & F must be __elements__ in their stadard state

__ex:__ $C(s, \text{graphite}) + 2H_2(g) \rightarrow CH_4(g)$

$\Delta H_f^\circ(CH_4) = -74.6\ \text{kJ/mol}$

* if $R \rightarrow P$ are elements → compounds and $\Delta H_f^\circ > 0$
then $R \rightarrow P$ are compounds → elements $\Delta H_f^\circ < 0$

* $\Delta H^\circ_{rxn} = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$

Lecture Notes

a. Some common elements are found in molecular form in nature and have $\Delta H_f^\circ = 0$

$H_2(g), N_2(g), O_2(g), F_2(g), Cl_2(g), Br_2(g), F_2(g)$

$C(s, \text{graphite}) \quad \Delta H_f^\circ = 0$

b. Some ΔH_f are positive

$C(s, \text{graphite}) \rightarrow C(s, \text{diamond})$

$\Delta H_f^\circ = 1.88\ kJ/mol$

$C(s, \text{graphite}) \rightarrow C(g)$

$\Delta H_f^\circ = 716.8\ kJ/mol$

c. Some ΔH_f° are negative

$C(s, \text{graphite}) + 2H_2(g) \rightarrow CH_4(g)$

$\Delta H_f^\circ = -76.4\ kJ/mol$

Demo: $2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s)$

- very exothermic
- forms molten Fe

$\Delta H_{rxn}^\circ = \Sigma \Delta H_f^\circ(\text{products}) - \Sigma \Delta H_f^\circ(\text{reactants})$

$$\Delta H_{rxn}^\circ = [\Delta H_f^\circ\ 2(\overset{0}{\cancel{Fe}}(s)) + (Al_2O_3)] - [\Delta H_f^\circ\ 2(\underset{0}{\cancel{Al}}(s)) + FeO_3]$$

given data table

$\Delta H_{rxn}^\circ = -1669\ kJ - (-824\ kJ)$

$\Delta H_{rxn}^\circ = -845\ kJ/rxn \nearrow |-850\ kJ|$ is released, produced

exothermic reactions, enthalpy of products less than that of reactants ex. 15g Al reacts w/ excess iron (II) oxide. How much heat was released? MM Al = 26.98g

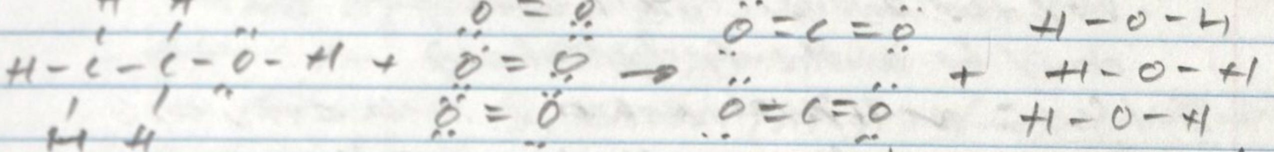
$$15g\,Al\left(\frac{1\,mol\,Al}{26.98g\,Al}\right)\left(\frac{1\,rxn}{2\,mol\,Al}\right)\left(\frac{-850\,kJ}{1\,rxn}\right) = -236\,kJ$$

ex. What mass of iron is formed when 725 kJ of heat is released? Mw(Fe) = 55.8g

$$725\,kJ\left(\frac{2\,mol\,Fe}{850\,kJ}\right)\left(\frac{55.8g\,Fe}{1\,mol\,Fe}\right) = 95.2g\,Fe$$

ex. Ethanol is a possible fuel. Use average bond energies to calculate ΔH_{rxn} for the combustion of ethanol

$$CH_3CH_2OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$



means exothermic so neg values

Textbook: $\Delta H_{rxn} = \sum \Delta H(\text{broken}) + \sum \Delta H(\text{formed})$

Eqn Sheet: $\Delta H_{rxn} = \sum \Delta H(\text{broken}) - \sum \Delta H(\text{formed})$

values are on the equation sheet

$\sum \Delta H_{broken}$ (reactants)

$= 5(C-H) + 1(C-C) + 1(C-O) + 1(O-H) + 3(O=O)$

$= 5\,mol(414\,\frac{kJ}{mol}) + 1\,mol(347\,\frac{kJ}{mol}) + 1\,mol(360\,\frac{kJ}{mol})$

$+ 1\,mol(464\,kJ/mol) + 3\,mols(498\,kJ/mol) = 4735\,kJ$

$\sum \Delta H_{formed} = -4\,mol(C=O) + (-6\,mol)(O-H)$

$= -4(799\,kJ/mol) - 6\,mol(464\,kJ/mol) = -5980\,kJ$

Σ special from textbook

$\Delta H_{rxn} = 4735\,kJ - 5980\,kJ = -1245\,kJ$

Independent Notes / Exam 4 11.17.23

Salt Solutions: 5% of exam

Cations:

- if a cation is a CA of a WB, then the solution will be acidic
- group 1, 2, or other +1 cations have negligable effect on pH an in water will be neutral
- the addition of cations to pure water will not result in a basic solution

Anions:

- if an anion is the CB of a WA, then the solution will be basic
- if an anion is the CB of a SA, then the anion has negligable effect
- very few anions contain hydrogens that could be acidic (polyprotics)

Buffers: ∼ 16% of exam

"a solution that results in a ΔpH upon addition of a SA or SB"

- buffers resist change because they contain:
  - acid to neutralize added OH^-
  - base to neutralize added H^+
- buffers are created by combining:
  - WA/WB w/ CB/CA, so both are in solution
  - adding SB to WA or SA to WB
    - must add less SB/SA b/c of limiting reagents

*pH ≈ pK_a (of acid chosen)

if $HA \rightleftharpoons H^+ + A^-$, then $K_a = \frac{[H^+][A^-]}{[HA]}$

$\Rightarrow [H^+] = K_a \frac{[HA]}{[A^-]}$, and:

Buffer Capacity: *$pH = pK_a \pm 1$

- $pH = pK_a - \log([HA]/[A^-])$
- $pH = pK_a + \log([A^-]/[HA])$

Maximum Buffer Capacity: $[HA] = [A^-]$

*can use mols if V_f is the same for both $[HA]$ & $[A^-]$ ie. in same flask

Titrations: ~ 22% of exam

"allow us to obtain information about a solution"

ie. "understand how pH changes in result of adding titrant"

SA + SB or SB + SA:

1. Treat as limiting/excess reagent reaction
2. Determine $[H_3O^+]$ or $[OH^-]$ and its pH

* at equivalence point, pH = 7 b/c $n_{[H_3O^+]} = n_{[OH^-]}$ and in pure water $[H^+] = 1.0 \cdot 10^{-7}$ M

WA + SB:

- Before $[OH^-]$ is added
  - → use ICE and K_a or H.H.
- At ½ of the equivalence point
  - – $pH = pK_a$
- At the equivalence point
  - – use $K_b = K_w / K_a$
- After the equivalence point
  - – determine the excess $[OH^-]$ and use $pOH \Rightarrow 14 - pH$
- In between stages
  - – determine [WA] and [CB] in solution
  - – use H.H.

* in a WA, pH at equivalence point > 7 *

WB + SA: "opposite of WA + SB"

- $K_b \rightarrow K_a$
- $[OH^-] \rightarrow [H^+]$

Ionic Compounds: 11% of exam completely?

- the salt of a metal/nonmetal dissolves" into ions
- K_{sp}: solubility product equilibrium

  $AB(s) \rightleftharpoons aA^+(aq) + bB^-(aq)$, $K_{sp} = [A^+]^a[B^-]^b$
- A large K_{sp} means high concentration of ions
  - → high solubility, strong electrolyte
- A small K_{sp} means low concentration of ions
  - → low solubility, weak electrolyte
- S: molar solubility (concentration of salt that dissolves in mol/L) * use ICE *

Thermodynamics: ~11-16% of exam

System: what is being studied

Surroundings: Everything else

Universe: systems + surroundings

Types of Systems:

1. open system - can exchange matter and energy w/ surroundings ex. coffee mug
2. closed system - can only exchange energy w/ surroundings ex. coffee mug
3. isolated system - no matter or energy can be exchanged ex. perfect coffee thermos

Work: achieving motion against an opposing force

Energy: capacity to do work

E/U: internal energy (total energy of a system)

1. Kinetic: energy due to motion
2. Potential: energy due to position or composition
3. Chemical: energy due to chemical bonds

ΔE: change in internal energy ($E_f - E_i$)

- if $\Delta E < 0$, exothermic
- if $\Delta E > 0$, endothermic

if E flow from system to surroundings, $\Delta E_{sys} < 0$, but $\Delta E_{surr} > 0$

* $E_{universe}$ is constant

$\Delta E_{total} = \Delta E_{sys} + \Delta E_{surr} = 0$

$\Delta E_{sys} = -\Delta E_{surr}$

* $\Delta E = q + w$ (heat + work)

- if heat flows into the system, or work is done on the system, $q > 0$ and $w > 0$ and the system gains energy
- if heat flows out of a system, or work is done by the system, $q < 0$ and $w < 0$ and the system loses energy

exothermic: heat flows out of a system

endothermic: heat flows into a system

adiabatic: no heat flows ($q=0$)

C_s: specific heat capacity - "the quantity of heat required to raise the temperature of 1g of a substance by 1°C"

in $\frac{J}{g°C}$ or $\frac{J}{gK}$

*$\Delta q = m C_s \Delta T$ C_m: molar heat capacity,

*$\Delta q = n C_m \Delta T$ in $\frac{J}{mol°C}$ or $\frac{J}{mol K}$

$T_f > T_i \Leftrightarrow \Delta T > 0 \Leftrightarrow \Delta q > 0 \Leftrightarrow$ endothermic

$T_f < T_i \Leftrightarrow \Delta T < 0 \Leftrightarrow \Delta q < 0 \Leftrightarrow$ exothermic

$q_{sys} = -q_{surr}$

*$W = -P_{ext} \Delta V$, "negative b/c $\Delta V > 0$ and work is being done by the system (pushing against the surroundings)" $\Delta V > 0 \Leftrightarrow$ expansion

L·atm = 101.3J

State Function: a property whose value is independent of path (ΔV or ΔE)

Enthalpy: ~22% of exam

"heat of reaction (ΔH), is a state function"

$\Delta H = \Delta E + P_{ext} \Delta V$

if this process occurs at a constant P_{ext} (like a chemical reaction in an open container), then $\Delta H = \Delta q$.

$\Delta H > 0$, endothermic

$\Delta H < 0$, exothermic

3 ways to calculate/estimate ΔH:

1. relate ΔH_{rxn} to known reactions
   - start with measured value
   - use stoichiometry (1 rxn / 1 mol X)
   - if rxn is multiplied by a factor, then ΔH is multiplied by that factor
   - if rxn is reversed, then sign on ΔH_{rxn} is reversed
   - if a rxn can be expressed as a sum of steps, then $\Delta H_{rxn} = \sum \Delta H_{steps}$
2. use bond energies

* $\Delta H_{rxn} = \sum \Delta H_{\text{bonds broken}} + \sum \Delta H_{\text{bonds formed}}$

endothermic (+) exothermic (−)

* a reaction is exothermic when weak bonds are broken and strong bonds form

* a reaction is endothermic when strong bonds are broken and weak bonds form

3. from ΔH_f°

ΔH – enthalpy

f – from formation (from nature)

(°) – standard state ° – standard state

- 1 atm, 25°C, 1 M

* ΔH_f°: formation of a single product, quantity of 1 mol

$A + \frac{5}{2}B \rightarrow \underline{C}$

* A and B must be elements in their standard state *

* if R → P are elements → compounds, and $\Delta H_f^\circ > 0$, then R → P are compounds → elements and $\Delta H_f^\circ < 0$

* $\Delta H_f^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$

Some common elements are found in nature w/ $\Delta H_f^\circ = 0$:

- $H_2(g)$, $N_2(g)$, $O_2(g)$, $F_2(g)$, $Cl_2(g)$, $Br_2(g)$, $I_2(g)$, C(s, graphite)

Some $\Delta H_f^\circ > 0$: C(s, graphite) → C(g)

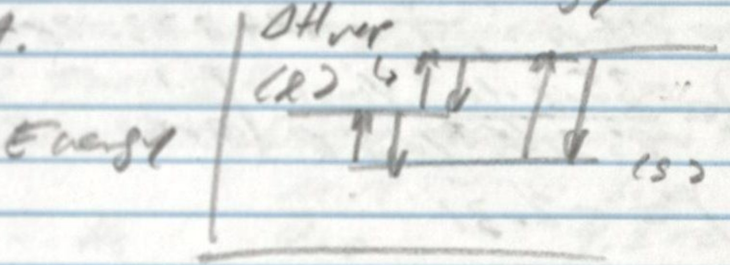
Some $\Delta H_f^\circ < 0$: C(s, graphite) + $2H_2(g) \rightarrow CH_4(g)$

Independent Notes / Final Exam Material 11.27.23

L.35. I. States of matter – (s), (l), or (g)

II. Phase Changes – require addition or removal of energy

A.



* vapor pressure – pressure of a gas in dynamic equilibrium w/ its liquid

ΔH_{vap} – amt of E required to go from (l) to (g)

B. Vapor pressure depends on temperature

Clausius – Clapeyron:

$$* \ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Boiling point: temperature at which the vapor pressure = P_{ext}

normal boiling point: temperature at which vapor pressure = 1atm = 760 torr

TTQ. Methanol (CH_3OH) has a normal boiling point of 64.4 °C and a $\Delta H_{vap} = 35.2\ ^{kJ}/_{mole}$ what is the vapor pressure at 12 °C?

Givens: $P_1 = 760\text{ torr}$, $T_1 = 64.4 + 273 = 337.4\text{K}$

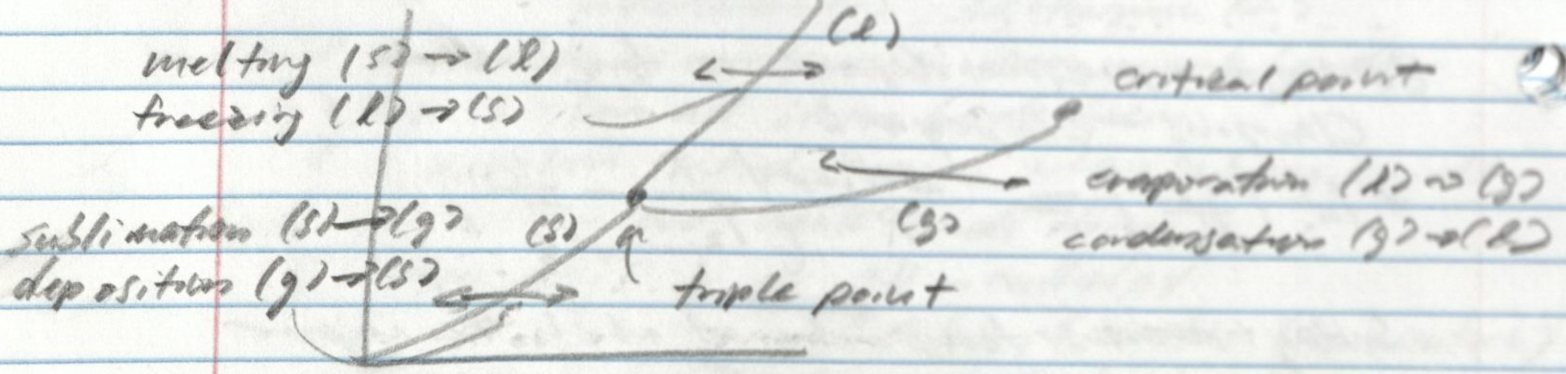
$P_2 = ?\text{ torr}$, $T_2 = 12 + 273 = 285\text{K}$

$$\ln\left(\frac{P_2}{760\text{torr}}\right) = \frac{-35.2 \cdot 10^3\ ^{J}/_{mol}}{8.314\ ^{J}/_{mol \cdot K}}\left(\frac{1}{285\text{K}} - \frac{1}{337.4\text{K}}\right)$$

$$\ln\left(\frac{P_2}{760\text{torr}}\right) = -2.31$$

$$P_2 = (760\text{ torr})\,e^{-2.31} = 75.4\text{ torr}$$

III. Substances changes can be plotted on a phase diagram



IV. Intermolecular Forces — are the attractions & repulsions of one molecule to another

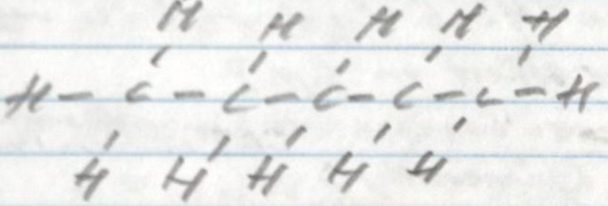
+ 1. Dispersion Forces: all molecules and atoms are attracted by dispersion forces due to a temporary dipole b/c of e^- movement

2 Factors:

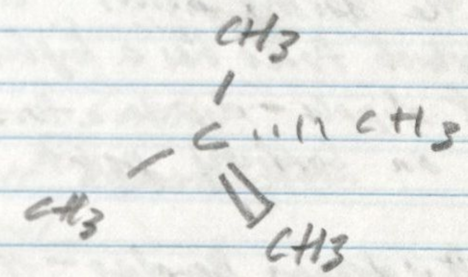
1) Polarizability — depends on the e^- cloud (size)

	M.M.	b.p.
He	4.0	4.2°C
Ar	39.95	87°C
Xe	131.30	165°C

2) Shape — surface area interactions



b.p. 36.1°C

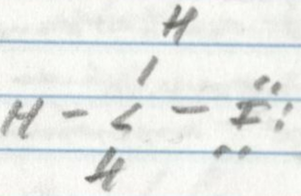
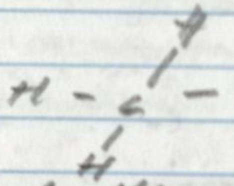


b.p. 9.5°C

6.34. 2. Dipole-dipole interactions — a polar molecule has a permanent dipole due to a separation of charges across a molecule

	b.p.	dipole "μ" – D=Debye
CH_3CH_2OH	78.3°C	1.66 D
H_2O	100°C	1.84 D
CH_4	−162°C	0

TTQ. Consider methyl iodide (CH_3I) and acetonitrile (CH_3CN).

1) MW are 142 and 41 amu respectively. Which molecule has more dispersion forces?

CH_3I

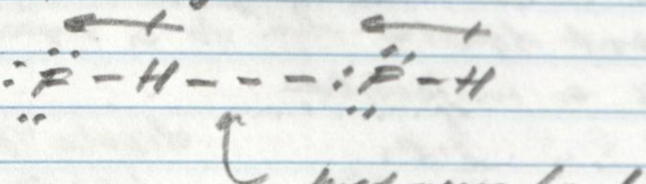
2) The dipole moments are 1.62D and 3.9D, respectively which molecule has more dipole-dipole forces?

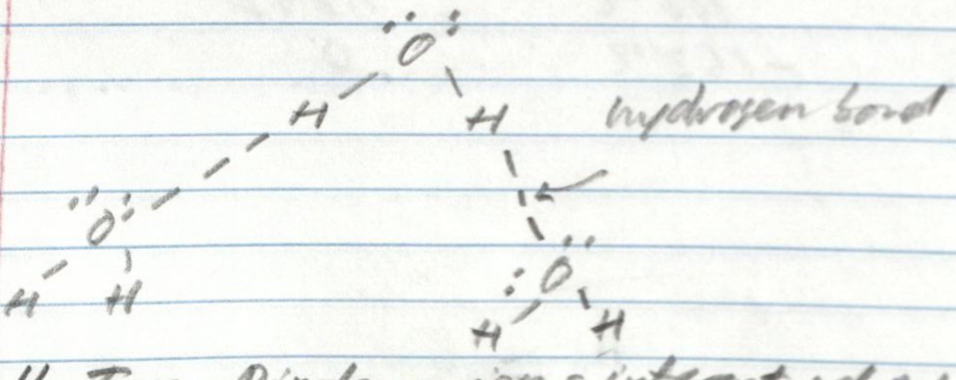
CH_3CN has more dipole-dipole interactions

3) The boiling point are 42.6 °C and 81.8 °C respectively which force has a higher effect on b.p.?

dipole-dipole forces have a larger effect on boiling point (generally)

3. Hydrogen Bonding - H bond to F, N, or O to undergo H-bonding w/ a lone pair of e⁻'s on a neighboring molecule





4. Ion-Dipole - ions interact w/ polar molecules

ex. salt melting ice on roads

I. Heating Curve Calculations

1) $-25°C \rightarrow 0°C$ heating the ice

$q = m\, C_{s,\,ice}\, \Delta T$

$= (18.0g)(2.09\ J/g°C)(25°C)$

MW ↑ ↑ in grams

$q = 941\ J = 0.941\ kJ$

2) $q = n \Delta H_{fus}$ ← heat of melting

$= (1\ mol)(6.02\ \frac{kJ}{mol}) = 6.02\ kJ$

3) $0 \rightarrow 100°C$ heating water

$q = (18.0g)(4.18\ J/g \cdot °C)(100°C)$

$q = 7.52\ kJ$

4) $H_2O(l) \rightarrow H_2O(g)$ boiling

$q = n \Delta H_{vap}$ ← heat of vaporization

$= (1.0\ mol)(40.7\ kJ/mol)$

$= 40.7\ kJ$

5) $100°C \rightarrow 125°C$ heating gas

$q = m\, C_s\, \Delta T$

$= (18.0g)(2.01\ J/g \cdot °C)(25°C)$

$= 904\ J = 0.904\ kJ$

Sum the q's:

$q_{total} = 0.941\ kJ + 6.02\ kJ + 7.52\ kJ + 40.7\ kJ + 0.904\ kJ$

$= 56.1\ kJ$

Lecture Notes 11.27.23

I. Entropy and the Second Law of Thermodynamics

A. Definitions:

spontaneous process – a process that occurs without ongoing outside intervention

$$C(s, \text{diamond}) \xrightarrow{\text{very slow kinetics}} C(s, \text{graphite})$$

spontaneous

↖ thermodynamics

thermodynamics – graphite is more stable than a diamond

kinetics – how fast a process occurs (another class)

* entropy (S) – a state function that increases with the number of energetically equivalent ways to arrange the components of a system — "randomness of a system"

B. Boltzmann

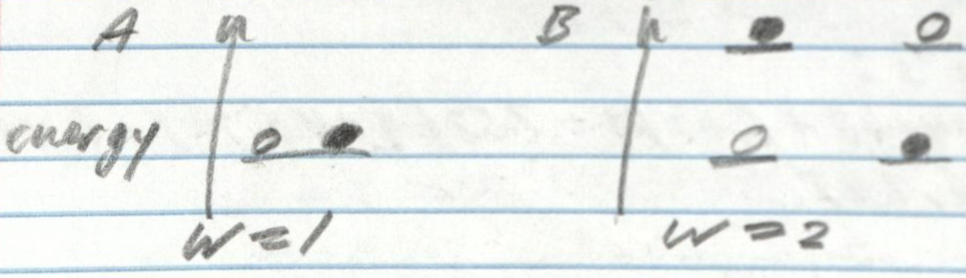
* $S = k_B \ln W$

k_B – Boltzmann's constant $= \frac{R}{N_A} = 1.38 \cdot 10^{-23}$ J/K

↖ avogadro's #

W – # of microstates

note: units for entropy are J/K



* in this case $S_B > S_A$

* for a system with n = # of possibilities, n! = # of microstates

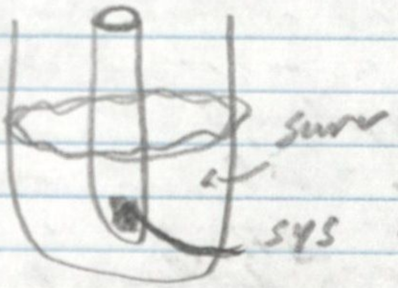
C. 2nd Law of Thermodynamics

* 1) $\Delta S_{universe} > 0$ for any spontaneous reaction

2) for an isothermal process (constant T),

* $\Delta S = \frac{\Delta q_{rev}}{T}$ where T is constant

reversable - an idealized process that occurs very slowly such that the system is in a state of equilibrium



$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$

for a chemical process at constant temperature and pressure

recall:

4) $q_{surr} = -q_{sys} = -\Delta H_{sys}$ (at constant P)

5) since surroundings are infinite and T is constant:

* $\Delta S_{surr} = \frac{-\Delta H_{sys}}{T}$

in chemistry, this is the mathematical definition of entropy

* a process is irreversible when the change occurs in such a way that the system and the surroundings cannot be restored to their original state by reversing the change *

II. Relating ΔH to ΔS

A process that emits heat to its surroundings:

- exothermic, $\Delta H < 0$

will increase entropy of the surroundings:

- $\Delta S_{surr} > 0$

A process that absorbs heat:

- endothermic, $\Delta H > 0$

will decrease the entropy of the surroundings:

- $\Delta S_{surr} < 0$

Putting equations together:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S_{univ} = \Delta S_{sys} - \frac{\Delta H_{sys}}{T}$$

Lecture Notes 11.29.23

III. Calculate ΔS°_{rxn}

$\Delta S^\circ_{rxn} = S^\circ_{products} - S^\circ_{reactants}$

recall (°) means standard state, standard T & P

S° are tabulated in Appendix III (given on exams)

* T is relevant

ex. $Cr_2O_3(s) + 3CO(g) \rightarrow 2Cr(s) + 3CO_2(g)$

find ΔS°_{rxn}: get data from tables

$\rightarrow$ * $\Delta S^\circ_{rxn} = \sum n_p S^\circ_{products} - \sum n_r S^\circ_{reactants}$

$\Delta S^\circ_{rxn} = 2S^\circ(Cr(s)) + 3S^\circ(CO_2)$
$- 1S^\circ(Cr_2O_3) - 3S^\circ(CO)$

$\Delta S^\circ_{rxn} = 2(23.8\ J/K) + 3(213.8\ J/K)$
$- 1(81.2\ J/K) - 3(197.7\ J/K) = +14.7\ J/K$

IV. Patterns and Trends to help explain entropy

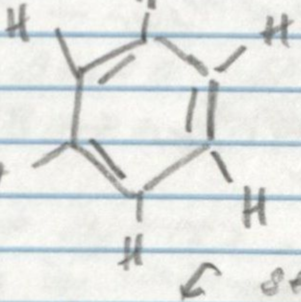
A. States (phases) of matter

* $S_{(s)} < S_{(l)} < S_{(g)}$

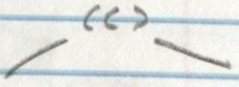
* B. Entropy increases as mass increases

C. Allotropes have different entropies

graphite



hexagon



$S_{diamond} < S_{graphite}$ (because diamond is structured in cube form while graphite can 'slip' as sheets of hexagons)

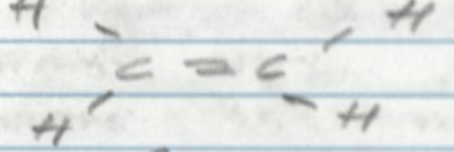
D. Molecular complexity (will trump size)

$S(Ar) < S(NO)$

$S(CO) < S(CO_2)$ (earlier example)

$CO(g)$: $C_2H_4(g)$:

$:C\equiv O:$



$S_{carbon\ monoxide} < S_{ethene}$

* the more complex a compound is the higher its entropy *

TTQ: Predict the sign of ΔS_{rxn} for each process (T is constant)

(+) $NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$

(+) $Au(s) \rightarrow Au(l)$

V. Third Law of Thermodynamics

* the entropy of a perfect crystal at zero Kelvin = 0 (theoretical)

Spontaneity, ΔH, ΔS, and ΔG:

recall: $\Delta S_{univ} = \Delta S_{sys} - \Delta H/T$ @ constant T

rearrange:

multiply by T and −1:

$$\underbrace{-T\Delta S_{univ}} = \Delta H_{sys} - T\Delta S_{sys}$$

* $\Delta G = \Delta H_{sys} - T\Delta S_{sys}$

Gibbs Free Energy

* $\Delta G < 0$ for a reaction to be spontaneous

↙

if $\Delta H < 0$ and $\Delta S > 0$, $\Delta G < 0$

Independent Notes / Missed lecture 12/1 12.3.23

*$\Delta G < 0$ for a reaction to be spontaneous

if $\Delta H < 0$ (exothermic)

and $\Delta S > 0$ (entropy increasing),

reaction will always be spontaneous

* The Effects of ΔH_{sys}, ΔS_{sys}, and T on spontaneity:

T is K so always positive

1) if $\Delta H > 0$ and $\Delta S < 0$,

$\Delta G = \Delta H - T\Delta S$,

then ΔG must be > 0 at all temperatures

is NOT SPONTANEOUS

ex. $3O_2(g) \rightarrow 2O_3(g)$, $\Delta H^\circ_{rxn} = 285.4$ kJ

2) if $\Delta H < 0$ and $\Delta S > 0$,

$\Delta G = \Delta H - T\Delta S$

$\Delta G < 0$ at all T, SPONTANEOUS

ex. $2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$, $\Delta H^\circ_{rxn} = -163.2$ kJ

3) if $\Delta H < 0$ & $\Delta S < 0$, $\Delta G = \Delta H - T\Delta S$

$(-) - (-)$

@ low T $\Delta G < 0$ SPONTANEOUS

@ high T $\Delta G > 0$ NOT SPONTANEOUS

ex. $H_2O(l) \rightarrow H_2O(s)$, $\Delta H^\circ_{rxn} = -6.01$ kJ

4) $\Delta H > 0$ and $\Delta S > 0$, $\Delta G = \Delta H - T\Delta S$

@ low T $\Delta G > 0$ NOT SPONTANEOUS

@ high T $\Delta G < 0$ SPONTANEOUS

ex. $H_2O(l) \rightarrow H_2O(g)$, $\Delta H^\circ_{rxn} = 40.7$ kJ @ 100°C or 373K ex- $3H_2(g) + Fe_2O_3 \rightarrow 2Fe(s) + 3H_2O(g)$ @ 25°C

Is this reaction spontaneous?

Will Temperature change affect spontaneity?

Strategy: find ΔH from ΔH_f° } from tables

And ΔS from ΔS°

then plug into $\Delta G = \Delta H - T\Delta S$

$\Delta H = \Delta H_f^\circ(H_2O(g)) - \Delta H_f^\circ(Fe_2O_3)$

$\Delta H^\circ_{rxn} = 3(-214.8\,kJ) - 1(-824.2\,kJ)$

$= +98.8\,kJ$

$\Delta S^\circ = \Sigma n\Delta S^\circ(\text{products}) - \Sigma n\Delta S^\circ(\text{reactants})$

$\Delta S^\circ = 2(27.3\,J/K) + 3(188.8\,J/K)$

$- 3(130.7\,J/K) - 1(87.4\,J/K)$

$= 141.5\,J/K = 0.1415\,kJ/K$

$T = 25°C = 298\,K$

$\Delta G = 98.8\,kJ - (298\,K)(0.1415\,kJ/K)$

$= 56.6\,kJ$

$\Delta G > 0$ NOT SPONTANEOUS

↑T to make it spontaneous

At what T does the rxn become spontaneous?

* $0 = \Delta H - T\Delta S$, solve for T

$0 = 98.8\,kJ - T(0.1415\,kJ/K)$

$\frac{-98.8\,kJ}{-0.1415\,kJ/K} = 698\,K$

III. Calculating ΔG°

($^\circ$): standard conditions

1) ΔG°_{rxn}, can be found using ΔH° & ΔS°
information from tables

2) ΔG° – from tables for ΔG

* $\Delta G^\circ_{rxn} = \sum n \Delta G^\circ_f$ (products) $- \sum n \Delta G^\circ_f$ (reactants)

IV. ΔG for non standard conditions

$H_2O(l) \rightleftharpoons H_2O(g)$. $\Delta G^\circ_{rxn} = 8.59$ kJ/mol

ΔG°_{rxn} is not spontaneous!

But water spilled on the floor will evaporate
if p (atm) $\neq 1$ atm

* $\Delta G_{rxn} = \Delta G^\circ_{rxn} - RT \ln Q$

Q = reaction quotient

$Q = \dfrac{[P]^x}{[R]^y}$ $(xP \rightarrow yR)$

* if you ae at standard conditions:

$p = 1$ atm

$M = 1$ M

$Q = 1$

so $\Delta G = \Delta G^\circ$

but the correction factor accounts for
other factors in the environment

Lecture Notes $H_2O(l) \rightleftharpoons H_2O(g)$ 12.4.23

ex. Prove that 25°C water is in equilibrium with water vapor at $P = 0.0313$ atm

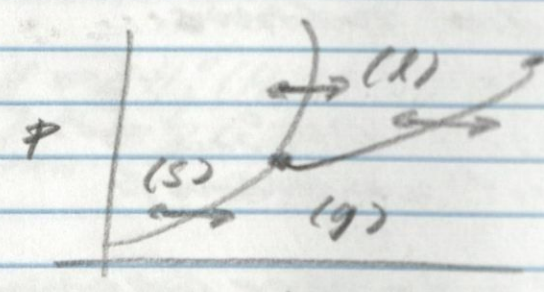
$\Delta G = \Delta G^\circ_{rxn} + RT \ln Q$

$\Delta G = 8.59\,kJ/mol + 0.008314\,kJ/mol \cdot K\,(298\,K) \ln\left(\frac{0.0313}{1}\right)$

from table/given ; look for correct units ;

$\Delta G = 8.59\,kJ/mol - 8.59\,kJ/mol$

$\Delta G = 0$, spontaneous



equilibrium points along line

II. Relating ΔG to K_{eq}

$\Delta G_{rxn} = 0$ @ equilibrium

and $Q = K_{eq}$ @ equilibrium

$0 = \Delta G^\circ_{rxn} + RT \ln K_{eq}$

$* \Delta G^\circ_{rxn} = -RT \ln K$

if $\Delta G^\circ_{rxn} = 0$, then $K = 1$

if $\Delta G^\circ_{rxn} > 0$, then $K < 1$

if $\Delta G^\circ_{rxn} < 0$, then $K > 1$

TTQ: Calculate K_{eq} of $N_2O_4(g) \rightarrow 2NO_2(g)$ @ 25°C

Given: $\Delta G^\circ_f(N_2O_4) = 99.8\,kJ/mol$

$\Delta G^\circ_f(NO_2) = 51.3\,kJ/mol$

$\Delta G^\circ_{rxn} = 2\Delta G^\circ_f(NO_2) - 1\Delta G^\circ_f(N_2O_4)$

$= 2(51.3\,kJ/mol) - 99.8\,kJ/mol = 2.8\,kJ/mol$

$K = e^{-\left[\frac{2.8\,kJ/mol}{0.008314\,kJ/mol \cdot K\,(298\,K)}\right]} = 0.32$

VI. Dependence of Keq on T

A. V'ant Hoff Eqn

$\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$

$\Delta G^\circ_{rxn} = -RT\ln K$

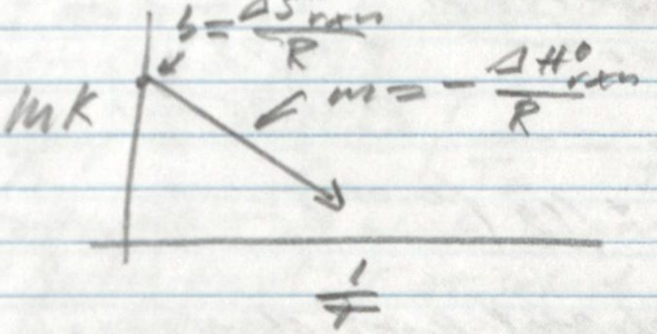
so $-RT\ln K = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$

if divide both sides by $-RT$

* $\ln K = -\frac{\Delta H^\circ_{rxn}}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ_{rxn}}{R}$

↑ only variable is T

analogous to $y = mx + b$



B. If reaction is done at 2 different temperatures

* $\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H^\circ_{rxn}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

* $\ln K_2 - \ln K_1 = \frac{-\Delta H^\circ_f}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

TTQ. Keq for ammonia is $6.8 \cdot 10^5$ at 298K. Predict its value at 400K.

Solve for K_2

$K_2 = e^{\left[\frac{-\Delta H^\circ_f}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \ln K_1\right]}$

$K_2 = 7.82 \cdot 10^7$

"synthesis of ammonia" means

balanced → $N_2 + 3H_2 \rightarrow 2NH_3$

→ $\frac{1}{2}\underline{N_2} + \frac{3}{2}\underline{H_2} \rightarrow NH_3$ ← must be 1 mol

elements: (g) at standard conditions

Lecture Notes | Course Review 12.6.23

Strong acids: HNO_3, H_2SO_4, $HClO_4$,
HCl, HBr, HI

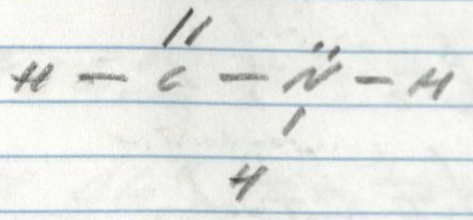
Strong bases: $LiOH$, $NaOH$, KOH
$Sr(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$

ex. 100 mL of 0.2 M CN^- is titrated with 75 mL 0.1 M $HClO_4$. Find pH of soln.

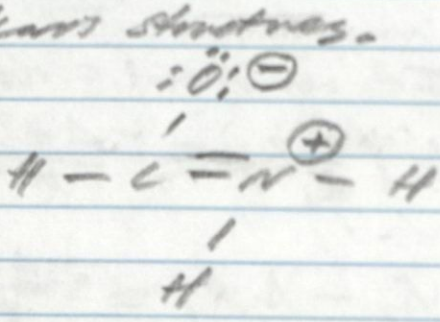
CN^- +	$HClO_4$ →	HCN +	ClO_4^-
.02 mol	.0075 mol		
−.0075	−.0075	+.0075	
0.0125 mol		0.0075 mol	

$$pH = pK_a + \log\left(\frac{0.0125\text{ mol}}{0.0075\text{ mol}}\right)$$

ex. Fill in the skeletal Lewis structures.



major



minor

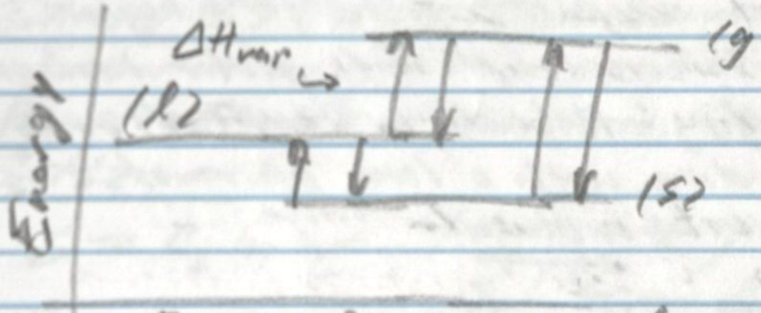
$* \; Hz = \nu = s^{-1}$

ex. 21σ, 5π in aspirin (wrong answer)

* know phase diagrams

Independent Notes / Final Exam Material Notes 12.9.23

Phase Changes: requires addition or removal of energy



Vapor Pressure: pressure of a gas in dynamic equilibrium with its liquid (depends on T)

ΔHvap: amount of E required to go from (l) → (g)

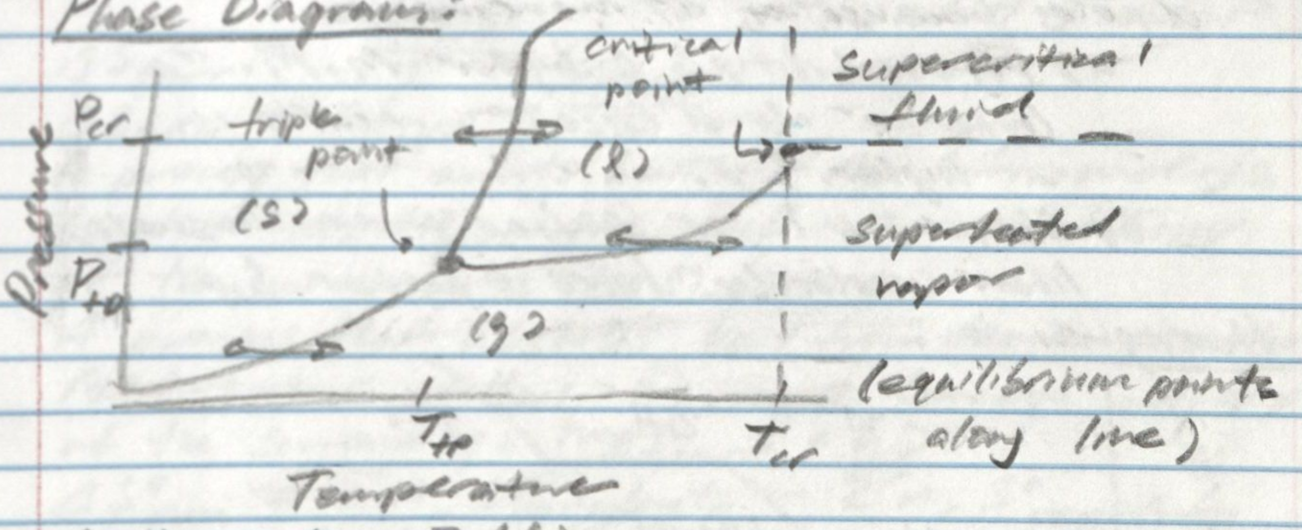
Clausius-Clapeyron:

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Boiling Point: T at which vapor pressure = P_{ext}

Normal Boiling Point: T at which vapor pressure = 1 atm = 760 torr

Phase Diagram:

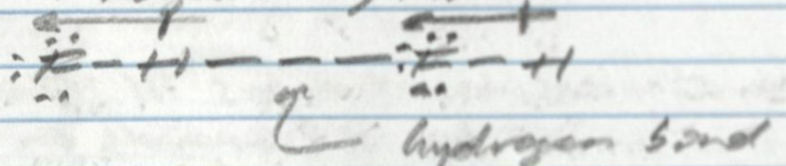


Melting: (s) → (l)
Freezing: (l) → (s)
Evaporation: (l) → (g)
Condensation: (g) → (l)
Sublimation: (s) → (g)
Deposition: (g) → (s)

Intermolecular Forces: attractions and repulsion of one molecule to another

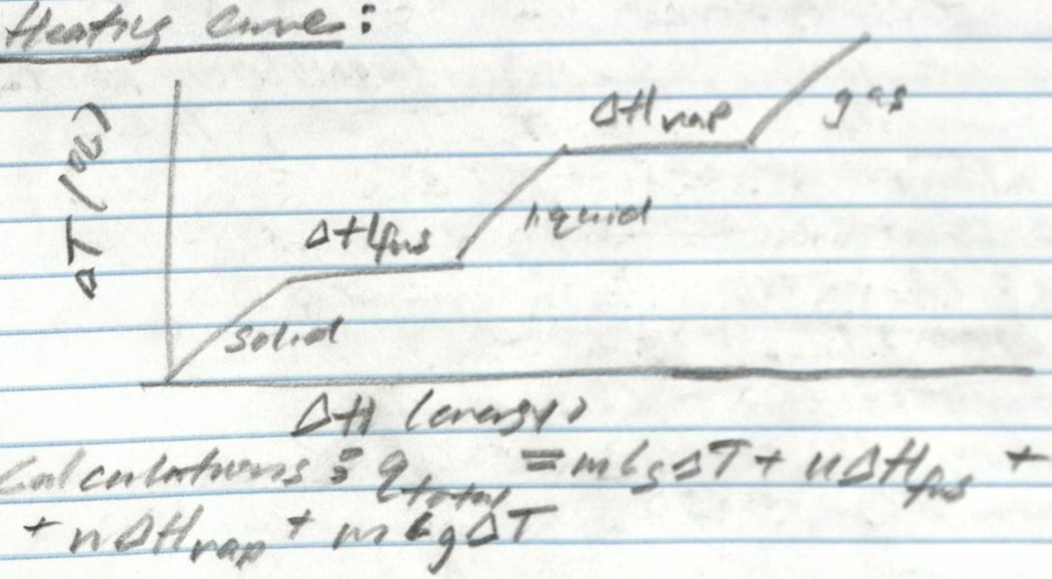
(from strongest to weakest) – stronger = higher b.p.

1. Ion–Dipole: ions react with polar molecules
2. Hydrogen Bonding: H bonds with F, N, or O undergo H-bonding with a lone pair of e^-'s on a neighboring molecule



3: Dipole–dipole: a polar molecule has a permanent dipole due to a separation of charges across a molecule
   dipole "D" increases with boiling point "b.p."
4: Dispersion Forces: all molecules an atoms experience dispersion forces due to temporary dipoles because of e^- movement
   a) Polarizability: a higher M.M. "a larger e^- cloud (size)" results in a higher b.p.
   b) Shape: a larger surface area "usually linear molecules" have a higher b.p.

Heating Curve:



Calculations: $q_{total} = mc_s\Delta T + n\Delta H_{fus} + mc_l\Delta T$
$+ n\Delta H_{vap} + mc_g\Delta T$

Spontaneous Process: a process that occurs without ongoing outside intervention

Entropy (S): a state function that increases with the number of energetically equivalent ways to arrange the components of a system, "randomness of a system"

Boltzman:

$S = k_b \ln W$ (units are J/K)

k_b = Boltzman's constant $= \frac{R}{N_A} = 1.38 \cdot 10^{-23}$ J/K

$W = n!$ # of microstates $\uparrow$ avogadro's number

$\Delta S_{universe} > 0$ for spontaneous processes

For an Isothermal Process (constant T):

$\Delta S = \frac{\Delta q_{rev}}{T}$ ← an idealized process such that the system is at a state of equilibrium

$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$ (for a chemical process at constant T and P)

$\Delta S_{surr} = \frac{-\Delta H_{sys}}{T}$

$\Delta S_{univ} = \Delta S_{sys} - \frac{\Delta H_{sys}}{T}$

A process that emits heat to its surroundings (exothermic, $\Delta H_{sys} < 0$), will increase entropy of the surroundings ($\Delta S_{surr} > 0$)

A process that absorbs heat from the surroundings (endothermic, $\Delta H_{sys} > 0$), will decrease entropy of the surroundings ($\Delta S_{surr} < 0$)

$\Delta S^\circ_{rxn} = \Sigma n_p S^\circ_{products} - \Sigma n_r S^\circ_{reactants}$

(°): standard state, standard T and P (0°C and 1 atm)

Patterns and Trends to Explain Entropy:

A. States: $S_{(s)} < S_{(l)} < S_{(g)}$

B. S increases as mass increases

C. S increases with weaker allotropes

$S_{perfect\ crystal} = 0 < S_{diamond} < S_{graphite}$

D. S increases with molecular complexity

$S(Ar) < S(NO) < S(CO_2)$

$\Delta G = \Delta H_{sys} - T\Delta S_{sys} = -T\Delta S_{univ}$ (in J or kJ)

$\Delta G < 0$ for a reaction to be spontaneous

- if $\Delta H < 0$ ad $\Delta S > 0$, rxn always spontaneous
- if $\Delta H > 0$ and $\Delta S < 0$, rxn never spontaneous
- if $\Delta H < 0$ ad $\Delta S < 0$, rxn sometimes spontaneous
  - ∘ at low T, $\Delta G < 0$, spontaneous
  - ∘ at high T, $\Delta G > 0$, not spontaneous
- if $\Delta H > 0$ ad $\Delta S > 0$, rxn sometimes spontaneous
  - ∘ at low T, $\Delta G > 0$, not spontaneous
  - ∘ at high T, $\Delta G < 0$, spontaneous

reaction becomes spontaneous when $0 = \Delta H_{sys} - T\Delta S_{sys}$

Calculating ΔG°:

1) $\Delta G^\circ_{rxn} = \Delta H^\circ - T\Delta S^\circ$ w/ info from tables
2) $\Delta G^\circ_{rxn} = \sum n\Delta G^\circ_f$ (products) $- \sum n\Delta G^\circ_f$ (reactants) w/ info from tables

Calculating ΔG (non standard conditions):

$$\Delta G_{rxn} = \Delta G^\circ_{rxn} + RT\ln Q$$

$$Q = \frac{[P]^x}{[R]^y}, \quad xP \rightarrow yR$$

$(^\circ)$: $P = 1\text{ atm}$, $M = 1M$, $Q = 1$, $\Delta G = \Delta G^\circ$

$\Delta G_{rxn} = 0$ at equilibrium (ad $Q = K_{eq}$)

$\Delta G^\circ_{rxn} = -RT\ln K$

if $\Delta G^\circ_{rxn} = 0$, $K = 1$

if $\Delta G^\circ_{rxn} > 0$, $K < 1$

if $\Delta G^\circ_{rxn} < 0$, $K > 1$

linear w/respect to $1/T$

$$-RT\ln K = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$$

$$\ln K = -\frac{\Delta H^\circ_{rxn}}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ_{rxn}}{R}$$

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H^\circ_{rxn}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln K_2 - \ln K_1 = \frac{-\Delta H^\circ_f}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Independent Notes / Exam 1 Review 12.10.23

Unit Conversions:

$$\text{units given} \cdot \left(\frac{\text{units needed}}{\text{units given}}\right) = \text{units needed}$$

Subatomic Particles:		charge	mass	amu
electron	e^-	-1	$9.109 \cdot 10^{-31}$ kg	0u
proton	p^+	$+1$	$1.672 \cdot 10^{-27}$ kg	1u
neutron	n	0	$1.672 \cdot 10^{-27}$ kg	1u

\# of protons: defines element

\# of neutrons: defines isotope

\# of electrons: equal to # of protons (in a neutral atom)

ion: charged atom / molecule with different # of p^+ and e^-

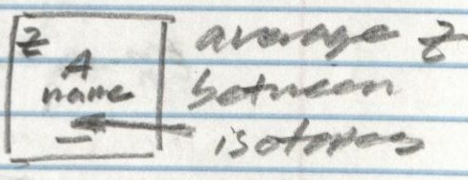
atomic # (Z): # of protons

mass # (A): # of protons + neutrons

Element Annotation:

$^{A}_{Z}X$ X: Element symbol

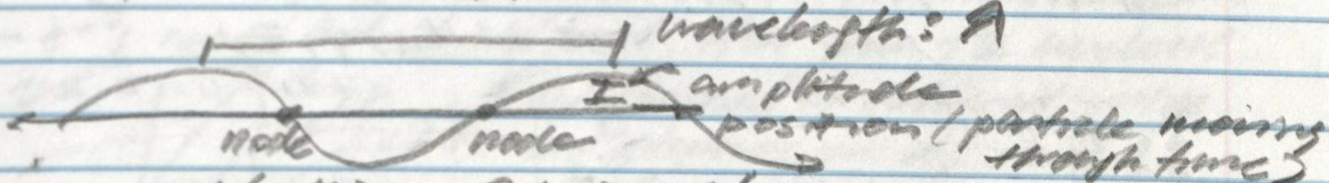
A: mass #, Z: atomic #



1 mol = n = $6.022 \cdot 10^{23}$: unit of measurement

Formula / Molecular Weight: mass of 1 mol of compound or molecule

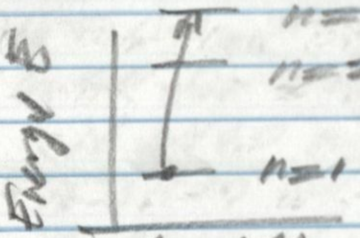
Quantum Mechanics of an Atom: in classical mechanics, an atom cannot exist



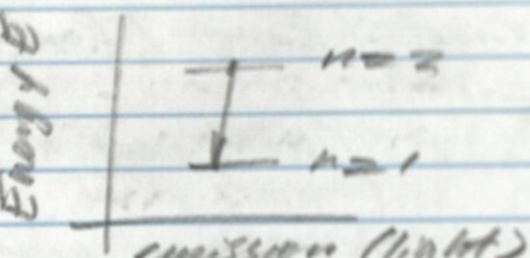
speed (m/s) = λ (m) ν (1/s, Hz), $c = \lambda\nu$

$E = h\nu$, h = plank's constant = $6.626 \cdot 10^{-34}$ Js

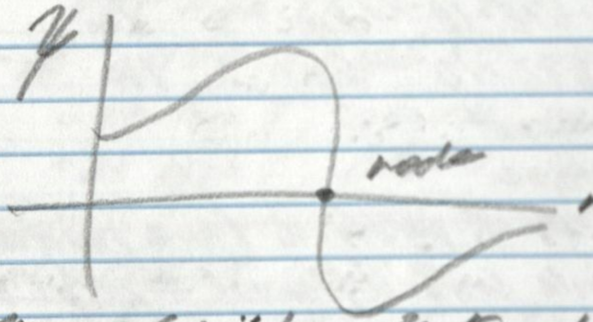
$E = h\left(\frac{c}{\lambda}\right)$, if $\nu\uparrow$, then $E\uparrow$
if $\lambda\uparrow$, then $E\downarrow$

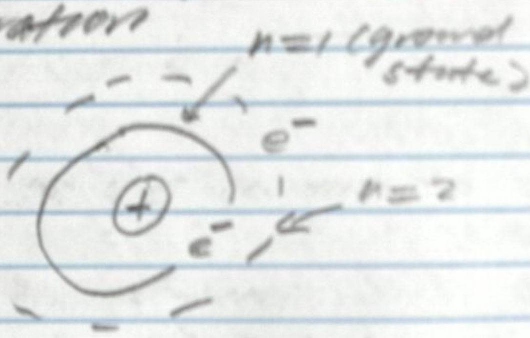


absorbtion
excitation



emission (light)
relaxation





Ψ(r): Schrödinger's Equation: wave function for e⁻'s where r = distance from nucleus to e⁻

$E_n = -\frac{Rh}{n^2}$, R = Rydberg's Constant, $3.29 \cdot 10^{15} s^{-1}$

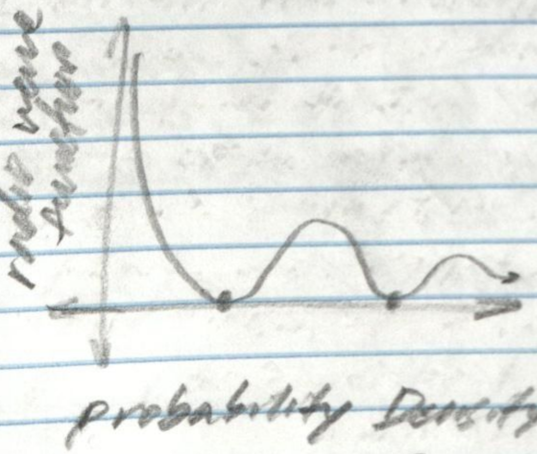
n = discrete e⁻ energy level

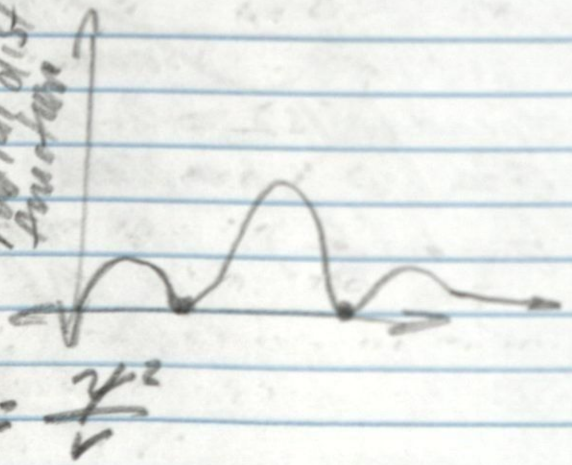
$\Delta E = E_f - E_i = h\nu$

$\Delta E = -Rh\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$ (emissions always negative)

$\psi(r) = \psi(x,y,z)$: wave function of e⁻

$\psi^2(r) = \psi^2(x,y,z)$: probability of finding e⁻ at (x,y,z)





probability Density = $\frac{\psi^2}{V}$

as V↓, $\frac{\psi^2}{V}$↑ to ∞

Quantum Numbers: help explain likely position of e^-

$n \rightarrow$ orbital size and energy $\rightarrow$ positive integer ≥ 1

$l \rightarrow$ orbital angular momentum $\rightarrow$ $0 \leq l \leq n-1$ (shape)

$m_l \rightarrow$ magnetism $\rightarrow$ $-l \leq m_l \leq l$ (orientation)

Node: probability of finding $e^- = 0$

Radial Nodes: $\psi(r) = 0$, $\psi^2(r) = 0$

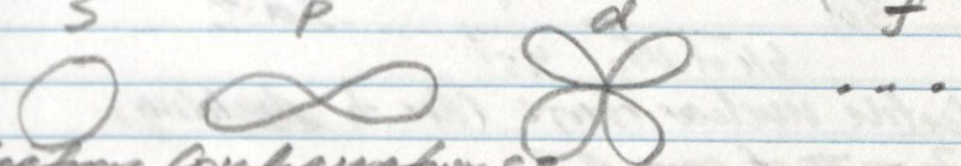
Angular Nodes:

l letter: s, p, d, f

l number: 0 1 2 3 (# of angular nodes)

Total Nodes = $n-1$

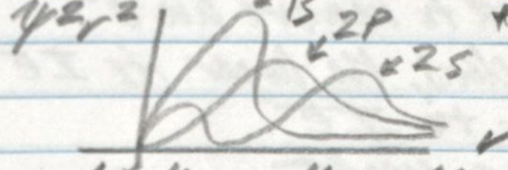
Total Nodes = radial nodes + angular nodes



Electron Configurations:

$m_s \rightarrow$ spin $\rightarrow$ $\frac{1}{2}$ (up), $-\frac{1}{2}$ (down)

- each orbital can carry 2 e^-'s (usually w/ opposite spins)
- each e^- has it's own unique set of quantum numbers
- e^-'s repel and shield each other from the nucleus



* this happens at different rates and depends on l, so l affects orbital energy

- orbitals with only 1 e^- are called degenerate orbitals
- for a group of degenerate orbitals (of the same energy) add e^-'s with parallel m_s before pairing e^-'s
- order of adding e^-'s: look at PT

  $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < \ldots$

  d-block: $n-1$, f-block: $n-2$
- add or subtract e^-'s to account for ions
  - same e^- configuration: isoelectric

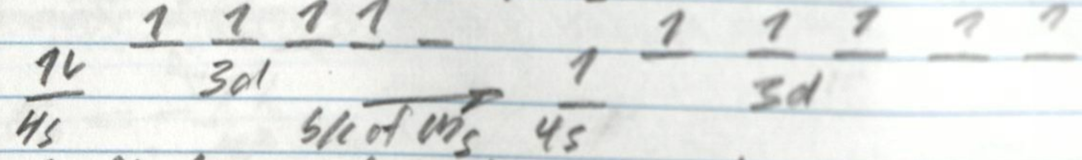
Valence Shell Electrons:

- outer e^- ≠ valence e^- = outer shell e^-
- for main group elements (s, p), v.s.e. are e^-'s with highest n
- for (d, f) block elements, v.s.e include e^-'s with highest n and outermost d or f block e^-'s *if* d or f block not filled

Periodic Trends:

1. Noble Gases (18) have most stable e^- configuration
2. V.S.E. are most reactive e^-'s
3. Shielding and Z_{eff} affect periodic trends
4. filled and half-filled shells are stable e^- configurations

Cr: $[Ar]4s^2 3d^4 \rightarrow [Ar]4s^1 3d^5$

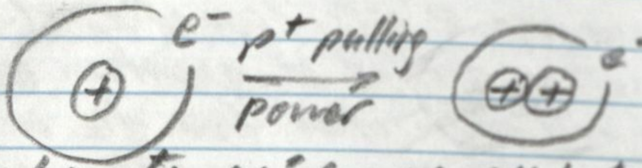


Z_{eff}: effective nuclear charge (due to shielding)

$Z_{eff} = Z - \#$ of core e^-

Atomic Radius: atoms get larger as you move down and left

Ionic Radius: cations are smaller than anions



Ionization Energy: energy required to remove an e^-

1. The farther an e^- is from the nucleus, the larger its IE
2. The larger the Z_{eff}, the larger the IE
   - IE increases as you go right

First IE: $M(g) + IE_1 = M^+(g) + e^-$

Second IE: $M^+(g) + IE_2 = M^{2+}(g) + e^-$

Electron Affinity: the energy released (−) when an atom gains an e^- to become an anion

1. No trend going down the PT
2. |EA| increases as you go right
   - p-block gain e^-'s to become noble gases