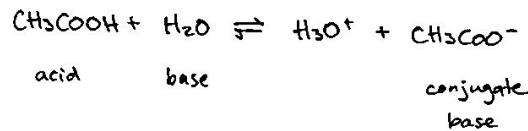


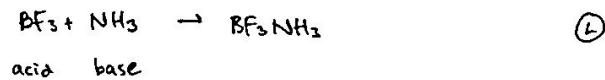
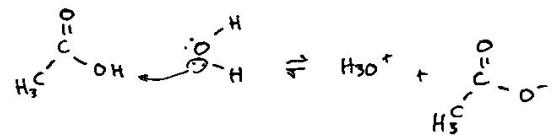
&lt;&lt; Definition of Acid &amp; Base

	<u>Scheme</u>	<u>Acid</u>	<u>Base</u>
(A)	Arrhenius	$[H_3O^+] \uparrow$ in $H_2O$	$[OH^-] \uparrow$ in $H_2O$
(B)	Bronsted-Lowry	$H^+$ donor	$H^+$ acceptor
(C)	Lewis	Bind on $e^-$ pair ( $e^-$ pair acceptor)	offers on $e^-$ pair ( $e^-$ pair donor)

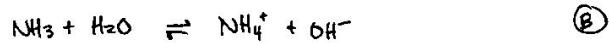
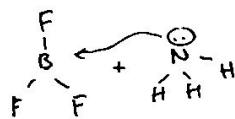


(A)(B)(C)

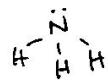
If (A)(B), then should be (C).



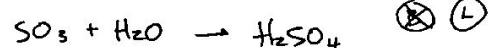
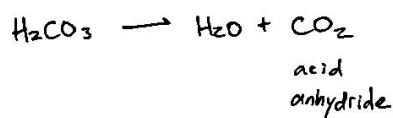
(C)



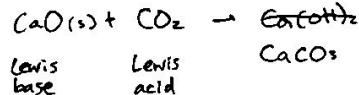
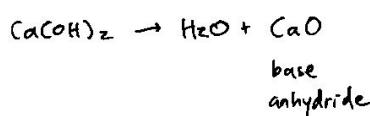
(B)



&gt; acid anhydride - an oxoacid with all waters removed so only an oxide remains

> base anhydride - compound left after removing  $H_2O$  from a base

(X) (C)



> amphoteric - substance that can act as acid or base



Since  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$  when neutral,  $[\text{H}_3\text{O}^+]^2 = 10^{-14}$ ,  $[\text{H}_3\text{O}^+] = 10^{-7}$

$$\text{pH} = 7$$

> strong acid - acid that dissociates completely in  $\text{H}_2\text{O}$

> strong base - base that dissociates completely in  $\text{H}_2\text{O}$

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$\text{pOH} = -\log[\text{OH}^-]$$

**EX1** pH of 0.1M NaOH soln?

$$[\text{Na}^+] = 0.1\text{M}$$

$$[\text{OH}^-] = 0.1\text{M}$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

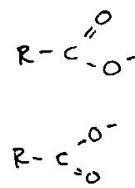
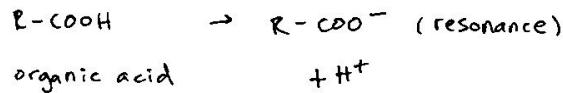
$$10^{-14} = [\text{H}_3\text{O}^+](10^{-1}\text{M})$$

$$[\text{H}_3\text{O}^+] = 10^{-13}\text{M}$$

$$\text{pH} = 13$$

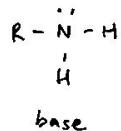
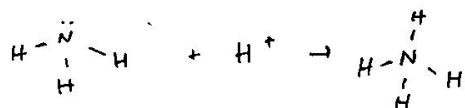
$$\text{pH} + \text{pOH} = 14$$

&lt;&lt; Recap

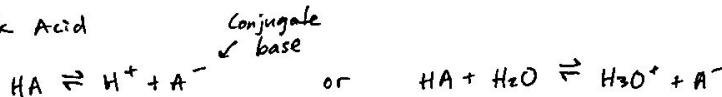


stable!

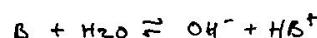
$$K > 1$$



&lt;&lt; Weak Acid



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



$$K_b = \frac{[\text{OH}^-][\text{HB}^+]}{[\text{B}]}$$

$$\rho K_a = -\log K_a$$

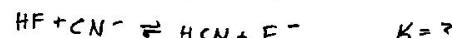
$$\rho K_b = -\log K_b$$

For any acid-base conjugate, the strength is inversely proportional.

$$K_a K_b = K_w = 10^{-14} = [\text{H}^+][\text{OH}^-] @ \text{STP}$$

$$\rho K_a + \rho K_b = 14$$

EX



↑ Base

↑ Base

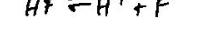
most  
dangerous  
acids  
(but weak acid)

$$K_{\text{HF}} =$$

$$6.6 \times 10^{-4}$$
 stronger acid  $\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$

$$K_{\text{HCN}} = 6.17 \times 10^{-10}$$

weaker acid

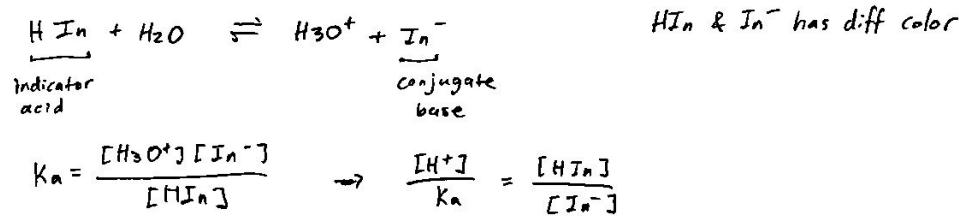


Safety moment

$$K = \frac{K_{\text{HF}}}{K_{\text{HCN}}} = \frac{6.6 \times 10^{-4}}{6.17 \times 10^{-10}} = \sim 10^6 \quad \text{to the right}$$

<< Indicator

> substance changes color upon protonation / lossing H<sup>+</sup>



if [H<sup>+</sup>] > K<sub>a</sub>, mostly [HIn]

if [H<sup>+</sup>] < K<sub>a</sub>, mostly [In<sup>-</sup>]

**Ex** 1.000 mol acetic acid CH<sub>3</sub>COOH in 1.000 L H<sub>2</sub>O. Find pH.

$$\text{H}_3\text{C}-\overset{\text{O}}{\underset{\text{OH}}{\text{C}}} \quad K_a = 1.76 \times 10^{-5} = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$\begin{array}{c|ccc} I & 1 & 0 & 0 \\ C & -x & +x & +x \\ E & 1-x & x & x \end{array} \quad \frac{x^2}{1-x} = K_a \quad (1 \gg x)$$
$$x^2 \approx K_a$$

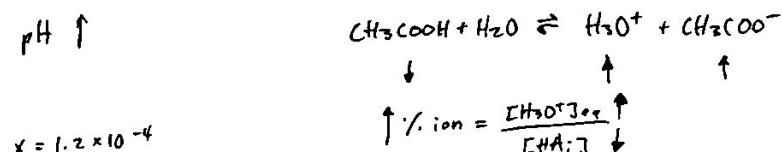
check by percent ionization.

$$\% \text{ ionization} = \frac{[\text{H}^+]_{\text{eq}}}{[\text{HA}]_i}$$
$$= \frac{4.2 \times 10^{-3} \text{ M}}{1 \text{ M}} = 0.42\%$$
$$x = \sqrt{K_a} = 4.2 \times 10^{-3}$$
$$[\text{H}^+] = 4.2 \times 10^{-3} \text{ M}$$
$$\text{pH} = 2.38$$

**Ex** if 0.001 mol CH<sub>3</sub>COOH

% ionization ↑ by Le Chatelier Principle

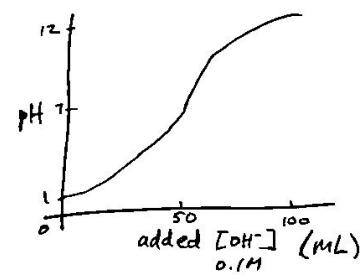
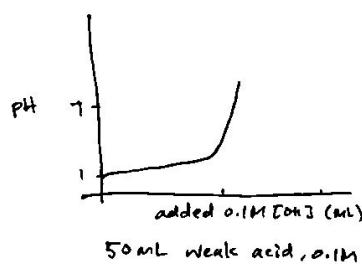
pH ↑



pH = 3.9

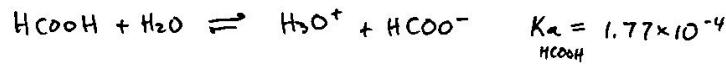
% ionization = 12.4%.

&lt;&lt; Buffer

> substance added to ~~solt~~ soln that resists  $\Delta \text{pH}$ .

- slower at first
- think % ionization
- not all  $\text{H}^+$  are out

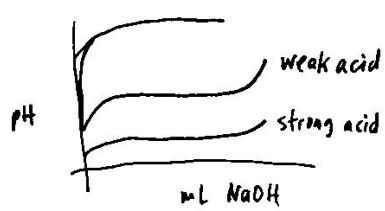
[EX] 1.00 mol  $\text{HCOOH}$   
0.5 mol  $\text{NaHCOO}$  } 1L Find pH.



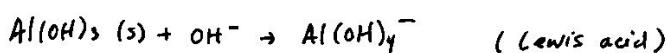
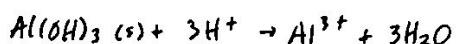
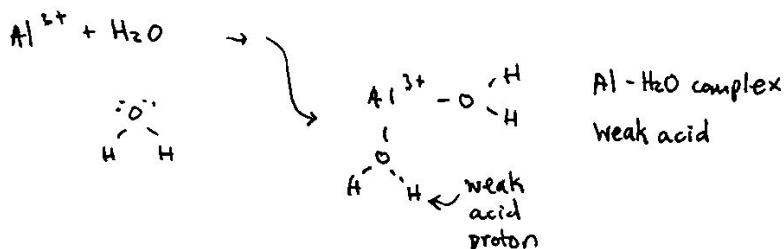
	$\text{NaHCOO}$	$\rightarrow \text{Na}^+ + \text{HCOO}^-$
I	1	0 0.5
C	-x	+x +x
E	$1-x$	x $0.5+x$

$$\frac{x(0.5+x)}{1-x} = K_a_{\text{HCOOH}}$$

$$\text{pH} = 3.45$$



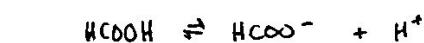
&lt;&lt; Demo

 $\text{Al}(\text{OH})_3$  is amphoteric

&lt;&lt; Buffer Example

[Ex]  $1.00\text{ mol HCOOH}$   
 $0.50\text{ mol NaCOO}$  } 1 L soln  $\rightarrow \text{pH} = 3.45$

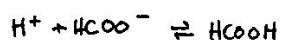
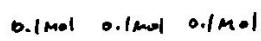
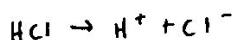
+ 0.1 mol HCl, Find pH



I	1.00 mol	0.50 mol	0.4 mol
C	-x	+x	+x
E	1.0-x	0.4+x	x

$$\frac{(0.4+x)x}{1.0-x} = K_a \rightarrow \text{pH} = 3.31$$

$$x = 4.9 \times 10^{-4}$$



/ use H-H eq:

$$\text{pH} = \text{pK}_a - \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$= 3.75 + \log \left( \frac{0.5}{1.0} \right) = 3.45$$

&lt;&lt; H-H Equation

$$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \approx \frac{[\text{H}^+][\text{A}^-]_0}{[\text{HA}]_0} \quad \begin{matrix} \text{Approximation} \\ \text{When solving ICE table.} \end{matrix}$$

$$[\text{H}^+] = K_a \frac{[\text{HA}]_0}{[\text{A}^-]_0}$$

$$-\log [\text{H}^+] = -\log K_a - \log \frac{[\text{HA}]_0}{[\text{A}^-]_0}$$

$$\boxed{\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]_0}{[\text{HA}]_0}} \quad \begin{matrix} \text{it is an approx.} \end{matrix}$$

10 Jan 2020

buffer

CHEM 155

**Exe** 0.05 M NaOH Add how much NaOH for pH = 4?

500mL 0.1 M  $\text{KH}_2\text{PO}_4$

$pK_a = 3.75$

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

$$4.0 = 3.75 + \log \frac{[A^-]}{[HA]} \quad \text{let } x = \text{mol A}^- \text{ added}$$

$$4.0 = 3.75 + \log \frac{\text{mol A}^-}{\text{mol HA}}$$

$$4.0 = 3.75 + \log \frac{x}{0.05 - x}$$

$$10^{-0.25} = \frac{x}{0.05 - x}$$

$$x = 0.032 \text{ mol}$$

$$0.032 \text{ mol} \quad \frac{1L}{0.05 \text{ mol}} = 0.640 \text{ L}$$

~~~ Titration Example

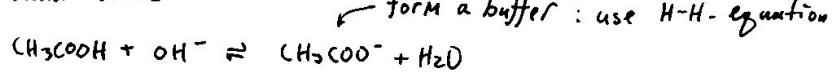
**Ex1** 100mL 0.100M CH<sub>3</sub>COOH analyte  
0.100M NaOH titrant

→ Initial point

pH = -log [H<sup>+</sup>], use K<sub>a</sub> use ICE, then  
pH = 3.88

→ To equiv pt.

$$V_{\text{add}} = 30 \text{ mL}$$



$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]_0}{[\text{HA}]_0} = \text{pK}_a + \log \frac{\text{mol A}^-}{\text{mol HA}} = 4.75 + \log \frac{0.003 \text{ mol}}{0.01 \text{ mol} - 0.003 \text{ mol}} = 4.38$$

→ Equiv. pt.

200 mL of 0.05M CH<sub>3</sub>COO<sup>-</sup>

$$K_b = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{K_w}{K_a} = 5.68 \times 10^{-10} = \frac{x^2}{0.05 - x}$$

ICE

→ After Equiv. pt.

$$x = 5.33 \times 10^{-6}$$

[OH<sup>-</sup>] ≈ excess added NaOH after equiv. pt.

(Strong Acid-Strong Base Q)

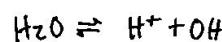
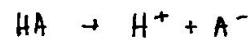
~~~ Deeper Look

**Ex2** Dissolve HA & NaA

$$[\text{HA}]_0 = c_a$$

$$[\text{NaA}]_0 = c_b$$

### Reactions



conservation of A material

conservation of charge

### Equations

$$[\text{Na}^+] = c_b = [\text{A}^-]$$

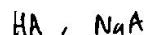
$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

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

$$c_a + c_b = [\text{HA}] + [\text{A}^-]$$

$$[\text{Na}^+] + [\text{H}^+] = [\text{A}^-] + [\text{OH}^-]$$

&lt;&lt; Derivation



$$c_a \quad c_b$$

$$\textcircled{1} \rightarrow \textcircled{5} \quad c_b + [\text{H}^+] = [\text{A}^-] + [\text{OH}^-]$$

$$\textcircled{6} \Leftrightarrow \textcircled{7} \quad [\text{A}^-] = c_b + [\text{H}^+] - [\text{OH}^-] \quad \textcircled{6}$$

$$c_a + c_b = [\text{HA}] + \underset{\textcircled{8}}{c_b + [\text{H}^+] - [\text{OH}^-]} \quad \textcircled{8}$$

$$[\text{Na}^+] = c_b \quad \textcircled{1}$$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \textcircled{2}$$

$$K_w = [\text{H}^+][\text{OH}^-] \quad \textcircled{3}$$

$$c_a + c_b = [\text{HA}][\text{A}^-] \quad \textcircled{4}$$

$$[\text{Na}^+] + [\text{H}^+] = [\text{A}^-] + [\text{OH}^-] \quad \textcircled{5}$$

$$[\text{HA}] = c_a - [\text{H}^+] + [\text{OH}^-] \quad \textcircled{7}$$

$$\textcircled{6}, \textcircled{7} \Leftrightarrow \textcircled{2} \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+](c_b + [\text{H}^+] - [\text{OH}^-])}{c_a - [\text{H}^+] + [\text{OH}^-]} \quad \textcircled{9}$$

$$\textcircled{10}: \quad [\text{OH}^-] = \frac{K_w}{[\text{H}^+]} \quad \textcircled{10}$$

$$\textcircled{10} \rightarrow \textcircled{9}: \quad [\text{H}^+]^3 + (c_b + K_a)[\text{H}^+]^2 - (K_w + c_a K_a)[\text{H}^+] - K_a K_w = 0$$

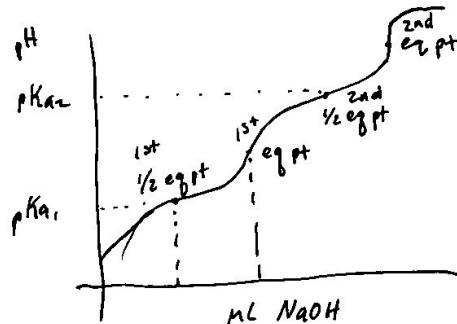
EX1       $1.00 \times 10^{-5} \text{ M HCN}$       Find pH  
 (15.20)       $K_a = 6.17 \times 10^{-10}$        $K_w = 1 \times 10^{-14}$       | Don't use ICE mindlessly, as it assumes no  $\text{H}_2\text{O}$  autoionization.  
 $c_a = 1 \times 10^{-5} \text{ M}$   
 $c_b = 0$

$$[\text{H}^+] = 10^{-7}$$

Guess  $[\text{H}^+] = 1 \times 10^{-7}$ , as the dissociation shall  $\ll \text{H}_2\text{O}$  autoionization, which is the whole purpose of this prob.

Use python,  $[\text{H}^+] = 1.29 \times 10^{-7} \text{ M}$

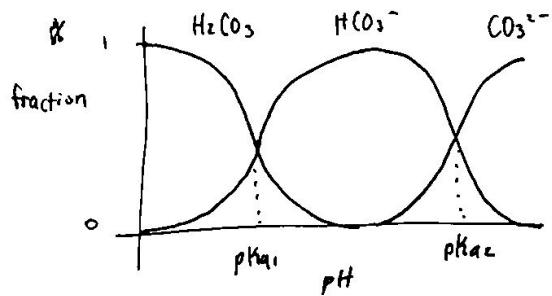
&lt;&lt; Polyprotic Acid



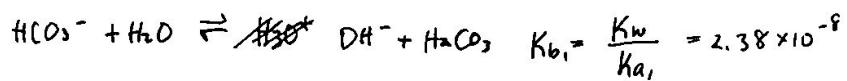
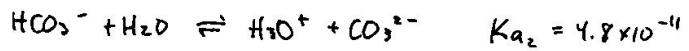
$$\text{pH} = \text{p}K_{a_1} + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$@ \frac{1}{2} \text{ eq pt}, \quad [\text{A}^-] = [\text{HA}], \quad \text{pH} = \text{p}K_{a_1}$$

<< pH effect on conc. of species



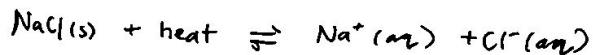
[EX2] Add NaHCO<sub>3</sub> to water



$K_{\text{b}_1} > K_{\text{a}_2}$ , should be basic

if [amphoteric] very big,  $\text{pH} \approx \frac{1}{2} (\text{pK}_{\text{a}_1} + \text{pK}_{\text{a}_2}) = 8.35$

[EX3]



(dissolution usually endothermic,  
but it's entropically favored)

17 Jan 2020

## Selective Precipitation &amp; Metal Sulfide

CHM 155

&lt;&lt; Recap



**EX1** 10.0mL  $1 \times 10^{-4}$  M NaCl      Does ppt form?  
 10.0mL  $1 \times 10^{-3}$  M AgNO<sub>3</sub>

$$K_{sp} = 1.6 \times 10^{-10}$$

$$[Ag^+] = 10.0\text{mL} \times \frac{[1 \times 10^{-3}\text{ mol}]}{1000\text{mL}} \times \frac{1}{20.0\text{mL}} = 5 \times 10^{-4} \text{ M}$$

$$[Cl^-] = 5 \times 10^{-5} \text{ M}$$

$$Q = [Ag^+][Cl^-] = (5 \times 10^{-4} \text{ M})(5 \times 10^{-5} \text{ M}) = 2.5 \times 10^{-8} \gg K_{sp} \rightarrow \text{ppt forms}$$

If add NaCl,  $[Ag^+] \downarrow$  by Le Chatelier Principle - common ion effect.

**EX2** Ni(OH)<sub>2</sub> molar solubility?       $K_{sp} = 1.6 \times 10^{-16} = [Ni^{2+}][OH^-]^2$

0.1 M NaOH

$$\text{Let } x = [Ni^{2+}]$$

in NaOH ...



|    |      |            |
|----|------|------------|
| 0- | 0    | 0.1        |
| -  | $+x$ | $+2x$      |
| -  | $x$  | $0.1 + 2x$ |

$$K_{sp} = x(2x)^2$$

$$K_{sp} = 4x^3$$

$$x = \sqrt[3]{\frac{K_{sp}}{4}} = 3.4 \times 10^{-6} \text{ in H}_2\text{O}$$

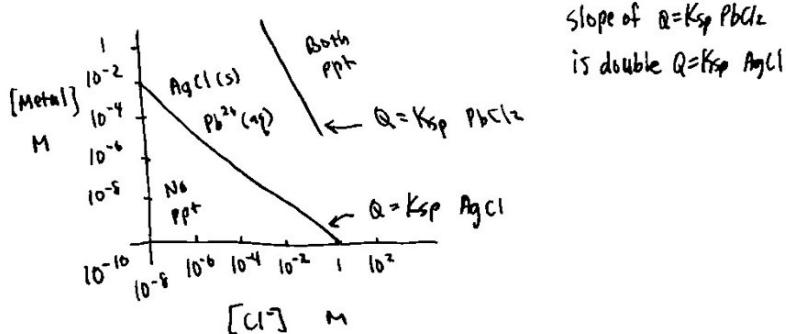
$$x(0.1 + 2x)^2 = K_{sp}$$

$$x = \frac{K_{sp}}{(0.1)^2} = 1.6 \times 10^{-14} \text{ in 0.1 M NaOH}$$

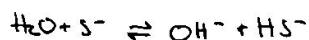
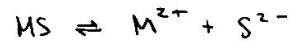
&lt;&lt; Selective precipitation

**EX3** AgCl       $K_{sp} = 1.6 \times 10^{-10}$

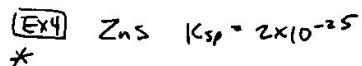
PbCl<sub>2</sub>       $K_{sp} = 2.4 \times 10^{-4}$



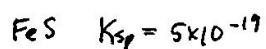
<<< Metal Sulf



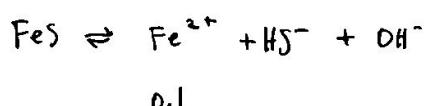
$$K_{sp} = [M^{2+}][HS^{2-}][OH^-] \quad \text{acidic soln}$$



highest  $[H^+]$ ? ~~that's not true~~



$$[Fe^{2+}] = 0.1M, [H_2S] = 0.1M$$



0.1

$$K_a(H_2S) = 9.1 \times 10^{-8} = \frac{[H^+][HS^-]}{[H_2S]}$$

Let  $x = [H^+]$

$$K_a = \frac{x[HS^-]}{0.1}$$

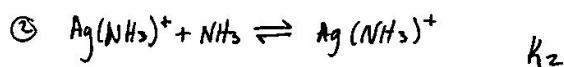
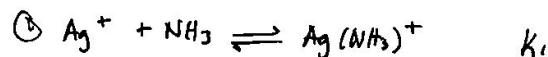
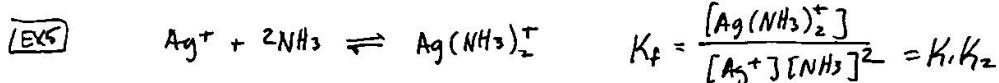
$$K_{sp}(FeS) = [Fe^{2+}][HS^-][OH^-]$$

$$\frac{0.1 K_a}{x} = [HS^-] = \frac{9.1 \times 10^{-9}}{x}$$

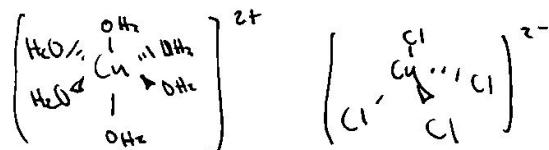
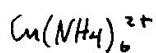
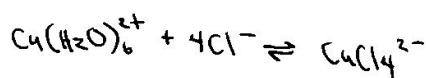
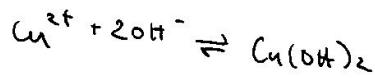
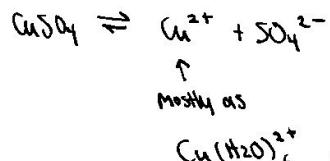
$$K_{sp} = (0.1) \left( \frac{9.1 \times 10^{-9}}{x} \right) \left( \frac{K_w}{x} \right)$$

$$x = \sqrt{\frac{(0.1)(9.1 \times 10^{-9})K_w}{K_{sp}}} = \sqrt{1.82 \times 10^{-5}} = 4.26 \times 10^{-3}$$

$$pH = 2.36$$



→ Demo



## &lt;&lt; Applications of Electrochemistry

- car, phone, batteries
  - Neurons, cellular action potentials
  - power of life, redox rxn
  - metal refining
- } electron transfer reactions

**EX1** 11.1 V, 5200 mAh

$$[E] = \text{J} \quad E = \frac{11.1 \text{ J}}{1 \text{ C}} \times \frac{5.2 \text{ C}}{1 \text{ s}} \times 1 \text{ h} \times \frac{3600 \text{ s}}{1 \text{ h}} = 200 \text{ kJ}$$

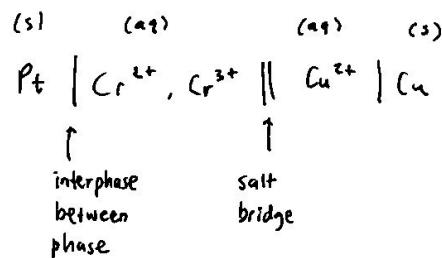
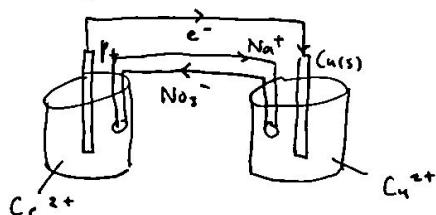
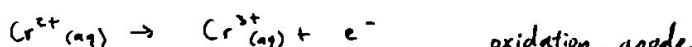
$$[V] = \text{V} = \text{J/C}$$

$$[I] = \text{A} = \text{C/s}$$

## &lt;&lt; Vocabulary

> anode - electrode that oxidation occurs "an ox"

> Cathode - electrode that reduction occurs "red cat"



## &lt;&lt; Faraday's Law

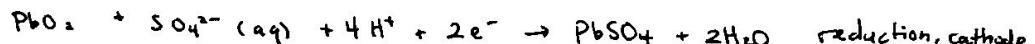
• can do stoichiometry to e<sup>-</sup>

• Conservation of charge

• 1 mol e<sup>-</sup>'s charge is 1 Faraday

$$\frac{6.022 \times 10^{23} \text{ e}^-}{1 \text{ mol}} \times \frac{1.6022 \times 10^{-19} \text{ C}}{\text{e}^-} = 96485 \text{ C/mol e}^- = 1 \text{ F}$$

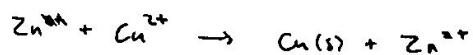
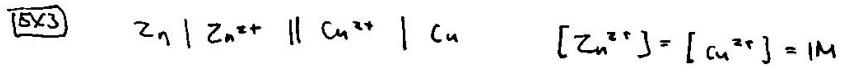
**EX2** Pb(s) + SO<sub>4</sub><sup>2-</sup>(aq) → PbSO<sub>4</sub> + 2e<sup>-</sup> oxidation, anode



How much Pb consumed for powering 300mA for 15 min?

$$300 \times 10^{-3} \text{ A} \times \frac{1 \text{ s}}{1 \text{ A}} \times 15 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{1 \text{ mol e}^-}{96485 \text{ C}} \times \frac{1 \text{ mol Pb}}{2 \text{ mol e}^-} \times \frac{207.2 \text{ g}}{1 \text{ mol Pb}} = 0.29 \text{ g}$$

- voltage - potential energy per charge  $IV = 1J/1C$
- $W_{elec} = -Q\Delta V = -Q\Delta E$ , where  $V=E$  is voltage
- Sign Conventions  
 $\Delta G^\circ = -Q\Delta E \stackrel{<0}{\cancel{\text{if spontaneous}}}$  if spontaneous for galvanic cells, thus  $\Delta E > 0$ .



$\Delta E^\circ = 1.10 \text{ V}$  ← cell potential - diff of voltage between rxn @ equilibrium.

$$\Delta G^\circ = -Q\Delta E^\circ = - \frac{2 \text{ moles}}{e^-} \times \frac{96485 \text{ C}}{\text{mol}} \times \frac{1.1 \text{ J}}{\text{C}} = -212 \text{ kJ/mol}$$

$\boxed{\Delta G^\circ = -nF\Delta E^\circ}$ , where  $n$  is # of  $e^-$  transferred.

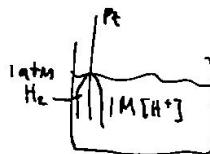
24 Jan 2020

## pH Influence on Cell Potential

CHEM 155

## &lt;&lt; Standard Reduction Potential

- use SHE, standard hydrogen electrode, as 0.00 V



| $E^\circ_{\text{red}}$ |
|------------------------|
| spontaneous reduction  |
| Au      +1.68 V        |
| SHE    0.00 V          |
| spontaneous oxidation  |
| Li      -3.045 V       |

think "penny experiment"

→ Common Mistake



$$E^\circ_{\text{red}} = 0.34 \text{ V}$$

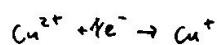


$$E^\circ_{\text{red}} = 0.522 \text{ V}$$



$$E^\circ_{\text{red}} = 0.158 \text{ V}$$

$$\textcircled{1} - \textcircled{2} \Rightarrow \textcircled{3}$$



$$E^\circ = 0.34 - 0.522 = \left[ \begin{array}{l} \text{inconsistent!} \\ \text{since we did not} \\ \text{balance } e^- \end{array} \right] \left. \begin{array}{l} \text{we're adding} \\ \text{intensive properties!} \end{array} \right]$$

→ Proof

$$\Delta G^\circ = -nF\Delta E^\circ$$

$$\Delta G_3^\circ = \Delta G_1^\circ - \Delta G_2^\circ$$

$$-nF\Delta E_3^\circ = -n_1F\Delta E_{1a}^\circ + n_2F\Delta E_2^\circ$$

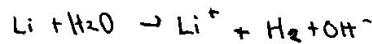
$$\Delta E_3^\circ = \frac{n_1\Delta E_1^\circ - n_2\Delta E_2^\circ}{n_3} = \frac{2\Delta E_1^\circ - \Delta E_2^\circ}{1} = 2\Delta E_1^\circ - \Delta E_2^\circ$$

$$\Delta E_3^\circ = 2(0.34 \text{ V}) - 0.522 \text{ V} = 0.158 \text{ V} \quad \checkmark$$

should use  
this instead  
(iff for eg)

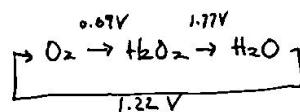
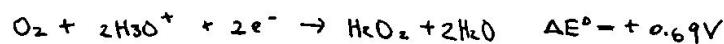
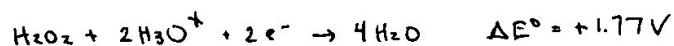
•  $\Delta G^\circ$  is additive•  $\Delta E^\circ$  is not simply additive.

→ DEMO

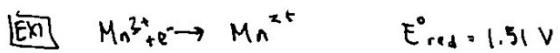


→ Disproportionation

&gt; Disproportionation - one species is both oxidized &amp; reduced.



✗ Disproportionated  
species are  
unstable.



$Mn^{2+}$  is stable vs. disproportionation reaction.

<< Nernst Equation

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \leftarrow -nFE = -nFE^\circ + RT \ln Q$$

$$\Delta G^\circ = -nF\Delta E^\circ$$

$$\boxed{\Delta E = \Delta E^\circ - \frac{RT}{nF} \ln Q}$$

Nernst Equation

• Nernst eq helps determine  $\Delta E$  vs concentration.

$$\begin{aligned} \Delta G^\circ &= -nF\Delta E^\circ \\ \Delta G^\circ &= -RT \ln K \end{aligned} \quad \left\{ \quad -nF\Delta E^\circ = -RT \ln K$$

$$\boxed{\Delta E^\circ = \frac{RT}{nF} \ln K}$$



$$\Delta E^\circ = \frac{RT}{nF} \ln K \quad n=2$$

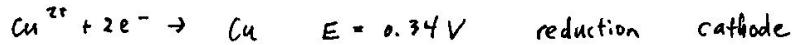
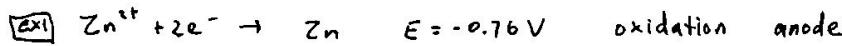
$$K = \exp\left(\frac{\Delta E^\circ nF}{RT}\right) = 1.6 \times 10^{37}$$

27 Jan 2020

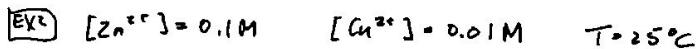
## Electrolysis

CHEM 152

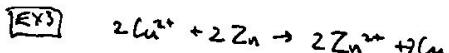
&lt;&lt; Review



$$E_{\text{cell}} = E_{\text{red}}(\text{cath}) - E_{\text{red}}(\text{anode}) = 0.34 \text{ V} - (-0.76 \text{ V}) = 1.10 \text{ V}$$



$$E = E^{\circ} - \frac{RT}{nF} \ln Q = E^{\circ} - \frac{0.0257}{n} \ln Q = 1.10 \text{ V} - \frac{0.0257}{2} \ln \frac{0.1 \text{ M}}{0.01 \text{ M}} = \underline{\underline{1.07 \text{ V}}}$$



$\Delta E_{\text{cell}}$  does not change,  $\Delta G^{\circ}$  changes (double),  $n$  doubles,  $Q$  changes.

$$Q = \frac{[Zn^{2+}]^2}{[Cu^{2+}]^2} \quad n = 4 \quad \leftarrow \text{these changes cancels out and}$$

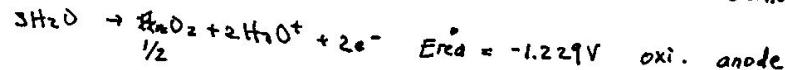
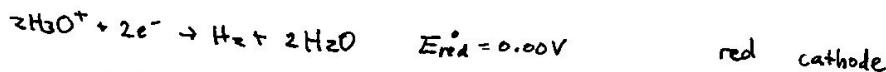
keep  $E_{\text{cell}}$  the same.

$$E_n^{\circ} = E^{\circ} - \frac{0.0257}{2n_0} \ln \left( \frac{[Zn^{2+}]_0}{[Cu^{2+}]_0} \right)^2$$

$$= E^{\circ} - \frac{0.0257}{n_0} \ln \frac{[Zn^{2+}]_0}{[Cu^{2+}]_0}$$

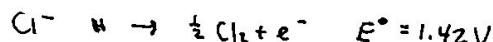
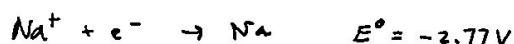
$$\approx E^{\circ}$$

&lt;&lt; Electrolysis of Water



> overpotential - extra potential needed to drive electrochem rxn @ a finite rate.

&lt;&lt; Deeper Look

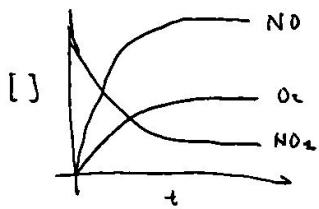


$H_2O$  has a high overpotential

## kinetics

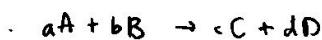
### «« Kinetics

- $\text{C(diamond)} \rightarrow \text{C(graphite)}$   $\Delta G^\circ = -2.9 \text{ kJ/mol}$ , but large activation barrier.
- $2 \text{NO}_2(g) \rightarrow 2 \text{NO} + \text{O}_2$



rate : change of concentration of a reactant/product over time.

$$[\text{rate}] : \frac{\text{mol}}{\text{L} \cdot \text{s}}$$



$$r \equiv -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

29 Jun 2020

## Kinetics

CHEM 151

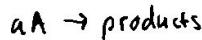
## &lt;&lt; Differential Rate Laws

$$\text{Differential: } \frac{d[A]}{dt}$$

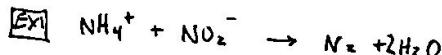
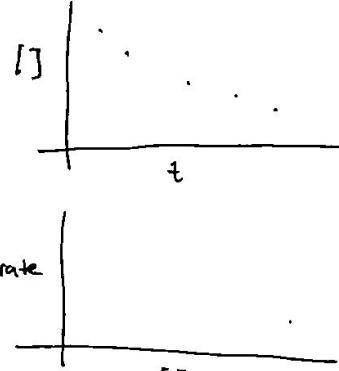
$$\text{Integrated: } [A](t)$$

$$\text{Average: } \frac{\Delta[A]}{\Delta t}$$

## &lt;&lt; Reaction Order



- rate  $\propto k[A]^n$ ,  $n$  = order of rxn
- $n$  can be integer, fraction, even negative
- $n=1$ , first order rxn  $k[A]$
- $n=2$ , second order rxn  $k[A]^2$
- $n=0$ , zeroth order rxn  $k$



| experiment | $[\text{NH}_4^+]$ | $[\text{NO}_2^-]$ | rate                  |
|------------|-------------------|-------------------|-----------------------|
| 1          | 0.100             | 0.005             | $1.35 \times 10^{-7}$ |
| 2          | 0.100             | 0.010             | $2.7 \times 10^{-7}$  |
| 3          | 0.200             | 0.010             | $1.08 \times 10^{-6}$ |

expect:

$$\text{rate} = k[\text{NH}_4^+]^n [\text{NO}_2^-]^m$$

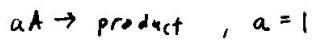
$$\textcircled{1} \text{ Constant } [\text{NH}_4^+] = \frac{\text{exp 2}}{\text{exp 1}} = \frac{2.7 \times 10^{-7}}{1.35 \times 10^{-7}} = \frac{k[\text{NH}_4^+]^n [0.01]^m}{k[\text{NH}_4^+]^n (0.005)^m} \quad m=1$$

$$\textcircled{2} \text{ constant } [\text{NO}_2^-] : \frac{\text{exp 3}}{\text{exp 2}} = \frac{1.08 \times 10^{-6}}{2.7 \times 10^{-7}} = \frac{k(0.100)^n [\text{NO}_2^-]}{k(0.200)^n [\text{NO}_2^-]} \quad n=2$$

$$\textcircled{3} k : 1.35 \times 10^{-7} = k(0.100)^2 (0.005) \quad k = 2.7 \times 10^{-3} \text{ L}^2/\text{(mol}^2\text{s})$$

- $k$  has diff unit for diff rxn

<< Integrated Rate Law



→ First Order Rxn

$$\text{rate} = k[A] = -\frac{d[A]}{dt}$$

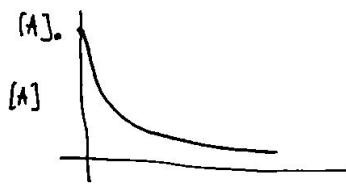
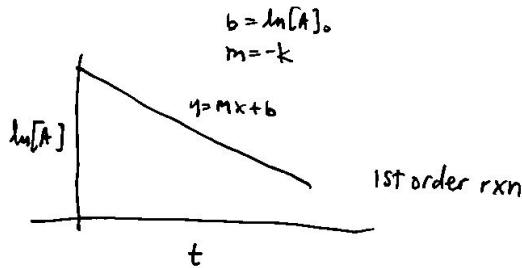
$$\frac{d[A]}{dt} = -k[A]$$

$$\int_{[A]_i}^{[A]_f} \frac{d[A]}{[A]} = \int_{t_i}^{t_f} -k dt$$

$$\ln \frac{[A]_f}{[A]_i} = -k(t_f - t_i) \quad \text{let } t_i = 0,$$

$$\frac{[A]_f}{[A]_i} = e^{-kt_f}$$

$$[A]_f = [A]_i e^{-kt_f}$$



• plot  $\ln[A]$  vs  $t$ , if linear, then 1st order rxn.

→ half-life

> half-life - time it takes for  $1/2$  reactant to be consumed (used in 1st order rxn)

$$\text{For } [A] = [A]_0 e^{-kt}, @ t=t_{1/2}, [A] = \frac{1}{2} [A]_0,$$

$$\frac{1}{2} [A]_0 = [A]_0 e^{-kt}$$

$$\frac{1}{2} = e^{-kt}$$

$$t = \frac{\ln 2}{k} \quad \leftarrow \text{if given half-life, } k \text{ is given.}$$

**Q** half life = 20 min. how long for 27.24% reactant consumed?

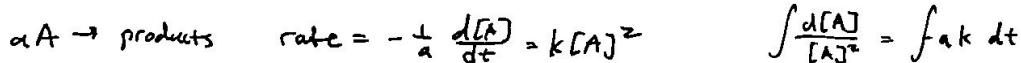
$$t_{1/2} = \frac{\ln 2}{k} \rightarrow k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{20 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} = 5.70 \times 10^{-4} \text{ s}^{-1}$$

$$[A] = (1 - 0.2724) [A]_0 = 0.7276 [A]_0$$

$$0.7276 [A]_0 = [A]_0 \left( e^{-5.70 \times 10^{-4} t} \right)$$

$$t = \boxed{550 \text{ s}}$$

→ Second-Order Rxn



$$\frac{d[A]}{dt} = -a k [A]^2$$

<< 2<sup>nd</sup> order rate law

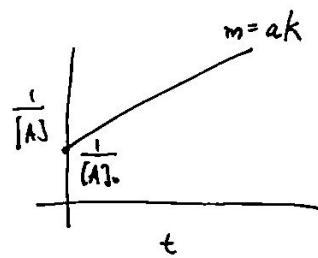
$$\frac{d[A]}{dt} = -ak[A]^2$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = - \int_{t_0}^t ak dt, \text{ let } t_0 = 0$$

$$-\frac{1}{[A]_t} + \frac{1}{[A]_0} = -akt$$

$$\frac{1}{[A]_t} = akt + \frac{1}{[A]_0} \quad \leftarrow \text{plotting for linear}$$

$$[A]_t = \frac{1}{\frac{1}{[A]_0} + akt} \quad \leftarrow \text{2nd order integrated rate}$$



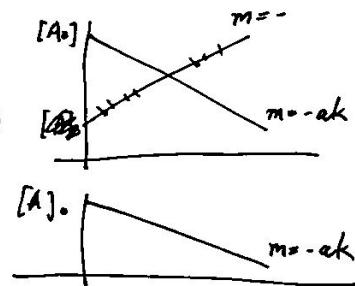
<< 0.5<sup>th</sup> order rate law

$$-\frac{1}{a} \frac{d[A]}{dt} = k[A]^0$$

$$\int_{[A]_0}^{[A]_t} d[A] = -k \int_{t_0}^t dt$$

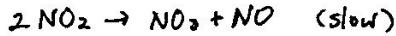
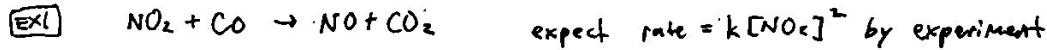
$$[A]_t = -akt + [A]_0$$

- solid & gas
- catalyzed rxn  
(alcohol dehydrogenase)



<< Reaction Mechanism

- elementary step (rxn)
- rxn mechanism - a series of elementary steps in which rxn occurs.



•  $\text{NO}_2$  is intermediate, since it's not product/reactant, but is formed.

→ molecularity of elementary steps

•  $A \rightarrow \text{prod}$

unimolecular

$k[A] = \text{rate}$

•  $2A \rightarrow \text{prod}$

bimolecular

$k[A]^2 = \text{rate}$

$A + B \rightarrow \text{prod}$

$k[A][B] = \text{rate}$

•  $3A \rightarrow \text{prod}$  → trimolecular

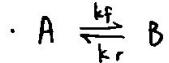
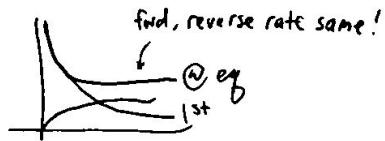
•  $B \times 2A + B \rightarrow \text{prod}$

rate =  $k[A]^3$

rate =  $k[A]^2[B]$

<< Deviation from theory

→ Equilibrium



$$k_f[A] = k_r[B]$$

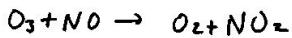
$$\frac{k_f}{k_r} = \frac{[B]}{[A]} = K_{eq}$$

<< Multiple step Rxn

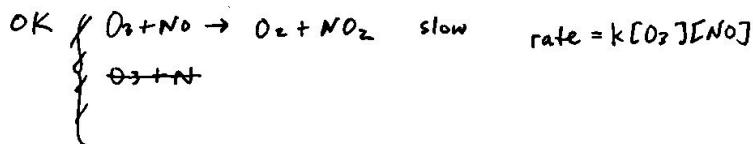
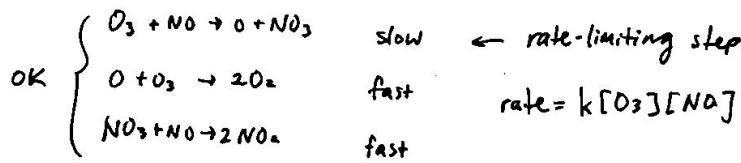
$$K_{eq} = K_1 K_2 K_3 = \frac{K_f_1 K_f_2 K_f_3}{k_r_1 k_r_2 k_r_3}$$

→ slow step @ later

[Ex2]



experiment: rate =  $k[O_3][NO]$



[Ex3] Same rxn above

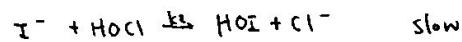
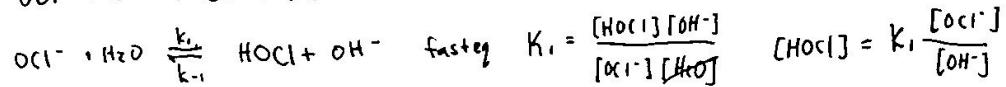
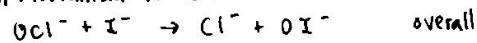


$$K_{eq} = \frac{[NO_2]}{[NO]^2}$$

$$\Rightarrow [N_2O_2] = K_{eq}[NO]^2$$

$$\text{rate} = k K_{eq} [NO]^2 [O_3][NO_2]$$

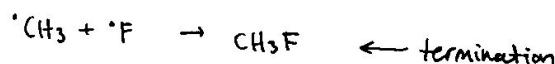
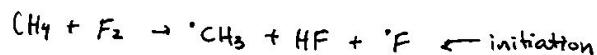
«« Rxn Mechanism Problem



$$\text{rate} = k_2 [\text{I}^-][\text{HOCl}] = K_1 k_2 [\text{I}^-] \frac{[\text{OCl}^-]}{[\text{OH}^-]}$$

«« Chain Rxn

> Rxn that has 3 steps { initiation - generate reactive intermediate  
 propagation - regenerate reactive intermediates  
 termination - intermediates react to form stable species

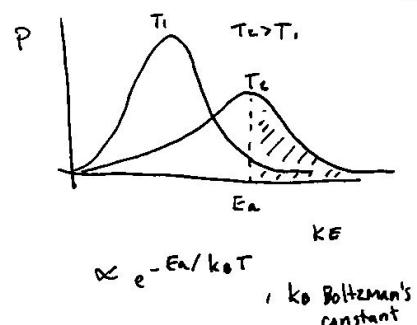


«« Temperature Dependence of Rxn Rate

- Molecules collide to react
- Not all collisions have enough KE to react

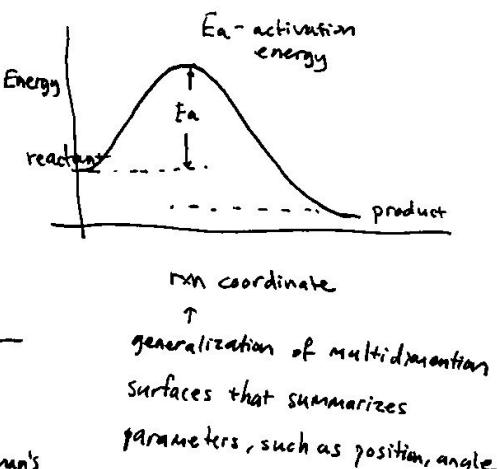
$$\frac{N_l}{N_e} = \frac{g_l e^{-E_l/kT}}{g_e e^{-E_e/kT}}$$

↑ degeneracy



$$\propto e^{-E_a/k_e T_e}$$

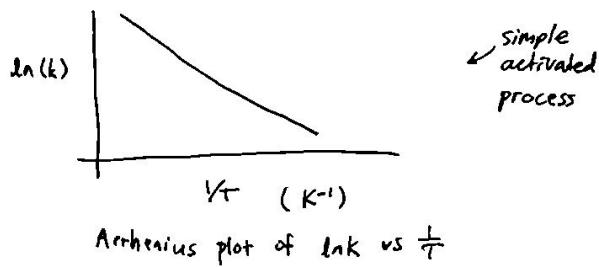
,  $k_e$  Boltzmann's constant



$$\text{rate} = v_0 e^{-E_a/k_B T}$$

↑  
attempt  
frequency

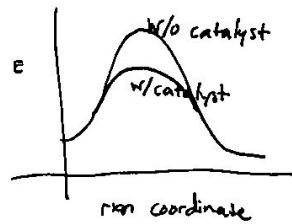
$$\text{rate} = k_{\text{obs}} [A][B]$$



$$\ln\left(\frac{k_{T_1}}{k_{T_2}}\right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{by two Arrhenius eq.}$$

<< Catalysis

- heterogeneous - two phase
- homogeneous - same phase
- catalyst - substance in rxn that's neither produced nor consumed.



7 Feb 2020

## Nuclear Chemistry

CHEM 155

&lt;&lt; Review

$$E^2 = M_0 c^4 + P^2 c^2$$

$$\begin{cases} M_0 > 0, P = 0 \\ M_0 = 0, P > 0 \end{cases}$$

$$E = M c^2$$

$$E = P c$$

$$1\text{amu} = \frac{1}{12} \text{ mass } (^{12}_6\text{C}) = 1.66 \times 10^{-27} \text{ kg}$$

$$1\text{mol} = \# \text{ of } ^{12}_6\text{C} = 12.0 \text{ g exactly}$$

&lt;&lt; Binding Energy

$$6p^+ = 6 \times 1.6726 \times 10^{-27} \text{ kg}$$

$$6n^0 = 6 \times 1.6749 \times 10^{-27} \text{ kg}$$

$$12.095 \text{ kg/mol}$$

$$\text{mass proton} \quad \text{mass neutron}$$

$$\Delta E = (ZM_p + NM_n - M_A) c^2$$

$$\begin{matrix} \uparrow & \uparrow & \curvearrowright \\ \# \text{ proton} & \# \text{ neutron} & \text{mass atom} \end{matrix}$$

$$m_e = 511 \text{ keV}/c^2$$

$$m_p = 938.2 \text{ MeV}/c^2$$

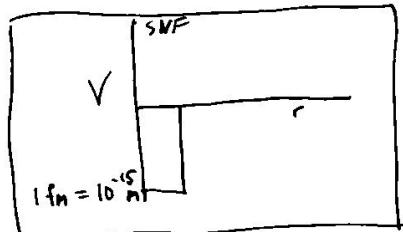
$$m_n = 939.8 \text{ MeV}/c^2$$

&gt; nucleon - particles in nucleus

- Fe nucleus is most stable

$$\cdot V = \frac{q_1 q_2}{4\pi \epsilon_0 r}$$

→ Strong Nuclear Force



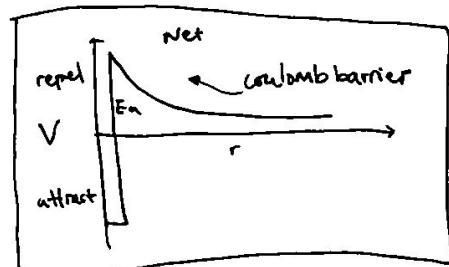
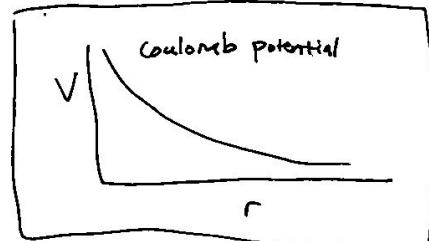
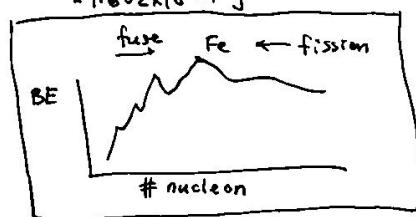
heavier than regular C!

 $8.55 \times 10^{-12} \text{ J/mol}$  Missing energy

$$1 \text{ eV} = 1 \text{ e}^- \cdot 1 \text{ eV}$$

$$= 1.602 \times 10^{-19} \text{ C} \times \frac{1 \text{ J}}{1 \text{ C}}$$

$$= 1.602 \times 10^{-19} \text{ J}$$



<< Conservation Laws

1. charge
2. energy (Mass)
3. momentum
4. Barion number
5. lepton number

> barions barion # charge

|           |     |    |
|-----------|-----|----|
| $p^+$     | +1* | +1 |
| $p^-$     | -1  | -1 |
| $n_1$     | +1  | 0  |
| $\bar{n}$ | -1  | 0  |

lepton lepton # charge

|             |       |    |    |
|-------------|-------|----|----|
| $(p^-)$     | $e^-$ | +1 | -1 |
| $(p^+)$     | $e^+$ | -1 | +1 |
| $\bar{v}_e$ |       | -1 | 0  |
| $v_e$       |       | +1 | 0  |

<< Nuclear Decay

$(\beta^-)$



$$\frac{^{14}C}{^{12}C} = 1.3 \times 10^{-12} \quad 15.3 \text{ decays / (min} \cdot \text{g C)}$$

carbon dating

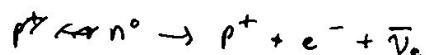
> Barion = proton + neutron

lepton =  $e^-$  + positron + neutrino

EX1  $M_n = 934.5 \text{ MeV}/c^2$

$$M_p = 938.2 \text{ MeV}/c^2$$

$$m_e = 511 \text{ keV}/c^2$$



energy goes to KE

charge conserved

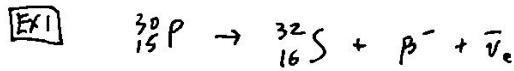
barion :  $1 = 1 + 0$

lepton :  $0 = 0 + 1 - 1$

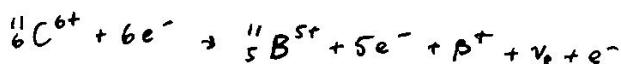
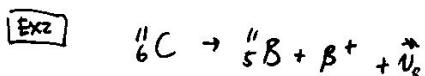
↑  
electron-favored  
neutrino  
anti-Matter

## » Nuclear Decay

- $\beta^-$  decay
- $\beta^+$  decay
- $\alpha$  decay
- $\beta\bar{\nu}_e$  capture
- $\gamma$  decay
- IC (internal conversion)

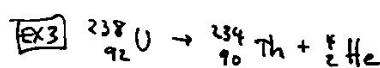


• spontaneous if  $\Delta M \leq 0$

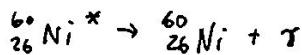
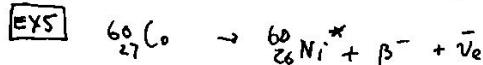
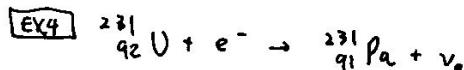


$$\begin{aligned}\Delta M &= M_{\text{product}} - M_{\text{reactant}} \\ &= m(^{16}_5B + 2e^-) - m(^{16}_6C)\end{aligned}$$

$$\Delta E = -0.96 \text{ MeV}$$



$$\begin{aligned}\Delta M &= m(^{234}_{90}Th + ^{4}_{2}He) \\ &\quad - m(^{238}_{92}U)\end{aligned}$$



## » Radiation &amp; Tissue

- chemical bond energy unit: eV
- ionizing radiation energy unit: keV, MeV
  - excite  $e^-$
  - dissociate bonds

→ Radiation

$$\text{Gray (Gy)} = 100 \text{ rad} = 1 \text{ J/kg}$$

$$\text{Sievert (Sv)} = 1 \text{ J/kg} \cdot QF \quad \leftarrow \text{Biological dose}$$

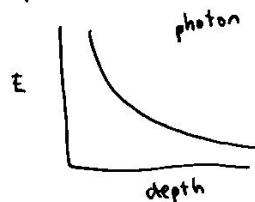
$\uparrow$  quality factor

$$LD_{50} = 500 \text{ rem} = 55 \text{ Sv}$$

→ Quality factor (QF)

| type | $\alpha$ | $\beta$ | $\tau$ | $n^o$   | $n^o$    | $\beta^+$ | heavy ion |
|------|----------|---------|--------|---------|----------|-----------|-----------|
| QF   | 1-20     | 1       | 1      | <keV: 3 | >keV: 10 | 1-10      | 20        |

→ Depth vs Dose



**EX6**



$$t_{1/2} = 8.04 \text{ days}$$

5mg  $^{131}\text{I}$ , at 16 kg, KE = 400 keV A = ? dose in 5 days = ?

$$(1) \text{ Activity} = \text{decays/sec} = \frac{dN}{dt}$$

$$k = \frac{\ln 2}{t_{1/2}} = 9.97 \times 10^{-7} \text{ s}^{-1}$$

$$\frac{dN}{dt} = -kN_0 = -(9.97 \times 10^{-7} \text{ s}^{-1})(2.3 \times 10^{16}) = 2.3 \times 10^{10} \text{ Bq}$$

$$N = 5\text{mg} \times \frac{1\text{g}}{10^3\text{mg}} \times \frac{1\text{mol}}{(31\text{g})} \times \frac{6.02 \times 10^{23}}{1\text{mol}} = 2.3 \times 10^{16}$$

$$(2) N_t = N_0 e^{-kt}$$

$$\text{dose} = (\Delta N)(KE)$$

$$N(5) =$$

<< Beta Decay Problem

$$\boxed{\text{Ex1}} \quad \frac{dN_{\text{new}}}{dt} = 15.3 \text{ decay/g/min} = -k N_{\text{old}}$$

$$\frac{dN_{\text{old}}}{dt} = \frac{400}{200g} \frac{15.3 \text{ decay/g/min}}{= \frac{2}{5} \text{ decay/min}} = -k N_{\text{old}}$$

<< Geochronology

$$P_t = P_0 e^{-kt} \Rightarrow P_0 e^{kt} P_t$$

$$D_t = P D_0 + (P_0 - P_t) = 0 + (P_t e^{kt} - P_t)$$

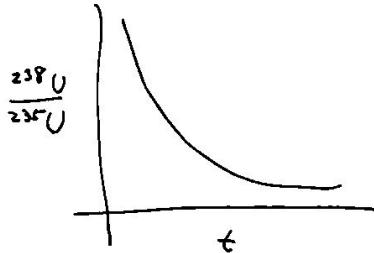
$$D_t = P_t (e^{kt} - 1)$$

$$^{206}\text{Pb} = ^{238}\text{U} (e^{k_{238}t} - 1) \quad \text{known } [^{238}\text{U}], [^{238}\text{U}], k_{238}, \text{ find } t.$$

$$\text{similarly, } ^{207}\text{Pb} = ^{235}\text{U} (e^{k_{235}t} - 1)$$

$$\text{find their ratio: } \frac{^{206}\text{Pb}}{^{207}\text{Pb}} = \frac{^{238}\text{U} (e^{k_{238}t} - 1)}{^{235}\text{U} (e^{k_{235}t} - 1)}$$

$$\boxed{\text{Ex2}} : \frac{^{238}\text{U}}{^{235}\text{U}} = 137.88 \quad (\text{today})$$



**Q3:** Given [U], find [Th]

first find the decay from U to Th, but Th is also decaying,

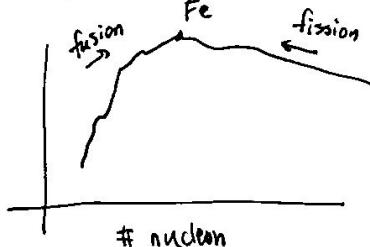
use steady state approximation, since  $U \rightarrow Th$  is ~~fast~~ slow,

$Th \rightarrow Pa$  is fast, Th is about constant intermediate.

$$A \xrightarrow{B \xrightarrow{C}} \frac{dN_B}{dt} \approx 0 = k_u N_u - k_{Th} N_{Th}$$

$$B = Th$$

<< Nuclear fission & Fusion



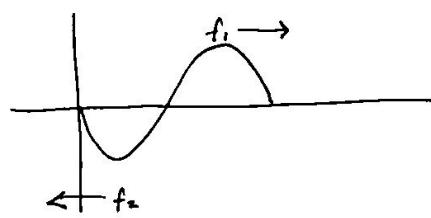
Wave

$$f_1(x,t) = A \sin(\omega t - kx) \quad \text{as } t \uparrow, x \uparrow$$

$$f_2(x,t) = A \sin(\omega t + kx) \quad \text{as } t \uparrow, x \downarrow$$

$t$ , time

$x$ , x-position



14 Feb 2020

## Intro to Wave &amp; Classical Problems

CHM 155

&lt;&lt; Wave function

$$f(x,t) = A \sin(\omega t - kx)$$

wave traveling to the right

$\omega = 2\pi\nu$        $k = \frac{2\pi}{\lambda}$

angular frequency      wave number

Amplitude at position and time

$$\lambda = \frac{\pi}{k} = \frac{\pi}{\frac{2\pi}{\lambda}} = \frac{\lambda}{2}$$

$$\text{speed} = \frac{\text{distance}}{\text{time}} = \frac{\lambda}{\nu^{-1}} = \lambda\nu$$

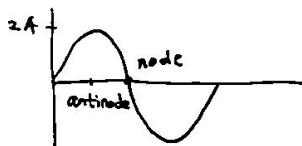
$$c = \lambda\nu \quad \text{for electromagnetic radiation}$$

λ wavelength  
 ν frequency  
 c speed (of light)

&lt;&lt; Linear property

$$\begin{aligned} & A \sin(kx - \omega t) + A \sin(kx + \omega t) \\ &= 2A \sin(kx) \cos(-\omega t) \\ &= 2A \sin(kx) \cos(\omega t) \\ &\quad \overline{T} \\ &\quad \text{Amplitude} \end{aligned}$$

$$\sin(u) + \sin(v) = 2 \sin\left(\frac{u+v}{2}\right) \cos\left(\frac{u-v}{2}\right)$$

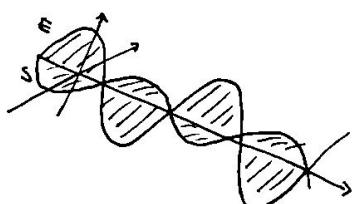


$$\boxed{\text{Ex1}} \quad c = \lambda\nu$$

$$\text{speed of sound } c = 345 \text{ m/s}, \nu = 23.13 \text{ Hz}$$

$$2 = \frac{c}{\nu} = \frac{345 \text{ m/s}}{23.13 \text{ Hz}} = 14.9 \text{ m}$$

&lt;&lt; # Wave-Particle Duality



$$E(x,t) = E_0 \cos(\omega t - kx)$$

$$\text{light intensity} \propto |E_0|^2$$

$$\text{Speed of light} = \frac{1}{\sqrt{\epsilon_0 \mu_0}} = 3 \times 10^8 \text{ m/s} \quad \text{in vacuum}$$

$$= \frac{c}{n} \quad \text{in other matter, } n \text{ is index}$$

$$\boxed{\text{Ex2}} \quad \text{green light } \nu \approx 532 \text{ nm}, \nu = ?$$

$$c = \lambda\nu \Rightarrow \nu = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ m/s}}{5.32 \times 10^{-9} \text{ nm}} = 5.66 \times 10^{14} \text{ s}^{-1}$$

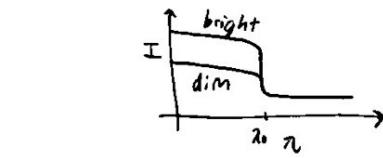
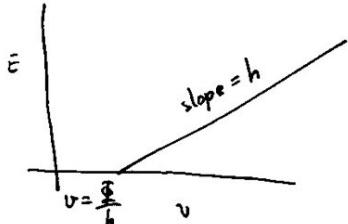
~<< Classic Mechanics



Classically,  $I \propto [E_0]^2$ ,  $I$  is intensity

Planck's  
constant  
 $\sqrt{v}$   
Work  
fxn

$$E_{max} = \frac{1}{2}mv^2 = h\nu - \Phi$$



| E with respect<br>to vacuum | (eV) | $\Phi$ (eV) |
|-----------------------------|------|-------------|
| Cs                          | -2.1 | 2.1         |
| K                           | -2.3 | 2.3         |
| Ca                          | -2.7 | 2.7         |
| Al                          | -4.1 | 4.1         |

ionization energy  
standard reduction  
potential  
work fxn

[Ex3] Max KE & velocity of photoelectron emitted from K surface with laser of  $\lambda = 325\text{ nm}$ .

$$E_{max} = h\nu - \Phi$$

$$E = h\nu = \frac{hc}{\lambda} = \frac{1240 \text{ eV} \cdot \text{nm}}{\lambda} = \frac{1240 \text{ eV} \cdot \text{nm}}{325 \text{ nm}} = 3.81 \text{ eV}$$

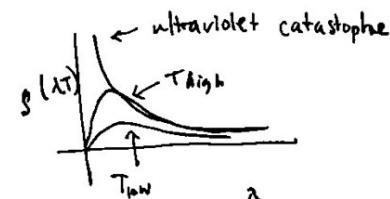
$$\frac{1}{2}mv^2 = E_{max} = h\nu - \Phi$$

$$\frac{1}{2}mv^2 = 3.81 \text{ eV} - 2.3 \text{ eV}$$

$$\frac{1}{2}mv^2 = 1.5 \text{ eV} \Rightarrow \times \frac{1.6 \times 10^{-9} \text{ J}}{1 \text{ eV}}$$

$$v = 1.0 \times 10^6 \text{ m/s}$$

<< Blackbody Radiation



$$\text{Emissivity} = n h \nu$$

19 Feb 2020

## Matter Wave &amp; Bohr's Model

CHM 155

↳ de Broglie Matter Wave

$$E^2 = M_0 c^4 + p^2 c^2$$

for photon,  $M_0 = 0$ ,  $E = pc$ 

$$E = \frac{hc}{\lambda}$$

also for photon

$$\frac{hc}{\lambda} = pc$$

$$p = \frac{h}{\lambda}$$

for photon

• De Broglie relation :  $p = \frac{h}{\lambda}$  for all matter**Ex1** Calculate  $\lambda$  for baseball.  $m = 145 \text{ g}$ ,  $v = 100 \text{ mph} = 44 \text{ m/s}$ 

$$p = mv = (0.145 \text{ kg})(44 \text{ m/s}) = 6.38 \text{ kg m/s}$$

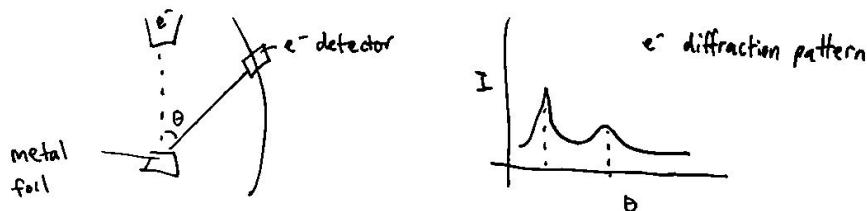
$$\lambda = \frac{h}{p} = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{6.38 \text{ kg m/s}} = 10^{-34} \text{ m}$$

**Ex2** Calculate  $\lambda$  for 2eV e<sup>-</sup>.  $KE = 2 \text{ eV}$ 

$$KE = 2 \text{ eV} \cdot \frac{1.6 \times 10^{-19} \text{ J}}{1 \text{ eV}} = 3.2 \times 10^{-14} \text{ J} = \frac{1}{2} M v^2$$

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ J}}{(838000 \text{ m/s})(9.1 \times 10^{-31} \text{ kg})} = 8.7 \times 10^{-10} \text{ m}$$

↳ Davisson &amp; Germer Experiment



↳ Quantization of Energy

- e<sup>-</sup> only has specific energy level
- photon absorption & emission is due to excitation & relaxation of e<sup>-</sup>
- $\Delta E = h\nu = \frac{hc}{\lambda}$  (ΔE is energy diff between e<sup>-</sup> levels)

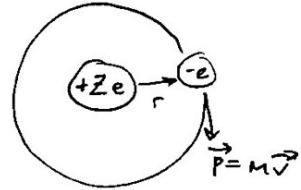
<< Bohr's Model

$$\frac{1}{\lambda} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

↑  
depend  
on material

- Coulomb force between  $e^-$  and nucleus :  $F = \frac{Q_1 Q_r}{4\pi\epsilon_0 r^2}$

$$F = -\frac{Ze^2}{4\pi\epsilon_0 r^2}$$



- $F_{\text{centripetal}} = -\frac{mv^2}{r} = -\frac{Ze^2}{4\pi\epsilon_0 r^2}$  due to changing  $\vec{r}$ ,  $\vec{a}$ , and  $\vec{F}$

• but classical Mechanics says : accelerating charges emit em radiation.

• Possible orbit :

$$mv_r = \hbar n \quad \hbar = \frac{h}{2\pi}$$

21 Feb 2020

## Bohr's Model &amp; Wave Function

CHEM 155

&lt;&lt; Bohr's Model

$$mv^2 = n\frac{h}{r}$$

$$v = \frac{n\frac{h}{r}}{m_e r}$$

$$\frac{Z e^2}{4\pi r_0 v^2} = \frac{n^2 h^2 m_e}{m_e^2 r^2} \Rightarrow r_n = \frac{n^2 h^2 4\pi E_0}{Z m_e e^2} = \frac{n^2}{Z} a_0 \quad \text{Bohr radius}$$

$$a_0 = 0.529 \text{ Å}$$

$$\begin{aligned} E_{\text{total}} = KE + PE &= \frac{1}{2} m v^2 - \frac{Z e^2}{4\pi E_0 r} = \frac{-Z^2 m_e e^4}{(6\pi^2 c_0^2 n^2 h^2)} + \frac{1}{2} \frac{Z^2 m_e e^4}{(6\pi^2 c_0^2 n^2 h^2)} \\ &= -\frac{(13.6 \text{ eV}) Z^2}{n^2} \end{aligned}$$

PE = -2 KE

virial theorem

**Ex1** max velocity of photo  $e^-$  from  $\text{He}^+$  ion at ground state  
 $Z=2$

$$\frac{1}{2} m v^2 = E_{\text{photon}} - IE$$

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{1240 \text{ eV} \cdot \text{nm}}{12.4 \text{ nm}} = 100 \text{ eV}$$

$$IE = 0 - (13.6 \text{ eV} \frac{Z^2}{n^2}) = +13.6 \text{ eV} \left(\frac{2^2}{1}\right) = +54.4 \text{ eV}$$

$$KE = 100 \text{ eV} - 54.4 \text{ eV} = 45.6 \text{ eV}$$

$$v = 4 \times 10^6 \text{ m/s}$$

&lt;&lt; De Broglie Wave

$$\lambda = \frac{h}{p} = \frac{h}{mv}; \quad mv^2 = \frac{n^2 h^2}{2\pi}$$

$$2\pi r = \frac{nh}{mv} = n\lambda$$

&lt;&lt; Wave Function

$\psi(x, y, z, t)$  - wave fn gives amplitude of matter wave at point  $(x, y, z)$  at time  $t$ ?

$\psi^* \psi dx dy dz$  - probability of finding the particle at point  $(x, y, z)$  at time  $t$ .

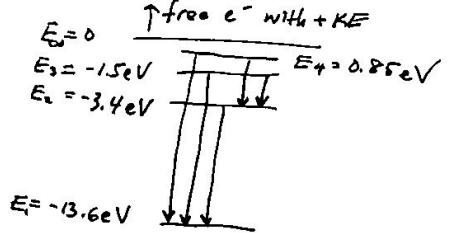
$\psi^*$  - complex conjugate

to  $(x+dx, y+dy, z+dz)$

$$z = a + bi$$

$$z^* = a - bi$$

$$z^* z = a^2 + b^2 \quad (\text{real & positive})$$



normalization  $\int_{-\infty}^{\infty} |\psi|^2 dx = 1$

**Ex3** e<sup>-</sup> in 1D box  $\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right)$ , L is length of box.

probability of finding e<sup>-</sup> in left half?

$$\int_0^{\frac{L}{2}} \psi^* \psi dx$$

$$= \int_0^{\frac{L}{2}} \frac{2}{L} \sin^2\left(\frac{2\pi x}{L}\right) dx$$

$$= \frac{2}{L} \int_0^{\frac{L}{2}} \sin^2\left(\frac{2\pi x}{L}\right) dx$$

$$= \frac{2}{L} \int_0^{\frac{L}{2}} \frac{1}{2} - \frac{1}{2} \cos\left(\frac{4\pi x}{L}\right) dx$$

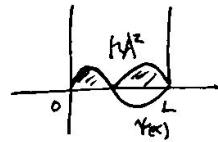
$$= \frac{2}{L} \left[ \int_0^{\frac{L}{2}} \frac{1}{2} dx - \frac{1}{2} \int_0^{\frac{L}{2}} \cos\left(\frac{4\pi x}{L}\right) dx \right]$$

$$= \frac{2}{L} \left[ \left[ \frac{1}{2}x \right]_0^{\frac{L}{2}} - \frac{1}{2} \left[ \frac{L}{4\pi} \sin\left(\frac{4\pi x}{L}\right) \right]_0^{\frac{L}{2}} \right]$$

$$= \frac{2}{L} \left[ \frac{L}{4} - \frac{L}{8} \cdot 0 \right]$$

$$= \frac{1}{2}$$

$$\sin^2 x = \frac{1}{2} - \frac{1}{2} \cos 2x$$



24 Feb 2020

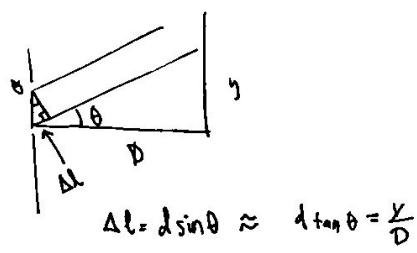
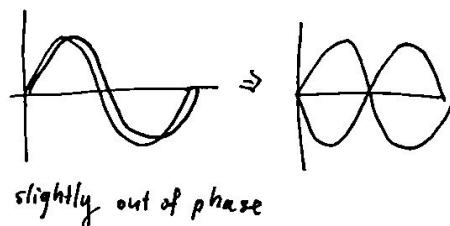
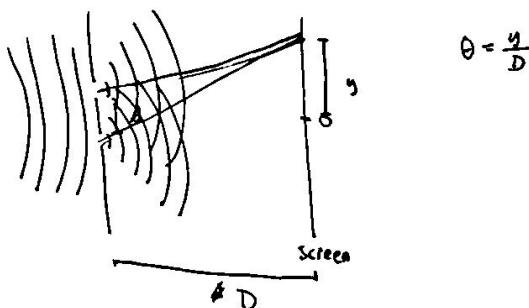
## Uncertainty Principle &amp; Schrödinger Equation

CHEM 155

&lt;&lt; Wave Functions

 $\psi^* \psi dV$  is probability density $= |\psi|^2 dV$  is probability

&lt;&lt; Young's Double Slit Experiment



$$\Delta l = d \sin \theta \approx d \tan \theta = \frac{y}{D}$$

$\Delta l = n\lambda$  for constructive interference

$$d \sin \theta = n\lambda \approx \frac{dy}{D}$$

$$y \approx \frac{n\lambda D}{d}$$

&lt;&lt; Heisenberg Uncertainty Principles

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}$$

$\Delta x$  is uncertainty in  $x$  position

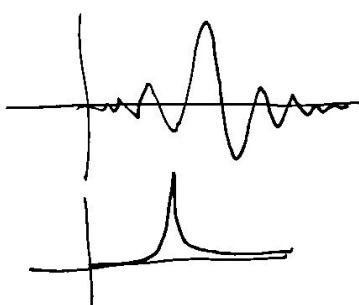
$\Delta p_x$  is uncertainty in momentum in  $x$  direction

$$\psi(x,t) = A \sin(kx - \omega t)$$



$$\lambda = \frac{h}{p}$$

$$\Delta p_x = 0, \Delta x = \infty$$



particle-wave packet

**Ex1**  $e^-$  confined in  $1\text{ \AA}$ .  $\Delta x = 1\text{ \AA} = 10^{-10}\text{ m}$

$$\Delta p_x \geq \frac{\hbar}{2\Delta x} = \frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s}}{4\pi \cdot 2 (10^{-10} \text{ m})} = 9.27 \times 10^{-25} \text{ kg m/s}$$

$$\Delta v \geq \frac{\Delta p_x}{m} = \frac{9.27 \times 10^{-25} \text{ kg m/s}}{9.1 \times 10^{-31} \text{ kg}} = 5.8 \times 10^5 \text{ m/s}$$

« Schrödinger Equation

$$\hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t}$$

↑  
Hamiltonian  
operator      wave  
fxn

Schrödinger Equation (time dependent)

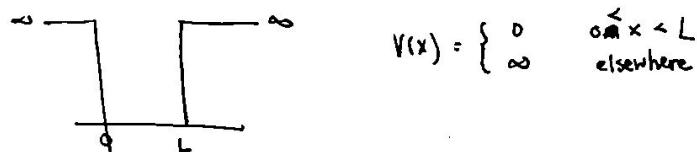
$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

↑  
Mass  
of  
particle      ↓  
potential  
energy      ↑  
total  
energy

Schrödinger Equation (time independent)

KE term       $\hat{H}\psi = E\psi$        $\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$

**Ex2** Particle in a box (Infinite Square Well)



$$\text{for } 0 < x < L : -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi$$

$$\frac{d\psi}{dx} \neq -\frac{2mE}{\hbar^2}\psi = 0 \Rightarrow \frac{d^2\psi}{dx^2} + k^2\psi = 0$$

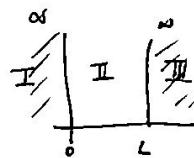
- Normalization
- Single valued
- Continuous
- Continuous first derivative

• Particle in a box.

$$\frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0$$

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0, \quad k = \sqrt{\frac{2mE}{\hbar^2}}$$



$$\psi(x) = A \sin(kx) + B \cos(kx)$$

- boundary conditions
  - { normalizable :  $\int_{-\infty}^{\infty} \psi^* \psi dx = 1$
  - single valued : it's a fn, can only have one probability
  - continuous  $\psi$
  - continuous  $\psi'$  (except if  $V = \infty$ )

• For region I,  $\psi(x) = 0$

• For region III,  $\psi(x) = 0$

} at  $x=0$  and  $x=L$ ,  $\psi(x)=0$

$$\psi(0) = A \sin(k \cdot 0) + B \cos(k \cdot 0) = 0$$

$$B \cos(k \cdot 0) = 0$$

$$B = 0$$

$$\psi(L) = A \sin(kL) \neq 0$$

$$kL = n\pi$$

$$k = \frac{n\pi}{L} \quad (\text{also notice } k = \sqrt{\frac{2mE}{\hbar^2}})$$

$$\frac{n\pi}{L} = \sqrt{\frac{2mE}{\hbar^2}} \Rightarrow \frac{n^2\pi^2}{L^2} = \frac{2mE}{\hbar^2} \Rightarrow$$

$$E = \frac{n^2 \hbar^2}{8mL^2}$$

• energy is quantized

•  $E \propto \frac{1}{m}$

•  $E \propto \frac{1}{L^2}$  (think uncertainty principle)

•  $E \propto n^2$  (energy spacing)

$$E_3 = 9E_1$$

$$E_2 = 4E_1$$

$$E_1 = \frac{\hbar^2}{8mL^2}$$

$$\psi(x) = A \sin\left(\frac{n\pi x}{L}\right)$$

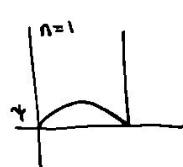
$$\int_{-\infty}^{\infty} \psi^* \psi dx = 1$$

$$= \int_0^L A^2 \sin^2\left(\frac{n\pi x}{L}\right) dx = 1$$

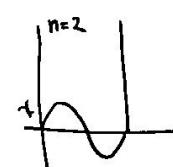
$$= A^2 \int_0^L 1 dx$$

$$A = \sqrt{\frac{2}{L}}$$

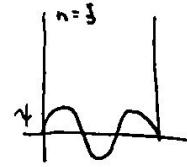
$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$



ground state



1<sup>st</sup> excited state



2<sup>nd</sup> excited state



3<sup>rd</sup> excited state

node: 0

1

2

3

<< Particle in a 3D Box

$$\psi(x,y,z) = A \sin\left(\frac{n_x \pi x}{L_x}\right) \cdot \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right)$$

$$E = \frac{\pi^2 \hbar^2}{8M} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

If  $L_x = L_y = L_z = L$ , there will be degeneracy:

$$E = \frac{\hbar^2}{8ML^2} (n_x^2 + n_y^2 + n_z^2)$$

Egrrond state:  $E(111)$

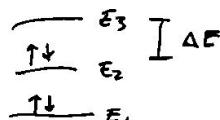
$E_{\text{1st excited}}: E(211) \quad E(121) \quad E(112)$

**EX1**  $\text{H}_2 \text{C}=\text{CH}-\text{CH}=\text{CH}_2$  what  $\lambda$  of light to excite  $e^-$  from  $n=2 \rightarrow n=3$

1) Length of box? End to end  $L \approx 5.8 \text{ \AA}$

2) #  $e^-$  in box?  $4e^-$  in  $\pi$  bond system.

3) Mass of particle?  $m_e$   $\uparrow$  lowest energy  $\Delta E = (\Delta E_3 - E_2)$



<< Hydrogen Atom

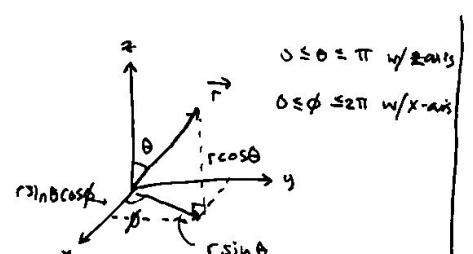
$$V(r) = -\frac{Z e^2}{4\pi \epsilon_0 r}$$

$$r = \sqrt{x^2 + y^2 + z^2}$$

$$z = r \cos \theta$$

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$



$$\begin{aligned} &= \frac{\hbar^2}{8mL^2} (3^2 - 2^2) \\ &= \frac{6.626 \times 10^{-34} \text{ J s}}{8(9.11 \times 10^{-31} \text{ kg})(5.8 \times 10^{-10} \text{ m})^2} (3^2 - 2^2) \\ &= 8.96 \times 10^{-19} \text{ J} \end{aligned}$$

$$\Delta E = h\nu = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{E} = 221 \text{ nm}$$

$n = \text{node} + 1$

$l = \text{node} = 0, \dots, n-1$

$m = -l, \dots, l$

quantum number

$n$  - principle quantum number  
 $l$  - orbital quantum number  $\rightarrow$  angular momentum  
 $m$  - magnetic quantum number  
 projection of  $l$  on  $z$ -axis

$$\nabla \psi = E \psi \quad V = -\frac{Ze^2}{4\pi \epsilon_0 r}$$

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi = E \psi$$

$$\nabla \cdot \nabla = \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$

$$\psi(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi)$$

$$E_n = -13.6 \text{ eV} \frac{Z^2}{n^2}$$

&lt;&lt; Review

- $\psi^* \psi dx$  - probability of finding the particle at  $dx$

wave fn boundary conditions : normalization, single valued, continuous  $\psi, \psi'$

particle in a box  $\psi_n(r) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi r}{L}\right)$

$$E_n = \frac{\pi^2 \hbar^2}{8mL^2}$$

$\psi(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi)$

$\downarrow$   
has  $\exp(-\sigma)$ ,  $\sigma \equiv \frac{2r}{a_0}$

(energy)  $E = \frac{(-13.6 eV) Z^2}{n^2}$

n - principle  $n=1, 2, 3, \dots$

l - orbital angular momentum  $l=0, \dots, n-1$

$m_l$  - magnetic  
(projection of L on z-axis)  $m_l = -l, \dots, l$

$m_s$  - spin

- in spherical coord.,  $dV = dr d\theta d\phi$

$$= r^2 \sin\theta dr d\theta d\phi$$

&lt;&lt; Radial Probability Density

- Radial probability density  $P(r) dr = |\psi|^2 4\pi r^2 dr$

$$\psi_{100} = \psi_{1s} = \frac{1}{\sqrt{4\pi}} \frac{1}{a_0 \sqrt{2}} e^{-r/a_0}$$

$$P(r) = |\psi_{1s}|^2 \cdot 4\pi r^2$$

$$= \frac{1}{4\pi} \frac{4}{a_0^3} e^{-2r/a_0} 4\pi r^2$$

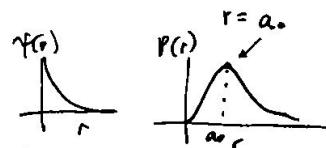
$$= \frac{4}{a_0^3} r^2 \exp(-2r/a_0)$$

$$\frac{dP}{dr} = \frac{4}{a_0^3} \left[ 2r \exp(-2r/a_0) + r^2 \exp(-2r/a_0) \cdot \left( -\frac{2}{a_0} \right) \right]$$

$$= \frac{8 \exp(-2r/a_0)}{a_0^3} r \left( 1 - \frac{r}{a_0} \right) = 0$$

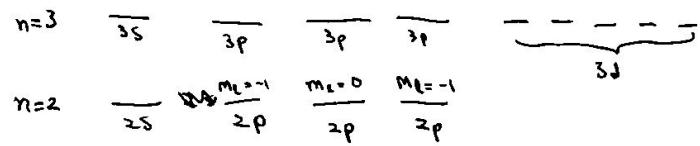
$$1 - \frac{r}{a_0} = 0$$

$$r = a_0$$



$\uparrow$  has to take volume into account: volume is larger away from nucleus.  
as  $r \uparrow$ ,  $P \uparrow$ .

<< Energy level of H atom

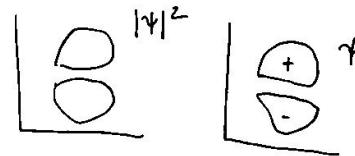


$$E = \frac{(-13.60 \text{ eV}) Z^2}{r^2}$$

He :  $1s^2$   ~~$= 1s + 2s$~~

## &lt;&lt; Review

- an atomic orbital is a one  $e^-$  wave fn
  - probability of finding an  $e^-$  at a point in H atom is given by the one  $e^-$  atomic orbital of H atom
  - Most likely distance to find  $e^-$  in ground state H atom:  $P_{\text{max}}(r) = a_0$
- quantum number



$$\begin{array}{lll} n = 1, 2, 3 & \text{principl quant #} & E_n = -13.60 \text{eV} \frac{Z^2}{n^2} \\ l = 0, \dots, n-1 & \text{orbital angular momentum} & L^2 = l(l+1) \pi^2 \\ m_l = -l, \dots, l & \text{magnetic quant #} & L_z = m_l \hbar \\ m_s = \frac{1}{2}, -\frac{1}{2} & \text{spin} & \end{array} \quad \left. \begin{array}{l} \text{specify spacial} \\ \text{wave fn.,} \\ \text{come from Schrodinger eq} \end{array} \right\}$$

## → Differentials

$$dV = r^2 \sin\theta dr d\theta d\phi$$

$$p(r)dr = |\psi|^2 4\pi r^2 dr \quad \leftarrow \text{Radial probability density}$$

## → Electron Density

- $m_l=0$  is  $p_z$
- $m_l=1, -1$  is NOT  $p_x, p_y$
- $p_x, p_y$  is linear combination of  $Y_m(\theta, \phi)$
- There are  $n-1$  radial nodes

## → Energy level of H atom



Same

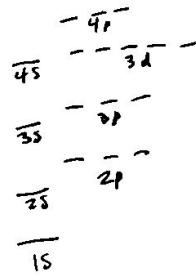
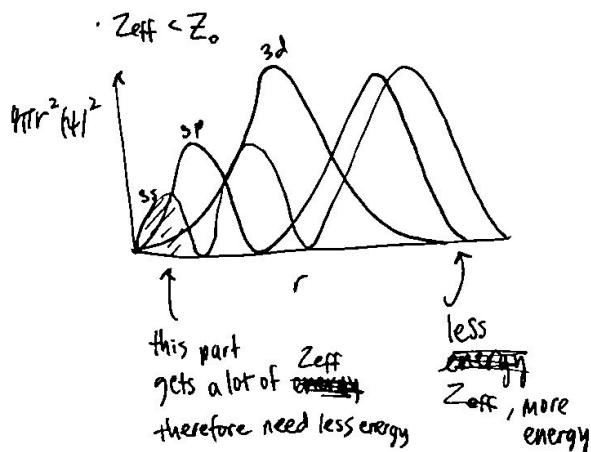
- for 1  $e^-$  atom, energy depends only on  $n$ , so  $3s, 3p, 3d$  are degenerate
- multi  $e^-$  atom does NOT follow due to screening, pauli exclusion principle, hund's rules

## &lt;&lt; Pauli Exclusion Principle

- no 2  $e^-$  can have the same 4 quant #.

$$\uparrow \quad 1s^1, 2s^1, 2p^3$$

## « Effective Nuclear charge & Shielding / Screening



**EX1**  $\begin{array}{c} \uparrow \downarrow 2s \\ \uparrow \downarrow 1s \end{array}$   $\begin{array}{c} \uparrow \downarrow 1s(1) \\ \uparrow \downarrow 1s(2) \\ \uparrow \downarrow 2s(3) \\ \uparrow \downarrow 2s(4) \end{array}$   $\xrightarrow{\# \text{ of } e^-}$   
 $\downarrow$   $1s^2 2s^2$    
this denotes approx of wave fun

## « Aufbau principle

- we build up electron config from the lowest energy level

## « Hund's Rule

- Empirical
- unpaired  $e^-$  are favored
- parallel spins are favored
- they minimize  $e^-e^-$  repulsion & maximize  $e^-$ -nuclear attraction

→ Exception

Arg: instead of  $[Kr] 5s^2 4d^9$

we have  $[Kr] 4d^{10} 5s^1$ , since filling the  $d$  shell is favored.  $5s$  has lower energy,  
being the balance  $e^-$

**EX2** For Carbon  $1s^2 2s^2 2p^2$

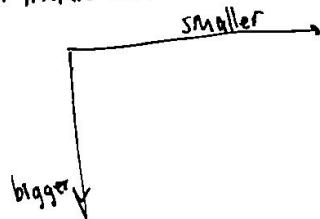
|                       |            |            |
|-----------------------|------------|------------|
| $\uparrow$            | $\uparrow$ | $\uparrow$ |
| $\uparrow \downarrow$ | $2s$       | $2p$       |
| $\uparrow \downarrow$ | $1s$       |            |

**EX3** V:  $Z=23$

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$   
 $\underbrace{[Ar]}_{\substack{\uparrow \\ \text{balance } e^-}} 4s^2 3d^3$

## « Periodic Trend

→ Atomic Size

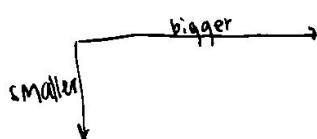


- across a period: same shell, but larger  $Z$   
see radial wave fun
- across a group, the  $\propto 1/r$  term decreases.

→ Ionization Energy - energy needed to remove  $e^-$

$$V(r) = \frac{-Ze^2}{4\pi\epsilon_0 r}$$

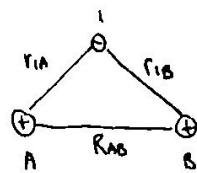
small size, large ionization energy



- filled & half filled orbitals are particularly stable

## &lt;&lt; Molecular Orbital

- Consider  $H_2^+$



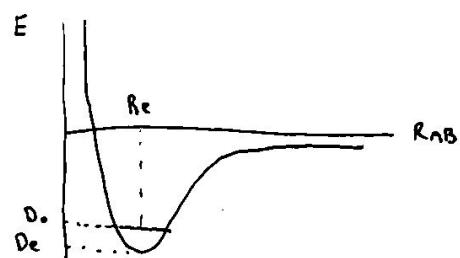
$$\hat{H} = KE_A + KE_B + KE_e + PE_{1A} + PE_{1B} + PE_{AB}$$

- Use Born-Oppenheimer Approx

$\rightarrow$  Born-Oppenheimer Approx

- $e^-$  is much lighter than proton
- proton moves very slowly,  $e^-$  moves fast
- wave fn is separable:  $\psi = \psi_{e^-} + \psi_{\text{nuclei}}$
- $E_{\text{total}} = E_{e^-} + E_{\text{nuclei}}$

Bond energy VS Distance between two nuclei



$R_e$  - equilibrium bond length

$D_e$  - depth of potential

$D_0$  - experimentally measured

- caused by zero point energy
- nuclei like particle in a box

## &lt;&lt; MO-LCAO

- standard basis vectors

$$\vec{i} = \hat{x} = \langle 1, 0, 0 \rangle$$

$$\vec{j} = \hat{y} = \langle 0, 1, 0 \rangle$$

$$\vec{k} = \hat{z} = \langle 0, 0, 1 \rangle$$

$\rightarrow$  H atom

Molecular orbital H atom wave fun

$$\downarrow$$

$$\phi_{\text{MO}} = C_A \psi_{1SA} + C_B \psi_{1SB}$$

A

B

$|C_A|^2 = |C_B|^2$  due to indistinguishable  
 $e^-$  & proton

- only outer shell  $e^-$  are involved in MO formation
- only AO's of similar energy mix significantly.

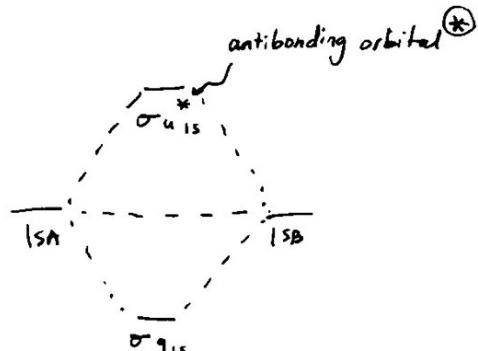
$\rightarrow H_2^+$

$$C_A \psi_{1SA} + C_B \psi_{1SB}$$

$$|C_A|^2 = |C_B|^2$$

$$\sigma_{g_{1S}} = C_{g_{1S}} (\psi_{1SA} + \psi_{1SB}) \quad \text{ground state}$$

$$\sigma_{u_{1S}}^* = C_{u_{1S}}^* (\psi_{1SA} - \psi_{1SB}) \quad \text{first excited state}$$



$\sigma = s = (l=0) = \text{no node parallel to bond axis}$   
 $\pi = p = (l=1) = \text{one nodal plane parallel to bond axis}$

$g = \text{gerade} = \text{even}$   
 $u = \text{ungerade} = \text{odd}$

\* - antibonding  
 $\overline{\sigma}$  - bonding  
 $\overline{\pi}$  - nothing

H<sub>2</sub> e<sup>-</sup> config:  $\sigma_{g_{1S}}^2$

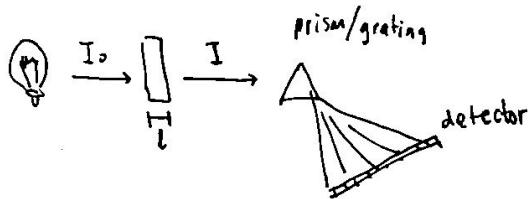
H<sub>2</sub> e<sup>-</sup> config:  $\sigma_{g_{1S}}^2 \sigma_{u_{1S}}^{*2}$

$\rightarrow$  bond order

$$\cdot \frac{1}{2} [\# \text{ of bond } e^-] - [\# \text{ of antibonding } e^-]$$

H<sub>2</sub>:  $\frac{2-2}{2} = 0$

H<sub>2</sub>:  $\frac{2-2}{2} = 0$



$$T = \frac{I}{I_0}$$

→ Beer-Lambert Law

$$I = I_0 10^{-\epsilon cl}$$

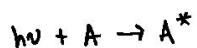
$\epsilon$  - molar extinction coefficient  
(decadic)  
 $c$  - concentration  
 $l$  - path length

$$[\epsilon] = M^{-1} \text{ cm}^{-1}$$

$$[c] = M$$

$$[\lambda] = \text{cm}$$

→ Nature of the law



1st order in  $hv$  and  $A$ .

$$\frac{dI}{dx} = -\alpha c I$$

$$\int_{I_0}^{I_f} \frac{dI}{I} = \int_0^l -\alpha c dx$$

$$\ln \frac{I_f}{I_0} = -\alpha c l \quad \text{let } \epsilon = \frac{\alpha}{\epsilon n(l)}$$

$$I = I_0 10^{-\epsilon cl}$$

$$\epsilon = 2.62 \times 10^{20} \sigma$$

( $\sigma$  is cross-section in  $\text{cm}^2$ )

$$A = -\log(T) = -\log\left(\frac{I}{I_0}\right)$$

(absorbance / optical density)

$A=1$ , 10% light get through

$A=2$ , 1% light get through

→ Vibrational Spectroscopy

$$hv = \Delta E = E_i - E_e$$

- electronic  $\sim 1 \text{ eV}$  UV-vis
- vibrational  $\sim 0.1 \text{ eV}$  IR
- rotational  $\sim 0.001 \text{ eV}$  microwave

$$(m_1, m_2)$$

$$-\mu$$

$k$  depend on bond strength

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

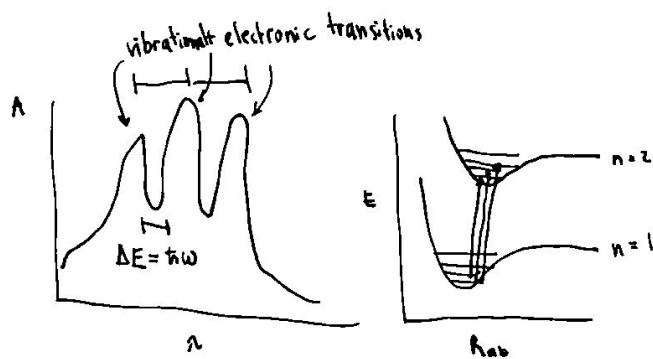
$$\omega = \sqrt{\frac{k}{\mu}} \leftarrow \begin{array}{l} \text{spring constant} \\ \text{reduced mass} \end{array}$$

$$E_n = (n + \frac{1}{2}) \hbar \omega, \quad \omega = \sqrt{\frac{k}{m}}$$

✓ vibrational energy is evenly spaced!  
 $\Delta n=1$  is selection rule

Selection rule:  
 $\Delta n=1$

- At room temperature, all molecules are in vibrational ground state (almost)
- generally, vibration excitation accompanies electronic excitation



## &lt;&lt; Valence Bond Theory

- describe molecules with localized bonds

- mixed use with MO theory

→  $\sigma$  bond

- $\lambda = 0$ , zero orbital angular momentum

- localized "pairing bond"

→  $\pi$  bond

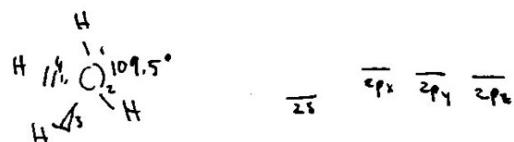
- $\lambda = 1$

- can be delocalized

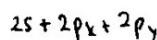
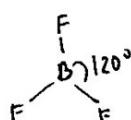
→ hybridization

- take linear combination of AO to create new directional orbital on an atom,  
on the same atom

[EX1] Methane :  $sp^3$



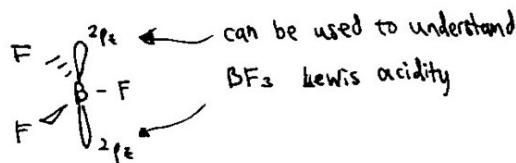
[EX2]  $\text{BF}_3$  -  $sp^2$ , trigonal planar



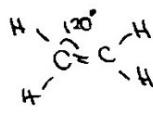
( $2p_z$  unhybridized)

$$c_1 \psi_{c_2s} + c_2 \psi_{c_2p_x} + c_3 \psi_{c_2p_y} + c_4 \psi_{c_2p_z}$$

four coefficients  
four hybridized orbitals  
four combinations = 4 wave funcns

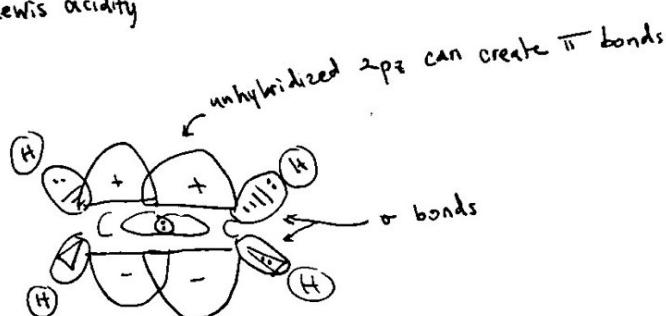


[EX3]  $\text{C}_2\text{H}_4$  ethene



steric # = 3

$sp^2$



total of 12 valence e<sup>-</sup>

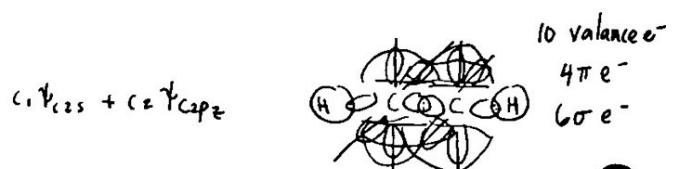
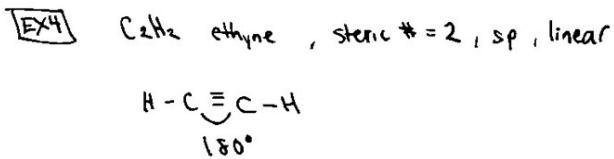
10 e<sup>-</sup> goes to σ bond ( $sp^2$ )

2 e<sup>-</sup> goes to π bond

LUMO →  $\pi^*$

HOMO ↑ ↓  $\pi$



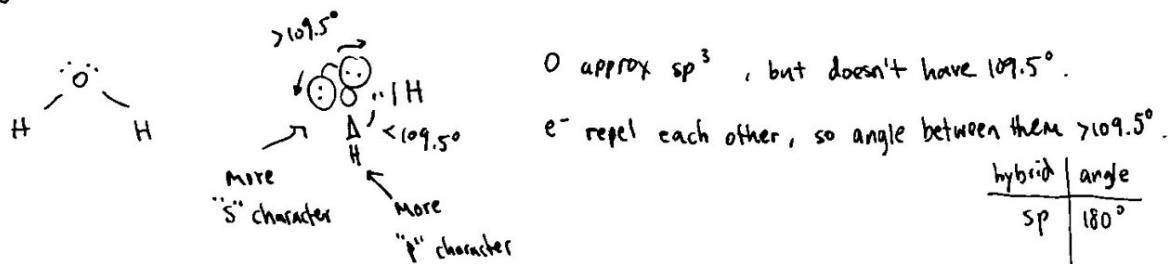


11 Mar 2020

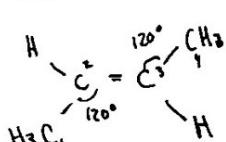
## Valence Bond Theory

CHEM 155

**EX1** H<sub>2</sub>O

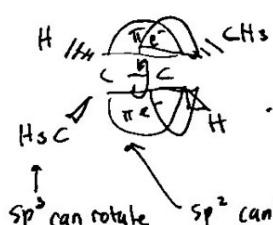


**EX2** trans-2-butene



How many of the carbon atoms will always lie in the same plane?

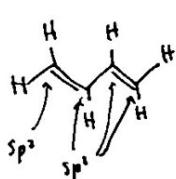
- 4. 1:  $\text{sp}^3$
- 2:  $\text{sp}^2$
- 3:  $\text{sp}^2$
- 4:  $\text{sp}^3$



if not in same plane, the  $\pi$  bond will not be aligned, increasing the energy of the system (not favored!)

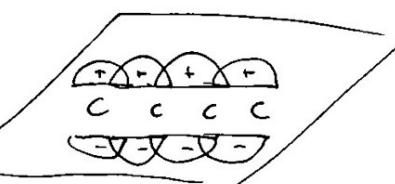
if  $\pi$  bond e<sup>-</sup> is excited to  $\pi^*$ , the molecule can rotate.

**EX3** 1,3-butadiene, a  $\pi$  conjugated molecule with all C in  $\text{sp}^2$ .

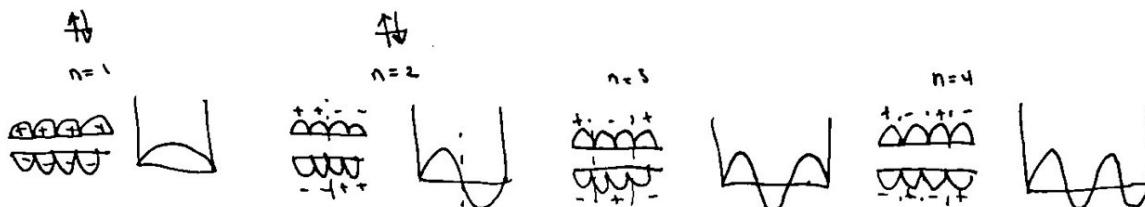


all 4 C are in the same plane

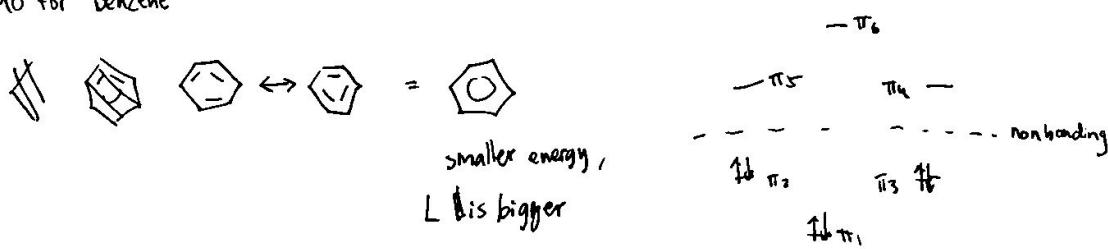
Shorter than normal C-C bond due to the double bonds



# atomic orbitals = # molecular orbital



→ Pi MO for benzene



→ Hybridization

|                      | steric # | # of AO needed | Hybridization                  |
|----------------------|----------|----------------|--------------------------------|
| linear               | 2        | 2              | sp                             |
| trigonal planar      | 3        | 3              | sp <sup>2</sup>                |
| tetrahedral          | 4        | 4              | sp <sup>3</sup>                |
| trigonal bipyramidal | 5        | 5              | sp <sup>3</sup> d              |
| octahedral           | 6        | 6              | sp <sup>3</sup> d <sup>2</sup> |

Modern theory rejects the involvement of d

### << Spectroscopy

- spectroscopy probes transitions between quantized energy levels to learn about molecular structure
- UV-visible - electrons in bond
- infrared - vibrations in bond (quantized)
- Raman
- Microwave - rotations
- NMR - flip spin
- X-ray photoe<sup>-</sup>spectroscopy - e<sup>-</sup> in core level