

## Chapter 5:

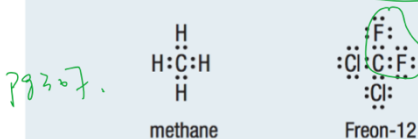
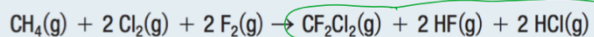
1.  $q = mc\Delta T$  and  $H_{\text{system}} = -H_{\text{surrounding}}$

## 2. Bond energy

Textbook page 309 – 310

**Sample Problem 2: Using Bond Energies and Lewis Diagrams to Estimate  $\Delta H$** 

Using the bond energies in Table 1, calculate the enthalpy change for the reaction in which methane gas,  $\text{CH}_4(\text{g})$ , is combined with chlorine gas and fluorine gas to produce Freon-12 gas,  $\text{CF}_2\text{Cl}_2(\text{g})$ . **Figure 2** shows the Lewis structures of methane and Freon-12. The balanced chemical equation for the formation of 1 mol of Freon-12 is



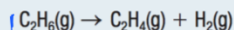
$$\begin{aligned} \Delta H &= \sum \text{reactants (required)} - \sum \text{products (released)} \\ &= [4 \times (\text{C-H}) + 2 \times (\text{Cl-Cl}) + 2(\text{F-F})] - [2 \times (\text{C-F}) + 2(\text{C-Cl}) \\ &\quad + 2 \times (\text{H-F}) + 2(\text{H-Cl})] \\ &= 4(413) + 2(239) + 2(154) - \dots \\ &= -1194 \text{ kJ, exothermic} \end{aligned}$$

$\Delta H < 0$

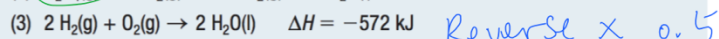
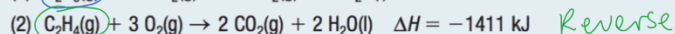
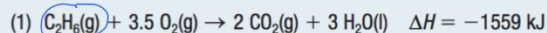
## 3. Hess's Law

## Example 2:

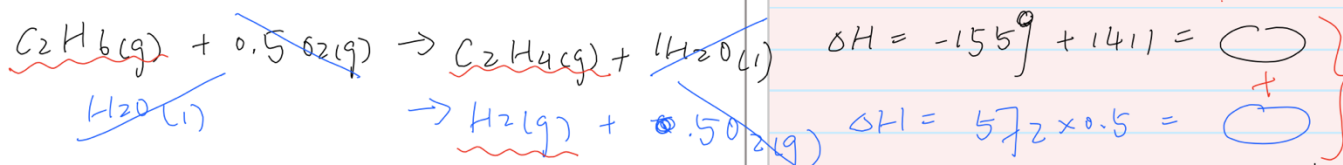
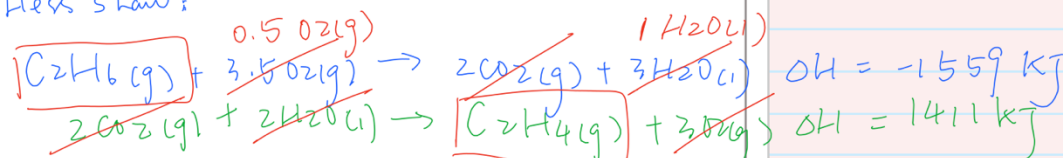
Ethene gas,  $\text{C}_2\text{H}_4(\text{g})$ , is the raw material for the synthesis of the plastic polyethylene. Engineers designing a process to make ethene from ethane gas,  $\text{C}_2\text{H}_6(\text{g})$ , need to know the change in enthalpy of the desired reaction represented by the following balanced chemical equation:



The engineers have the following thermochemical equations:

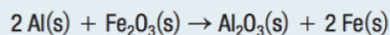


Hess's law:



#### 4. Standard enthalpy of formation

Using standard enthalpies of formation in Table 1, calculate the standard change in enthalpy for the thermite reaction represented by the balanced equation



$$\Delta H = \left( \Delta H_{\text{Al}_2\text{O}_3\text{(s)}} + 2\Delta H_{\text{Fe(s)}} \right) - \left( 2\Delta H_{\text{Al(s)}} + \Delta H_{\text{Fe}_2\text{O}_3\text{(s)}} \right)$$

$$\text{Example 2: } = (-1675.7 + 0) - (0 + -824.2) = -851.5 \text{ kJ}$$

Until recently, liquid methanol was used to fuel high-performance engines in race cars.

Gasoline is a mixture of hydrocarbons, but assume for this problem that gasoline is

### Chapter 6:

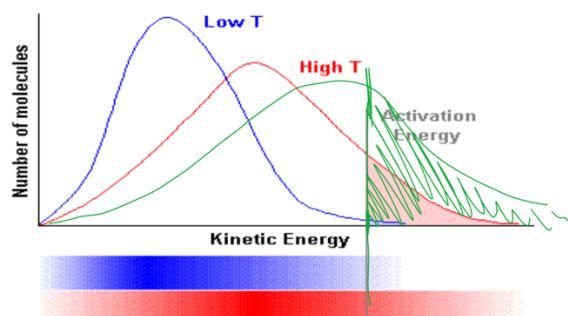
#### 5. Reaction rate

- Dinitrogen pentoxide gas decomposes to produce nitrogen dioxide gas and oxygen gas. If the rate of appearance of  $\text{NO}_2\text{(g)}$  is  $2.0 \times 10^{-2} \text{ mol/L}\cdot\text{s}$  at 90s.

- Determine the rate of appearance of  $\text{O}_2\text{(g)}$  at the same point in time  $\frac{2 \times 10^{-2}}{4} = 5.0 \times 10^{-3} \text{ mol/L}\cdot\text{s}$
- Determine the rate of disappearance of  $\text{N}_2\text{O}_5\text{(g)}$  at the same point in time  $\frac{2 \times 10^{-2}}{4} \times 2 = \boxed{\phantom{000}}$



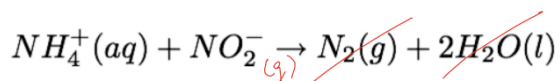
#### 6. Factor affecting rate of reaction and collision theory (6.2 – 6.3)



as well as catalyst...

#### 7. Rate Law (6.5)

##### Example



Experiment Number	Initial $\text{NH}_4^+$ Concentration (M)	Initial $\text{NO}_2^-$ Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	$5.4 \times 10^{-7}$
2	0.0200	0.200	$10.8 \times 10^{-7}$
3	0.0400	0.200	$21.5 \times 10^{-7}$
4	0.0600	0.200	$32.3 \times 10^{-7}$
5	0.200	0.0202	$10.8 \times 10^{-7}$
6	0.200	0.0404	$21.6 \times 10^{-7}$
7	0.200	0.0606	$32.4 \times 10^{-7}$
8	0.200	0.0808	$43.3 \times 10^{-7}$

$$\text{Rate} = k [\text{NH}_4^+\text{(aq)}]^1 [\text{NO}_2^-\text{(g)}]^1$$

$$5.4 \times 10^{-7} \text{ M/s} = k (0.0100 \text{ M})^1 (0.2 \text{ M})^1$$

$$k = \frac{5.4 \times 10^{-7}}{(0.01)(0.2)} \text{ s/M}$$

$$k = 2.7 \times 10^{-4} \text{ s/M}$$

$$\text{Rate} = 2.7 \times 10^{-4} [\text{NH}_4^+\text{(aq)}]^1 [\text{NO}_2^-\text{(g)}]^1$$

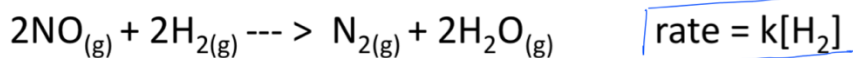
##### Find the Rate Law

$$\text{Rate} = k [\text{NH}_4^+\text{(aq)}]^m [\text{NO}_2^-\text{(g)}]^n$$

observed initial rate is doubled as  $[\text{NH}_4^+\text{(aq)}]$  is double  $\rightarrow m = 1$

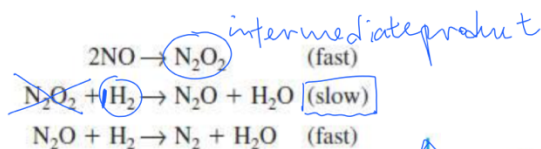
$[\text{NO}_2^-\text{(g)}]$   $\rightarrow n = 1$

## 8. Reaction mechanism and rate determining step

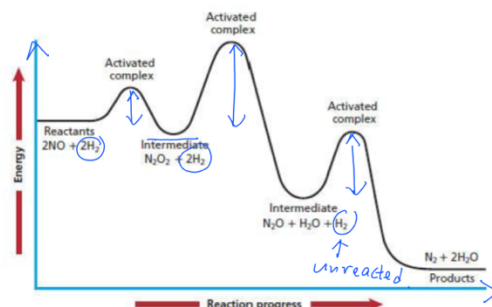


$$\text{rate} = k[\text{NO}]^2[\text{H}_2]$$

The mechanism for the above reaction occurs in three steps:



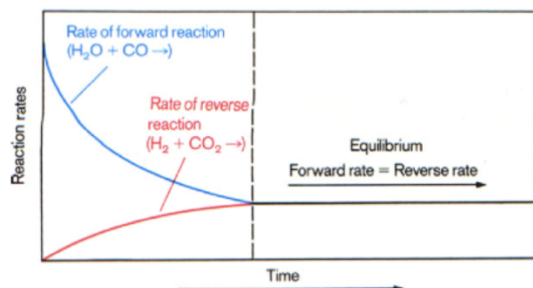
- \* only look at "slowest"
- \* NO intermediate molecule in Rate law.



## Chapter 7:

## 9. Reaction rate and change of concentration in dynamic equilibrium

Changes in reaction rates of the forward and reverse reaction for:

$$\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{H}_2 + \text{CO}_2$$


Rate of forward reaction decreases while reverse increases till the concentrations reach a level at which the rate of the forward and reverse reactions is the same. The system has reached equilibrium.

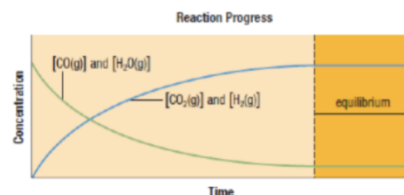
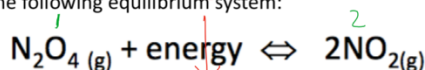


Figure 2 Changes in concentrations over time, when equal amounts of carbon monoxide gas and water vapour are allowed to react in a closed vessel

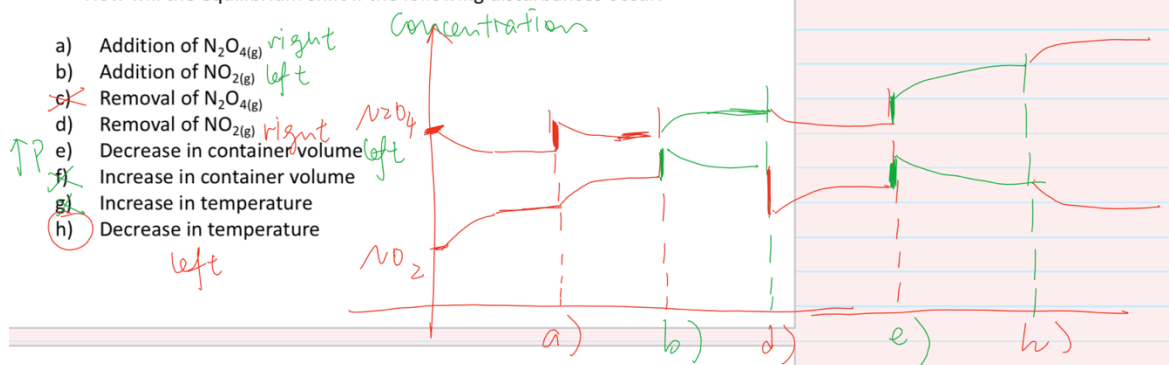
## 10. Le Chatelier's Principle and drawing diagram with disturbances (7.5)

- Consider the following equilibrium system:



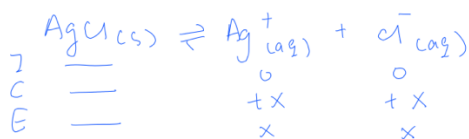
- How will the equilibrium shift if the following disturbances occur:

- Addition of  $\text{N}_2\text{O}_4(g)$  right
- Addition of  $\text{NO}_2(g)$  left
- Removal of  $\text{N}_2\text{O}_4(g)$  left
- Removal of  $\text{NO}_2(g)$  right
- Decrease in container volume left
- Increase in container volume right
- Increase in temperature right
- Decrease in temperature left



# 11. $K_{sp}$ (solubility product), molar solubility or mass per volume solubility (7.6)

What is the solubility of silver chloride in g/L if  $K_{sp} = 1.6 \times 10^{-10}$ ? (mass per volume solubility)



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

$$x = 1.26 \times 10^{-5} \text{ mol/L}$$

$$\text{solubility} = \left( 1.26 \times 10^{-5} \text{ mol} \times 143.32 \text{ g/mol} \right) / \text{L}$$

$$= 1.81 \times 10^{-3} \text{ g/L}$$

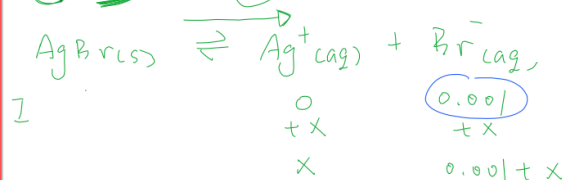
Textbook pg 464 / sample problem 3.

# 12. Trial ion product, predict precipitation and common ion effect

• What is the molar solubility of AgBr in

a) Pure water?  $K_{sp} = 5.4 \times 10^{-3}$  @  $25^\circ\text{C}$

b) 0.0010 M NaBr?



$$K_{sp} = (0.001 + x)x = 5.4 \times 10^{-3}$$

$$\text{Approximation} = \frac{0.001}{5.4 \times 10^{-3}} = 0.185 < 500$$

$$x^2 + 0.001x - 5.4 \times 10^{-3} = 0$$

$$x = \frac{-0.001 \pm 0.147}{2}$$

$$x = 0.073 \text{ mol/L}$$

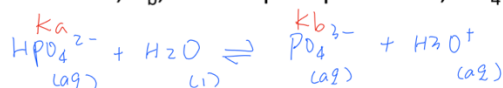
molar solubility of AgBr

## Chapter 8:

# 13. Arrhenius theory of acid-base & Bronsted and Lowry; strength of conjugate acid and conjugate base (8.1)

# 14. Ion-product constant, PH and POH (8.2)

The hydrogen phosphate ion,  $\text{HPO}_4^{2-}(\text{aq})$ , has a  $K_a$  of  $1.3 \times 10^{-13}$  at SATP. What is the base ionization constant,  $K_b$ , for the phosphate ion,  $\text{PO}_4^{3-}(\text{aq})$ ?



$$K_a = \frac{[\text{PO}_4^{3-}][\text{H}_3\text{O}^+]}{[\text{HPO}_4^{2-}]} = 1.3 \times 10^{-13}$$

$$K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{1.3 \times 10^{-13}} = \boxed{\phantom{0000}}$$



$$K_b = \frac{[\text{HPO}_4^{2-}][\text{OH}^-]}{[\text{PO}_4^{3-}]}$$

You could check the product of  $K_a$  of  $\text{HPO}_4^{2-}$  and  $K_b$  of  $\text{PO}_4^{3-}$  is equal to  $K_w = 10^{-14}$ .

15. Use % ionization to calculate  $K_a$  or  $K_b$  & use  $K_a$  or  $K_b$  to calculate pH (vice versa) and calculate related to polyprotic acids (8.4)

④ Example: Pg 522.

ascorbic acid  $[H_2C_6H_6O_6] = 0.1 M$ ,  $pH = ?$ ,  $[...] = ?$   
 $H_2C_6H_6O_6 + H_2O \rightleftharpoons HC_6H_6O_6^- + H_3O^+$   $K_{a1} = 7.9 \times 10^{-5}$

I	0.1	0	0
C	-x	+x	+x
E	0.1-x	x	x

Use approximation method, we can simplify:  $K_{a1} = \frac{x^2}{0.1}$

$$x = 2.8 \times 10^{-3} M$$

$$pH = -\log 2.8 \times 10^{-3} = \underline{2.55}$$

Then let see if  $K_{a2}$  will affect pH noticeable or not.

	$HC_6H_6O_6^- + H_2O \rightleftharpoons C_6H_6O_6^{2-} + H_3O^+$	$K_{a2} = 1.6 \times 10^{-12}$	
or I	$2.8 \times 10^{-3}$	0	$2.8 \times 10^{-3}$
C	-x	+x	+x
E	$2.8 \times 10^{-3} - x$	x	$2.8 \times 10^{-3} + x$

Approximation:  $\frac{2.8 \times 10^{-3}}{K_{a2}} \gg 500$ .

$$K_{a2} = \frac{(2.8 \times 10^{-3})x}{2.8 \times 10^{-3}}$$

$$x = 1.6 \times 10^{-12} M$$

$$pH = -\log (2.8 \times 10^{-3} + 1.6 \times 10^{-12}) = \underline{2.55}$$

At equilibrium:

$$[H_2C_6H_6O_6] = 0.1 - 2.8 \times 10^{-3} = 0.0972 M$$

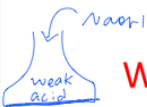
$$[HC_6H_6O_6^-] = 2.8 \times 10^{-3} - 1.6 \times 10^{-12} \approx 2.8 \times 10^{-3} M$$

$$[C_6H_6O_6^{2-}] = 1.6 \times 10^{-12} M$$

$$[H^+] = 2.8 \times 10^{-3} + 1.6 \times 10^{-12} \approx 2.8 \times 10^{-3} M$$

16. Analysis acid-base properties of salt (8.6) & hydrolysis of amphiprotic ions

17. Titration (I only put an example we did in class about weak acid/base titration, read textbook for strong acid/base titration)



### Titrations Involving Weak Acids and Strong Bases

- To calculate the  $[H^+]_{(aq)}$ , and pH after a certain amount of strong base has been added, we must deal with the weak acid ionization equilibrium.

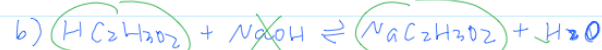
**Practice:**  $K_a = 1.8 \times 10^{-5}$

A 20.00 mL sample of 0.600 mol/L ethanoic acid,  $HC_2H_3O_2(aq)$  (a weak acid), is titrated with a standardized 0.300 mol/L solution of sodium hydroxide,  $NaOH(aq)$  (a strong base). Predict the amount of unreacted ethanoic acid and the pH of the solution

- before titration begins
- Before equivalence point when 20.00 mL of NaOH has been added
- At the equivalence point when 40.00 mL of  $NaOH(aq)$  has been added
- Beyond the equivalence point when a total of 60.00 mL of  $NaOH(aq)$  has been added



$$\begin{array}{ccc} 0.6 & 0 & 0 \\ 0.6-x & +x & +x \end{array} \dots\dots$$



$$n(\text{HC}_2\text{H}_3\text{O}_2) = 0.02\text{L} \times 0.6\text{mol/L} = 0.012\text{mol}$$

$$n(\text{NaOH}) = 0.02\text{L} \times 0.3\text{mol/L} = 0.006\text{mol}$$

$$\text{Before reaction} \quad 0.012 \quad 0.006 \quad 0$$

$$\text{after reaction} \quad 0.006 \quad 0 \quad 0.006$$

$$[\text{HC}_2\text{H}_3\text{O}_2] = \frac{0.006\text{mol}}{0.02\text{L} + 0.02\text{L}} = 0.15\text{M}$$

$$[\text{C}_2\text{H}_3\text{O}_2^-] = 0.15\text{M}$$



$$\begin{array}{ccc} I & 0.15 & 0.15 & 0 \\ C & -x & -x & +x \\ E & 0.15-x & 0.15+x & x \end{array}$$

$$K_a = 1.8 \times 10^{-5} = \frac{(0.15+x)x}{0.15-x}$$

$$\Rightarrow x \Rightarrow \text{pH}$$

$$n = C \cdot V$$

c) before reaction

after reaction

$$\text{HC}_2\text{H}_3\text{O}_2$$

$$\text{NaOH}$$

$$\text{NaC}_2\text{H}_3\text{O}_2$$

$$\rightarrow \text{Na}^+$$

$$\rightarrow \text{C}_2\text{H}_3\text{O}_2^-$$

strong conjugate base of a weak acid.



$$\frac{0.012\text{mol}}{0.02\text{L} + 0.04\text{L}}$$

$$= 0.2\text{M}$$

$$\begin{array}{ccc} 0.2 & 0 & 0 \\ 0.2-x & x & x \end{array}$$

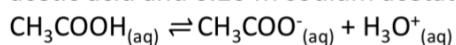
$$K_b = \frac{10^{-14}}{1.8 \times 10^{-5}} = \frac{x^2}{0.2-x}$$

$$5.56 \times 10^{-10} = \dots\dots\dots$$

$$\text{pH} = 9.1 \text{ basic.}$$

## 18. Buffer system

Calculate the pH of a buffer that contains 0.20 M acetic acid and 0.20 M sodium acetate.



$$\begin{array}{ccc} I & 0.2 & 0.2 & 0 \\ C & -x & +x & +x \\ E & 0.2-x & 0.2+x & x \end{array}$$

$$K_a = 1.8 \times 10^{-5} = \frac{(0.2+x)x}{0.2-x}$$

$$x = 1.8 \times 10^{-5}$$

$$\text{pH} = -\log 1.8 \times 10^{-5} = 4.74$$

$$\text{pK}_a = -\log K_a$$

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

$$K_a = \frac{(0.2 + [\text{H}^+]) \cdot ([\text{H}^+])}{(0.2 - [\text{H}^+])}$$

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

$$\log K_a = \log \frac{[\text{A}^-] \cdot [\text{H}^+]}{[\text{HA}]} = \log \left( \frac{[\text{A}^-]}{[\text{HA}]} \cdot \frac{[\text{H}^+]}{1} \right)$$

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

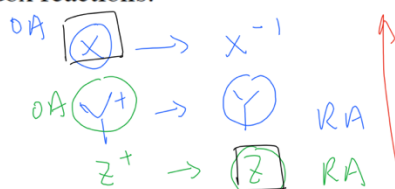
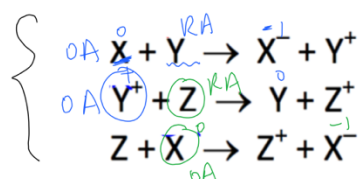
$$-\text{pK}_a = \log \frac{[\text{A}^-]}{[\text{HA}]} - \text{pH}$$

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

## Chapter 9 and chapter 10:

19. Identifying Oxidation reaction, reduction reaction, oxidizing agent, reducing agent, oxidation number, and strength of OA and RA. (9.1 – 9.2)

ex. Consider the following spontaneous redox reactions:



What is the relative strengths of oxidizing agents (strongest to weakest)?

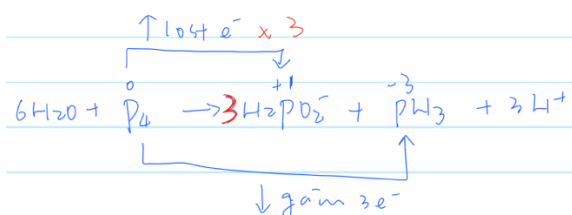
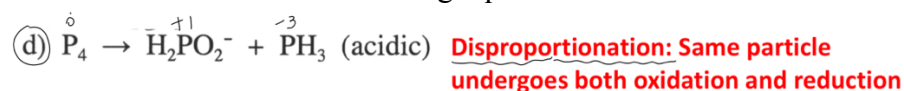


R.A strongest → weakest

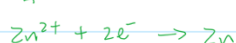
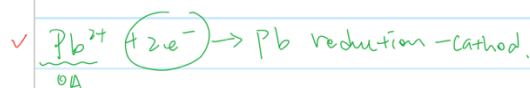
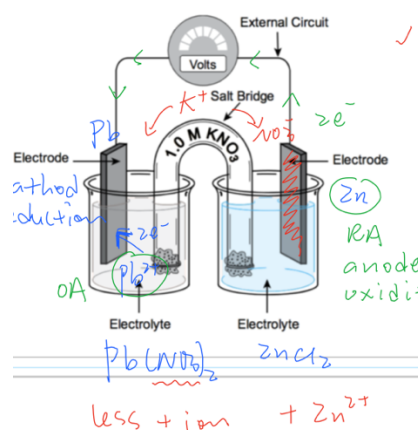
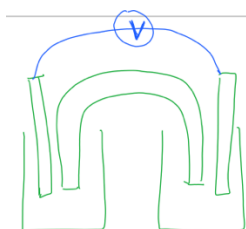


ex. A solution containing  $\text{Pd}^{2+}$  reacts spontaneously with

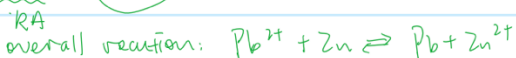
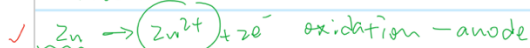
20. Two different method of balancing equations in acidic or basic solution (9.3)



21. Galvanic cells (10.1 – 10.2): identify name and function of different parts of galvanic cells, identify cathode, anode, direction of electron flow, half-cell reaction, how salt bridge balance excess of charge accumulation, etc... Calculate cell potential and determine if it is spontaneous or non-spontaneous...



reverse it

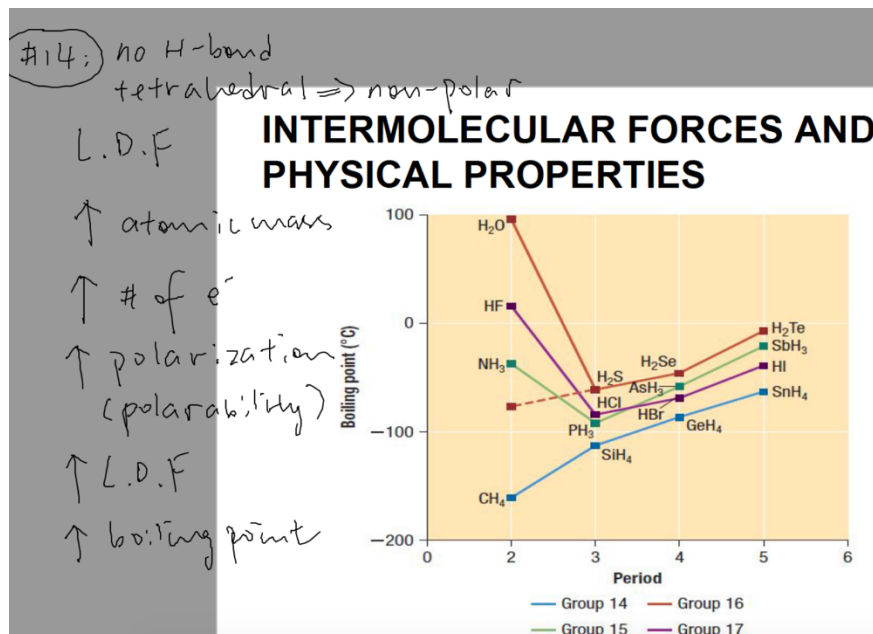
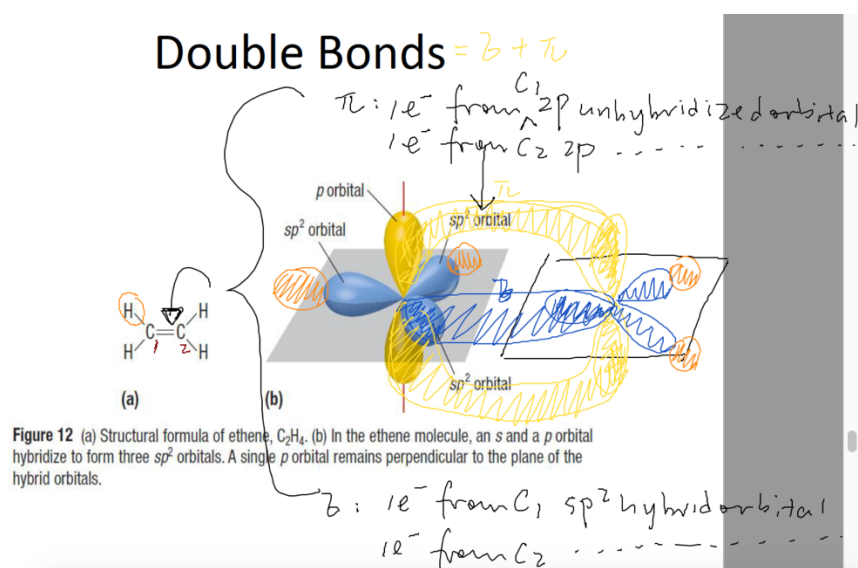




22. Preventing corrosion
23. Selecting preferred reaction in galvanic cell
24. Molten binary salt electrolysis
25. Aqueous solution electrolysis
26. Overpotential effect

### Chapter 3:

27. Quantum numbers, Pauli Exclusion Principle, Aufbau principle; electron configuration, energy-level diagram, Cr and Cu exception, determine possible charges (3.4 – 3.5)
28. Lewis structure, VSEPR 3D structure of central atoms, bond and molecular polarity, hybridization
29. intermolecular forces: dipole-dipole, hydrogen bond, London dispersion forces, polarizability; physical properties (ranking melting and boiling point)...





**Practice**

**• Predict the hybridization and describe the three dimensional structure of propene**

**O:**  $2p^4$   $\uparrow\downarrow$   $\uparrow$   $\uparrow$   
 $2s^2$   $\uparrow\downarrow$

**sp<sup>2</sup>**  $\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow$

**P:**  $1$

half-filled p orbital for  $\pi$  bond

**POF<sub>3</sub>**

central atom

$5 + 6 + 3 \times 3 = 22$   
 $- 8$   
 $14e^-$   
 formal charge:  $14e^-$   
 $P: 5 - 4 = +1 \rightarrow 0$   
 Valence  $e^-$  - # of bond - # of lone pairs  $e^-$   
 $O: 6 - 1 - 6 = -1 \rightarrow 0$   
 $F: 7 - 1 - 6 = 0 \checkmark$

$\sigma$  bond:  $1e^-$  P  $sp^3$  +  $1e^-$  O  $sp^2$   
 $\pi$  bond:  $1e^-$  P  $3d$  +  $1e^-$  O  $2p$

$AX_4 \rightarrow$  tetrahedral

**P:**  $3p^3$   $\uparrow$   $\uparrow$   $\uparrow$   
 $3s^2$   $\uparrow\downarrow$

$\downarrow$   
 $3d^1$   $\uparrow$   $\leftarrow$  promoted from  $3s$   
 $3p^3$   $\uparrow\downarrow$   $\uparrow$   
 $3s$   $\uparrow\downarrow$

$\downarrow$   
 $d$   $\uparrow$  unhybridize  
 $sp^3$   $\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow\downarrow$  hybridize

**CO<sub>3</sub><sup>2-</sup>**

$\left[ \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \end{array} \right]^{2-}$

C: trigonal planar

ground state:  $2p^2$   $\uparrow$   $\uparrow$   
 $2s^2$   $\uparrow\downarrow$

$\downarrow$

(excited) promoted state:  $2p^3$   $\uparrow$   $\uparrow$   $\uparrow$   
 $2s^1$   $\uparrow$

$\downarrow$

hybridized state:  $2p^1$   $\uparrow$  unhybridized  $\rightarrow \pi$  bond.  
 $2sp^2$   $\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow\downarrow$  hybridized  $\rightarrow \sigma$  bond.

**O:**  $2p^4$   $\uparrow\downarrow$   $\uparrow$   $\uparrow$   
 $2s^2$   $\uparrow\downarrow$

ground state  $\downarrow$

$2p$   $\uparrow$   $\pi$   
 $2sp^2$   $\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow$  hybridized state.

$\sigma$  bond:  $1e^-$  C  $2sp^2$  +  $1e^-$  O  $2sp^2$   
 $\pi$  bond:  $1e^-$  C  $2p$  +  $1e^-$  O  $2p$ .

Homework:  $SF_4$   
 $CH_3OH$   
 $SO_4^{2-}$