

## Complex equilibrium problems---how to set them up!

Need to write all equilibria involved + Charge Balance and Mass Balance equations!~-

Charge balance: sum of all negative charges in solution must equal sum of all positive charges in solution to maintain electroneutrality in the bulk solution!

$$\text{general eqn: } n_1[C_1] + n_2[C_2] + \dots = m_1[A_1] + m_2[A_2] + \dots$$

where C represents cations, A are the anions, and n and m are the charges on the ionic species respectively!

e.g., What is charge balance for solution containing 0.01 M NaCl + 0.01 M Na<sub>2</sub>SO<sub>4</sub>?

$$[Na^+] + [H^+] = [Cl^-] + 2[SO_4^{2-}] + [OH^-] \quad \text{----can neglect } H^+ \text{ and } OH^- \text{ in this case---}$$
$$0.03 = 0.01 + 2(0.01)$$

Mass balance (material balance) ---conservation of matter!

for acetic acid in soln:  $F = [\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^-]$

for phosphoric acid:  $F = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]$

Treating System Equilibria:

1. write all pertinent rxns
2. write charge balance equation for all ionic species
3. write mass balance equations (there may be more than one)
4. write the equilibrium constant for each rxn (use activity coefficients)
5. count the equations and unknowns---need same number of eqns as unknowns to solve
6. Solve for unknowns----can often simplify by assuming certain #s are very small!

simple example: what is the pH of  $10^{-8}$  M KOH? (it is not pH 6.0 of course)

only 1 pertinent rxn:  $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$

charge balance:  $[\text{K}^+] + [\text{H}^+] = [\text{OH}^-]$

mass balance:  $[\text{OH}^-] = [\text{K}^+] + [\text{H}^+]$

$$[\text{K}^+] = 1.00 \times 10^{-8} \text{ M}$$

equilibrium constants:  $K_w = [\text{H}^+]\gamma_{\text{H}^+} [\text{OH}^-]\gamma_{\text{OH}^-}$

Can write three equations, three unknowns (but  $[\text{K}^+]$  is known)

Can use chemical intuition---ionic strength of solution is low---so we don't need to worry about activity coefficients!!  $\gamma = 1$  in all cases!

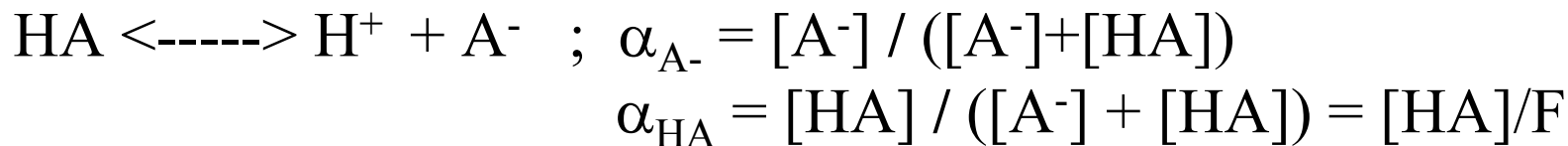
use charge balance equation:  $1 \times 10^{-8} + [\text{H}^+] = K_w/[\text{H}^+]$

yields quadratic:  $[\text{H}^+]^2 + 1 \times 10^{-8}[\text{H}^+] - K_w = 0$

two solns:  $9.6 \times 10^{-8}$  &  $-1.1 \times 10^{-7}$  M

must have positive value---hence  $\text{pH} = -\log(9.6 \times 10^{-8}) = \mathbf{7.02}$

## Fractional composition equations:



For acid with formal conc. of F;  $F = [\text{HA}] + [\text{A}^-]$

$$[\text{A}^-] = F - [\text{HA}]$$

therefore:

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

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

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

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

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

$$K_a F = [\text{A}^-]( [\text{H}^+] + K_a )$$

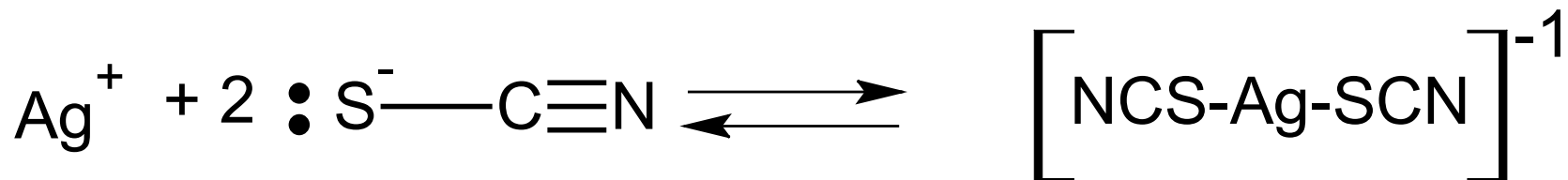
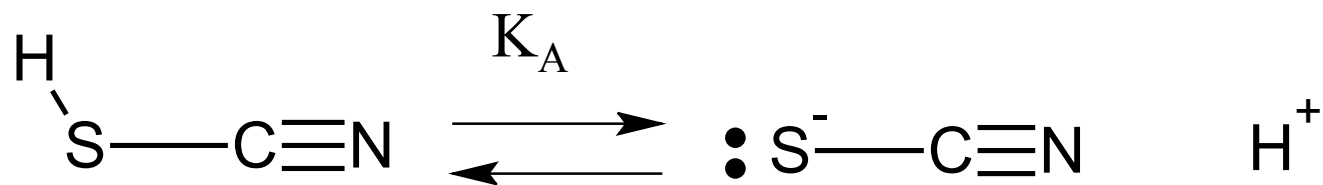
$$\alpha_{\text{HA}} = \frac{[\text{HA}]}{F} = \frac{[\text{H}^+]}{[\text{H}^+] + K_a}$$

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

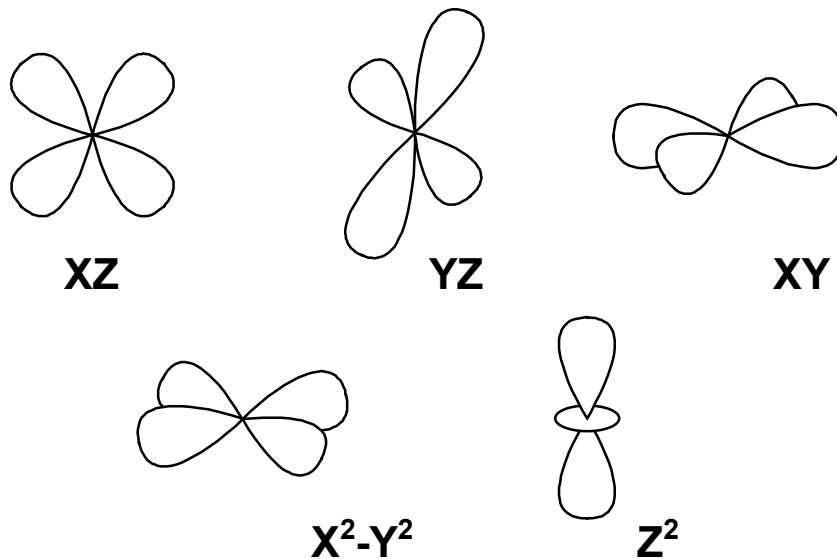
# Chapter 12

## EDTA and Complex Titrations

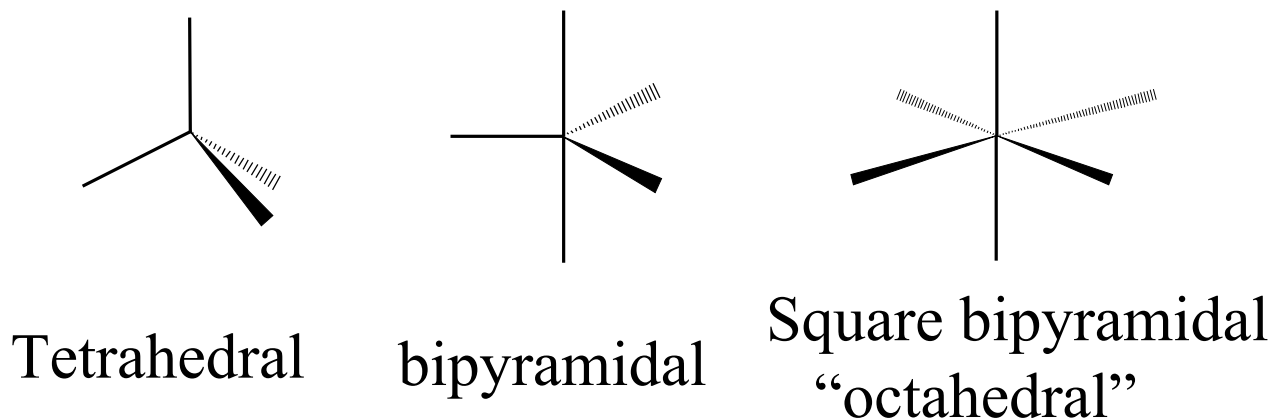
# Metal Ligands



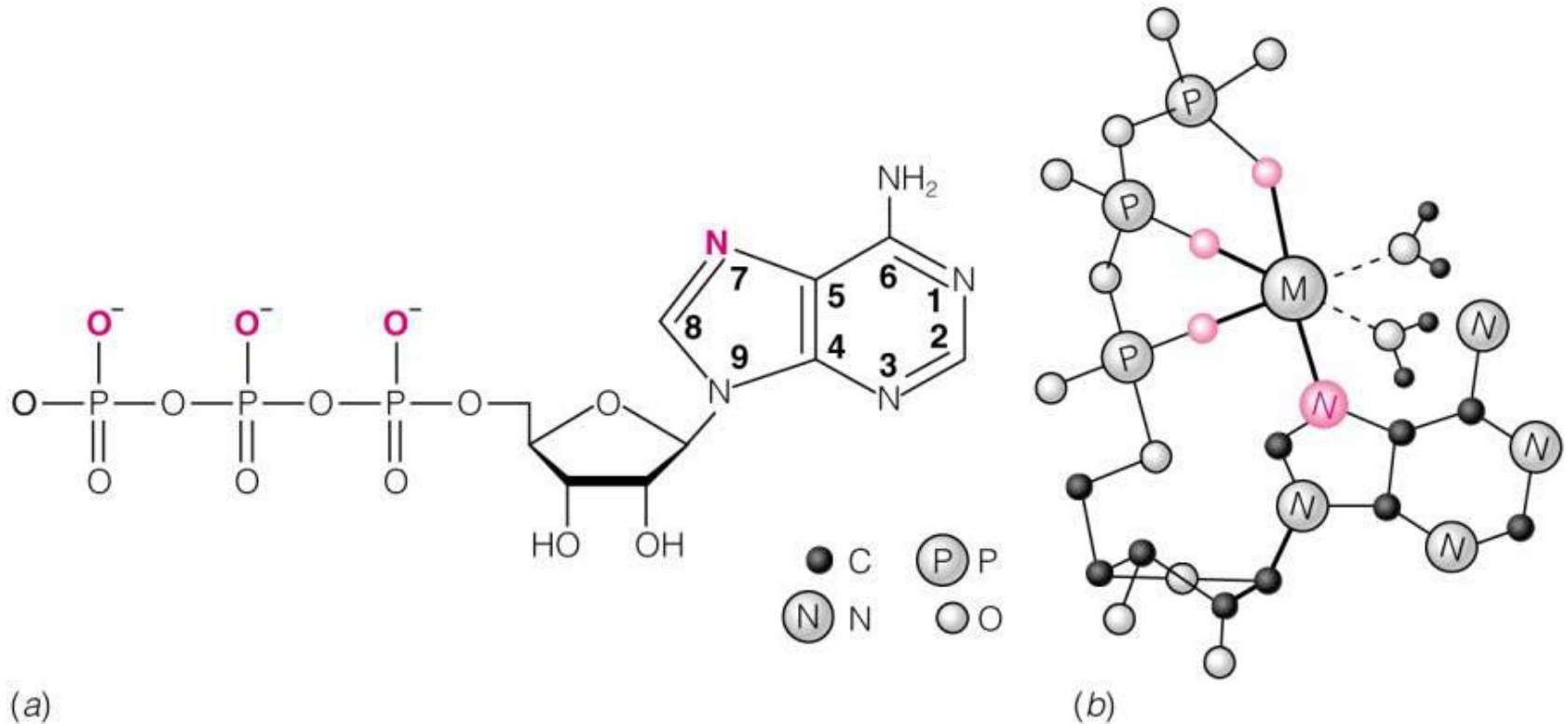
# d-Atomic Orbitals (from metal ions)



Stick models of the common bonding configurations



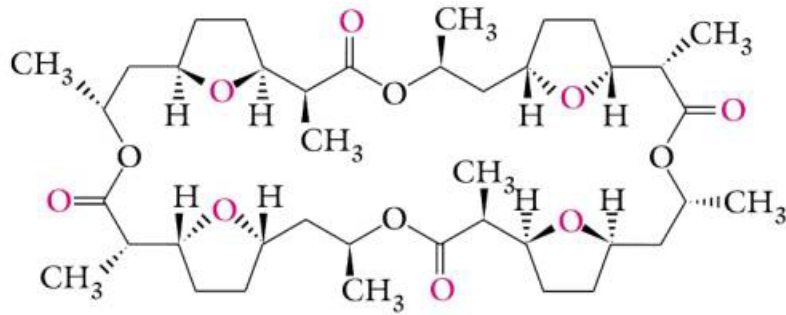
# ATP binds $Mg^{2+}$ ( $M^{2+}$ )



Adenosine triphosphate: four bonds to  $Mg^{2+}$  from ATP, two bonds from water to give octahedral coordination



# Nonactin selectively binds $\text{NH}_4^+$ and $\text{K}^+$



Structure of nonactin with ligand atoms highlighted

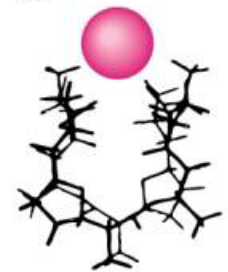
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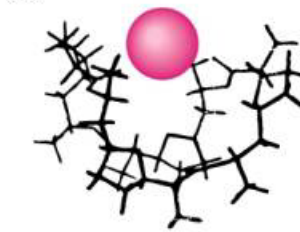
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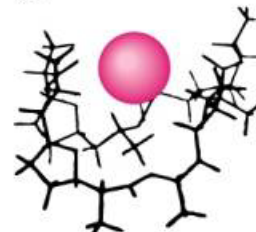
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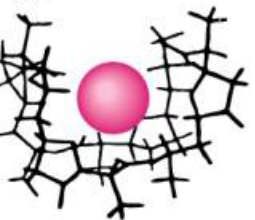
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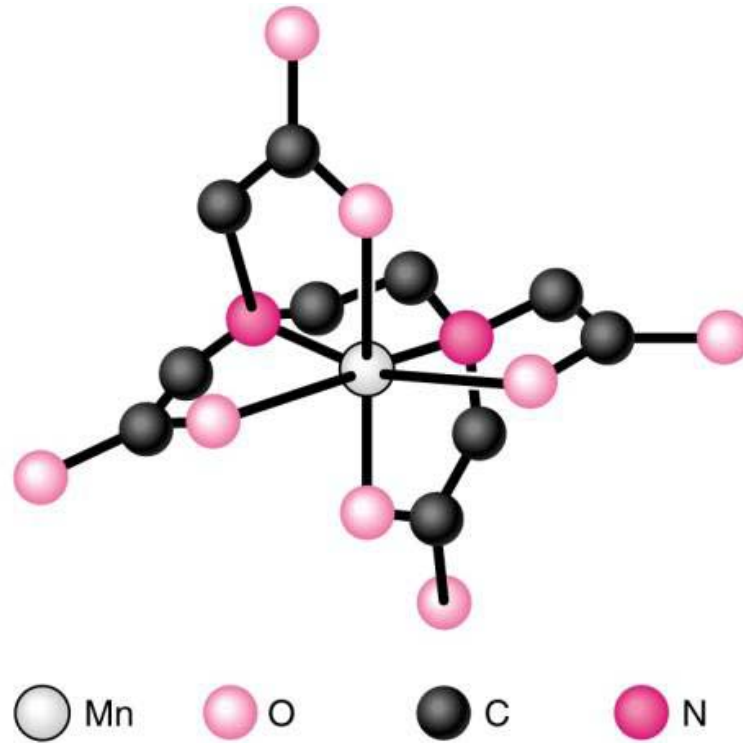
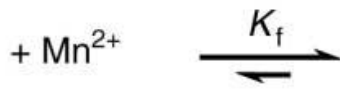
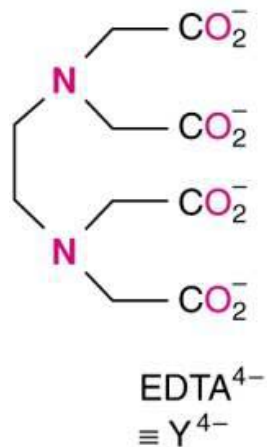


*Chelate*, derived from the Greek word for a lobster's claw

Carries  $\text{K}^+$  charge across nerve cell membranes

Usually monovalent alkali cations are not chelated, this is a highly specialized exception  
Compounds of this type use to make ion-selective membrane electrodes

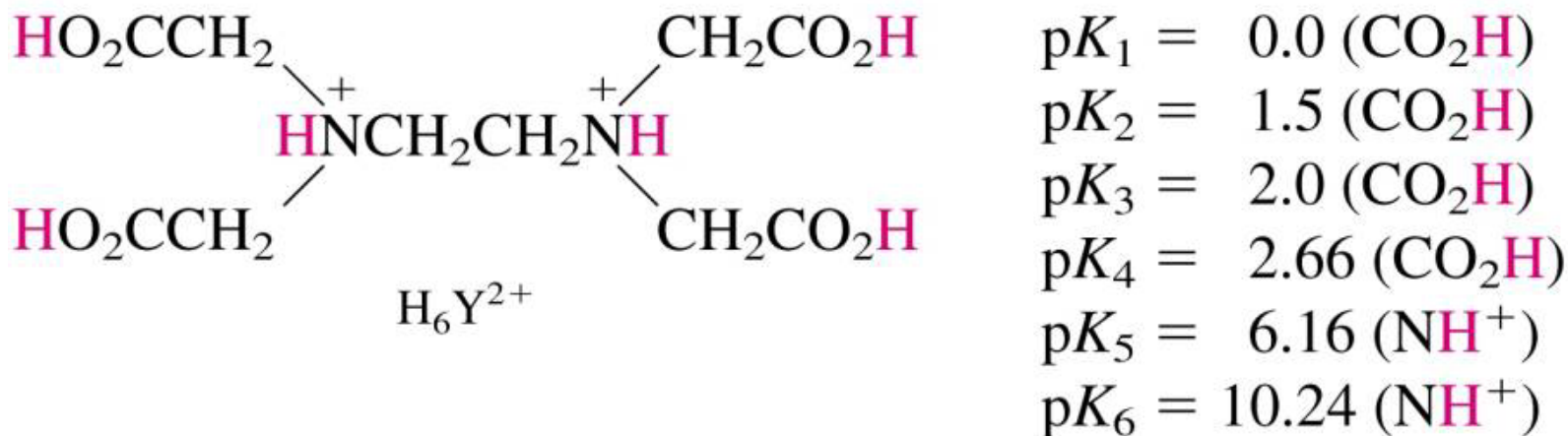
# EDTA binds....



Almost every ion except alkalis with a high  $K_F$   
 $K_f$  = formation constant!

•  $K_F$  found in Table 12-1 page 259

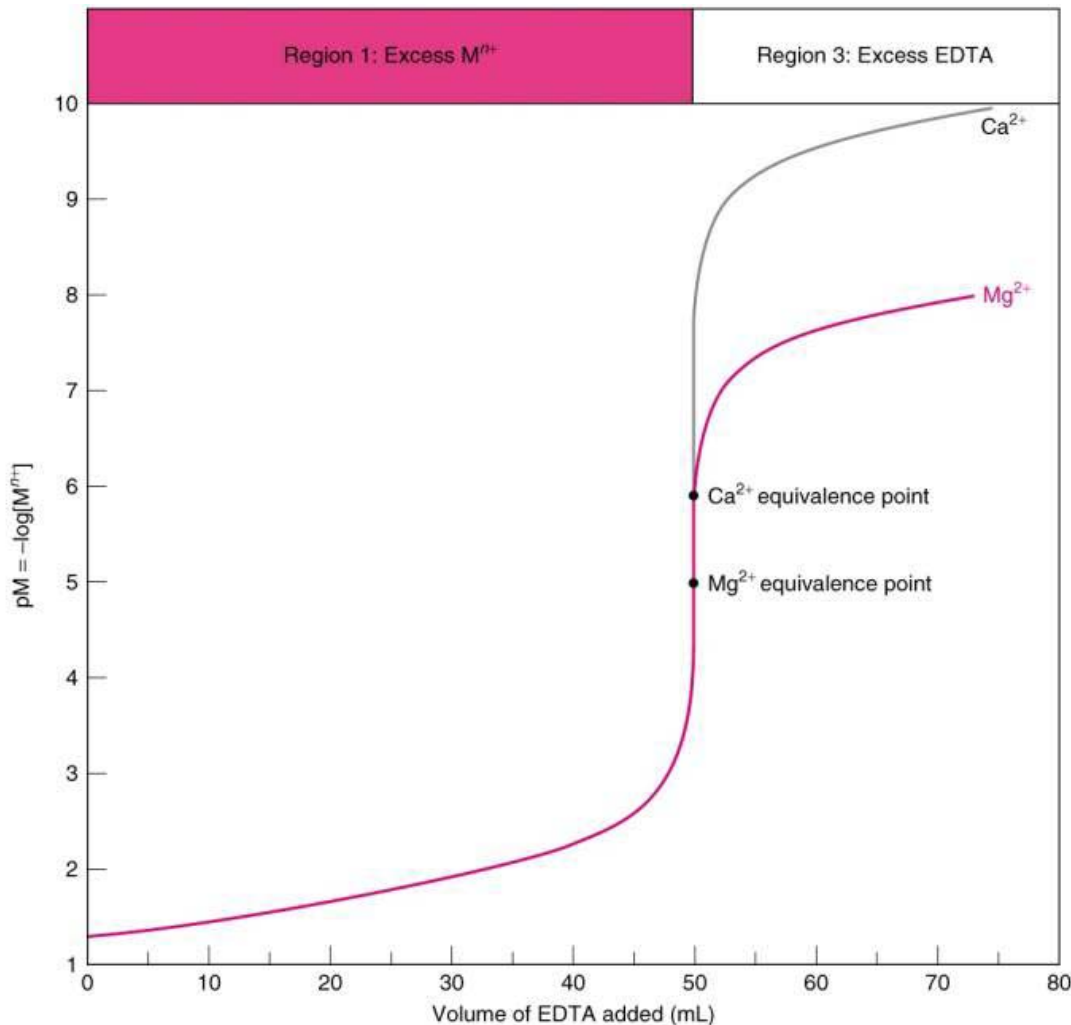
# EDTA is a Hexaprotic Acid



So at low pH the ligands for metal chelation are going to be tied up with protons  
This is going to shift our  $K_F$  equilibria.



# EDTA Titration of $M^{2+}$



$$-pK_F(Ca^{2+})=10.69$$

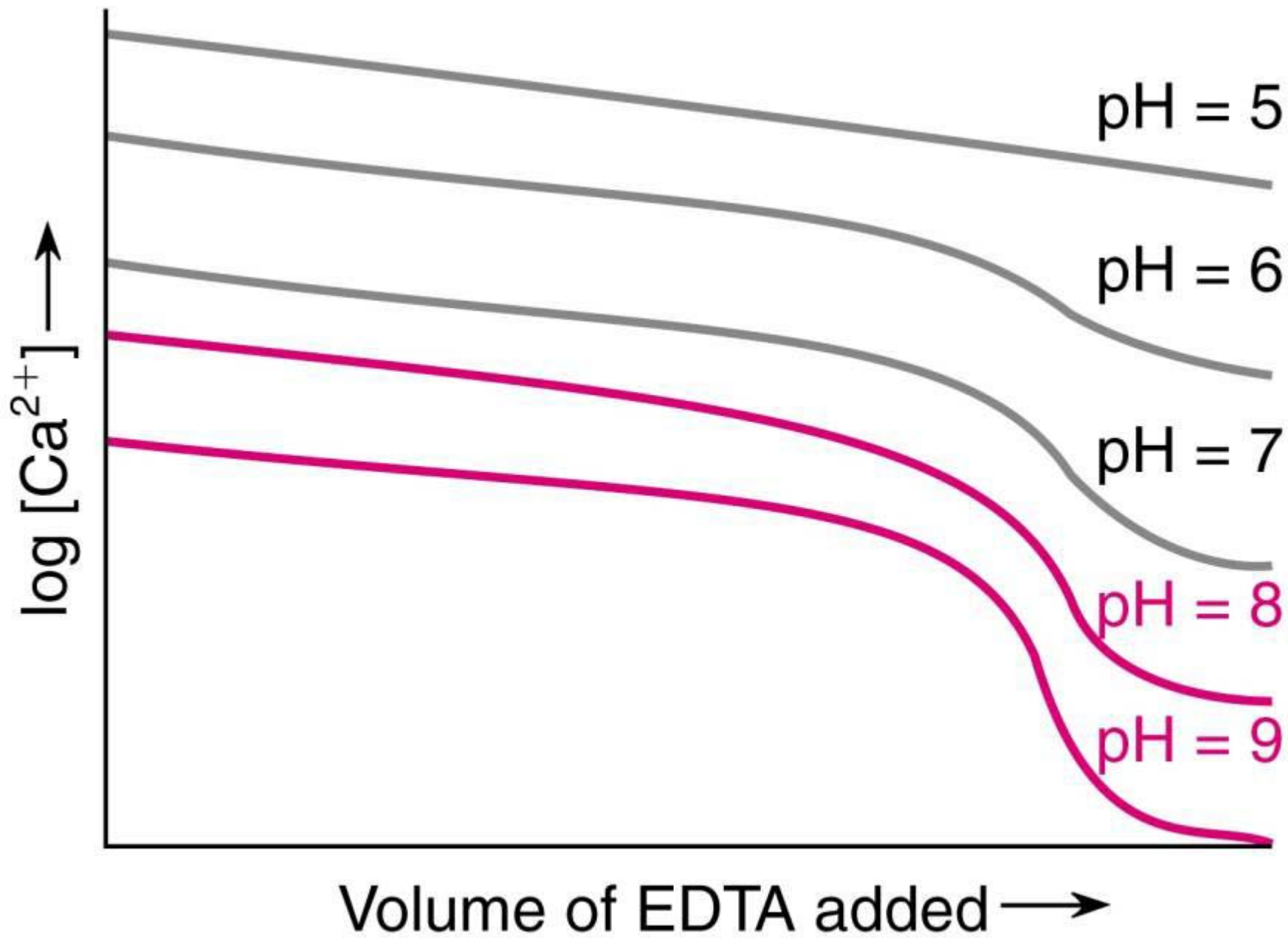
$$-pK_F(Mg^{2+})=8.79$$

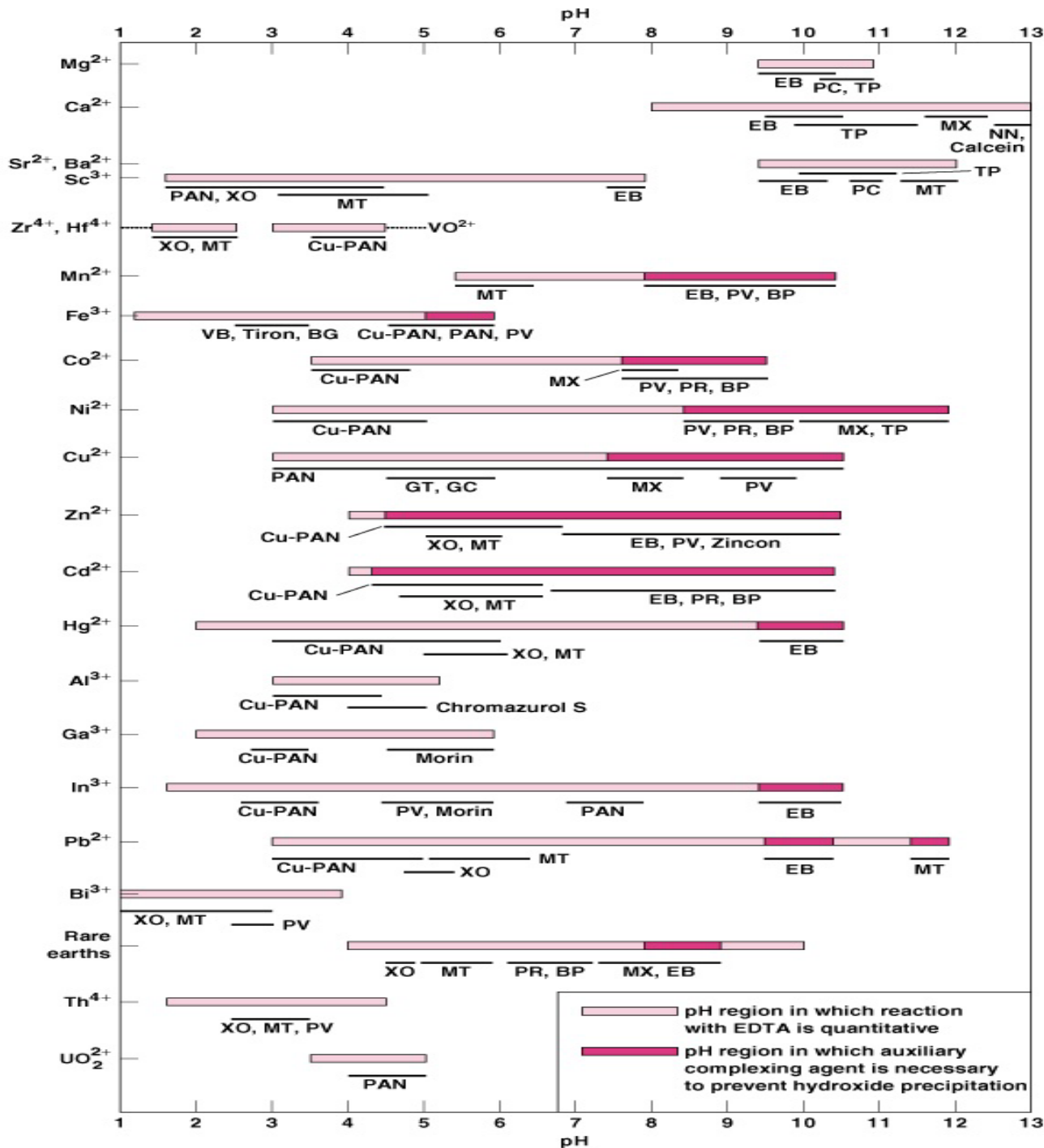
@  $pH > 12$

used to measure total  
water hardness---

$[Mg] + [Ca]$ ---endpoint  
gives total when both  
present in solution!

Actual titration at  $pH=10$





Conditions for titration of various cations with EDTA!- pH range allowed is dictated by several parameters including  $K_{sp}$  of Metal ion-(OH)<sub>n</sub>- and  $K_f$  with Y<sup>-4</sup> (EDTA)

# Fraction (Dissociation)

- Fraction of EDTA present in  $Y^{-4}$  form

$$\alpha_{Y^{-4}} = \frac{[Y^{-4}]}{F_{EDTA}}$$
$$= \frac{[Y^{-4}]}{[H_6Y^{+2}] + [H_5Y^+] + [H_4Y] + [H_3Y^{-1}] + [H_2Y^{-2}] + [HY^{-3}] + [Y^{-4}]}$$

- Depends on the pH of the solution  
dominant form only above  $pH > 10$

See Table 12-3 on page 267



# Conditional Formation Constant-effective equilibrium constant for complex formation when pH less basic ( $\alpha_{Y^{4-}} < 1$ )



$$K_f = \frac{[MY^{n-4}]}{[M^{n+}][Y^{-4}]}$$

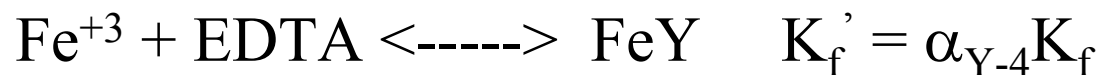
$$K_f = \frac{[MY^{n-4}]}{[M^{n+}]\alpha_{Y^{-4}}[EDTA]}$$

$$K'_f = K_f \alpha_{Y^{-4}} = \frac{[MY^{n-4}]}{[M^{n+}][Y^{-4}]} = \text{conditional formation const.}$$

where  $\alpha$  is found from the table 12-3 (p. 267 ECA)---becomes smaller number as pH decreases!

**$Y^{-4}$  is not the only form of EDTA that complexes with  $M^{n+}$  !?**

How much free  $\text{Fe}^{+3}$  in solution of  $\text{FeY}^-$  at 0.10 M at pH 4.00 and pH 1.00?



at pH 4.0;  $K_f' = (3.8 \times 10^{-9}) (1.3 \times 10^{25}) = 4.9 \times 10^{16}$

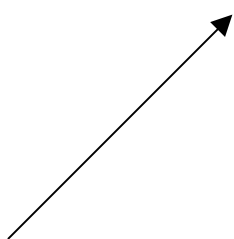
at pH 1.0;  $K_f' = (1.9 \times 10^{-18}) (1.3 \times 10^{25}) = 2.5 \times 10^7$

$$K_f' = \frac{[\text{FeY}^-]}{[\text{Fe}^{+3}][\text{EDTA}]}$$

$$K_f' = \frac{0.1 - x}{x^2} = 4.9 \times 10^{16} \text{ at pH 4.0}$$

$$x = 1.4 \times 10^{-9} \text{ M at pH 4.0}$$

$$x = 6.4 \times 10^{-5} \text{ M at pH 1.0}$$



use successive approx. method, or quadratic formula!

Using such calculations you can plot theoretical titration curve as  $\text{pM}^{n+}$  vs. vol EDTA----can calculate free  $\text{M}^{n+}$  for any conc. of EDTA for titration at given pH!  
note:  $\text{pM} = -\log [\text{M}^{n+}]$

# Types of EDTA Titrations

- Direct: add enough EDTA to complex all  $M^{n+}$  analyte-- get colorimetric or electrochemical endpoint!
- Back: add excess EDTA to  $M^{n+}$ , analyte; titrate excess EDTA with another  $M^{+n}$  (used when analyte precipitates in absence of EDTA, analyte blocks indicator, or analyte reacts with EDTA too slowly to titrate!)
- Displacement: excess  $M_2$ -EDTA complex is added to analyte which displaces  $M_2$  from the EDTA (it binds stronger);  $M_2$  is titrated with more EDTA (direct) (used when no good indicator for analyte  $M^{n+}$ )
- Indirect: anions (as analyte) can be precipitated (filtered) with excess metal,  $M^{n+}$ , excess  $M^{n+}$  can be directly titrated with EDTA

# Metal Ion Indicators

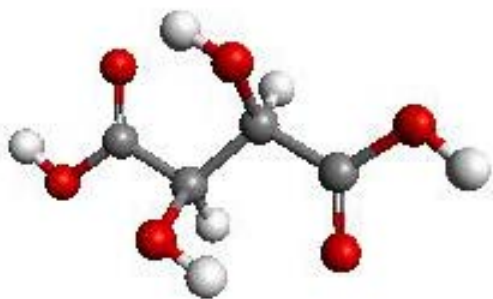
- Visible-Chromophores (dyes) change absorbance (or fluorescence) spectra when bound to certain metal ions--  
-dyes are also acids/bases---so pH in which they can be used is restricted to get proper color change!
- Indicator must bind metal ion less strongly than EDTA does!!
- Change in color indicates the presence of available metal ions
- Eriochrome black T---MgIn --> red  
first excess of EDTA pulls Mg away from indicator--  
yields blue color!
- This is similar to a displacement titration
  - EDTA displaces the indicator as the most favorable ligand (chelate) for the analyte

# Masking Agents

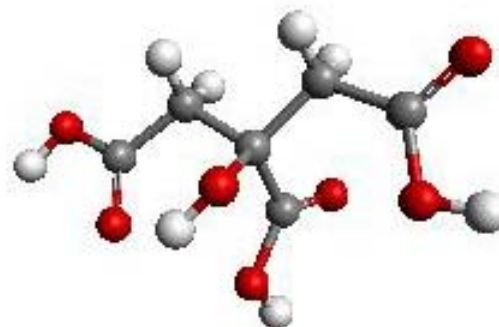
- Other metal ions (besides the analyte) can also be complexed by EDTA during a titration.
- The apparent amount of EDTA (mol) at the titration endpoint would not be equal to the mol of analyte
- Adding other complexing agents that have a higher affinity for the spectator ions (larger  $K_f$ ) reduces the EDTA consumed, improves the accuracy of the analysis

Lack of Selectivity Makes it Nearly Impossible to Use EDTA Titrations if Very Complex Samples!

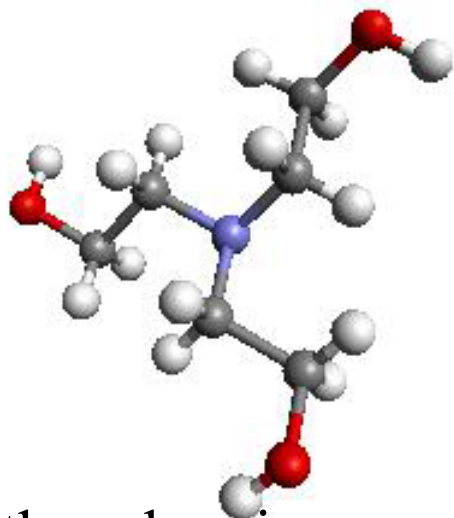
# Masking Agents / Auxiliary Ligands



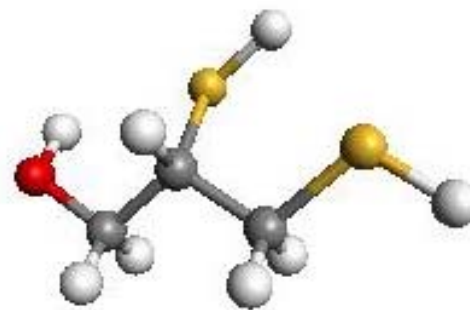
Tartaric Acid



Citric Acid



triethanol amine



dimercaptopropanol

# Introduction to Electroanalytical Chemistry!

(chapter 13--ECA)

## Methods:

Potentiometry: measure voltage of galvanic cell--and relate  $E_{\text{cell}}$  to concentration/activity of given analyte

Amperometric/Voltammetric: Apply external voltage to electrochemical cell (electrolyte cell) and measure current response!

Can also use both methods as detection systems for titrations---using chelating agents, or redox titrants!

All electrochemistry is based on Redox reactions!---  
species gains electrons (reduction) and species lose electrons (oxidation)

Electric charge-(q) is measured in coulombs (C)

a single charge has  $1.602 \times 10^{-19} \text{ C}$  ; 1 mole of charge has  
 $(1.602 \times 10^{-19} \text{ C}) \times (6.022 \times 10^{23} \text{ mol}^{-1}) = 9.649 \times 10^4 \text{ C/mol} = F =$   
**Faraday's constant!**

Faraday's law: moles reacted =  $q/nF$  ; n = number of electrons in  
or  $q = nF(\text{moles reacted})$  reaction!

Current is proportional to moles reacted for electrochemical reaction:

current = amperes =  $1 \text{ C/sec}$  ;

What would be current required to reduce  $\text{Sn}^{+4} + 2 \text{ e}^- \text{ ----} \rightarrow \text{Sn}^{+2}$   
at a platinum electrode as a rate of  $4.24 \text{ mmol/h}$ ?

What would be rate per second?  $4.24 / 3600 = 1.18 \times 10^{-6} \text{ mol/sec}$   
current =  $\text{C/s} = q/\text{sec} = (1.18 \times 10^{-6} \text{ mol/sec}) \times n \times F (\text{C/mol}) =$   
 $= 0.227 \text{ A (amps)}$



## Voltage and work----

Electrical potential difference---difference in charge between two points!---this potential difference is a measure of the work required to bring (move) electrons from one point to the other!-----

has units of Volts (V)

and work done or needed to be done has units of Joules (J)

$$\text{joules (work)} = E \text{ (volts)} \times q \text{ (charge)}$$

One joule of energy is used to move one coulomb of charge between two points that differ by 1 volt!

therefore-- 1 volt = joules/C

In potentiometry---we measure the desire for charge to flow from one electrode to another (we don't actually let the charge flow)---charge will only want to flow if there is a voltage difference!