STONY BROOK

CHE 134

A brief review

Engaged in 10 Exercises

1. Calorimetric Determination of Enthalpy of Reactions
2. Complexometric Titration of Calcium
3. Kinetic Study of a Bleaching Reaction
4. Synthesis and IR Analysis of Aspirin
5. Colorimetric Determination of Iron in Multivitamins
6. Aspirin Purity by pH Titration
7. Determination of Molar Mass and pK_a of unknown acid by pH Titration
8. Identification of Plastics
9. Determination of Vitamin C in Food Products.
10. Electrochemistry and the Nernst Equation

Recurrent Concepts

Chemical Reactions / Equations

Stoichiometry / Mole Relationships

Limiting Reagents

Concentration Measures / Dilution

Organic Structure Representation

Strong/Weak Acids / pK_a

Significant Figures

Statistical Measures (Avg, Avg/ Dev etc.)

Recurrent Concepts

pH and [H^+]

Redox Reactions

Colorimetry

Graphs

Precision

Accuracy

Reproducibility

The most recent 3 exercises.

Questions will be detailed

Polymer Properties & IR

Titrations – Vitamin C

Electrochemistry & Nernst Equation

Polymer Properties & IR

Group IR absorptions

Beilstein Test

Heat behavior

Density Determination

Structure/Property Relations

Melting behavior

The packaging plastics

DISTINGUISHING CHARACTERISTICS

1 (PETE) POLYETHYLENE TEREPHTHALATE
Monomer contains C, H and O,
BENZENE ring and *ESTER* LINKAGES
C=O bonds (1720 cm^{-1})

2 (HDPE) HIGH DENSITY POLYETHYLENE
Hydrocarbon - only C and H

3 (V) POLYVINYL CHLORIDE
Monomer contains C, H and C-Cl bonds

4 (LDPE) LOW DENSITY POLYETHYLENE
Hydrocarbon - only C and H

5 (PP) POLYPROPYLENE
Hydrocarbon - only C and H

6 (PS) POLYSTYRENE
Hydrocarbon - only C and H
Monomer contains BENZENE ring but
no C=O bonds.

7 (OTHER)

Titrations – Analysis (4)

End / Equivalence point	Buffers for pH control
Indicators / Signals	Oxidation State Control
Ion selective indicator-EBT	Polydentate Ligands (EDTA)
Standardization	Selective Complexation
Titers	Effective Molar Mass (EMM)
Glass Electrode	Acid Base Titration Curves

Titration Reaction

Vitamin C Determination: **Oxidation**

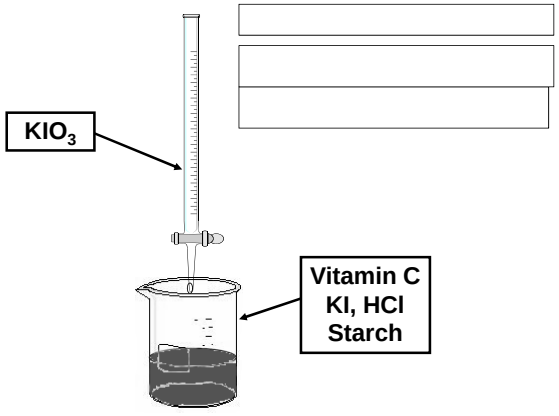
$IO_3^- + 5\ I^- + 6\ H^+ \rightarrow 3\ I_2 + 3H_2O$

$C_6H_8O_6 + I_2 \rightarrow C_6H_6O_6 + 2\ H^+ + 2\ I^-$

I_2 + STARCH $\rightarrow$ **[STARCH - I_2]**

Solution is made acidic using buffer to enhance first reaction

Indicator is Starch which gives blue color with I_2



Calculations:

Weigh pure Vitamin C		125.6 mg
Titrate with KIO_3 – net volume		24.72 mL
Calculate Titer of KIO_3	123.6/24.72	5.081 mg/mL
Use KIO_3 on unknown sample		
Titrate with KIO_3 – net volume		22.37 mL
Titer provides amount of Vitamin C		23.37 mL X 5.081 mg/mL
Unknown sample contains		118.7 mg

Electrochemistry & Nernst Equation

Concepts:

Oxidation / Reduction	Electric potential
Cell/Half Cell	Nernst Equation
Concentration Cell	Reduction Potential
Solubility Product	Salt Bridge
Basic Electrical Units	Anode, Cathode

$$\mathcal{E} = \mathcal{E}^0 - \frac{\mathcal{R}T}{n\mathcal{F}} \ln Q$$

Q = Equilibrium Expression

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Electrochemistry

$$Cu\,(s) + 2Ag^+\,(aq) \rightarrow 2Ag\,(s) + Cu^{2+}\,(aq)$$

$$Cu \mid Cu^{2+}\,(M_1) \parallel Ag^+\,(M_2) \mid Ag$$

$Cu^{2+}\,(aq) + 2e^- \rightarrow Cu\,(s)$ $\quad \mathcal{E}^0 = 0.337$ v

$Ag^+\,(aq) + e^- \rightarrow Ag\,(s)$ $\quad \mathcal{E}^0 = 0.7994$ v

$\Delta\mathcal{E}^0 = 0.7994 - 0.337 = 0.462$ v

$$\mathcal{E} = \mathcal{E}^0_{Ag} - (\mathcal{R}T/2\mathcal{F}) \ln (1/[Ag^+]^2) - \{\mathcal{E}^0_{Cu} - (\mathcal{R}T/2\mathcal{F}) \ln 1/[Cu^{2+}]\}$$

$$\mathcal{E} = \mathcal{E}^0_{Ag} - \mathcal{E}^0_{Cu} - (\mathcal{R}T/2\mathcal{F}) \ln [Cu^{2+}]/[Ag+]^2$$

Voltages, Equilibrium Constants, ΔG and K_{eq}

$$Cu\,(s) + 2Ag^+\,(aq) \rightarrow 2Ag\,(s) + Cu^{2+}\,(aq)$$

$$\mathcal{E} = \mathcal{E}^0 - \frac{\mathcal{R}T}{n\mathcal{F}} \ln Q \qquad Q = \frac{[Cu^{2+}]}{[Ag^+]^2}$$

$\Delta G^0 = -n\mathcal{F}\mathcal{E}^0 = -\mathcal{R}T \ln K$ $\quad \Delta G^0 = -88.72$ kJ/mol Cu

$\Delta\mathcal{E}^0 = -(-88.72) / 2 \times 96485 = 0.4599$ v

$\mathcal{R}T \ln K = n\mathcal{F}\mathcal{E}^0$ $\quad K = 10^{n\mathcal{F}\mathcal{E}^0/2.303\mathcal{R}T}$

$K = 10^{-\Delta G0\,/2.303\,\mathcal{R}T} = 10^{15.55} = 3.55 \times 10^{15}$

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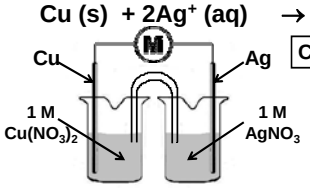
$$Cu\,(s) + 2Ag^+\,(aq) \rightarrow 2Ag\,(s) + Cu^{2+}\,(aq)$$



$Cu \mid Cu^{2+}\,(1\text{ M}) \parallel Ag^+\,(1\text{M}) \mid Ag$

$$\mathcal{E} = 0.462 - \frac{0.0295}{} \log \frac{[Cu^{2+}]}{[Ag^+]^2}$$

Initially, $\mathcal{E} = 0.462$ v

0.1 M	1 M	$\mathcal{E} = 0.521$ v
1 M	0.1 M	$\mathcal{E} = 0.403$ v
0.1 M	5.3×10^{-8} M	$\mathcal{E} = 0.000$ v
1 M	1.7×10^{-8} M	$\mathcal{E} = 0.000$ v

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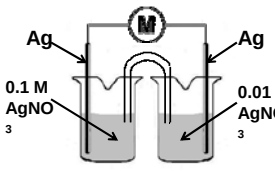
Concentration Cells



$Ag(s) + Ag^+(0.01) \rightarrow Ag(s) + Ag^+(0.1)$

$Ag \mid Ag^+\,(M_1) \parallel Ag^+\,(M_2) \mid Ag$

$\Delta\mathcal{E}^0 = 0$ v, $\Delta G^0 = -n\mathcal{F}\Delta\mathcal{E}^0 = 0$

$$\mathcal{E} = 0.000 - \frac{\mathcal{R}T}{\mathcal{F}} \ln \frac{[Ag^+]_1}{[Ag^+]_2}$$

A concentration difference suffices to produce a potential. E.g., for a 1 electron change, a factor of 10 in concentration produces:

$$\mathcal{E} = 0.000 - 0.0592 \log \frac{0.10}{0.01} = -0.0592 \text{ V}$$

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Other Exercises

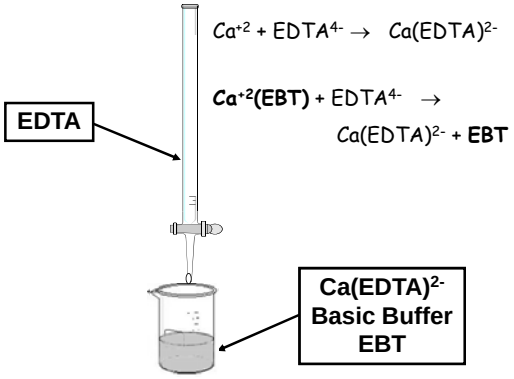
Other Titration Reactions

Calcium Determination:

Ca^{+2} + **EBT** → ***Ca(EBT)$^{+2}$***

Ca^{+2}(EBT) + $EDTA^{4-}$ → $Ca(EDTA)^{2-}$ + **EBT**

Solution is made ***basic*** using ammonia buffer to enhance formation of the 4- form of EDTA



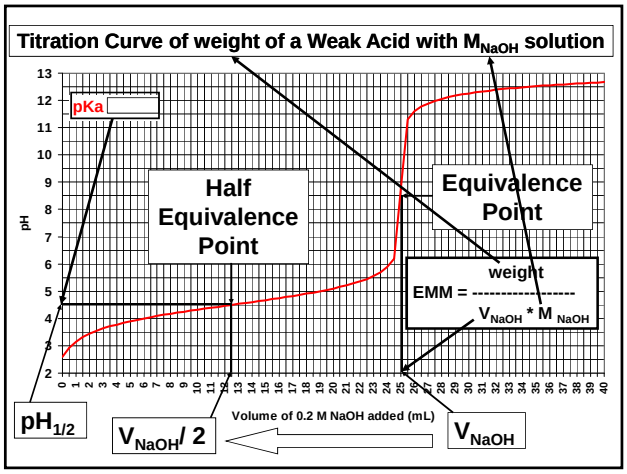
Calculations:

Concentration of EDTA = 0.04653
Weigh entire Pill = 0.9438 g

Weigh Unknown Sample	251.8 mg
Titrate with Na_2H_2EDTA – of known concentration – net volume	12.37 mL
Not enough titrant!	
Adjust unknown weight 12.37/251.8 = 25/x x = 509	
Weigh new Unknown Sample	521.3 mg
Titrate with Na_2H_2EDTA – of known concentration – net volume	22.37 mL
Conc provides mmol of Ca	25.56 mL X 0.04653 mmol/mL
Unknown sample contains	1.189 mmol
Convert mmol to weight (of $CaCO_3$)	
1.189 mmol X 100.1 mg/mmol	119.0 mg

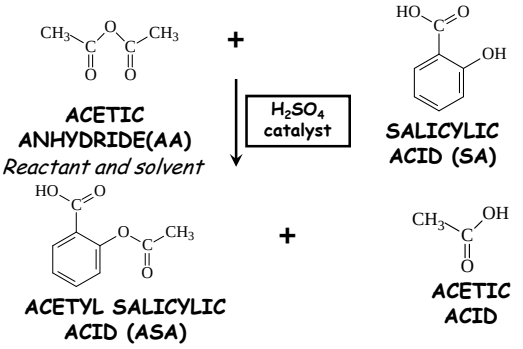
Weigh entire Pill = 0.9438 g

Weigh new Unknown Sample	521.3 mg
Unknown sample contains	119.0 mg
Entire pill contains	119.0 / 521.3 = x / 943.8
	215.4 mg



Synthesis of Aspirin

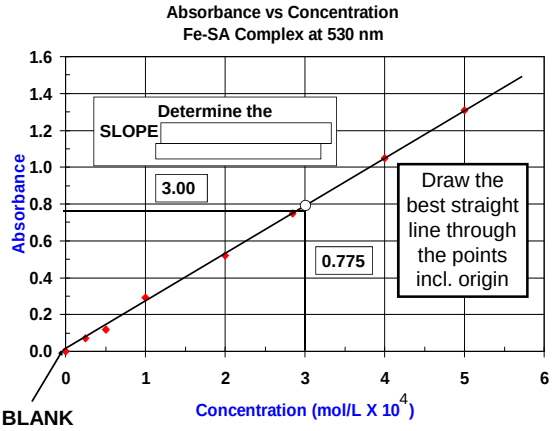
- Logic of Synthesis
- Starting Materials / Product
- Product Isolation / Crystallization
- Theoretical & Percent Yield
- Melting Point Determination
- Product Purity
- Non-aqueous Solvents
- Organic Reactions
- Organic Functional Groups



$$SA^{2-} + Fe(H_2O)_6^{3+} \rightarrow FeSA(H_2O)_4^{+1} + 2H_2O$$

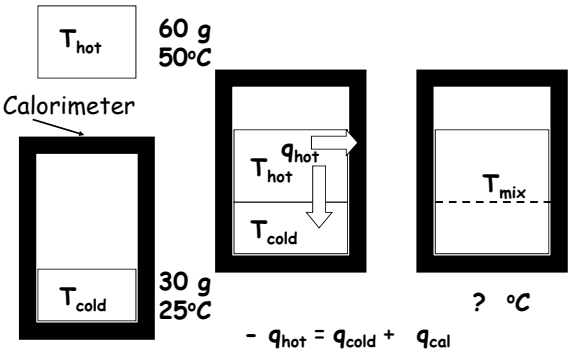
Spectrophotometry (2)

- Absorbance
- % Transmittance
- Absorption Spectrum
- Analytical Wavelength
- Beer's Law / Beer's Law Plot
- Blank
- Quantitative Dilution



Calorimetry (1)

- 1st Law of Thermodynamics
- Calorimeter
- Calorimeter Constant
- Heat
- Enthalpy
- Hess's Law
- Temperature Measurement
- Specific Heat



Kinetics (1)

- First Order Kinetics
- Second Order Kinetics
- Rate / Rate Law
- Reactant order
- Linear plots from non-linear data
- Time measurement
- Specific Rate

for ***first*** **order (m = 1)**

$$[MG^+] = [MG^+]_0 e^{-qt}$$

taking the natural logarithm of each side produces:

$$\ln [MG^+] = \ln [MG^+]_0 - q\,t$$

Linear plots *vs* time with slope q

for *second* order (m = 2)
We have

$$\frac{1}{[MG^+]} = \frac{1}{[MG^+]_0} + q\,t$$

The Last Week in Lab

Final Quiz Check Out TA Evaluation

Monday, May 5 @ 5:00 PM Makeup Exercise

All students take final quiz in the section in which they are registered

Students in Lab Sections 1 & 2 who are registered to do the make-up exercise will check out after completing the exercise

Students in other Lab Sections (3,4,5,6,7) doing make-up will take quiz & check out with their own sections