you-try-it-08.xlsx

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For use with:

Brian M. Tissue, *Basics of Analytical Chemistry and Chemical Equilibria,* (John Wiley: New York, 2013).

http://www.achem.org

Worksheets in this file

notes	This page with background information.
8.A balancing redox reactions	Identify oxidation states and balance reactions.
8.B Nernst equation	Calculate potential as a function of concentration and temperature.
8.C Potentiometry	Use standards to calibrate an ion-selective electrode meassurement.
8.D Voltammetry	Plot scan rate and concentration dependence for cyclic voltammetry.

Background

Refer to Chapter 8 in the text for equations and explanations.

Each worksheet has instructions in the blue shaded box.

For step-by-step help see you-try-it-08guide.pdf.

You-Try-It 8.A

Balancing Redox Reactions

Table 8.A.1 lists a series of unbalanced redox reactions.

1. Identify the atoms that undergo a change in oxidation state and write half reactions.
2. Balance each half reaction.
3. Combine half reactions to eliminate electrons.

Table 8.A.1

case	reactants				products		
1	$CH_3CH_2OH(l)$	+	$O_2(g)$	→	$CH_3CHO(l)$		
	ethanol		oxygen		acetaldehyde		
2	$CH_3CH_2OH(l)$	+	$Cr_2O_7^{2-}(aq)$	→	$CH_3COOH(l)$	+	$Cr^{3+}(aq)$
	ethanol		dichromate ion		acetic acid		chromium ion
3	$CH_3CH_2OH(l)$	+	$O_2(g)$	→	$CH_3CH_2OH(l)$	+	$H_2O_2(g)$
	glucose		oxygen		gluconic acid		hydrogen peroxide
4	$CH_3CH_2OH(l)$	+	$O_2(g)$	→	$CH_3CH_2OH(l)$	+	$CO_2(g)$
	glucose		oxygen		ethanol		carbon dioxide

case	notes
1	reaction in the liver
2	colorimetric breathalyzer (catalyst and spectator ions not shown)
3	sensor reaction
4	fermentation reaction

You-Try-It 8.B **Nernst Equation**

Table 8.B.1 lists Nernst equation parameters for a Ag/AgCl reference electrode.

1. Use the data in Table 8.B.2 to predict reference electrode potential as the composition of the internal reference solution changes.
   You may assume that the listed concentrations are equal to activity.

2. Use the data in Table 8.B.3 to determine how temperature affects the reference electrode potential.

3. Use the data in Table 8.B.4 to calculate cell voltage as a function of [Zn^{2+}] for the following cell:
   Ag | AgCl | 0.1 M Cl^- || Zn^{2+} | Zn
   Plot the results to confirm the log dependence.

Table 8.B.1. Nernst equation parameters.

E°	0.222	V
R	8.314	J/mol·K
T	298	K
n	1	
F	96485	C/mol

Sample calculation for the half reaction:

$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$

$E = E^\circ - (RT/nF)\ \ln(Q)$

for Q = [Cl^-] = 3.00 M

E = 0.194 V

Table 8.B.2. Internal solution dependence for Ag/AgCl reference electrode. T = 298 K.

[Cl^-] (M)	E (V)
0.10	
1.00	
2.00	
3.00	
3.50	

Table 8.B.3. Temperature effects for Ag/AgCl reference electrode. [Cl^-] = 3.0 M.

T (C)	T (K)	E (V)
5		
10		
15		
20		
25		
30		
37		

Table 8.B.4. Cell voltage for a zinc indicator electrodes.

[Zn^{2+}] (M)	E_Zn (V)	E_{cell} (V)
1.0E-05		
1.0E-04		
1.0E-03		
1.0E-02		
1.0E-01		

Nernst equation parameters for 8.B.4.

E_Ag/AgCl	0.281	V
E°	-0.762	V
R	8.314	J/mol·K
T	298	K
n	2	
F	96485	C/mol

You-Try-It 8.C **Potentiometry**

Tables 8.C.1 and 8.C.2 list data for standards and test portions using a homemade chloride ISE.
The indicator electrode was a silver wire and the reference electrode was constructed of Cu/$CuSO_4$.*
All solutions were measured in 1 M $NaNO_3$ ionic strength adjustment buffer.

1. Construct a calibration curve from the standard data.

2. Determine the chloride concentration in the test solutions.

Table 8.C.3 lists measurements for this ISE of the 10 ppm standard with added NaOH.
All test solutions were made up to 20.0 mL after adding the OH^- spike.
Supporting information is below the data table.

3. Determine the selectivity coeffient for hydroxide ion for this ISE.

*Lisensky, G.; Reynolds, K. “Chloride in Natural Waters,” J. Chem. Ed. 1991, 68, 334.

Table 8.C.1. Chloride standards.

Cl^- standards (ppm)	log[Cl^-]	Voltage (mV)
10		148
100		103
1000		50
10000		-7

slope = mV/decade
intercept = mV

Table 8.C.2. Unknown measurements.

test portion	Voltage (mV)	[Cl^-] (ppm)
tap water	134	
well water	120	
DI water	170	
meat tenderizer	72	

The ISE equation for chloride is:
E = intercept − (slope)log[Cl^-]

The meat tenderizer solution contained 62 mg of product dissolved in 100 mL of water. 0.062 g sample
Bonus question: What is the weight percent of NaCl in this product?

Cl and NaCl formula weights: 35.45 g/mol 58.44 g/mol

% NaCl

Table 8.C.3. Standard addition of OH^- to determine *k*.

added NaOH (mL)	$[OH^-]$ (ppm)	Voltage (mV)	*k*
0.0		147	
0.2		145	
0.4		140	
0.6		138	

average:

Supporting Information

NaOH conc:	0.1	M NaOH
NaOH f.w.:	40	g/mol
NaOH conc:	4000	ppm NaOH
test volume:	20	mL

The ISE equation for chloride and hydroxide is:

E = intercept − (slope)log($[Cl^-]+k\,[OH^-]$)

You-Try-It 8.D **Cyclic Voltammetry**

The adjacent figures show typical cyclic voltammograms for ascorbic acid (vitamin C).
The one-electron oxidation reaction is irreversible and only one peak appears.
Measurements were made with a 1.6 mm diameter Pt working electrode and Ag/AgCl reference electrode.

Table 8.D.1 lists measured peak currents for 0.015 M ascorbic acid as a function of scan rate.

1. The Randles-Sevcik equation predicts a square root dependence on scan rate.
   Plot the data to check this prediction.
2. Use the slope of the plot to calculate the diffusion coefficient for ascorbic acid.
   The equation and relevant parameters are below Table 8.D.1.

Table 8.D.2 lists measured peak currents for a series of standard ascobic acid solutions and a test portion.

3. Plot the standard data to generate a calibration curve.
4. Determine the ascorbic acid concentration in the test portion.
   Use the sample information to compare the measurement to the stated ingredients.

Table 8.D.1 Ascorbic acid peak current as a function of scan rate.

Scan Rate (V/s)	Peak Current (A)	(Scan Rate)^0.5 (V/s)^0.5	Peak Current (μA)
0.10	6.50E-05		
0.50	1.42E-04		
1.00	2.25E-04		
5.00	4.70E-04		

Randles-Sevcik equation:

$i_p = (2.69\times10^5)n^{3/2}AcD^{1/2}v^{1/2}$ where:

n is number of electrons	1			
A is electrode area in cm^2	0.020	cm^2	0.16	cm dia electrode
c is bulk analyte concentration in mol/cm^3	0.000015	mol/cm^3	0.001	L/cm^3
D is analyte diffusion coefficient in cm^2/s				
and v is scan rate in V/s				

slope = $(2.69\times10^5)n^{3/2}AcD^{1/2}$ = D = cm^2/s

Table 8.D.2 Ascorbic acid standards and unknown.

Conc (M)	Peak Current (A)	Peak Current (µA)
0.000	5.00E-07	0.50
0.005	2.11E-05	21.08
0.010	4.32E-05	43.18
0.015	6.21E-05	62.06
0.020	8.42E-05	84.17
juice	1.14E-05	11.40

Calibration Function

slope:	µA/M
intercept:	µA

Test portion: M

The label on the juice container listed 108 mg vitamin C per 240 mL serving.
Use the formula weight (176.1 g/mol) to determine the amount of vitamin C in one serving of juice.

176.1 g/mol	L	g	mg vit C

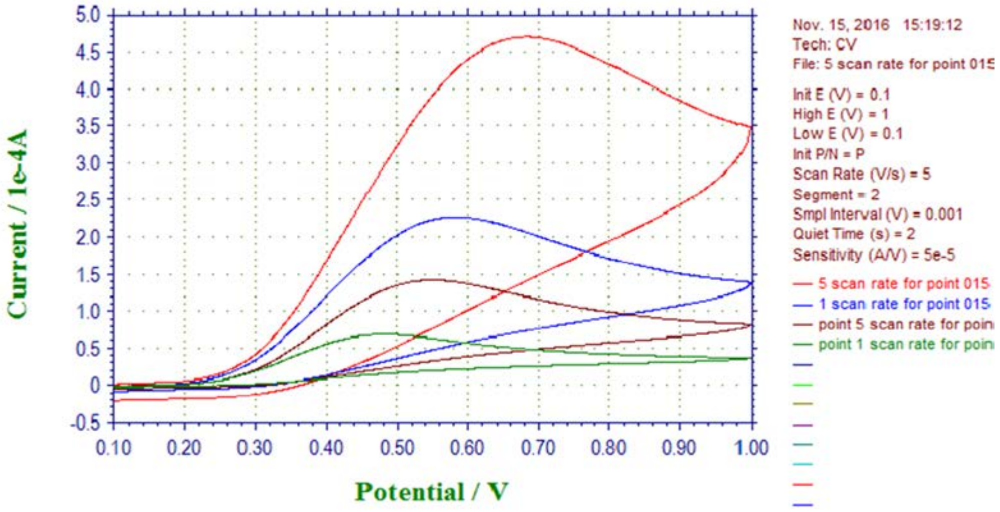

Figure 8.D.1. Cyclic Voltammograms of 0.015 M vit C in 0.5 M KCl at scan rates of 0.1 (green), 0.5 (brown), 1 (blue), and 5 (red) V/s.

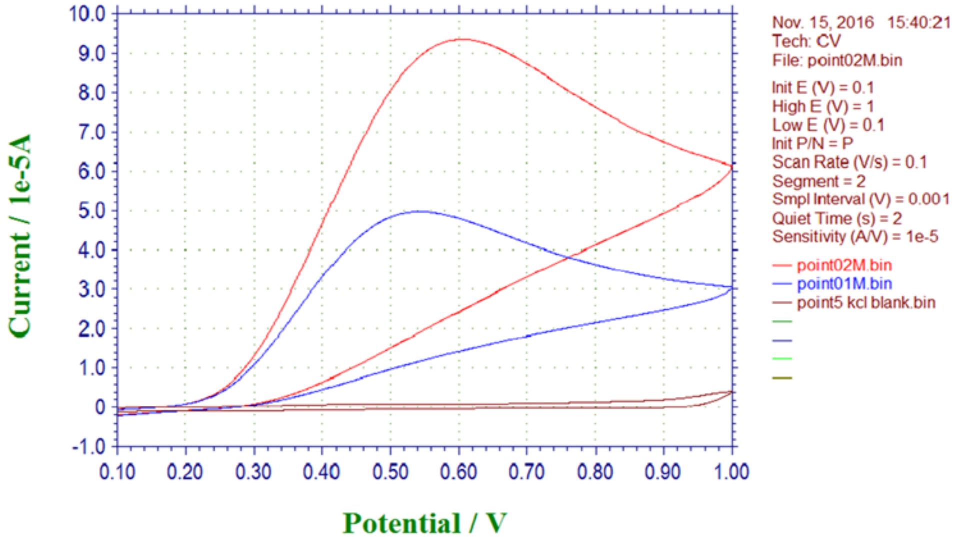

Figure 8.D.2. Cyclic Voltammograms of 0.5 M KCl blank (brown), 0.01 M vit C (blue), and 0.02 M vit C (red). Scan rate = 0.1 V/s.