

you-try-it-08answers.xlsx

ver. 11/21/2018

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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 measurement.
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.

1. Atoms that change oxidation state are highlighted in red.
Electrons on the left indicate that reactant undergoes reduction.
Electrons on the right indicate that reactant undergoes oxidation.
Half reactions are unbalanced.
Answers to instructions 2 and 3 are not shown.

Table 8.A.1

case	reactants	products
1	$\text{CH}_3\text{CH}_2\text{OH}(l)$ + $\text{O}_2(g)$ → $\text{CH}_3\text{CHO}(l)$	ethanol + oxygen → acetaldehyde
	$\text{CH}_3\text{C}\text{H}_2\text{OH}(l)$ → $\text{CH}_3\text{C}\text{HO}(l)$ + $2e^-$	
	$1e^-$ + $\frac{1}{2}\text{O}_2(g)$ → $\text{CH}_3\text{C}\text{HO}(l)$	
2	$\text{CH}_3\text{C}\text{H}_2\text{OH}(l)$ + $\text{Cr}_2\text{O}_7^{2-}(aq)$ → $\text{CH}_3\text{COOH}(l)$ + $\text{Cr}^{3+}(aq)$	ethanol + dichromate ion → acetic acid + chromium ion
	$\text{CH}_3\text{C}\text{H}_2\text{OH}(l)$ → $\text{CH}_3\text{COOH}(l)$ + $4e^-$	
	$3e^-$ + $\frac{1}{2}\text{Cr}_2\text{O}_7^{2-}(aq)$ → $\text{Cr}^{3+}(aq)$	
3	$\text{C}_6\text{H}_{12}\text{O}_6(aq)$ + $\text{O}_2(g)$ → $\text{C}_6\text{H}_{12}\text{O}_7(aq)$ + $\text{H}_2\text{O}_2(g)$	glucose + oxygen → gluconic acid + hydrogen peroxide
	$\text{C}_6\text{H}_{12}\text{O}_6(aq)^*$ → $\text{C}_6\text{H}_{12}\text{O}_7(aq)^*$ + $2e^-$	
	$2e^-$ + $\text{O}_2(g)$ → $\text{H}_2\text{O}_2(g)$	
4	$\text{C}_6\text{H}_{12}\text{O}_6(aq)$ → $\text{CH}_3\text{CH}_2\text{OH}(l)$ + $\text{CO}_2(g)$	glucose → ethanol + carbon dioxide
	$\text{C}_6\text{H}_{12}\text{O}_6(aq)^*$ → $\text{C}_6\text{H}_{12}\text{O}_6(aq)^*$	
	$\text{C}_6\text{H}_{12}\text{O}_6(aq)^*$ → $\frac{1}{2}\text{CO}_2(g)$	

Enzymes, catalysts, and spectator ions are not shown.

case	notes
1	reaction in the liver
2	colorimetric breathalyzer
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.

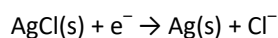
1. Use the data in Table 8.B.2 to predict reference electrode potential as the composition of the internal reference solution changes.
You may assume that the listed concentrations are equal to activity.
2. Use the data in Table 8.B.3 to determine how temperature affects the reference electrode potential.
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:



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

$$\text{for } Q = [Cl^-] = 3.00 \text{ M}$$

$$E = 0.194 \text{ V}$$

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

$[Cl^-]$ (M)	E (V)
0.10	0.281
1.00	0.222
2.00	0.204
3.00	0.194
3.50	0.190

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

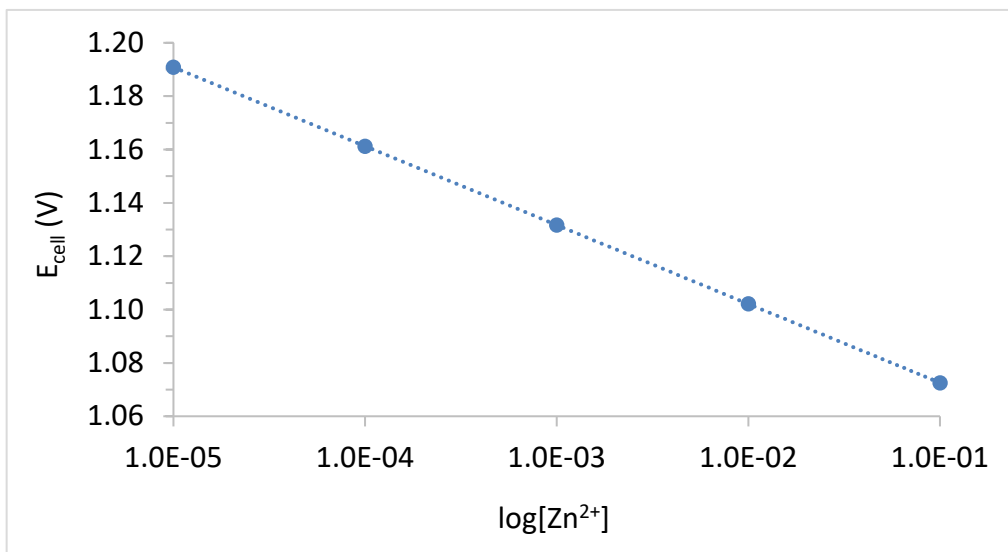
T (C)	T (K)	E (V)
5	278	0.196
10	283	0.195
15	288	0.195
20	293	0.194
25	298	0.194
30	303	0.193
37	310	0.193

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

$[Zn^{2+}]$ (M)	E_{Zn} (V)	E_{cell} (V)
1.0E-05	-0.910	1.191
1.0E-04	-0.880	1.161
1.0E-03	-0.851	1.132
1.0E-02	-0.821	1.102
1.0E-01	-0.792	1.073

Nernst equation parameters.

$E_{Ag/AgCl}$	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/CuSO₄.*

All solutions were measured in 1 M NaNO₃ 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 coefficient 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	1	148
100	2	103
1000	3	50
10000	4	-7

slope = -51.80 mV/decade
intercept = 203.0 mV

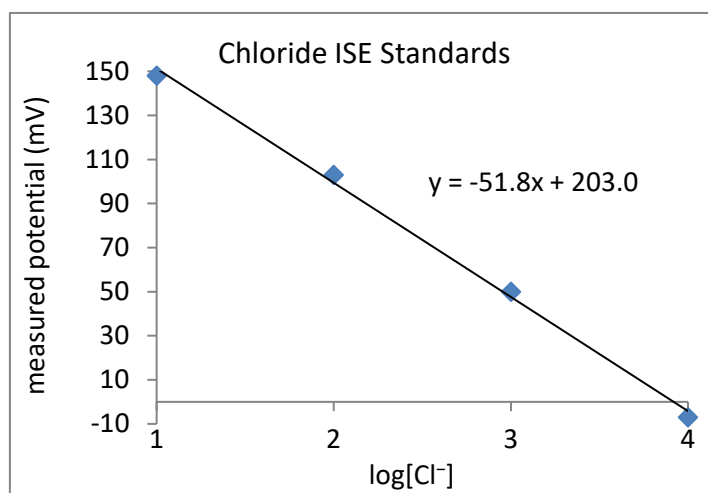


Table 8.C.2. Unknown measurements.

test portion	Voltage (mV)	[Cl ⁻] (ppm)
tap water	134	21.5
well water	120	40.0
DI water	170	4.3
meat tenderizer	72	338.0

The ISE equation for chloride is:
 $E = \text{intercept} - (\text{slope})\log[\text{Cl}^-]$

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

0.338
g/L Cl

0.0338
g Cl

9.535E-04
mol Cl

9.535E-04
mol NaCl

0.0557
g NaCl

0.899
fraction

89.9 % NaCl

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

added NaOH (mL)	[OH ⁻] (ppm)	Voltage (mV)	<i>k</i>
0.0	0.0	147	---
0.2	40.0	145	0.079
0.4	80.0	140	0.081
0.6	120.0	138	0.067

average: 0.075

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:

$$E = \text{intercept} - (\text{slope})\log([\text{Cl}^-] + k[\text{OH}^-])$$

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.

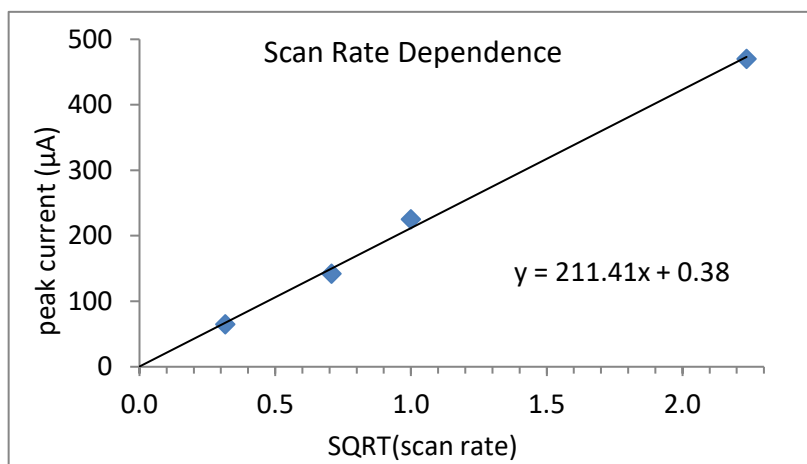
1. The Randles-Sevcik equation predicts a square root dependence on scan rate.
Plot the data to check this prediction.
2. Use the slope of the plot to calculate the diffusion coefficient for ascorbic acid.
The equation and relevant parameters are below Table 8.D.1.

Table 8.D.2 lists measured peak currents for a series of standard ascorbic 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	0.32	65.0
0.50	1.42E-04	0.71	142.0
1.00	2.25E-04	1.00	225.0
5.00	4.70E-04	2.24	470.0



$$i_p = (2.69 \times 10^5) n^{3/2} A c D^{1/2} v^{1/2} \text{ where:}$$

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

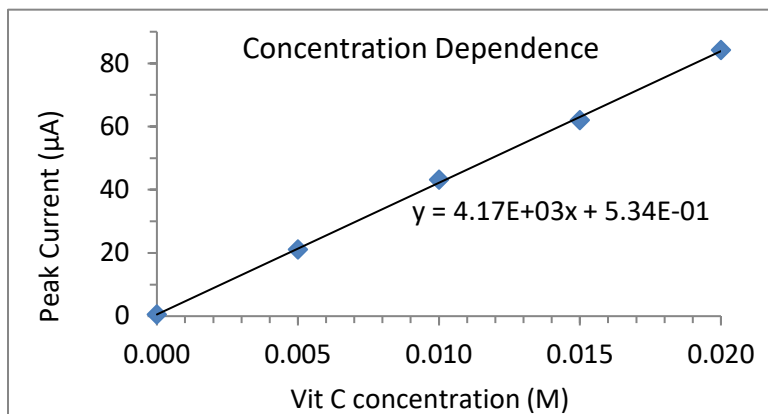
D is analyte diffusion coefficient in cm^2/s

and v is scan rate in V/s

$$\text{slope} = (2.69 \times 10^5) n^{3/2} A c D^{1/2} = 2.11\text{E-}04 \quad D = 6.8\text{E-}06 \quad \text{cm}^2/\text{s}$$

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:	4166.40	$\mu\text{A}/\text{M}$
intercept:	0.53	μA

Test portion: 2.61E-03 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	0.24	0.110	110
g/mol	L	g	mg vit C

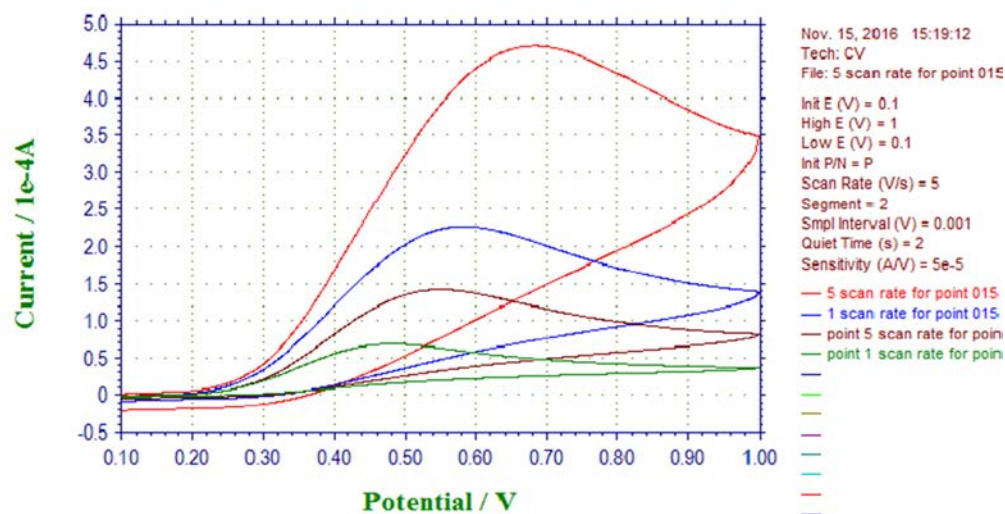


Figure 8.D.1. Cyclic Voltammograms of 0.015 M vit C in 0.5 M KCl at scan rates of 0.1 (green), 0.5 (brown), 1 (blue), and 5 (red) V/s.

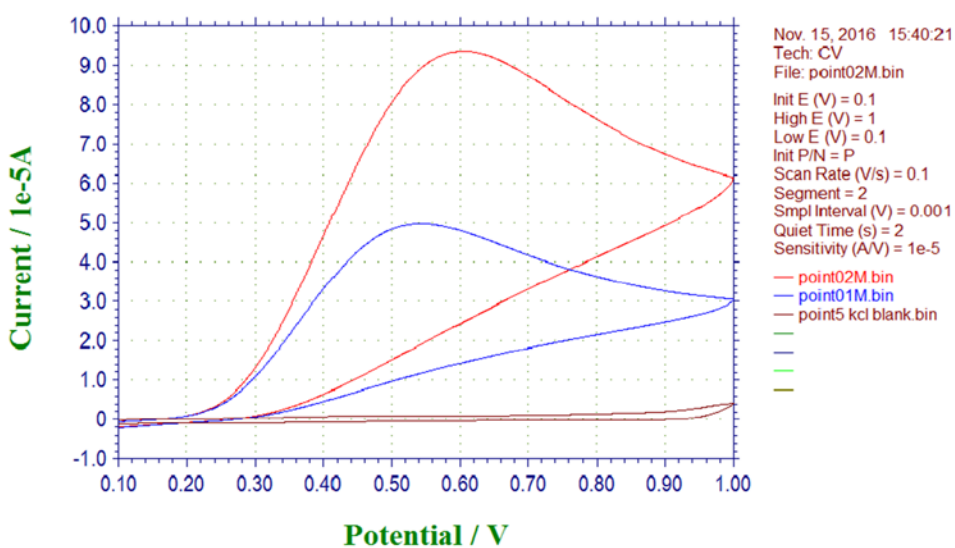


Figure 8.D.2. Cyclic Voltammograms of 0.5 M KCl blank (brown), 0.01 M vit C (blue), and 0.02 M vit C (red). Scan rate = 0.1 V/s.