you-try-it-09.xlsx
Step-by-Step Guide
ver. 8/10/2023

Abstract

This document provides step-by-step instructions for the workbook you-try-it-09.xlsx (saved from Microsoft® Excel® 365). Each worksheet contains data for practice exercises keyed to the You-Try-It boxes in Chapter 9 of:

> Brian M. Tissue, *Basics of Analytical Chemistry and Chemical Equilibria*, 2nd Ed. (John Wiley: New York, 2023).

General Advice

Work out or outline the first exercise of each worksheet on paper. Compare your result to the answer given in the worksheet. Next try writing formulas to do the calculations. If you do not get the same answer, error check your work by writing formulas step-wise to check intermediate steps. Try to write formulas to be general so that you can copy them to use for multiple cases.

Version History

6/21/2014	First draft.
7/26/2016	Revised formatting.
8/10/2023	Updated for 2nd edition.

For updates visit the text support website:

https://www.achem.org/

9.A Balancing Redox Reactions

This worksheet contains a table of unbalanced redox reactions. The exercise is to balance the redox reactions.

| Concepts	Concept Synopsis
oxidation state	Determining the number of electrons transferred in a half reaction requires that oxidation states of reactants and products be assigned correctly.
balancing redox reactions	Half reactions are combined so that electrons on each side of the half reactions cancel.

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.

These exercises are easiest to do on paper.

Case 1:

$CH_3CH_2OH(l)$	+		$O_2(g)$	$\rightarrow$		$CH_3CHO(l)$	+		H_2O
ethanol			oxygen			acetaldehyde			water

The approach is to identify atoms that change oxidation state and atoms or functional groups that do not change. In case 1, the methyl group is the same in both the ethanol and the acetic acid and we can ignore it. The other carbon in the ethanol does change. Remember that we give the bonding electrons to the more electronegative atom, or for a C-C bond, one electron to each carbon. The carbon atom in $-CH_2OH$ has 5 electrons around it rather than the 4 that is normal for carbon, so the oxidation state is -1. In acetaldehyde, the carbon atom in $-CH=O$ has 3 electrons around it rather than the 4 that is normal for carbon, so the oxidation state is $+1$. This change requires ethanol to lose two electrons and the half reaction is:

$$CH_3CH_2OH(l) \rightarrow CH_3CHO(l) + 2e^-$$
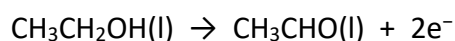
The oxygen atom in O_2 has an oxidation state of zero and the oxygen atom in H_2O has an oxidation state of -2. Two electrons are transferred for each oxygen atom. Since there

are two oxygen atoms in O_2, we need two water molecules on the right side and 4 electrons in the half reaction:

$$O_2(g) + 4e^- \rightarrow 2H_2O(l)$$
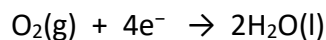
We multiply the ethanol half reaction by two to equalize the number of electrons in each half reaction:

$$2CH_3CH_2OH(l) \rightarrow 2CH_3CHO(l) + 4e^-$$
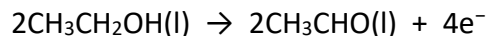
Now adding these two half reactions eliminates the electrons and the overall reaction is:

$$2CH_3CH_2OH(l) + O_2(g) \rightarrow 2CH_3CHO(l) + 2H_2O(l)$$
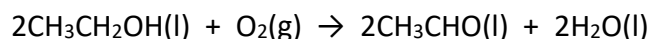
As a check, count the number of each atom on each side of the reaction.

| Left Side		Right Side	
C	4	C	4
H	12	H	12
O	4	O	4

The previous reaction is catalyzed by an enzyme in the liver. The next reaction is also the oxidation of ethanol, but the dichromate ion is a stronger oxidizing agent and the product is acetic acid.

Case 2
$$CH_3CH_2OH(l) + Cr_2O_7^{2-}(aq) + H^+(aq) \rightarrow CH_3COOH(l) + Cr^{3+}(aq)$$
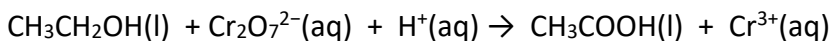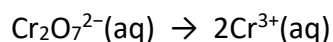
Our approach is the same as before, but in this case the carbon atom goes from an oxidation state is −1 in ethanol to +3 in acetic acid for a loss of 4 electrons from ethanol:

$$CH_3CH_2OH(l) \rightarrow CH_3COOH(l) + 4e^-$$
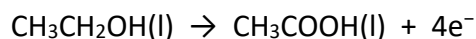
There are two chromium atoms on the left and one on the right, so first balance number of atoms:
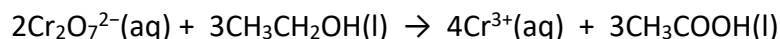
$$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$$

In the dichromate ion, $Cr_2O_7^{2-}$, oxygen is in the −2 oxidation state (our usual rule), and therefore chromium is in the +6 oxidation state to have an overall charge of 2−. Chromium is in the +3 oxidation state on the right side of the equation. Each chromium atom changes by 3 electrons, and since there are two chromium atoms present, the half reaction is:

$$Cr_2O_7^{2-}(aq) + 6e^- \rightarrow 2Cr^{3+}(aq)$$
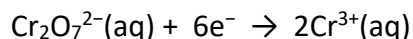
To make the number of electrons equal in both half reactions, we multiply the ethanol reaction by 3 and the dichromate half reaction by 2:

$$3CH_3CH_2OH(l) \rightarrow 3CH_3COOH(l) + 12e^-$$

$$2Cr_2O_7^{2-}(aq) + 12e^- \rightarrow 4Cr^{3+}(aq)$$
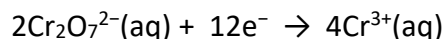
Now add the two half reactions together:

$$2Cr_2O_7^{2-}(aq) + 3CH_3CH_2OH(l) \rightarrow 4Cr^{3+}(aq) + 3CH_3COOH(l)$$

The next thing to do is to add H_2O to balance the number of oxygen atoms. There are 17 O atoms on the left and 6 O atoms on the right, so we add 11 waters on the right:

$$2Cr_2O_7^{2-}(aq) + 3CH_3CH_2OH(l) \rightarrow 2Cr^{3+}(aq) + 3CH_3COOH(l) + 11H_2O$$

The last thing to do is to add H^+ to balance the number of hydrogen atoms. There are 18 H atoms on the left and 34 H atoms on the right, so we add 16 H^+ on the left:

$$2Cr_2O_7^{2-}(aq) + 3CH_3CH_2OH(l) + 16H^+(aq) \rightarrow 4Cr^{3+}(aq) + 3CH_3COOH(l) + 11H_2O$$
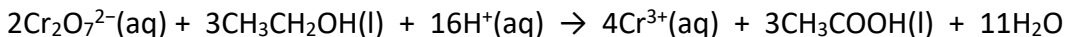
As a check, verify that charge balances: (−4 + 16) on the left equals (+12) on the right.

9.B Nernst Equation

This worksheet contains measurements of a reference electrode to see how it varies with composition of the internal solution and temperature.

Concepts	Concept Synopsis
Nernst equation	The Nernst equation
Electrochemical cell	The Nernst equation can be used for either a half-reaction or an overall reaction.

1. Use the data in Table 9.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.

Table 9.B.1 gives E^o and other constants. To the right of this table is the Nernst expression and a sample calculation for $[Cl^-]$ = 3.00 M. Note that I use concentration units for clarity, but the true response of the Nernst expression is to analyte activity, a.

	B	C	D	E	F	G	H	I
16								
17		**Table 9.B.1. Nernst equation parameters.**						
18		E^o	0.222	V		Sample calculation for the half reaction:		
19		R	8.314	J/mol·K		$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$		
20		T	298	K		$E = E^o - (RT/nF)$	$\ln(Q)$	
21		n	1			for $Q = [Cl^-] =$	3.00	M
22		F	96485	C/mol		$E =$	0.194	V
23								

Table 9.B.2 lists chloride concentrations with a second column to calculate the predicted E of the half-cell as a function of $[Cl^-]$.

In cell D27, type:
=$D$18-($D$19*$D$20/$D$21/$D$22)*LN(C27)

I place the constant values in cells (Table 9.B.1) and reference them in the formula. Doing so allows you to correct an error, or make a change such as temperature, in only one cell rather than changing multiple formulas.

Copy cell D27 into cells D28 through D31. The results should look like the following figure. As a check, [Cl⁻] = 1.0 M should equal E^o.

	B	C	D	E	F	G	H
24							
25		Table 9.B.2. Internal solution dependence for Ag/AgCl reference electrode. T = 298 K.					
26		[Cl⁻] (M)	E (V)				
27		0.10	0.281				
28		1.00	0.222				
29		2.00	0.204				
30		3.00	0.194				
31		3.50	0.190				
32							

2. Use the data in Table 9.B.3 to determine how temperature affects the reference electrode potential.

This exercise is essentially the same as part 1, but now we are varying T rather than [Cl⁻]. First convert the Celsius temperatures in Table 9.B.3 to Kelvin. In cell D36 type:
=C36+273

Copy this cell and paste in cells D37 through D42. In cell E36, type the following formula:
=$D$18-($D$19*$D36/$D$21/$D$22)*LN($H$21)

Copy cell E26 into cells E27 through E42. The results should look like the following figure.

	B	C	D	E	F	G	H
33							
34		Table 9.B.3. Temperature effects for Ag/AgCl reference electrode. [Cl–] = 3.0 M.					
35		T (C)	T (K)	E (V)			
36		5	278	0.196			
37		10	283	0.195			
38		15	288	0.195			
39		20	293	0.194			
40		25	298	0.194			
41		30	303	0.193			
42		37	310	0.193			

You can see that temperature effects are measurable but not large. Temperature drift is generally not a problem over a few hours. Making electrochemical measurements when standard solutions and unknown solutions have not been brought to the same temperature can introduce a bias in the results.

3. Use the data in Table 9.B.4 to calculate cell voltage as a function of [Zn^{2+}] for the following cell:

Ag | AgCl | Cl⁻ (0.1 M) || Zn^{2+} (variable) | Zn
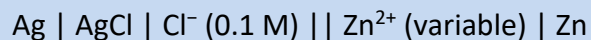
Plot the results to confirm the log dependence.

Table 9.B.4 lists a series of Zn^{2+} concentrations. Column D has spaces to find the voltage of the zinc half-reaction. The line notation shows that the cell has an Ag/AgCl cathode and a Zn anode. The zinc half-reaction therefore goes as an oxidation. We will see from the result that this cell is a galvanic cell, that is, the overall reaction is spontaneous. The zinc half-reaction is:

$$Zn(s) \leftrightarrow Zn^{2+} + 2e^- \qquad E^o = -0.762 \text{ V}$$

and the corresponding Nernst expression is:

$$E = E^o - \frac{RT}{nF} \log \frac{1}{[Zn^{2+}]}$$

The constants for this expression are in cells in column H. In cell D47 type:

=$H$47-($H$48*$H$49/$H$50/$H$51)*LN(1/C47)

Copy cell D47 and paste it into cells D48 through D51. Now use these values to find the cell voltage, E_{cell}, as a function of [Zn^{2+}].

The cell voltage is:

$$E_{cell} = E_{cathode} - E_{anode}$$

where the cathode is a Ag/AgCl reference electrode with a half-reaction potential of 0.281 V (cell H46).

In cell E47 type:

=$H$47-D47

Copy cell E47 and paste it into cells E48 through E51. Your results should look like the following figure:

	B	C	D	E	F	G	H	I
44								
45		Table 9.B.4. Cell voltage for a zinc indicator electrode				Nernst equation parameters.		
46		$[Zn^{2+}]$ (M)	E_{Zn} (V)	E_{cell} (V)		E_Ag/AgCl	0.281	V
47		1.0E-05	-0.910	1.191		E°	-0.762	V
48		1.0E-04	-0.880	1.161		R	8.314	J/mol·K
49		1.0E-03	-0.851	1.132		T	298	K
50		1.0E-02	-0.821	1.102		n	2	
51		1.0E-01	-0.792	1.073		F	96485	C/mol
52								

Now highlight cells C47 through C51 and cells E47 through E51. Insert a plot with Insert > Charts > Scatter. Double-click on the x-axis and check the box for Logarithmic scale. Enter axes titles and adjust formatting to your liking. You plot should look something like the following figure. Note we see the linear response when plotted versus a log scale.
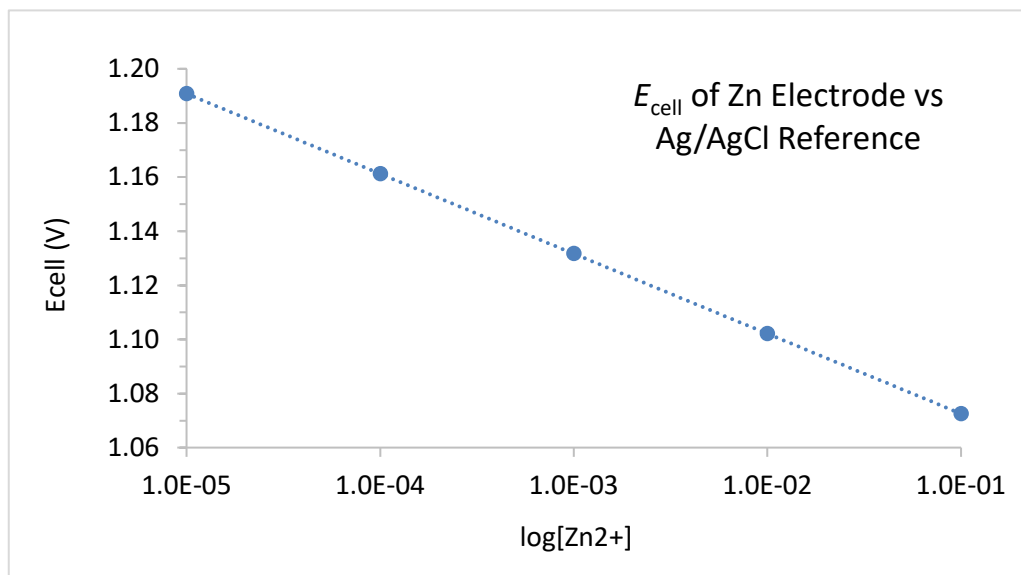
9.C potentiometry

This worksheet contains tables with measurements of [Cl⁻] using an ion-selective electrode. When all solutions are measured at equal ionic strength, it is possible to relate the unknown measurements to standard concentration to determine [Cl⁻].

Concepts	Concept Synopsis
Ion-selective electrodes	Ion-selective electrodes are a common and convenient means of measuring ion concentrations in solution.
Nikolsky equation	The Nikolsky equation relates the measured voltage of an ISE to analyte activity (see below).
selectivity	Ion-selective electrodes are not perfectly selective. Manufacturer information will usually state the interferences for a given analyte.

1. Construct a calibration curve from the standard data.

The general Nikolsky equation is:

$$E_{\mathrm{ISE}} = E_{\mathrm{const}} + \frac{0.0592\ \mathrm{V}}{z_{\mathrm{i}}} \log\bigl(a_{\mathrm{i}} + k_{\mathrm{i,j}}a_{\mathrm{j}} + k_{\mathrm{i,k}}a_{\mathrm{k}} + \ldots\bigr)$$

where E_{const} is an experimentally determined intercept, z_{i} is the charge of the analyte ion, and a_{i} is analyte activity. The k terms we will discuss in part 3. Neglecting the k terms and assuming [Cl⁻] is equally proportional to a_{Cl} in all solutions, this expression simplifies to:

$$E_{\mathrm{ISE}} = E_{\mathrm{const}} + \frac{(0.0592\ \mathrm{V})}{-1}\ \log[\mathrm{Cl}^-]$$

where the –1 in the denominator of the slope is the charge for the chloride ion.

Table 9.C.1 contains ISE measurements for a series of chloride standards. Since $E_{\mathrm{ISE}} \propto \log[\mathrm{Cl}^-]$, we will convert the concentrations to log[Cl⁻]. In cell D25 (see next figure), type:

    =log(C25)

Copy that formula into cells D26 through D 28 for the other concentrations.

	A	B	C	D	E
21					
22			**Table 9.C.1. Chloride standards.**		
23			**Cl⁻ standards**		
24			**(ppm)**	**log[Cl⁻]**	**Voltage (mV)**
25			10		148
26			100		103
27			1000		50
28			10000		-7
29					
30			slope =		mV/decade
31			intercept =		mV
32					
33					
34			**Table 9.C.2. Unknown measurements.**		
35			**test portion**	**Voltage (mV)**	**[Cl⁻] (ppm)**
36			tap water	134	
37			well water	120	
38			DI water	170	
39		meat tenderizer		72	
40					

Now highlight cells D25 through E28 and use Insert > Charts > Scatter to create a plot. Adjust axes, formatting, and insert a trendline. You should have something like the following figure:

Chloride ISE Standards

$y = -51.8x + 203.0$
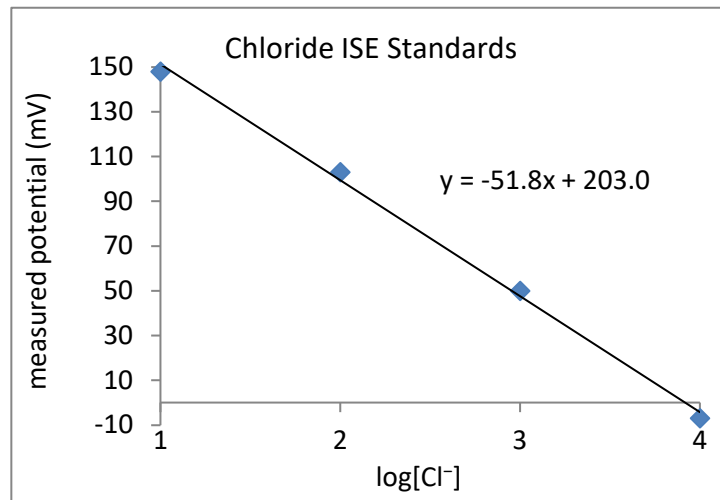
You can see from the trendline equation that the slope is rarely the 59.2 mV theoretical value.

I've also entered places below Table 9.C.1 to calculate the slope and intercept. In cells D30 and D31, respectively, type:

    =SLOPE(E25:E28,D25:D28)

    =INTERCEPT(E25:E28,D25:D28)

These values are the same as shown in the trendline equation above, but they are now easily referenced for use in subsequent formulas.

2.   Determine the chloride concentration in the test solutions.

Table 9.C.2 contains ISE measurements for several test solutions (see figure of Table 9.C.2 on previous page). The expression is the same as the trendline, rearranged to find x, which is $\log[Cl^-]$:

$$\log[Cl^-] = x = (y - 203\ mV)/(-51.8\ mV)$$

$$[Cl^-] = 10^{\wedge}\{(y - 203\ mV)/(-51.8\ mV)\}$$

We can use the slope and intercept in cells D30 and D31 to write the formula to find $[Cl^-]$ for each solution. In cell E36 type:

    =10^((D36-$D$31)/$D$30)

Copy this formula to cells E37 through E39 and you will get the following results:

	A	B	C	D	E
33					
34			Table 9.C.2. Unknown measurements.		
35			test portion	Voltage (mV)	[Cl⁻] (ppm)
36			tap water	134	21.5
37			well water	120	40.0
38			DI water	170	4.3
39			meat tenderizer	72	338.0
40					

The bonus question below Table 9.C.2 states that the meat tenderizer solution contained 62 mg of product dissolved in 100 mL of water. The concentration result in cell E39 can be used to determine the weight percent of NaCl in the meat tenderizer. You can follow the unit conversions in row 48 in the next figure to complete this calculation:

	B	C	D	E	F	G	H	I	J
44									
45		Cl and NaCl formula weights:		35.45	g/mol		58.44	g/mol	
46									
47		0.338	0.0338	9.535E-04	9.535E-04	0.0557	0.899	90	% NaCl
48		g/L Cl	g Cl	mol Cl	mol NaCl	g NaCl	fraction		

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

Table 9.C.3 contains ISE measurements for the 10-ppm standard solution after adding varying amounts of hydroxide ion, OH⁻, to the solution:

	B	C	D	E	F
51					
52		Table 9.C.3. Standard addition of OH⁻ to determine k.			
53		added NaOH	[OH⁻]	Voltage	k
54		(mL)	(ppm)	(mV)	
55		0.0		148	
56		0.2		145	
57		0.4		140	
58		0.6		138	
59					
60				average:	
61					
62		Supporting Information			
63		NaOH conc:	0.10	M NaOH	
64		NaOH f.w.:	40.0	g/mol	
65		NaOH conc:	4000	ppm NaOH	
66		test volume:	25.0	mL	

We can see from the measurements in column E that the chloride ISE has some sensitivity to OH⁻. Use the supporting information to convert the amount of added NaOH to [OH⁻] in ppm. In cell D55 type:

    =C55*$D$65/$D$66

Copy this formula into cells D56 through D58.

The expression for the chloride ISE including contributions to hydroxide interferences is:

$$E_{ISE} = E_{const} + \frac{(0.0592\ \text{V})}{-1}\ \text{Log}(\ [Cl^-] + k[OH^-]\ )$$

A k factor in the Nikolsky equation is a relative sensitivity for an interfering ion. It will be a value between 0 and 1, where 0 means no sensitivity to the interference and 1 indicates the interference responds the same as the analyte.

Rearranging this expression and inserting the experimental intercept and slope gives:

$$\frac{E_{ISE} - intercept}{slope} = \log([Cl^-] + k[OH^-])$$

$$10^\wedge\{(E_{ISE} - intercept)/slope\} = [Cl^-] + k[OH^-]$$

$$k = \frac{10^\wedge\{(E_{ISE} - intercept)/slope\} - [Cl^-]}{[OH^-]}$$

Converting this expression to a formula, in cell F56 type:

=(10^((E56-$D$31)/$D$30)-10)/D56

Copy this formula into F57 and F58. Find the average of the three values by typing in cell F60:

= AVERAGE(F56:F58)

The results are shown in the next figure:

	B	C	D	E	F
51					
52		Table 9.C.3. Standard addition of OH⁻ to determine k.			
53		added NaOH	[OH⁻]	Voltage	k
54		(mL)	(ppm)	(mV)	
55		0.0	0.0	148	---
56		0.2	32.0	145	0.099
57		0.4	64.0	140	0.101
58		0.6	96.0	138	0.083
59					
60				average:	0.094

The k value of 0.09 is not insignificant. For reference though, the pH of the solutions with added NaOH are near pH = 11. The chloride ISE will be accurate for solutions that have pH lower than ≈10. Knowing this characteristic allows an analyst to know when a correction might be necessary for a given unknown solution.

9.D voltammetry

This worksheet shows cyclic voltammograms for ascorbic acid (vitamin C). Two tables list peak current as a function of scan rate and for a series of standard solutions and an unknown sample.

Concepts	Concept Synopsis
voltammetry	Voltammetry can be used to study the kinetics and mechanisms of redox reactions. The measured peak current is directly proportional to analyte concentration, so it is also useful as a quantitative analytical method.

Table 9.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.

Two empty columns are labeled in Table 9.D.1 for the square root of the scan rate and to convert the peak current to microamps.

For row 23, the formulas for cells E23 and F23 are, respectively:
=SQRT(C23)
=D23*1000000

The results are:

	B	C	D	E	F
19					
20		Table 9.D.1 Ascorbic acid peak current as a function of scan rate.			
21		Scan Rate	Peak Current	(Scan Rate)^0.5	Peak Current
22		(V/s)	(A)	(V/s)^0.5	(µA)
23		0.10	6.50E-05	0.32	65.0
24		0.50	1.42E-04	0.71	142.0
25		1.00	2.25E-04	1.00	225.0
26		5.00	4.70E-04	2.24	470.0
27					

Highlight the data in cells E23:E26 and in F23:F26 and use "Insert > Charts > Scatter" to plot the data. Empty space is below Table 9.D.1 to place the chart. Add axis labels and a trendline. In the following figure I've also added a chart label and displayed the trend-

line equation on the chart. The plot shows a linear dependence as expected from the Randles-Sevcik equation.
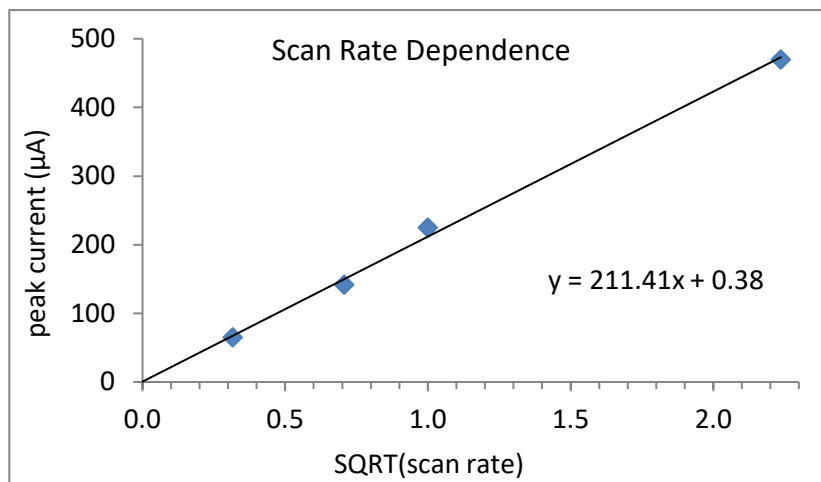
2. Use the slope of the plot to calculate the diffusion coefficient for ascorbic acid. The equation and relevant parameters are below Table 9.D.1.

The Randles-Sevcik equation for peak current, i_p, at 25 C is:

$$i_p = (2.69 \times 10^5)n^{3/2}AcD^{1/2}v^{1/2}$$

For the 2.69×10^5 prefactor, the variables and units are:

n is the number of electrons transferred.

A is electrode area in cm^2.

c is analyte concentration in the bulk solution in mol/cm^3.

D is diffusion constant with units of cm^2/s.

V is scan rate in V/s.

The oxidation of ascorbic acid is a one-electron process, the electrode dimension is listed as 1.6 mm diameter, and the analyte concentration is 0.015 M. Some of this information is already present in rows 45 and 46. In cell E50 I find the slope:

=SLOPE(D23:D26,E23:E26)

The slope of the plot of i_p versus $v^{1/2}$ is: $(2.69 \times 10^5)n^{3/2}AcD^{1/2}v^{1/2}$ and rearranging for D is:

$$D = (slope/2.69 \times 10^5 Ac)^2$$

In cell G50 I find D using:

=(E50/269000/F46/F45)^2

The results are:

|	A	B	C	D	E	F	G	H	I	J
42										
43			$i_p = (2.69\times10^5)n^{3/2}AcD^{1/2}v^{1/2}$ where:							
44			n is number of electrons			1				
45			A is electrode area in cm^2			0.020	cm^2	0.16	cm dia electrode	
46			c is bulk analyte concentration in mol/cm^3			0.000015	mol/cm^3	0.001	L/cm^3	
47			D is analyte diffusion coefficient in cm^2/s							
48			and v is scan rate in V/s							
49										
50			slope = $(2.69\times10^5)n^{3/2}AcD^{1/2}$ =		2.11E-04		D =	6.8E-06	cm^2/s	
51										

Table 9.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.

Highlight the data in cells D57:E61 and use "Insert > Charts > Scatter" to plot the data. Empty space is below Table 9.D.1 to place the chart. Add axis labels and a trendline. In the following figure I've also added a chart label and displayed the trendline equation on the chart. The plot shows a linear dependence as expected from the Randles-Sevcik equation.
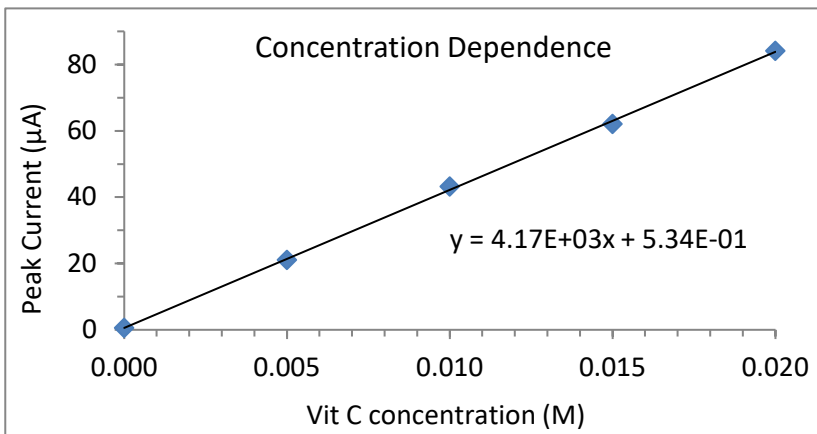
4. Determine the ascorbic acid concentration in the test portion.
    Use the sample information to compare the measurement to the stated ingredients.

I find the slope and intercept in cells D79 and D80, respectively, using:

=SLOPE(E57:E61,C57:C61)

=INTERCEPT(E57:E61,C57:C61)

The test portion concentration is found from the juice measurement using:

=(E62-$D$80)/$D$79

The results are:

	B	C	D	E	F	G	H	I
77								
78		**Calibration Function**						
79		slope:	4166.40	µA/M				
80		intercept:	0.53	µA				
81								
82		Test portion:	2.61E-03	M				
83								
84		The label on the juice container listed 108 mg vitamin C per 240 mL serving.						
85		Use the formula weight (176.1 g/mol) to determine the amount of vitamin C in one serving of juice.						
86		176.1	0.24	0.110	110			
87		g/mol	L	g	mg vit C			