Potentiometric Determination of the pK_a and the Equivalent Weight of a Weak Acid

Introduction

In this experiment you will use a pH meter to follow changes in H^+ concentration during a titration. The laboratory instructor as part of the briefing will explain operation of the pH meter to you. These instruments are expensive and the electrodes are fragile. They should be handled with care. You should be absolutely certain that you understand the correct technique for using the meter.

By plotting pH as a function of the volume of base added during the titration, a titration curve can be readily prepared (Figure 1). Titration curves provide the analyst with significant information concerning the identity of the weak acid. For a monoprotic acid, there will be one equivalence point (as shown in Figure 1). However, diprotic acids exhibit two equivalence points, triprotic acids exhibit three equivalence points, and so on. If the pK_a's for a polyprotic acid are sufficiently far apart (~2 units), then the equivalence points in the titration curve will be distinct. If the pK_a's are too close, the equivalence points merge into a single, irregular shaped equivalence point representing both pK_a's.

The pK_a for a monoprotic acid is readily determined from the titration curve by the following procedure. First, determine the volume of base required to reach the equivalence point. Divide this volume in half, and from inspection of the titration curve determine the pH of the solution at 1/2 of the volume of base necessary for equivalence. The pH at this point is the pK_a. This is readily confirmed from the Henderson-Hasselbach equation describing buffers:

$$pH = pKa + \log \frac{\left[A^-\right]}{\left[HA\right]}$$

where A^- represents the concentration of neutralized weak acid and HA is the concentration of unneutralized weak acid. At the equivalence point, all of the HA has been converted into A^-. This conversion required a finite volume of base. If half of the volume of base needed for total conversion is added, then half of the HA has been converted into A^-. The concentrations of HA and A^- will be equal, the ratio of $[A^-]/[HA]$ will be 1.00, the log of 1.00 is 0.00, and the pH = pK_a.

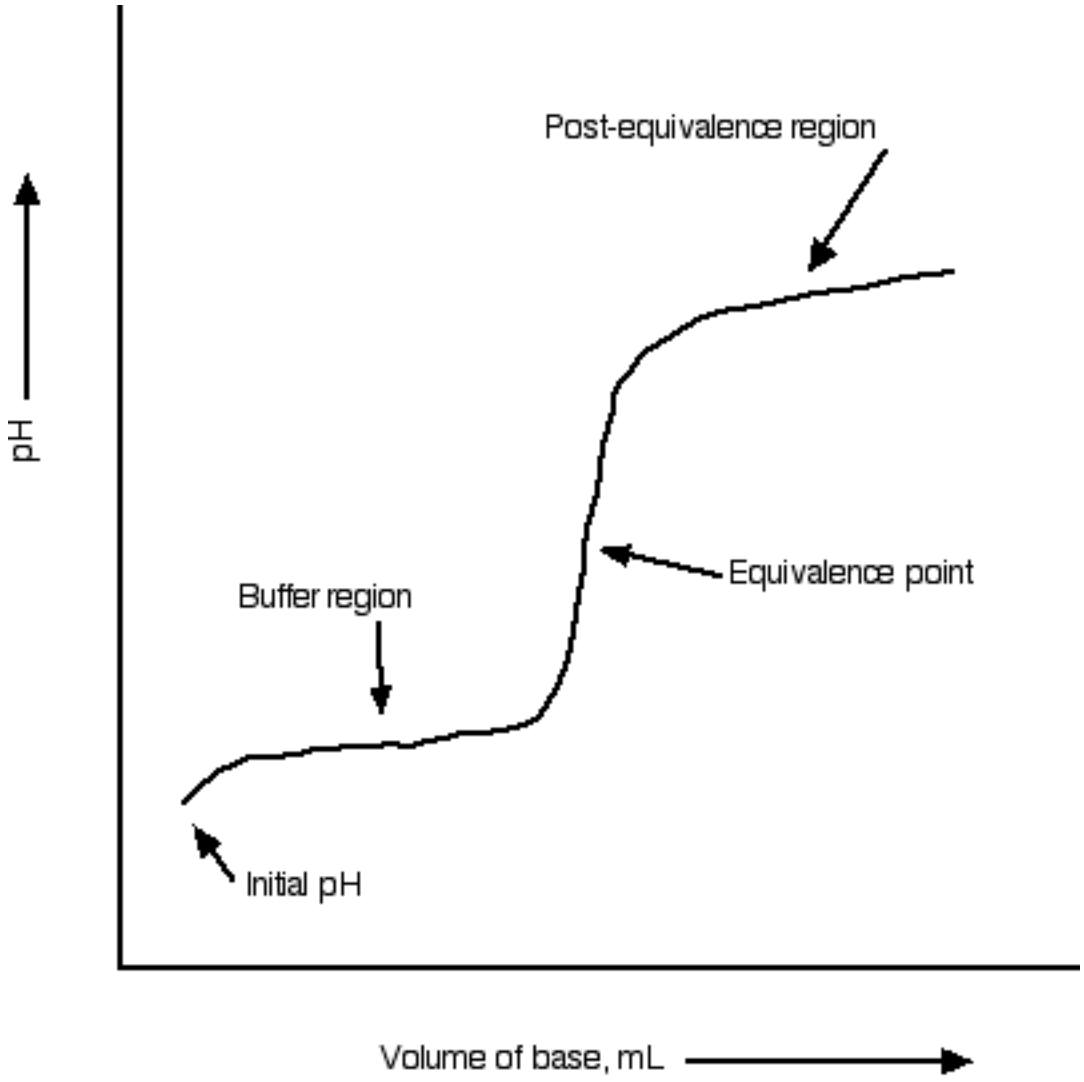

Figure 1. Titration curve for a monoprotic weak acid.

Solutions needed for this experiment:

Solutions prepared by the student	Solutions provided by the instructor
0.1N sodium hydroxide (standardized by student)	Phenolphthalein indicator (for standardization of sodium hydroxide solution only)

Specialized equipment needed:

In this experiment, you will be using a pH meter and electrode. Your laboratory instructor will demonstrate the proper calibration and use of this instrument during the laboratory briefing for this experiment.

Experimental Procedure

Preparation and standardization of sodium hydroxide solution.

1. Dry ~2 grams of potassium hydrogen phthalate (KHP) in the oven for 2 hours at 110 ^{o}C. Store the dried KHP in a desiccator.

2. Prepare 1 liter of 0.1N sodium hydroxide by adding about 500 mL of deionized water to a clean 1 liter plastic bottle. Add either 4.0 grams of solid sodium hydroxide, or 8.0 grams (~5.3 mL) of 50% sodium hydroxide solution. Shake the contents until the sodium hydroxide is completely dissolved and mixed, and then fill the bottle with deionized water. Cap the bottle and mix by shaking.

3. Using an analytical balance, dispense three 0.5-gram samples of KHP into separate beakers or flasks. Make sure you record the mass of KHP used to four decimal points. Add about 25 mL of water to each sample. The KHP should completely dissolve, but if it doesn't DON'T WORRY ABOUT IT.

4. To each KHP sample, add 2-3 drops of phenolphthalein solution.

5. Titrate each KHP sample with your sodium hydroxide solution to the first, pale pink endpoint that is stable for at least 10 seconds (Figure 2). The entire contents of the beaker/flask must be pale pink, and the palest endpoint possible is the most desirable. Record the volume of sodium hydroxide solution used.

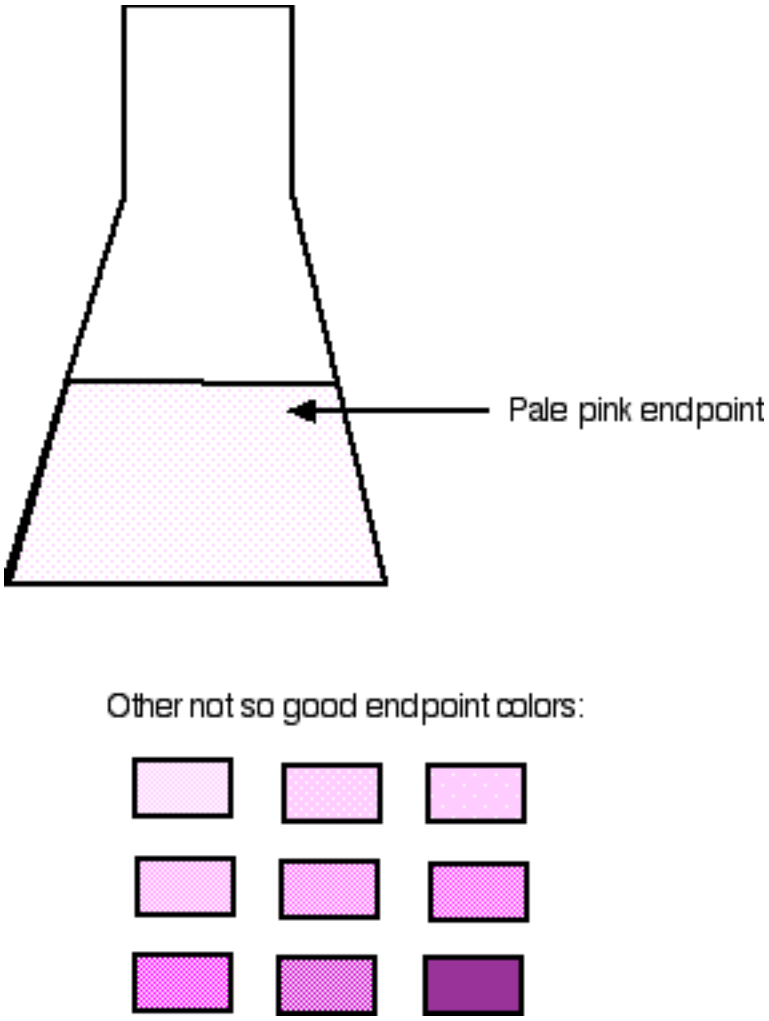

Figure 2. A correct pale pink endpoint, and examples of other possible (wrong) end points.

6. Calculate the average normality of your sodium hydroxide solution and label the solution appropriately. The formula weight of KHP is 204.23 g/mole. At the endpoint of the titration the number of moles of sodium hydroxide is equal to the number of moles of KHP. The molarity of the sodium hydroxide solution is equal to the moles of sodium hydroxide divided by the volume (in liters) of sodium hydroxide solution used at the endpoint. The normality of sodium hydroxide is equal to the molarity.

Titration of the weak acid.

1. Obtain an unknown weak acid sample from your instructor and record the unknown number. DO NOT dry the acid in the oven.

2. Using the analytical balance dispense 0.4 – 0.5 grams of the acid into a 250 mL beaker. Add about 50 mL of deionized water and a magnetic stir bar. Turn the magnetic stirrer on, and adjust it so that the solution is constantly and gently stirred. Rinse the pH electrodes with deionized water and place them in the beaker. Make certain that the stir bar does not hit the electrodes.

3. Record the initial pH of the weak acid solution.

4. Mount the burette in an appropriate position for the addition of sodium hydroxide to the beaker.

5. Add standard base to the unknown acid and record the total volume of base added and the pH reading. Try to record pH changes in intervals of 0.2 – 0.3 pH units, or volume increases of ~ 5 mL, whichever comes first.

6. Continue to titrate until you have reached the equivalence point. Normally, you will be able to tell that you are approaching the equivalence point when a small addition of base causes a dramatic increase in pH. When this happens, add additional smaller increments of sodium hydroxide solution (~ 0.1 - 0.2 mL). After you have reached the equivalence point, the small volumes of sodium hydroxide will not have significant effects on the pH. Return to adding ~5 mL increments of sodium hydroxide and continue the titration until you have reached a pH that is 2 – 3 pH units higher than the equivalence point pH, or until you reach a pH of 12 (whichever comes first).

7. Repeat the titration on a second sample of the unknown acid.

8. When you are finished, you should have two sets of data similar to that shown in the table below.

Total volume of base added	pH of solution
0.00 mL	4.65
5.13 mL	4.99
10.22 mL	5.31
etc.	etc.

9. For both sets of titration data, plot pH (y-axis) as a function of total volume of sodium hydroxide solution added (x-axis). Draw a smooth curve through all of the data points.

10. Determine the equivalence point volume of your two titrations. Detailed instructions on how to do this are at the end of this lab procedure (after the sample report).

11. From the equivalence point volume, calculate the equivalent weight of your acid using the following equations:

$$N_{(base)} \acute{} \; V_{(base,Liters)} = moles, OH^- = moles, H^+$$

$$\frac{grams_{Acid}}{moles, H^+} = \text{Equivalent weight, grams/mole}$$

12. Determine the pK_a for your acid by determining the pH at a volume equal to 1/2 of the equivalence point volume. Report the average equivalent weight and average pKa.

Laboratory Report

A sample lab report is shown at the end of this procedure.

WASTE DISPOSAL: All wastes can be poured down the sink.

SAMPLE REPORT

Equivalent Weight and pK_a
Unknown # 12.5
Washington Irving

	Sample 1	Sample 2	Average
Mass of unknown acid, g	0.5278	0.5093	
Vol. base at equivalence, mL	25.50	24.50	
Vol. base at 1/2 equivalence, mL	12.75	12.25	
Normality of base, N	0.1099	0.1099	
pKa, from titration curves	5.50	5.45	5.48
Equivalent weigh, g/mole	188.3	189.2	188.8

Sample calculations:

$$N_{(base)} \text{´ } V_{(base,Liters)} = moles, OH^- = moles, H^+$$

$$0.1099N \text{´ } 0.02550L = 0.00280245 moles, OH^- = 0.00280245 moles, H^+$$

$$\frac{grams_{Acid}}{moles, H^+} = \text{ Equivalent weight, grams/mole}$$

$$\frac{0.5278 grams_{Acid}}{0.00280245 moles, H^+} = 188.3 \frac{grams}{mole}$$

Attach one of your titration curves to the report.

How to Find the Equivalence Point from Your Titration Data

The simplest way of accurately finding the equivalence point from your titration data is to take the first and second derivatives. The sample spreadsheet below shows how to set up the columns and the calculations that need to be made, using the following instructions.

1. In an Excel spreadsheet, label columns from left to right as shown in the sample. Column "A" is "Total mL of base added", column "B" is "pH", and so on.

2. Column "C" is v' – the average of 2 consecutive volumes. Enter the formula shown in cell C2, and then use the fill down command.

3. Column D is f' – the change in pH divided by the change in volume for two consecutive measurements. Enter the formula shown in cell D2 and then use the fill down command.

4. Column E is v'' – the average volume of consecutive average volumes. Enter the formula shown in cell E2 and then use the fill down command.

5. Column F is f'' – the change in f' divided by the change in v'. Enter the formula shown in cell F2 and then use the fill down command.

Total mL of base added	pH	v' (mL)	f'(ΔpH/ΔV)	v'' (mL)	f'' (ΔpH^2/Δ^2V)
0.00	4.05	=(A2+A3)/2	=(B3-B2)/(A3-A2)	=(C2+C3)/2	=(D3-D2)/(C3-C2)
1.89	4.29	=(A3+A4)/2	=(B4-B3)/(A4-A3)	=(C3+C4)/2	=(D4-D3)/(C4-C3)
4.09	4.54	=(A4+A5)/2	=(B5-B4)/(A5-A4)	=(C4+C5)/2	=(D5-D4)/(C5-C4)
		Etc	Etc	Etc	Etc

When you have finished your calculations, you will have a data table that looks like Table 1 (below). If you plot pH (y-axis) vs. Total mL of base added (x-axis), you get an ordinary titration curve that looks like Figure 1.

If you plot f' (y-axis) vs. v' (x-axis), you get a first derivative plot that looks like Figure 2. The equivalence point volume is the volume giving the highest f' value; f' is 9.60, so the equivalence point volume is 21.89 mL.

If you plot f'' (y-axis) vs. v'' (x-axis), you get a second derivative plot that looks like Figure 3. The average volume corresponding to the highest value and lowest value is the equivalence point. These two volumes are 21.69mL (corresponding to f'' = 48.59) and 21.89 mL (corresponding to f'' = -41.69). The average of the two

volumes is 21.79 mL which agrees closely with 21.89 mL from the first derivative curve.

Finally, the pKa is the pH when 50% of the titration is complete (when 50% of the equivalence point volume of base has been added). If we use 21.89 mL as the equivalence point, 50% of this volume is 10.95 mL (10.945 rounded to 2 decimal places). The pH at this volume is the pKa. You may have to replot the data surrounding this pH and volume value in order to estimate the pKa to an acceptable number of significant figures.

TABLE 1

Vol Base, mL	pH	v'(mL)	f'(dpH/dV)	v''(mL)	'(dpH^2/d^2v
0.00	4.05	0.95	0.13	1.97	-0.01
1.89	4.29	2.99	0.11	4.09	-0.01
4.09	4.54	5.19	0.10	6.94	-0.01
6.28	4.75	8.69	0.08	10.59	0.00
11.10	5.12	12.50	0.08	14.33	0.01
13.89	5.34	16.17	0.10	17.56	0.03
18.44	5.80	18.96	0.17	19.24	-0.01
19.47	5.98	19.53	0.17	19.61	0.83
19.59	6.00	19.69	0.30	19.81	-0.38
19.79	6.06	19.94	0.21	20.04	0.33
20.08	6.12	20.14	0.27	20.20	-0.05
20.19	6.15	20.27	0.27	20.35	0.91
20.34	6.19	20.43	0.41	20.52	-0.24
20.51	6.26	20.61	0.37	20.72	-0.20
20.70	6.33	20.84	0.32	20.94	0.94
20.98	6.42	21.03	0.50	21.11	1.70
21.08	6.47	21.19	0.77	21.29	-0.18
21.30	6.64	21.40	0.74	21.49	1.35
21.49	6.78	21.59	1.00	21.67	15.25
21.69	6.98	21.75	3.36	21.80	48.59
21.80	7.35	21.85	8.22	21.92	9.50
21.89	8.09	21.99	9.60	22.06	-41.69
22.09	10.01	22.14	3.56	22.19	-19.19
22.18	10.33	22.24	1.64	22.29	-3.20
22.29	10.51	22.34	1.30	22.39	-2.00
22.39	10.64	22.44	1.10	22.49	-3.00
22.49	10.75	22.54	0.80	22.59	-1.00
22.59	10.83	22.64	0.70	22.69	-1.00
22.69	10.90	22.74	0.60	22.79	-1.00
22.79	10.96	22.84	0.50	22.89	0.00
22.89	11.01	22.94	0.50	23.22	-0.35
22.99	11.06	23.49	0.31	23.97	-0.14
23.99	11.37	24.45	0.18	24.92	-0.06
24.90	11.53	25.40	0.12	25.93	-0.03
25.90	11.65	26.45	0.09	27.15	-0.01
27.00	11.75	27.86	0.07	28.85	-0.01
28.71	11.87	29.85	0.05	30.94	0.00
30.99	11.98	32.04	0.04		
33.08	12.06				

FIG 1

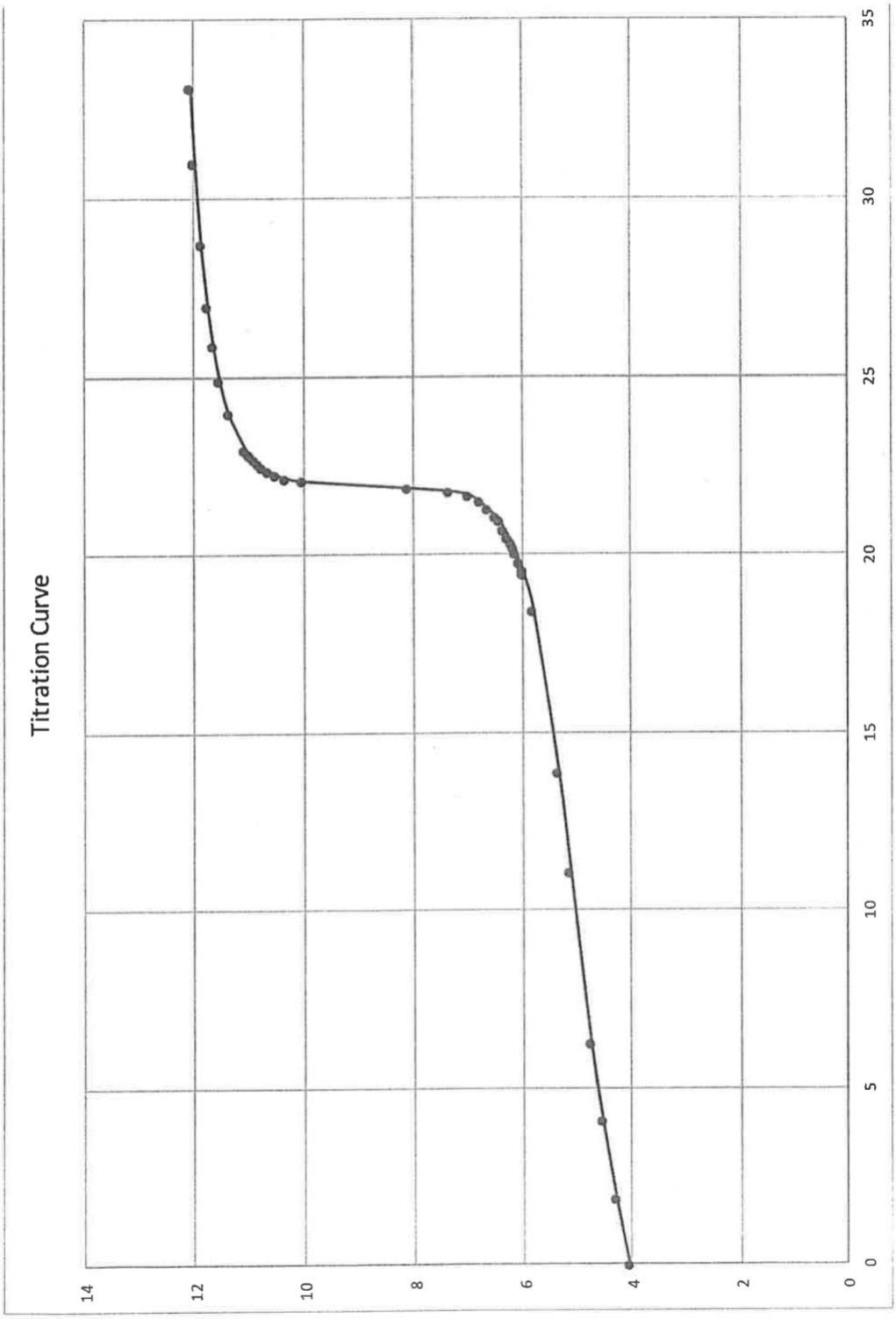

FIG 2

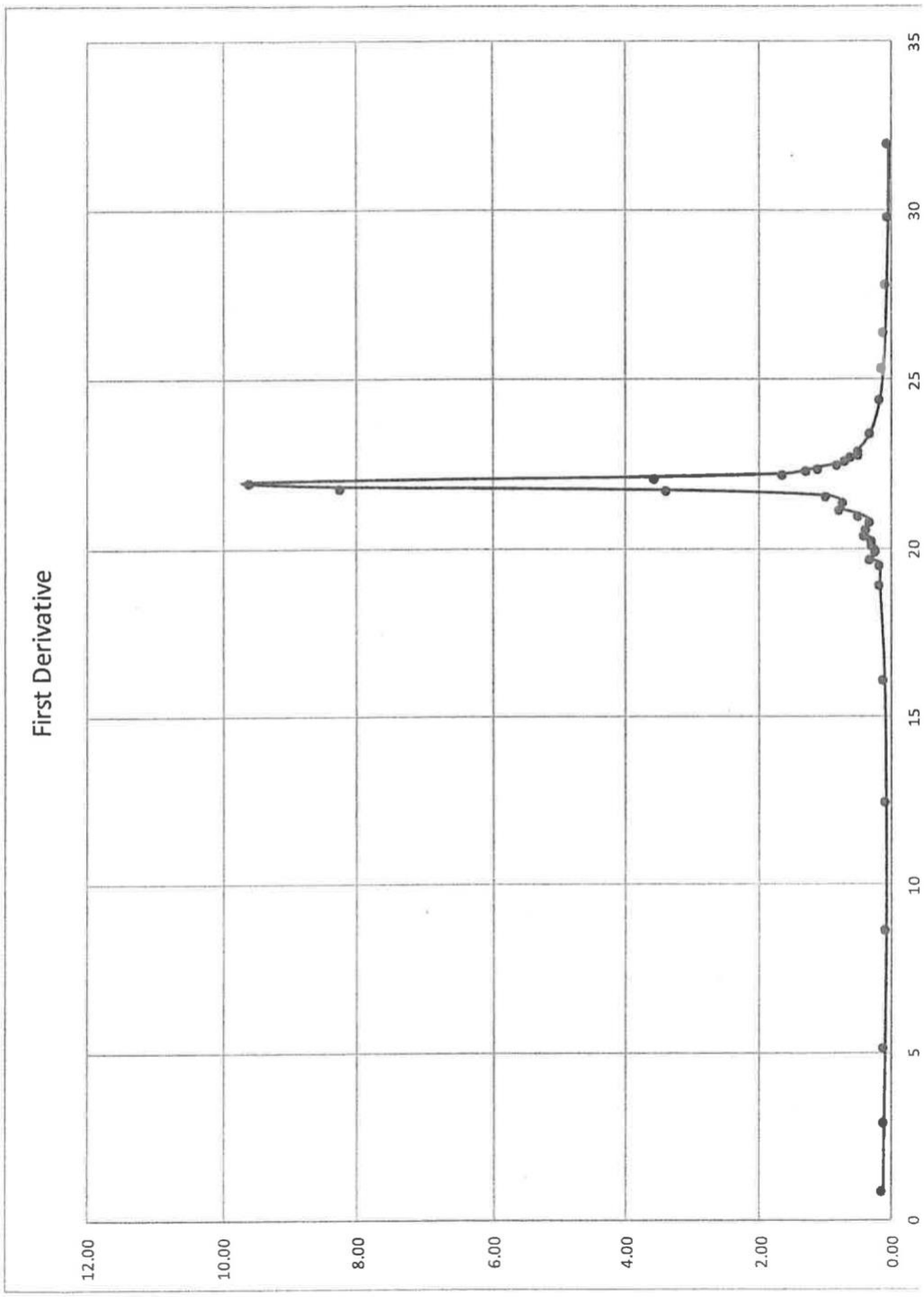
First Derivative
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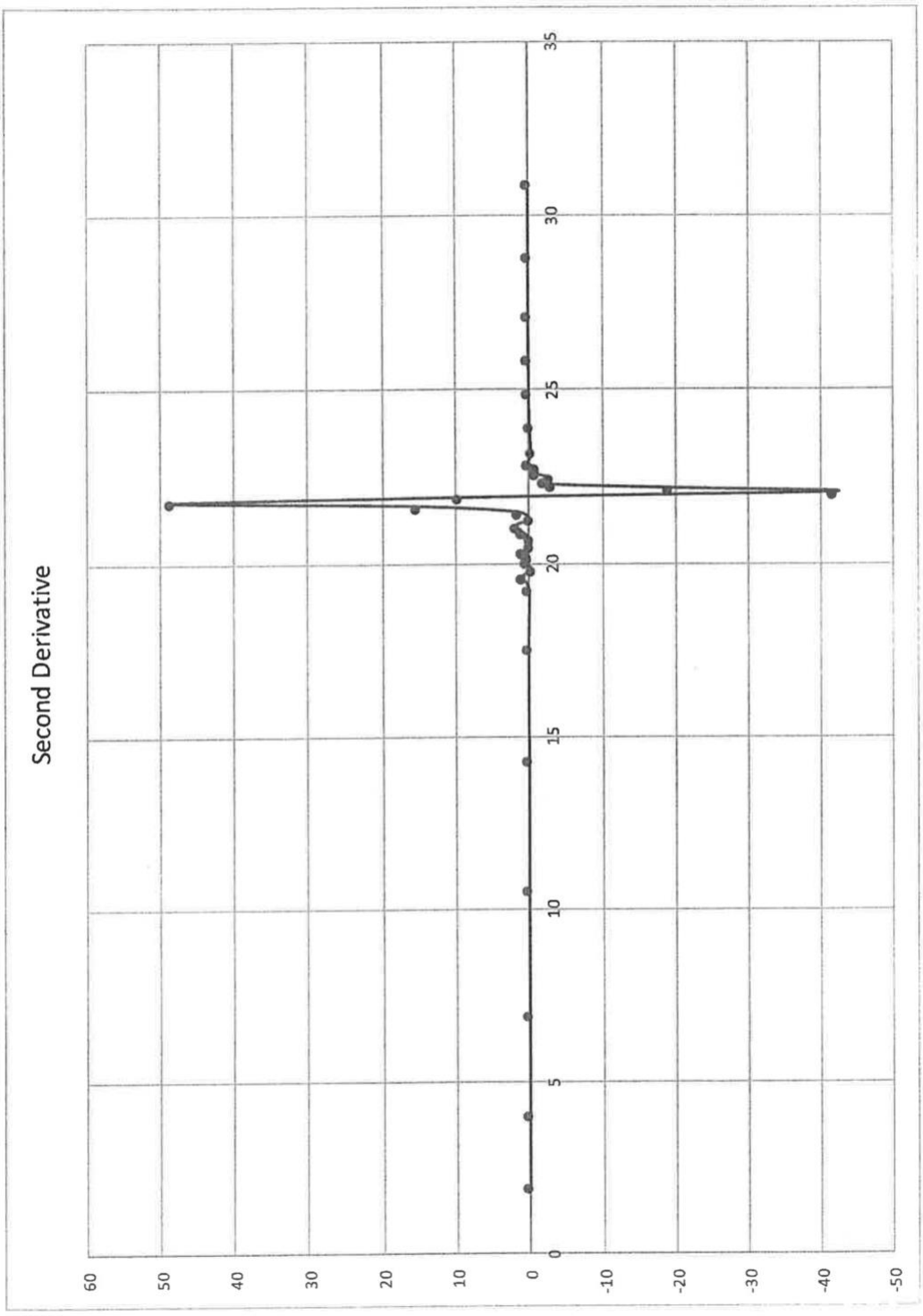
Fig 3


Second Derivative
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