

pH Titration of Maleic Acid

I. Introduction

In this experiment, a solution containing maleic acid, $\text{HO}_2\text{C}(\text{CH})_2\text{CO}_2\text{H}$, will be titrated with standardized NaOH solution. The titration will be monitored by measuring the pH of the solution after each addition of titrant. Analysis of the resulting titration curve will permit calculation of the exact molarity of the maleic acid solution. The first and second acid dissociation equilibrium constants for maleic acid will also be determined.

Maleic acid is a weak diprotic acid that can dissociate stepwise as shown in equations (1) and (2).



As the acid is titrated with strong base, the pH changes in a characteristic way giving rise to a 2-step titration curve. The rate of change of H^+ ion concentration increases until it reaches a maximum rate at the equivalence point.

The first and second equivalence points in this titration can be determined by the use of suitable indicators, or by following the pH of the solution and analyzing the resulting titration curve. The latter approach will be used by employing a pH meter with combination electrode and a graphical method known as a Gran plot. See your text for a discussion of the Gran plot.

II. Procedure

A. Preparation and standardization of 0.1 M NaOH (containing less than 0.001 M Na_2CO_3)

1. Weigh out approximately 3 g of reagent grade NaOH pellets in a 50-mL beaker. Add approximately 10 mL of deionized water and gently swirl for three seconds to dissolve the surface material containing Na_2CO_3 . Immediately decant the liquid from the beaker. Transfer the remaining NaOH pellets to a 250-mL Erlenmeyer flask and add about 100 mL of deionized water. Swirl until dissolved. Transfer the solution to a plastic bottle and add deionized water to make approximately 500 mL of solution. Cover the opening of the bottle with plastic film and tightly seal with a cap.

2. Standardization of 0.1 M NaOH

Weigh out approximately 2.5 g of potassium hydrogen phthalate and dry for 1 hour at 110°C . Store the dried sample in your desiccator. Accurately weigh out 0.4 to 0.45 g (to four significant figures) of dried primary standard potassium hydrogen phthalate (MW=204.22), place in a 250-mL Erlenmeyer flask and dissolve in 25 mL of deionized water. Add three drops of phenolphthalein indicator and titrate with the NaOH solution

to the first indication of a pink color that persists for at least 20 seconds. Calculate the molarity of the NaOH solution. Repeat the titration several times; the RMD should be no more than 2-3 ppt.

B. Calibrate your pH meter according to the directions on the following page.

C. Titration of the Maleic Acid

Transfer (with a Class A pipet) 10.00 mL of the maleic acid solution into a 250-mL beaker. Add 75.0 mL of deionized water, about 0.67 g KCl (establishes ionic strength at 0.1 M), and a small stirring bar. Rinse the combination electrode with deionized water, carefully blot dry and clamp in place in the above solution. Do not allow the electrode to be hit by the stirring bar.

Record the initial pH value and the pH value at various volumes of added NaOH solution. Stir the solution slowly and well after the addition of each volume increment (~1 mL), but read the pH of the solution when the stirrer is off if the pH value indicated on the meter is unstable. When the pH begins to increase rapidly with the addition of titrant near the second equivalence point, decrease the volume increments to 0.10-0.20 mL. Continue the titration to a pH of approximately 11. The titrant volume can be increased to ~1 mL after the pH is above 9.5. Once the pH of the solution is above 7, proceed with the titration as rapidly as possible to minimize absorption of CO₂ from the air. If you wish to calculate K_{a1} and K_{a2} by the rigorous method (Appendix C), then any rinse water volume must be noted and accounted for.

Carry out three additional titrations.

III. Calculations

A. Plot pH versus milliliters of NaOH added for each complete titration.

B. For the second equivalence point of each titration, prepare a Gran plot (a graph of $V_b \cdot 10^{-\text{pH}}$ versus V_b) using data collected between $0.9V_e$ and V_e . Fit the linear portion of this curve with a linear least-squares line and extrapolate it to the abscissa to find the equivalence point volume (V_e). Use the buret-corrected equivalence point volume to calculate the exact molarity of the maleic acid solution.

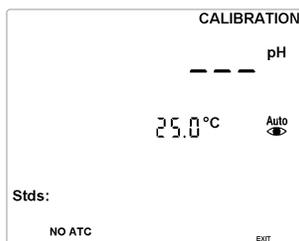
C. Estimate K_{a1} and K_{a2} for maleic acid by noting that $\text{pK}_{a1} \approx \text{pH}$ at the half-way point to the first equivalence point and $\text{pK}_{a2} \approx \text{pH}$ at the point halfway between the first and second equivalence points. See Appendix C for a rigorous calculation of K_{a1} and K_{a2}. Compare your values to literature values for a comparable ionic strength.

IV. Results

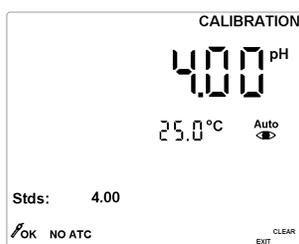
Report the mean molarity of your maleic acid solution and RMD, and your average K_{a1} and K_{a2} values.

Beckman 300 Series pH Meter Operating Instructions

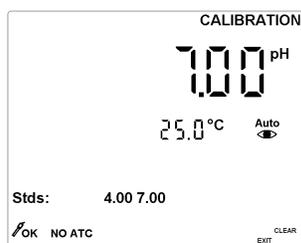
1. Press  to turn on the pH meter. Make sure you are in the pH mode, indicated by the pH icon to the right of the large numeric display. To enter pH mode press  until the pH icon appears.
2. Remove the Parafilm covering the reference junction of the electrode and rinse the electrode with deionized water. Blot excess.
3. Immerse the electrode in pH 4.00 standard buffer solution. The solution must reach at least the level of the white line on the electrode. Gently agitate for one minute. Check for air bubbles trapped on electrode bulb.



4. Press  to enter calibration mode. Press  two times to remove any existing calibration.



5. Press . When the  icon (located below large numeric display) stops flashing, the numeric display will show a pH of 4.00. The buffer value also appears in the lower left part of the display.
6. Remove the electrode from solution and rinse with deionized water. Blot excess.
7. Immerse the electrode in pH 7.00 standard buffer solution. The solution must reach at least the level of the white line on the electrode. Gently agitate for one minute. Check for air bubbles trapped on electrode bulb.
8. Press . When the  icon stops flashing, the numeric display will show a pH of 7.00. The buffer value also appears in the lower left part of the display.



9. Remove the electrode from solution and rinse with deionized water. Blot excess.
10. Immerse the electrode in pH 10.01 standard buffer solution. The solution must reach at least the level of the white line on the electrode. Gently agitate for one minute. Check for air bubbles trapped on electrode bulb.
11. Press . When the  icon stops flashing, the numeric display will show a pH of 10.01. The buffer value also appears in the lower left part of the display.
12. Press  to exit calibration mode. The  icon shown on the left of the display indicates a successful calibration.
13. Remove the electrode from solution and rinse with deionized water. Blot excess.
14. Press  **twice**, remove the electrode from solution and rinse the electrode with deionized water. Blot excess.
15. Immerse the electrode in sample. The solution must reach at least the level of the white line on the electrode. Gently agitate for one minute. Check for air bubbles trapped on electrode bulb.
16. Press . When the  icon stops flashing, the numeric display will show the pH of the solution. Measurement is now complete.
17. Repeat steps 13-15 for additional samples.
18. NOTE: If continuous pH monitoring is desired (as with a titration), press  to turn off the Auto Read function.
19. After the last pH measurement, press  **twice**, rinse the electrode thoroughly with deionized water and press  to turn off pH meter.
20. Wrap electrode with Parafilm as shown.

