

## 010 exercise

# Acidity and Acid Content of Beverages

SUSB-010

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## purpose

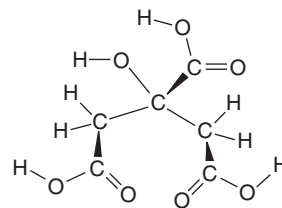
To determine the total acid content of various beverages, including fruit juices and soft drinks, by titration. To measure the pH using a pH meter.

## concepts

concentration units • available acid • acid strength • strong acid • weak acid • pH • monoprotic • polyprotic • equilibrium constant • acid ionization constant • indicator end point • standard solution

## [Background Information]

Most fruits contain water to the extent of 80% or more. Their solid and water soluble constituents are primarily carbohydrates. The end products of the metabolism of carbohydrates by most living organisms are carbon dioxide and water. The precursors to this final step are organic acids—usually of low molar mass. (The combination of atoms that characterizes an organic acid is the grouping  $-\text{COOH}$ .) A metabolic product in many plants is the six carbon acid, citric acid whose empirical formula is  $\text{C}_6\text{H}_8\text{O}_7$  and whose structure is shown below.



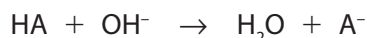
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All acids have a sour taste. They are used in conjunction with other flavorings to provide and control flavors in beverages such as carbonated drinks. Cola-type soft drinks are acidic partly due to the presence of phosphoric acid. Some acids, such as ascorbic acid (Vitamin C), and benzoic acid are used as preservatives as well. Carbonated drinks also have dissolved carbon dioxide which, in aqueous solution, behaves as an acid.

In this exercise, you will measure two characteristics of acids in beverages:

1. total amount of **available acid** (in the form of *replaceable* hydrogen ion,  $H^+$ ), determined by titration with base of known concentration, and
2. **acid strength**, in the form of *dissociated*  $H^+$  by determining the pH of the beverage using a pH meter.

The fundamental reaction for the determination of total available acid content is neutralization:



regardless of the source of the hydrogen ion. While we have written the acid as monoprotic, i.e., having one available hydrogen, some acids are polyprotic (have more than one available hydrogen); e.g., a molecule of citric acid contains three COOH groups, each of which will react with hydroxide ions, while malic acid (another acid common in fruits) has two COOH groups. For our current purposes, the number of COOH groups per molecule is irrelevant. We will neutralize the acid in such a way that virtually all of its acidic hydrogens react, measuring, therefore, the **total concentration of all of the acidic, -COOH, groups** in the solution.

Another characteristic of acids in aqueous solutions is their **strength**. Chemists measure the strength of aqueous acids by the extent to which the available  $H^+$  is actually present as the free ion. For example, 1 liter of a 1 M (moles/L = Molarity, designated M) solution of the **strong** acid, hydrochloric acid, has **1 mole of available  $H^+$** . [While we write  $H^+$ , remember that the hydrogen ion is actually present as the solvated ion, sometimes written as  $H_3O^+$ .] The concentration of hydrogen ion is 1 M. 1 liter of a 1 M solution of the **weak** acid, acetic acid, also has **1 mole of available  $H^+$** . How much of the  $H^+$  is actually present as the solvated ion? Direct measurement shows only  $4.3 \times 10^{-3}$  moles of  $H^+$  per liter. Equal amounts of both acids will require the same amount of base to neutralize them, but their amount of free hydrogen ion are very different.

## Acid Strength and Acid Ionization Constants

The strength of any acid, HA, is measured quantitatively by its **acid ionization constant**,  $K_a$ .  $K_a$  is the **equilibrium constant** for the reaction  $HA \leftrightarrow H^+ + A^-$ :

$$K_a = [H^+][A^-] / [HA]$$

where  $[H^+]$ , etc., denotes the concentration of the species in the bracket in moles/liter.

Strong acids have very large  $K_a$ 's ( $K_a \sim 1$  or greater). Weak acids have small  $K_a$ 's. Acetic acid, for example, has  $K_a = 1.8 \times 10^{-5}$ . The  $K_a$ 's for the consecutive removal of the three acidic hydrogens of citric acid are  $7.1 \times 10^{-4}$ ,  $1.7 \times 10^{-5}$  and  $4.1 \times 10^{-7}$  respectively.

## Definition of pH

Because  $H^+$  concentrations of aqueous solutions vary over a wide range (e.g., in 1 M HCl,  $[H^+] = 1.0$  M while in 1 M NaOH,  $[H^+] = 1.0 \times 10^{-14}$  M), it is convenient to introduce a special way to represent this concentration. When a quantity varies over a wide range of powers of 10, scientists often use a logarithmic scale to represent the quantity. In a logarithmic scale (using base 10), a change of 1 unit represents a difference in one order of magnitude (one power of 10) in the actual quantity. For hydrogen ion concentration, the scale is called pH.

$$\text{pH} = -\log_{10} [H^+] \text{ or, inversely, } [H^+] = 10^{-\text{pH}}$$

A solution with  $[H^+] = 1.0 \times 10^{-4}$  M has a pH of 4, and, in a solution with a pH of 3,  $[H^+] = 1.0 \times 10^{-3}$  M. What about a solution with a pH of 3.7? Expressing the concentration as  $10^{-3.7}$  is mathematically correct but, convention requires the conversion to a number in which the exponent is an integer. Modern day calculators are programmed to perform the conversion of an expression in the form  $10^x$  to its scientific notation equivalent ( $y \times 10^{-n}$ , where  $n$  is an integer). You should know how to perform such a conversion. A pre-lab question addresses this issue.

## The Indicator End Point

In this exercise, the total acid concentration is determined by titration with a standard NaOH solution. The **end point** of any titration is determined by a signal indicating that a desired condition has been attained. The signal in this titration is the change in color of the acid-base indicator, phenolphthalein. Phenolphthalein is colorless in acidic and neutral solutions ( $\text{pH} = 7$ ) and turns pink in solutions with pH of 9 or more.

This suggests two special considerations in the exercise:

1. The end point of the titration occurs when the pH of the solution reaches 9, i.e., when  $[H^+] = 1.0 \times 10^{-9}$  M. Will that pH correspond to the neutralization of all of the acid in the beverage? Consider a very weak acid with a  $K_a$  of  $1.0 \times 10^{-10}$ , i.e.,

$$\frac{[H^+][A^-]}{[HA]} = 1.0 \times 10^{-10}$$

When  $[H^+] = 1.0 \times 10^{-9}$  M (corresponding to  $\text{pH} = 9$ )

$$\frac{1.0 \times 10^{-9}[A^-]}{[HA]} = 1.0 \times 10^{-10} \quad \text{or} \quad \frac{[A^-]}{[HA]} = 0.1 = \frac{1}{10}$$

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i.e., approximately nine-tenths (actually 10/11ths = 91%) of the acid is still in the undissociated form. Has sodium hydroxide neutralized all of this acid? No.

Because of our choice of indicator, our measurement of total acid is limited to those acids with a  $K_a$  of  $10^{-8}$  or less (see Problem 4). Fortunately this includes most of the acids commonly found in fruit juices or soft drinks.

Phenolphthalein changes from colorless to *light pink* when the solution turns basic. **Many natural or added colors in beverages will obscure the color change. This should be kept in mind in choosing the type of beverage to be studied!**

The color change indicates the completion of the neutralization with some precision. At the beginning of the titration, the addition of base causes a small change in the pH of the solution as the weak acid increases its extent of dissociation. Near the end point, the weak acid is almost completely dissociated so that the addition of a small amount of base suddenly causes the pH to change from a solution which is characteristically acidic (i.e., below pH 7) to one which is basic. (The pH of a 0.1 M NaOH solution is 13.)

### Standard Solutions and Concentration Units

This exercise makes use of a standard, approximately 0.1 M, sodium hydroxide solution. Its concentration has been determined by titration with a primary standard and is indicated (with appropriate precision) in moles/L (or, equivalently, mmoles/mL) on the containers from which you obtain the base.

You are asked to report the concentration of total acid in the beverage in the same units (moles/L or, the equivalent, mmoles/mL). The computation is as follows. Suppose the concentration of the standard sodium hydroxide is 0.113 M and 28.85 mL of that solution is required to titrate 20.0 mL of the beverage to the phenolphthalein endpoint.

The number of mmoles of sodium hydroxide used is:

$$0.113 \text{ mmoles NaOH/mL} \times 28.85 \text{ mL} = 3.26 \text{ mmoles NaOH}$$

Since one mole of sodium hydroxide neutralizes one mole of available  $H^+$ , the number of mmoles of  $H^+$  neutralized must also be 3.26. That number of mmoles was in a beverage sample with a volume of 20.0 mL (or .0200 L). Therefore, the concentration of available  $H^+$  in the beverage sample is

$$3.26 \text{ mmoles}/20.0 \text{ mL} = [0.00326 \text{ moles}/0.0200 \text{ L} = ] 0.163 \text{ mmoles/mL} = 0.163 \text{ M.}$$

Suppose that the same, untitrated, beverage shows a measured pH of 3.70, i.e.,  $[H^+] = 2.0 \times 10^{-4} \text{ M}$ . If the acidity were all due to a single acid, HA, having one acidic hydrogen, we would have the following:



from which we can calculate, for that acid,

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{2.0 \times 10^{-4} \times 2.0 \times 10^{-4}}{0.163} = 2.4 \times 10^{-7}$$

a very weak, but still titratable acid. (Note that, within the specified precision, we can neglect the  $2.0 \times 10^{-4}$  compared to 0.163 in the concentration of HA in this calculation.)

## procedure

The procedure in this exercise depends to some extent on the type of beverage. Special procedures are indicated as required.

### CAUTION

Sodium hydroxide solutions are highly corrosive toward flesh and clothing, and must be handled with care. Safety goggles must be worn at all times in the laboratory. Any spills of sodium hydroxide solution must be cleaned up immediately and completely.

## Fruit juices

### 1. SAMPLE AND BURET PREPARATION

Record all of the relevant information regarding the beverage (type, brand, ingredients, etc.) in your laboratory notebook. Obtain 200 mL of standard sodium hydroxide solution in a clean, dry (why must it be dry?) 400 mL beaker. Cover the beaker with a watch glass and record the concentration of the solution in your notebook. Obtain one of your *assigned* burets and rinse the buret using three or four small (~3 – 5 mL) samples of the sodium hydroxide solution. Make sure that the buret tip has no trapped bubbles. Fill the buret and establish and record its initial reading (0.00 is not acceptable). Remember to record the identification number of the buret.

Throughout this exercise, we use a graduated cylinder to measure the volume of beverage that we titrate. In each instance, the cylinder must be read to its maximum precision (1/5th of the smallest division) and the volume recorded to that precision. E.g., if the smallest division on the cylinder is 1 mL, the volume of a liquid can be read to the nearest 0.2 mL (e.g., 20.4 mL). For a 20 mL sample, this constitutes a precision of  $100 \times 0.2 / 20 = 1\%$ .

Our objective will be to use **not less than** 20 mL of the sodium hydroxide solution. Since the concentration of acids in beverages varies widely, we must make a preliminary determination of how much juice is required to consume 20 mL of the base.

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## 2. PRELIMINARY TITRATION

Measure a 20.0 mL sample of the juice using a 100 mL graduated cylinder. Transfer the 20.0 mL sample into a clean 250 mL Erlenmeyer flask and rinse out the cylinder with your wash bottle (water) to insure complete transfer. Dilute with 20–30 mL of water to help to see the equivalence point. (Does adding the water change the amount of available acid?) The water is added to decrease the intensity of any intrinsic color of the juice and facilitate the observation of the end point.

Add 3–5 drops of phenolphthalein indicator to the juice sample. Titrate the sample slowly until the color change indicates that the titration has reached its end point. Carefully observe the color of the end point. If the color change cannot be detected, consider using a different type of juice. Record the final buret reading and compute the total volume of sodium hydroxide used (final buret reading—initial buret reading).

If the volume of sodium hydroxide required was between 20 and 40 mL, the 20 mL volume of juice will be used in the subsequent titrations. If the volume was between 10 mL and 20 mL, the volume of juice used in the subsequent titrations should be doubled to 40 mL. If the volume was greater than 40, the volume of juice used in future titrations should be halved to 10 mL. If the volume used was less than 10 mL or more than 40 mL, you should calculate the volume required to consume between 20 and 30 mL of the sodium hydroxide solution. (Round this value to the nearest multiple of 5 mL for purposes of Part 4.) You should also insure that you have enough of your beverage to be able to do the required number of titrations.

## 3. pH MEASUREMENT

(This part of the exercise can be done at any time during the laboratory period.)

Place ~20 mL of **undiluted** juice in a 50 mL beaker. (Unlike the total acid in the juice, its pH **will** depend on any added water.) Take the sample of juice to a pH meter and measure and record the value of the pH of the solution as instructed and with the appropriate precision. From the measured pH, calculate the free hydrogen ion concentration,  $[H^+] (= 10^{-pH})$ .

## 4. FINAL TITRATIONS

Transfer an appropriate amount of juice as determined in Part 2 into a clean 250 mL Erlenmeyer flask, using a 100 mL graduated cylinder. Be sure to record the volume transferred to the appropriate number of significant figures. Dilute the sample by adding an appropriate volume of water (how much will depend on the intensity of color of the beverage), add the phenolphthalein indicator and titrate the sample, recording all of the appropriate buret volume readings to the appropriate precision (0.02 mL).

Repeat the titration two more times. Compute the total acid concentration of your juice in each case, the average concentration, the average deviation of the concentration and the percent deviation. If the percent deviation is more than 3%, you should repeat the titration a fourth time. You may report the data for any three runs which produce a percent deviation less than 3%. Record all titration data in your notebook,

but **do not enter the data on the data sheet until you have decided which you wish to report**. Your grade will be reduced if you cross out any data on your data sheet. If you have done more than 3 titrations and cannot decide which ones to report, attach a supplementary sheet with your additional data.

You should also calculate an effective acid ionization constant for the juice (assuming the acid is a general monoprotic acid HX). For example, if the average concentration of total acid was 0.239 M and the pH before titration was 2.70, then

$$[\text{H}^+] = [\text{X}^-] = 10^{-2.70} = 2.0 \times 10^{-3} \text{ M.}$$

$$[\text{HX}] = 0.239 - 2.0 \times 10^{-3} = 0.237 \text{ M}$$

$$K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]} = \frac{2.0 \times 10^{-3} \times 2.0 \times 10^{-3}}{0.237} = 1.7 \times 10^{-5}$$

Note that, to the indicated precision of the total acid, we cannot neglect  $2.0 \times 10^{-3}$  compared to 0.239, but since our concentration is known to only two significant figures, our final answer will still not be affected by ignoring it.

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**[Data Sheet]**

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Notebook Grade: \_\_\_\_\_

Safety Grade: \_\_\_\_\_

Name \_\_\_\_\_

Date \_\_\_\_\_

Course/Section \_\_\_\_\_

Characterization of beverage: \_\_\_\_\_

## 1. Trial run

a. Molarity of NaOH solution \_\_\_\_\_ M

b. Volume of beverage used \_\_\_\_\_ mL

c. Final volume of NaOH \_\_\_\_\_ mL

d. Initial volume \_\_\_\_\_ mL

e. Volume NaOH delivered (c-d) \_\_\_\_\_ mL

## 2. Based on the trial run, calculate what volume of your beverage you should titrate to insure that you use 25 mL of the NaOH solution.

Calculated volume of beverage \_\_\_\_\_ mL

(Round this value to the nearest multiple of 5 mL for purposes of Part 4)

*(over)*

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3. pH and dissociated acid concentration

f. pH of *undiluted* beverage \_\_\_\_\_g.  $[H^+]$  of beverage from pH ( $10^{-pH}$ ) \_\_\_\_\_ M

4. Final Titrations

**Run 1****Run 2****Run 3**

h. Volume of beverage used \_\_\_\_\_ mL \_\_\_\_\_ mL \_\_\_\_\_ mL

i. Final buret reading \_\_\_\_\_ mL \_\_\_\_\_ mL \_\_\_\_\_ mL

j. Initial buret reading \_\_\_\_\_ mL \_\_\_\_\_ mL \_\_\_\_\_ mL

k. Volume NaOH delivered (i-j) \_\_\_\_\_ mL \_\_\_\_\_ mL \_\_\_\_\_ mL

l. Mmoles of NaOH used ( $k \cdot a$ ) \_\_\_\_\_ mmol \_\_\_\_\_ mmol \_\_\_\_\_ mmol

m. Total mmoles of acid in beverage (l) \_\_\_\_\_ mmol \_\_\_\_\_ mmol \_\_\_\_\_ mmol

n. Conc. of acid in beverage (m/h) \_\_\_\_\_ M \_\_\_\_\_ M \_\_\_\_\_ M

o. Average concentration of acid [HA] \_\_\_\_\_ M

p. Average deviation of acid concentration \_\_\_\_\_ M

q. % Deviation \_\_\_\_\_ %

r. Apparent  $K_a$  of acid in beverage,  $[H^+]^2/[HA]$  \_\_\_\_\_

# [Pre-laboratory Questions]

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Name

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Date

Course/Section

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1. Propionic acid,  $\text{CH}_3\text{CH}_2\text{COOH}$ , has a  $K_a$  of  $1.6 \times 10^{-6}$ . What is the pH of a solution containing 0.5 M  $\text{CH}_3\text{CH}_2\text{COOH}$  (undissociated) and 0.5 M  $\text{CH}_3\text{CH}_2\text{COO}^-$  (propionate ion)?

[Such a solution can be made by adding sodium propionate to a solution of propionic acid.]

2. What is  $[\text{H}^+]$  in a solution whose pH is 2.5 (in normal scientific notation)? What is the pH of a solution with  $[\text{H}^+] = 2.5 \times 10^{-2}$ ?

3. A student titrates 50.0 mL of apple juice and reports the following in the titration to the phenolphthalein end point with 0.1011 M NaOH.

Final buret reading: 17.86 mL

Initial buret reading: 1.XX mL (where XX is the last two digits of your student ID)

- a. What is the concentration of the total available acid in moles/L of the apple juice?

(over)

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- b. Assuming a drop is 0.05 mL, what will be the percentage error introduced into the result if the final buret reading is two drops past the actual endpoint?
  - c. What is the percentage error in the result if the true volume of the juice titrated was actually 51.0 mL?
  - d. If the measured pH of the pure apple juice is 4.0, what is the apparent  $K_a$  of the acid?
4. By analogy with the calculation of the ratio of concentrations of dissociated and undissociated acid of  $pK_a = 10$  when the pH is 9 in the **Indicator End Point Section** of the exercise, what is the ratio of dissociated to undissociated acid for an acid with  $pK_a = 8$  at the same pH? What would it be at a pH of 11?
5. Why does adding water to dilute the juice not change the available acid in the juice? Would it be likely to change the measured pH? Why or why not?