1

Acids, Bases, and Buffers

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1.1 Learning Outcomes

After completing this exercise, students will be able to:

1) Explain the roles of acids and bases in food products.
2) Measure the pH of selected food products.
3) Prepare and evaluate a buffer system.
4) Measure the buffering capacity of a common beverage.

1.2 Introduction

Many food components may be classified as acids or bases due to their capacity to donate or accept protons (hydrogen ions). These components perform numerous important functions including flavor enhancement, control of microbial growth, inhibition of browning, alteration of texture, prevention of lipid oxidation, and pH control.

Acids and bases are key metabolites in living plant and animal organisms, for example as intermediates in the TCA cycle, and are mostly retained when the plant is harvested or the animal is slaughtered so they are naturally present in foods. They may also be added during processing or synthesized during fermentation to produce desired characteristics in the final food product.

The concentration and relative proportion of acids and bases determine the pH of a food, an extremely important characteristic. pH can affect the flavor, color, texture, stability, and behavior in food processing situations. For example, commercial sterilization of acid foods (pH less than 4.6) [1] can be achieved under milder processing conditions than in foods with a higher pH.

1.2.1 Acids

Acids serve a variety of functions in foods including flavor enhancement, control of microbial growth, protein coagulation, emulsification, control of browning, buffering action, and metal chelation (to control lipid oxidation). All acids have a sour taste but different acids produce

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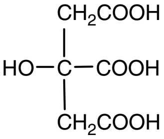
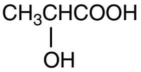
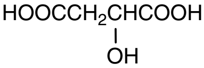
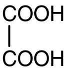
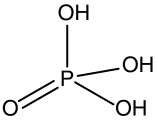
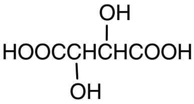
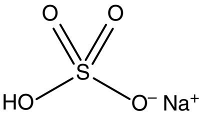
Table 1.1 Acids common in foods: structures and pK_a values.

Substance	**Structure**	**pK_a**	**Food found in**
Acetic acid	CH_3COOH	$pK = 4.75$	Vinegar, figs
Adipic acid	$HOOC(CH_2)_4COOH$	$pK_1 = 4.43$ $pK_2 = 5.62$	Beets
Butyric acid	$CH_3(CH_2)_2COOH$	$pK = 4.82$	Cheese, butter
Citric acid	 $\begin{array}{c} CH_2COOH \\ \mid \\ HO-C-COOH \\ \mid \\ CH_2COOH \end{array}$	$pK_1 = 3.06$ $pK_2 = 4.74$ $pK_3 = 5.40$	Oranges, lemons, apricots, tomatoes
Lactic acid	 $CH_3\underset{\substack{\mid \\ OH}}{CH}COOH$	$pK = 3.83$	Yogurt, buttermilk, cheese, beer
Malic acid	 $HOOCCH_2\underset{\substack{\mid \\ OH}}{CH}COOH$	$pK_1 = 3.40$ $pK_2 = 5.05$	Apples, apricots, grapes, oranges, tomatoes
Oxalic acid	 $\begin{array}{l} COOH \\ \mid \\ COOH \end{array}$	$pK_1 = 1.27$ $pK_2 = 4.27$	Spinach, potatoes, tomatoes
Phosphoric acid		$pK_1 = 2.12$ $pK_2 = 7.21$ $pK_3 = 12.32$	Tomatoes, acidulant used in soft drinks
Tartaric acid	 $HOOC\underset{\substack{\mid \\ OH}}{CH}\overset{\substack{OH \\ \mid}}{CH}COOH$	$pK_1 = 2.98$ $pK_2 = 4.34$	Grapes
Sodium hydrogen sulfate or sodium acid sulfate		$pK = 1.99$	Acidulant. Lowers pH without imparting acid taste. May be added to process water to enhance chlorine activity

distinctively different sour flavors. Thus, it is not enough to simply add any acid when attempting to produce a characteristic sour flavor in a food. Table 1.1 gives structures and pK values of some common food acids.

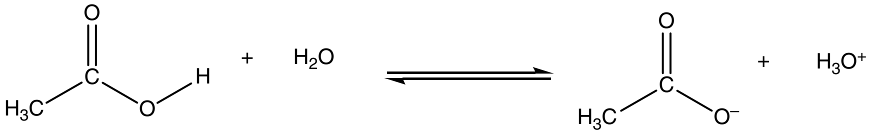
1.2.1.1 Food Acidulants

In the food industry, food additives that have acidic properties are commonly known as food acidulants. There are many approved food acidulants, but only a few are in wide use. They include organic acids like acetic acid, citric acid, fumaric acid, lactic acid, malic acid, and tartaric acid as well as the mineral acids phosphoric acid and sodium hydrogen sulfate. (See [2] for guidance in selecting food acidulants.)

1.2.1.2 Reactions of Food Acids

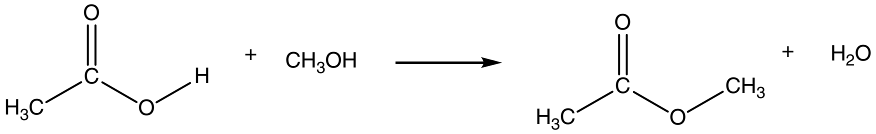
Most naturally occurring food acids are carboxylic acids. Carboxylic acids are weak acids compared with mineral acids such as HCl and H_2SO_4. Important reactions of carboxylic acids include the following:

Ionization:



Acetic acid Acetate ion

Reaction with alcohols to form esters:



Acetic acid Methanol Methyl acetate

1.2.2 Bases

Bases are also common food additives and are added for a variety of purposes. They may be added to modify the flavor, color, and texture, enhance browning, induce chemical peeling, and produce CO_2. Examples of bases used as food additives include dilute NaOH (to induce chemical peeling in fruits and vegetables, enhance browning, de-bitter olives, solubilize proteins), phosphate salts (to prevent protein coagulation in evaporated and condensed milks, produce a smooth texture in processed cheese), and $NaHCO_3$ (to give chocolate a darker color, produce CO_2 in leavening systems).

1.2.3 Buffers

Buffers stabilize the pH in foods. They are also used to neutralize foods which are too acidic. By using the salt of the acid already present, acidity is reduced without adding neutralization flavors. Many buffers are present naturally in foods. Animal products are usually buffered by amino acids, proteins, and phosphate salts. In plants, organic acids (such as citric, malic, oxalic, and tartaric) in conjunction with phosphate salts are the primary buffers. Table 1.2 shows the pHs of some common foods. Notice that most foods are buffered in the acidic range ($pH < 7$).

See Appendix III or your chemistry and biochemistry textbooks for a review of acid and base chemistry.

1.3 Apparatus and Instruments

1) pH meter equipped with a pH electrode
2) Analytical balance
3) Household blender
4) Centrifuge
5) Centrifuge tubes

Table 1.2 Approximate pH values for some common foods[a].

Food	pH	Food	pH
Lime juice	2.0	Yogurt	4.0–4.5
Lemon juice	2.2	Cheddar cheese	5.1–5.5
Vinegar	2.6	Beef, fresh	5.5–5.0
Rhubarb	3.0	Pork, fresh	5.6–6.9
Grape juice	3.1–3.2	Turkey, fresh	5.7–6.1
Wines	2.9–3.9	Tuna	6.0
Apple juice	3.5–3.9	Carrots, fresh	5.7–6.1
Strawberries	3.2–3.4	Potatoes, fresh	6.1
Peaches	3.8	Green beans, fresh	6.5–6.7
Pears	3.9	Milk, fresh	6.6
Grapefruit juice	4.0	Sweet corn, fresh	6.7
Orange juice	4.2	Egg yolk	6.0–6.9
Tomato juice	3.8–4.7	Egg white (pH increases as egg ages)	7.6–9.2

[a] Modified from [3] and [4].

6) Pipette and pipette bulb, 10 ml
7) Volumetric flask, 200 ml
8) Beakers, 150 ml
9) Burette, 25 or 50 ml
10) Burette holder and stand
11) Thermometer
12) Funnel
13) Graduated cylinder, 100 ml
14) Squeeze bottle for deionized water
15) Tissue
16) Weighing paper
17) Spatula
18) Stirring hot plate with stirring bars

1.4 Reagents and Materials

1) Citric acid, monohydrate. MW = 210 g mole^{-1}
2) KOH, 0.5 N
3) HCl, 0.5 N
4) HCl, 0.001 N
5) Sprite® (Coca Cola Company) or comparable lemon-flavored soda
6) Selected vegetables, e.g. fresh and canned tomatoes
7) Calibration buffers, pH 2 and 4

1.5 Procedures

1.5.1 Determining the pH of a Solid Food [5]

1) Cut a fresh tomato into small cubes and blend in a blender until a uniform slurry is formed, measure the temperature of the slurry.
2) Calibrate your pH meter.
3) Measure the pH of the slurry.
4) Centrifuge an aliquot of the slurry for 10 minutes at maximum speed.
5) Measure the pH of the supernatant.
6) Repeat Steps 1 through 5 using canned tomatoes.

1.5.2 Preparation of a Buffer and Determination of Buffer Capacity

1) Calculate the amounts of citric acid monohydrate and 0.5 N KOH required to prepare 200 ml of 0.05 M citrate buffer, pH 3. **Note**: Even though citric acid is a triprotic acid, calculations for this pH range are made using $pK_a = 3.06$.
2) Prepare 200 ml of the buffer.
3) Measure the pH of your buffer. Is it 3.0? If not, can you explain why?
4) Determine the buffer capacity of your buffer in the alkaline direction by titrating a 100 ml aliquot with 0.5 N KOH. Express buffer capacity as the number of moles of OH^- required to increase the pH of 1 l of the buffer by 1 pH unit.
5) Repeat Step 4 using 0.001 N HCl in place of the citrate buffer, i.e. determine the buffer capacity of 0.001 N HCl.
6) Determine the buffer capacity of your buffer and 0.001 N HCl by calculation. Compare your experimental results with your calculated answers. Explain any discrepancies between experimental and calculated values.
7) Determine the buffer capacity of Sprite® in the same way you did for your citrate buffer (Step 4 above).

1.6 Problem Set

1 The K_a for the weak acid HA is 4.0×10^{-6}. What is the pH of a 0.01 M solution of this acid? What is its pK_a?

2 How many grams of acetic acid and sodium acetate are required to prepare 1.0 l of 0.5 M acetate buffer, pH 4.5? The pK_a for acetic acid is 4.75.

3 Explain carefully how to prepare 1.0 l of 0.05 M phosphate buffer, pH 7.0 from $NaH_2PO_4 \cdot H_2O$ and 1.0 N NaOH or 1.0 N HCl. The molecular weight of sodium phosphate monohydrate monobasic is 138 g $mole^{-1}$. The pK_{a2} for H_3PO_4 is 7.21. **Hint**: To determine whether you will need to add NaOH or HCl, you need to calculate the pH of a 0.05 M solution of NaH_2PO_4.

4 Preparation of buffers using published tables.

a) Using Tables III.2a, III.2b, and III.2c in Appendix III, describe carefully how you would prepare 1 l of 0.1 M acetate buffer, pH 5.2 and 1 l of 1/15 M phosphate buffer, pH 7.6.

b) Using the Henderson–Hasselbalch equation (shown below), calculate the theoretical pH of these 2 buffers. Explain why the calculated pHs are not exactly the same as the pHs shown in the Appendix table.

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{\left[A^-\right]}{\left[HA\right]}$$

1.7 References

1 FDA (2019). Acidified & low-acid canned foods guidance documents & regulatory information [Internet]. FDA [cited 2020 Mar 5]. http://www.fda.gov/food/guidance-documents-regulatory-information-topic-food-and-dietary-supplements/acidified-low-acid-canned-foods-guidance-documents-regulatory-information (accessed 5 March 2020).
2 Bartek Ingredients, Inc (2020). Self teaching guide for food acidulants - Google search [Internet]. [cited 2020 Mar 5] p. 37. https://www.google.com/search?q=Self+teaching+guide+for+food+acidulants&rlz=1C1EJFC_enUS825US876&oq=Self+teaching+guide+for+food+acidulants&aqs=chrome..69i57j69i60.2887j0j4&sourceid=chrome&ie=UTF-8 (accessed 5 March 2020).
3 USDA ARS (2020). pH of selected foods [Internet]. [cited 2020 Mar 5]. https://pmp.errc.ars.usda.gov/phOfSelectedFoods.aspx (accessed 5 March 2020).
4 Bennion, M. (1980). *The Science of Food*. San Francisco: Harper & Row. 598 p.
5 AOAC Official Method 981.12 (1982). *pH of Acidified Foods*. AOAC International.

1.8 Suggested Reading

Lindsay, R.C. (2017). Food additives. In: *Fennema's Food Chemistry*, 5e (eds. S. Damodaran and K.L. Parkin), 803–864. Boca Raton: CRC Press, Taylor & Francis Group.

Segel, I.H. (1976). *Biochemical Calculations: How to Solve Mathematical Problems in General Biochemistry*, 2e. New York: Wiley. 441 p.

Answers to Problem Set

1 pH = 3.7; pK_a = 5.4.
2 14.68 g sodium acetate; 19.26 g acetic acid.
3 Use NaOH to adjust pH; dissolve 6 g NaH_2PO_4 (or 6.9 g $NaH_2PO_4 \cdot H_2O$) in water (~900 ml); using pH meter, titrate to pH 7.0 with 1.0 N NaOH; transfer to a volumetric flask and dilute to 1 l.
4 a) pH 5.2 acetate buffer: mix 768 ml 0.1 M sodium acetate and 232 ml acetic acid. pH 7.6 phosphate buffer: mix 128 ml 1/15 M KH_2PO_4 and 872 ml 1/15 M Na_2HPO_4.
b) Calculated pHs: Acetate buffer = 5.27; Phosphate buffer = 8.04.