

PROFESSIONAL DEVELOPMENT

AP[®] Chemistry
Acids and Bases

Special Focus

The College Board: Connecting Students to College Success

The College Board is a not-for-profit membership association whose mission is to connect students to college success and opportunity. Founded in 1900, the association is composed of more than 5,400 schools, colleges, universities, and other educational organizations. Each year, the College Board serves seven million students and their parents, 23,000 high schools, and 3,500 colleges through major programs and services in college admissions, guidance, assessment, financial aid, enrollment, and teaching and learning. Among its best-known programs are the SAT[®], the PSAT/NMSQT[®], and the Advanced Placement Program[®] (AP[®]). The College Board is committed to the principles of excellence and equity, and that commitment is embodied in all of its programs, services, activities, and concerns.

For further information, visit www.collegeboard.com.

The College Board acknowledges all the third-party content that has been included in these materials and respects the intellectual property rights of others. If we have incorrectly attributed a source or overlooked a publisher, please contact us.

Page 13, 18, 22, 23: Chemistry: Matter and its Changes, 4th edition, by James Brady and Fred Senese, Copyright (c) 2003 by John Wiley & Sons, Inc. Reprinted with permission of John Wiley & Sons, Inc.

Page 14, 15, 17: HILL/PETRUCCI/MCCREARY/PERRY, GENERAL CHEMISTRY, 4th edition, © 2005. Electronically reproduced by permission of Pearson Education, Inc., Upper Saddle River, New Jersey.

Page 18, 19: BROWN, THEODORE E.; LEMAY, EUGENE; BURSTEN, BRUCE E, CHEMISTRY: THE CENTRAL SCIENCE, 10th edition, © 2006. Electronically reproduced by permission of Pearson Education, Inc., Upper Saddle River, New Jersey.

Page 21, 23, 53: Chemistry: The Molecular Nature of Matter and Change, 2nd edition, by Martin S. Silberberg. © 2000 by The McGraw-Hill Companies, Inc. Used by permission.

Page 98: Figure 4.2, page 117 from Shriver & Atkins: Inorganic Chemistry, 4/e by Peter Atkins, et. al. (c) 2006 by D.F. Shriver, P.W. Atkins, T.L. Overton, J.P. Rourke, M.T. Weller, and F.A. Armstrong. Used with permission of W.H. Freeman and Company/Worth Publishers and Oxford University Press.

Page 100, 101: Inorganic Chemistry, by J.R. Bowser. Copyright © 1993 Brooks/Cole. Used by permission of the author.

Page 102: Principles of Descriptive Inorganic Chemistry by Gary Wulfsberg. © 1991 University Science Books. Used by Permission.

Contents

1. Introduction	1
Marian De Wane	
2. <i>Properties of Acids and Bases</i>	3
Arden P. Zipp	
3. <i>Weak Acids and Bases</i>	13
Valerie Ferguson	
4. <i>pH and the Properties of [H⁺] in Aqueous Solution</i>	29
Lew Acampora	
5. <i>Acid–Base Titrations</i>	39
Cheri Smith	
6. <i>Polyprotic Acids</i>	63
Lew Acampora	
7. <i>Salts and Buffers</i>	75
Adele Mouakad	
8. <i>Acidic and Basic Reactions of Oxides</i>	87
Marian DeWane	
9. <i>Misconceptions in Chemistry Demonstrated on AP[®] Chemistry Examinations</i>	91
George E. Miller	
10. <i>Acid–Base Chemistry Beyond AP</i>	97
Arden P. Zipp	
11. <i>Acids–Bases Lesson Plans</i>	105
Heather Hattori	
12. About the Editor	159
13. About the Authors	159

Introduction

Marian De Wane

Centennial High School
Boise, Idaho

In the broad expanse of the AP[®] curriculum, acid–base chemistry is vital. The following material consists of a series of chapters dealing with specific topics relating to acids and bases. Most chapters contain important teaching points and strategies, ideas for laboratory activities, demonstrations, and a sampling of questions and solutions from previous AP Chemistry Examinations. Each author has their own unique style, giving a different perspective on acids and bases. In sections with equilibrium reactions, please note the traditional formatting of arrows is \rightleftharpoons but the \leftrightarrow symbol has also been used in the text. On the AP test, the \leftrightarrow symbol is used. Either symbol is acceptable for scoring purposes.

Each chapter stands alone but in sequence. The first chapter is an introduction to the theories and properties of acids and bases required in the AP curriculum written by Arden Zipp. This is followed by a chapter by Valerie Ferguson on the properties of weak acids and bases and how calculations with them need to be treated differently. Lew Acampora explains the concepts of pH and H⁺, and the calculations required to determine pH. Cheri Smith follows this with acid–base titrations and how to do calculations.

More advanced topics are covered in the remaining chapters. Lew Acampora explains polyprotic acids, Adele Mouakad explains salts and buffering systems, and I provide an explanation of oxides. Even though understanding acids and bases is essential to the mastery of chemistry, students and teachers continue to have many misconceptions regarding the concepts. These misconceptions are addressed in a chapter by George Miller. Arden Zipp has addressed some current new acid–base theories in a chapter called Acid–Base Chemistry Beyond AP. A special lesson planning section by Heather Hattori is included as the ending chapter.

The contributing authors are all experienced AP teachers and university professors with years of experience. Each has attended several AP Readings, some as Table Leaders, Questions Leaders, or Chief Readers. To ensure consistency of content with the current AP Chemistry curriculum, the chapters were reviewed by an exceptional group of advisers, each of whom has served on the AP Chemistry Development Committee at one time or another. A special thank you goes to the head adviser of the project, George Miller, who provided invaluable assistance in the preparation of this document.

I gratefully acknowledge the assistance of each one of the dedicated and talented authors involved in the production of this AP Chemistry resource. It is my sincere hope that new and experienced teachers will find these materials useful for the instruction of AP Chemistry.

The Properties of Acids and Bases

Arden P. Zipp

SUNY Cortland

Cortland, New York

Acids and bases represent two of the most important classes of chemical compounds. Some of the properties of acids (such as their sour taste) and bases (bitterness) have been known to humans for hundreds of years even if their chemical explanations have not. The reactions of these substances are significant in many atmospheric and geological phenomena. In addition, acids and bases control many of the physiological processes in the human body and can catalyze a variety of chemical reactions. This chapter will address some of the fundamental aspects of acids and bases in order to set the stage for subsequent discussions.

In addition to taste, which was mentioned above but *is no longer used in the chemistry lab*, several other properties of acids and bases that can be observed readily are given below. Table 1 shows that they have some properties in common, while they do not share others.

Table 1

Properties of Acids and Bases

Acids			Bases		
1	conduct electricity in solution		1	conduct electricity in solution	
2	react with	product(s) formed	2	react with	product(s) formed
	many metals	H ₂		metal oxide and water	H ₂
	carbonates	CO ₂ , H ₂ O, a salt		metal ions	precipitates
	bicarbonates	CO ₂ , H ₂ O		bicarbonates	CO ₃ ²⁻ , H ₂ O
	a base	H ₂ O, a salt		an acid	H ₂ O, a salt
	dyes	colors, often reddish		dyes	colors, often bluish

Teaching Tip

Students will appreciate these properties more if they are demonstrated by the teacher, or better yet, investigated by students themselves. Inexpensive conductivity meters can be purchased or constructed to investigate the first property on the list while the others can be studied using well plates and solutions dispensed from dropper bottles.

Early History: Arrhenius Theory

Some of the properties in Table 1 were known to alchemists hundreds of years ago, and classification schemes were developed by many noted scientists during the 1600s and 1700s including Robert Boyle, Joseph Black, and Antoine Lavoisier.

However, the beginning of the modern understanding of acids is usually attributed to Svante Arrhenius, who, in his 1884 Ph.D. thesis, explained the electrical conductivity of aqueous solutions in terms of the presence of ions and attributed the unique behavior of acids to H^+ ions. According to Arrhenius, an acid is a substance that, when added to H_2O , increases the $[H^+]$, while a base is a substance that increases the $[OH^-]$.

Many of the reactions in Table 1 can be explained with the Arrhenius acid–base theory by the presence of H^+ or OH^- ions as shown in the equations below:

Acids	Bases
$2H^+ + M \text{ (e.g. Mg)} \rightarrow H_2 + M^{2+}$	$2OH^- + M_2O_3 \text{ (e.g. Al)} + 2H_2O \rightarrow H_2 + 2M(OH)_4^-$
	$xOH^- + M^{x+} \rightarrow M(OH)_x \text{ (s)}$
$2H^+ + CO_3^{2-} \rightarrow H_2O + CO_2$	$OH^- + HCO_3^- \rightarrow H_2O + CO_3^{2-}$
$H^+ + HCO_3^- \rightarrow H_2O + CO_2$	
$H^+ + OH^- \rightarrow H_2O$	$H^+ + OH^- \rightarrow H_2O$

State of H^+ in H_2O .

In the above equations the acid is represented as H^+ , a bare proton. However, it is generally agreed that the charge density of a proton is too large for it to exist in that form in aqueous solutions. Many texts represent protons as hydronium ions, H_3O^+ , as if each proton is bonded to a single H_2O molecule. Current evidence suggests, however, that the actual species has three additional H_2O molecules attached via hydrogen bonds to form $H_9O_4^+$. H^+ will be used in this volume but it should be recognized that the actual species is more complex. Interestingly, the same texts that make a point of using H_3O^+ usually show the hydroxide ion as OH^- even though it also appears to be hydrated, existing in H_2O as $H_7O_4^-$.

Strong and Weak Acids

Arrhenius related the degree of electrical conductivity to the strength of acids, thereby introducing the concept of strong and weak acids. Strong acids are those that ionize completely (or nearly so) in solution, while weak acids ionize only partially, i.e., have solutions that contain significant amounts of the parent acid and lower concentrations of H^+ . In terms of equations, the reaction of a strong acid goes completely to the right, so is written with a simple arrow while that for a weak acid is reversible and is depicted with a double-headed arrow.



Among the standard acids commonly encountered in aqueous solutions, six are strong.

HCl	hydrochloric acid	HNO ₃	nitric acid
HBr	hydrobromic acid	HClO ₄	perchloric acid
HI	hydroiodic acid	H ₂ SO ₄	sulfuric acid

All other acids behave as weak acids in water. Although strong and weak acids produce the same types of reactions, the rates at which these reactions occur vary depending on the concentration of free H^+ ions in solution. It should be noted that in the above table, only the first proton from H_2SO_4 can really be described as "completely ionized," the second proton has a measurable equilibrium constant.

Teaching Tip

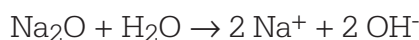
The difference between strong and weak acids can be made more concrete for students by demonstrations (or experiments) in which they compare the behavior of 1.0 M solutions of strong (e.g., HCl) and weak ($HC_2H_3O_2$) acids. Properties of interest include electrical conductivity and the rate of reaction with Mg metal (using a balloon attached to the mouth of a conical flask to capture the evolved H_2). Equal volumes of the weak and strong acids will produce the same volume of H_2 but the rates at which they do so will differ substantially. Reactions with calcium carbonate, capturing the CO_2 , work similarly. Students can measure how much time it takes for a short measured length of Mg ribbon or a measured scoop of calcium carbonate to dissolve completely.

Strong and Weak Bases

There are also six common strong bases that ionize completely in H_2O , though some have limited solubility, which should not be confused with amount of ionization.

LiOH	lithium hydroxide	$\text{Ca}(\text{OH})_2$	calcium hydroxide
NaOH	sodium hydroxide	$\text{Sr}(\text{OH})_2$	strontium hydroxide
KOH	potassium hydroxide	$\text{Ba}(\text{OH})_2$	barium hydroxide

A solution of a strong base in H_2O may be obtained by dissolving the appropriate solid hydroxide but may also be formed by reacting a solid metallic oxide with H_2O . For example, sodium oxide dissolves in H_2O according to the following equation:



Similar reactions to produce strongly basic solutions occur with several other anions but these will not be considered here. There are a variety of compounds that behave as weak bases, although few of these contain OH^- ions. These will be discussed further below.

Concentrations

Water itself is a weak acid, existing in equilibrium with its ions, H^+ and OH^- , as shown in the reversible equation:



where the square brackets, [], represent concentrations in moles per liter. When the above value of K is multiplied by $[\text{H}_2\text{O}]$, (55.5 M), the expression is $K_w = [\text{H}^+][\text{OH}^-]$ with a value of $K_w = 1.0 \times 10^{-14}$ at 25 °C. Using the K_w expression it is possible to calculate $[\text{H}^+]$ for any $[\text{OH}^-]$ and vice versa. In a 1.0 M solution of a strong acid, $[\text{H}^+] = 1.0$, while in a 1.0 M solution of a strong base, $[\text{OH}^-] = 1.0$ and $[\text{H}^+] = 1.0 \times 10^{-14}$. Because of this extremely wide range of $[\text{H}^+]$, an alternative method of comparing $[\text{H}^+]$ concentrations, called the pH scale, has been devised, where pH is defined as $-\log [\text{H}^+]$. Thus, a solution with $[\text{H}^+] = 1.0$ has a pH = 0.00 and one with $[\text{H}^+] = 1.0 \times 10^{-14}$ has a pH = 14.00.

In pure H_2O , $[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7}$ and pH = pOH = 7.00. Acid solutions are those in which $[\text{H}^+] > 1.0 \times 10^{-7}$ or pH < 7.00 while basic (alkaline) solutions have $[\text{OH}^-] > 1.0 \times 10^{-7}$, $[\text{H}^+] < 1.0 \times 10^{-7}$ or pH > 7.00. A more extensive discussion of pH and further calculations are provided in a later chapter.

Teaching Tip

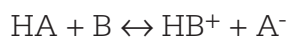
Students typically enjoy determining the pH values of common household materials (with indicator paper or drops of universal indicator). This activity can be useful for AP students if it is coupled with pH calculations and practice in $\text{pH} \leftrightarrow [\text{H}^+]$ or $\text{pOH} \leftrightarrow [\text{OH}^-]$ conversions.

Formation of Acidic or Basic Solutions

It is easy to see how adding a strong acid like hydrochloric acid, HCl, or even a weak acid such as ethanoic (acetic) acid, $\text{HC}_2\text{H}_3\text{O}_2$, to water will increase the concentration of $[\text{H}^+]$ above 1.0×10^{-7} as these species ionize completely (HCl, a strong acid) or partially ($\text{HC}_2\text{H}_3\text{O}_2$, a weak acid) to release H^+ ions. Similarly, the release of OH^- ions can be envisioned from the addition of one of the strong bases to H_2O . However, the production of acidic solutions by substances that contain no H^+ (or basic ones by substances that do not possess OH^-) is less apparent. Clearly, an acid–base theory other than that proposed by Arrhenius is required.

Brønsted-Lowry Acid–Base Theory

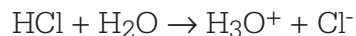
As outlined above, Arrhenius defined acids as substances that produce H^+ ions in H_2O and bases as species that produce OH^- ions. In 1923 Johannes Brønsted and Thomas Lowry independently described acids as proton donors and bases as proton acceptors, thereby broadening the concept of acids and bases significantly. In addition, they introduced the notion that acids and bases exist in pairs (called conjugate pairs) that differ by the presence (acid) or absence (base) of a proton. Further, they suggested that when acid–base reactions occur, stronger acids and bases react to form weaker acids and bases as in the equation below, where HA and A^- are a conjugate pair, and B and HB^+ are a conjugate pair:



Such reactions are reversible and the relative amounts of the various substances depend on the strengths of the acids (bases) involved. Where HA is a stronger acid than HB^+ and B is a stronger base than A^- , the equilibrium constant will be >1 . The strengths of Brønsted-Lowry acids and their conjugate bases are inversely related. This is because stronger acids donate protons more readily and, hence, their conjugate bases have lower attractions for protons (i.e., are weaker).

The Brønsted-Lowry theory includes as acids all the substances identified by Arrhenius as acids because they donate H^+ ions to water and would also classify the

OH^- ion as a base because it is a proton acceptor. For example, HCl acts as an acid according to both definitions in the equation:



because it releases an H^+ ion (Arrhenius) or donates a proton (Brønsted-Lowry). In this reaction, H_2O behaves as the base. However, the Brønsted-Lowry theory can also account for the acidic behavior of metal ions and nonmetallic oxides, neither of which contain H^+ ions. In addition, it can explain the basic behavior of weak bases such as ammonia.

Acidities of Metal Ions and Nonmetallic Oxides

Just as protons are hydrated (described above), most metal ions are also hydrated, usually with six H_2O molecules. In both instances lone pairs of electrons in H_2O molecules are attracted to the positive charge of the ion. For metal ions with large charge densities (due to high charges and/or small radii), the attraction for the oxygen of the H_2O may be strong enough to polarize the O-H bond and cause an H^+ ion to be released. This process is depicted in the equation:



The effect of charge and radius on the acidic behavior of selected metal ions is shown in the Table 2 below.

Table 2

Li⁺ slightly acidic	Be²⁺ weakly acidic		
Na⁺ neutral	Mg²⁺ weakly acidic	Al³⁺ acidic	
K⁺ neutral	Ca²⁺ slightly acidic	Sc³⁺ acidic	Ti⁴⁺ very acidic

Teaching Tip

The relative acidities of these (and other) metal ions can be shown by adding a few drops of universal indicator to solutions containing these ions and comparing the solution colors with those of pH standards.

The acidic behavior of nonmetallic oxides can be explained on the basis of their reaction with water to form oxyacids as represented in the equation for SO_2 :



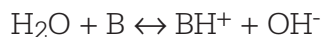
Such oxyacids ionize to release H^+ ions as:



Thus, the Brønsted-Lowry theory offers an explanation for the acidic behavior of both metal ions and nonmetallic oxides, neither of which contain H^+ . A more extensive discussion of oxides (both nonmetallic and metallic) is undertaken in a later section as is the relative acidities of oxyacids.

Behavior of Weak Bases

As mentioned above, there are six strong bases, each of which contains hydroxide ions. In contrast to the small number of strong bases, there are many substances that behave as weak bases. These substances produce an excess of OH^- ions in water even though they do not contain OH^- ions themselves. Most of these materials contain a nitrogen atom that can act as a Brønsted-Lowry base by accepting a proton, although some contain other atoms that can behave in this same manner. When a proton is abstracted from a water molecule, an excess of OH^- ions remains in the solution as shown in the equation:



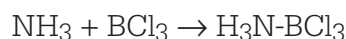
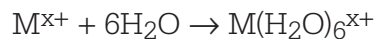
The $[\text{OH}^-]$ produced in such a reaction depends on the position of the above equilibrium, which is a function of the strength of B as a Brønsted-Lowry base. (H_2O is acting as the acid in this reaction.)

For ammonia, NH_3 , the most common weak base, $[\text{OH}^-] = 4.2 \times 10^{-3} \text{ M}$ in a 1.0 M NH_3 solution. Weak acids and bases will be treated in more detail in another section of this book.

Lewis Acid–Base Theory

By emphasizing the transfer of protons, the Brønsted-Lowry theory is able to account for several acid–base reactions that can not be treated by the Arrhenius theory. The same year that Brønsted and Lowry proposed their theory, G.N. Lewis noted that the reaction of a proton with a base involved the donation of a pair of electrons from the base to form a bond with the proton. He defined bases as electron pair donors, and acids as electron pair acceptors. Hence, Lewis acid–base reactions encompass

all Brønsted-Lowry reactions but also cover many processes that do not involve proton transfer. Examples of these include all cases in which a pair of electrons is donated, such as the hydration of metal ions and the reaction of ammonia with boron compounds:



This brief discussion of various aspects of acids and bases is intended to introduce the more extensive treatments in later chapters. Because of the importance of acids and bases in modern chemistry, this material has been tested frequently on the AP Chemistry Exam, both Part I and Part II.

Sample Part I

Released Exam 2002 Questions

An analysis of this released exam revealed a total of 9 questions (out of 75) related to acids and bases. Of these, the ones below are based solely on the above material.

21. In the laboratory, $H_2(g)$ can be produced by adding which of the following to 1.0 M $HCl(aq)$?

- I. 1 M $NH_3(aq)$
 - II. $Zn(s)$
 - III. $NaHCO_3(s)$
- (A) I only
 - * (B) II only
 - (C) III only
 - (D) I and II only
 - (E) I, II, and III

22. In liquid ammonia, the reaction represented below occurs.



In the reaction, NH_4^+ acts as

- (A) a catalyst
- (B) both an acid and a base
- * (C) the conjugate acid of NH_3

- (D) the reducing agent
 (E) the oxidizing agent

30. At 25°C, aqueous solutions with a pH of 8 have hydroxide concentration, $[OH^-]$, of

- (A) $1 \times 10^{-14} M$
 (B) $1 \times 10^{-8} M$
 * (C) $1 \times 10^{-6} M$
 (D) $1.0 M$
 (E) $8.0 M$

Sample Part II

Released Exam 2004 Questions

Question 4

- (c) A 0.1 M nitrous acid solution is added to the same volume of a 0.1 M sodium hydroxide solution

$$HNO_2 + OH^- \rightarrow NO_2^- + H_2O$$
- (d) Hydrogen iodide gas is bubbled into a solution of lithium carbonate:

$$2 HI + CO_3^{2-} \rightarrow 2 I^- + H_2O + CO_2$$
- (h) Concentrated hydrochloric acid is added to a solution of sodium sulfide:

$$2 H^+ + S^{2-} \rightarrow H_2S$$

Released Exam 2005 Questions

Question 4

- (d) Solid calcium carbonate is added to a solution of ethanoic (acetic) acid:

$$Na_2CO_3 + 2 HC_2H_3O_2 \rightarrow 2 C_2H_3O_2^- + H_2O + CO_2 + 2 Na^+$$
- (f) Boron trifluoride gas is added to ammonia gas:

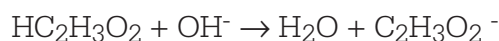
$$BF_3 + NH_3 \rightarrow F_3B-NH_3$$
- (g) Sulfur trioxide gas is bubbled into a solution of sodium hydroxide:

$$SO_3 + OH^- \rightarrow HSO_4^-$$

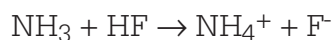
Released Exam 2006 Questions

Question 4

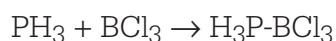
- (c) A solution of ethanoic (acetic) acid is added to a solution of barium hydroxide:



- (d) Ammonia gas is bubbled into a solution of hydrofluoric acid:



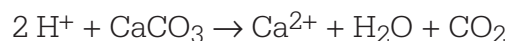
- (f) Hydrogen phosphide (phosphine) gas is added to boron trichloride gas:



Released Exam 2007 Questions

Question 4

- (b) (i) Excess nitric acid is added to solid calcium carbonate.



- (ii) Briefly explain why statues made of marble (calcium carbonate) displayed outdoors in urban areas are deteriorating.

The H^+ ions in acid rain react with the marble statues and the soluble compounds of calcium that are formed are washed away.

Bibliography

Brown, T. L., H. E. LeMay Jr., and B. E. Bursten. *Chemistry: The Central Science*, 5th ed. Englewood Cliffs, NJ: Prentice Hall, 1991.

Huheey, J. E., E. A. Keiter, and R. L. Keiter. *Inorganic Chemistry*, 4th ed. New York: Harper Collins, 1993.

Rayner-Canham, G., and T. Overton. *Descriptive Inorganic Chemistry*, 4th ed. New York: W.H. Freeman, 2006.

Salzberg, H. W. *From Caveman to Chemist*. Washington, DC: American Chemistry Society, 1991.

Weak Acids and Bases

Valerie Ferguson

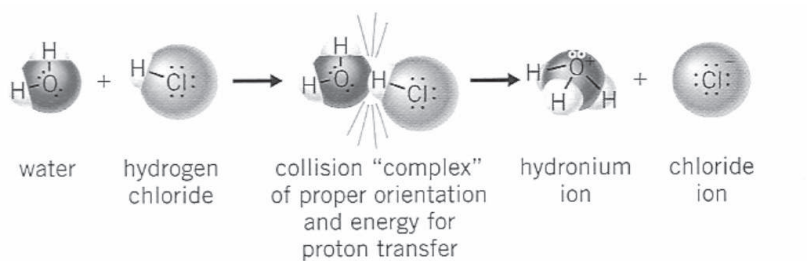
Moore High School

Moore, Oklahoma

Many substances dissolve in water to cause a change in the pH of pure water. Some of the substances ionize completely and others only partially ionize.

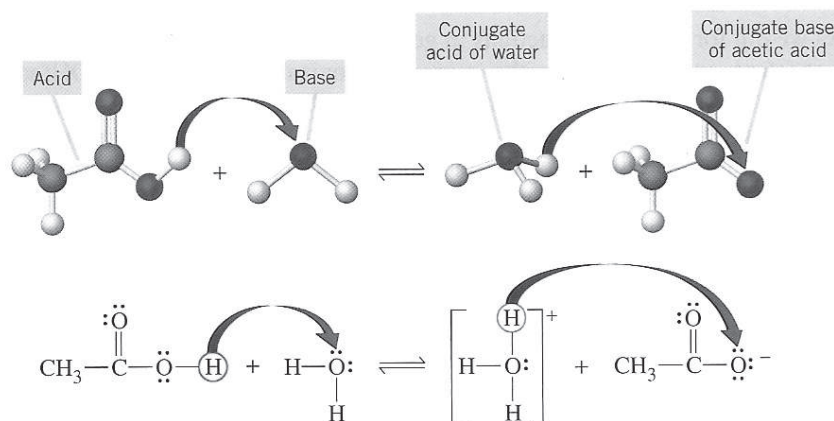
Strong acids and bases are strong electrolytes in water solutions, and are almost totally ionized. The reaction depicted below of a strong acid in water occurs with all of the HCl molecules in water. Since all of the HCl molecules are converted to H_3O^+ and Cl^- , the concentration of the hydronium ion is equal to the initial concentration of HCl in the solution. Strong acids and bases are not thought of as establishing equilibria since the reaction essentially goes to completion. However, equilibria never “turn off.” The equilibrium autodissociation of water is always present and operative in any aqueous solution even though the conjugate ion concentration (OH^- in acid, H_3O^+ in base) is extremely small.

Weak acid and base solutions are partially ionized. The Brønsted-Lowry



definition describes many acid and base interactions as a proton transfer from one particle to another. The particle that donates a proton is the acid and the particle accepting the proton is the base. The products of these reactions are called conjugate acids and conjugate bases. The acid and its product, the conjugate base, are a conjugate acid–base pair.

Conjugate acid–base pairs are two substances whose formulas differ by a proton. The example below illustrates a Brønsted-Lowry reaction with acetic acid in water.

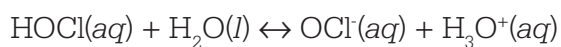


Examples from Prior AP Chemistry Examinations (2005 Form B)

$$K_a = [\text{H}_3\text{O}^+][\text{OCl}^-]/[\text{HOCl}] = 3.2 \times 10^{-8}$$

1. Hypochlorous acid, HOCl, is a weak acid in water.
The K_a expression for HOCl is shown above.

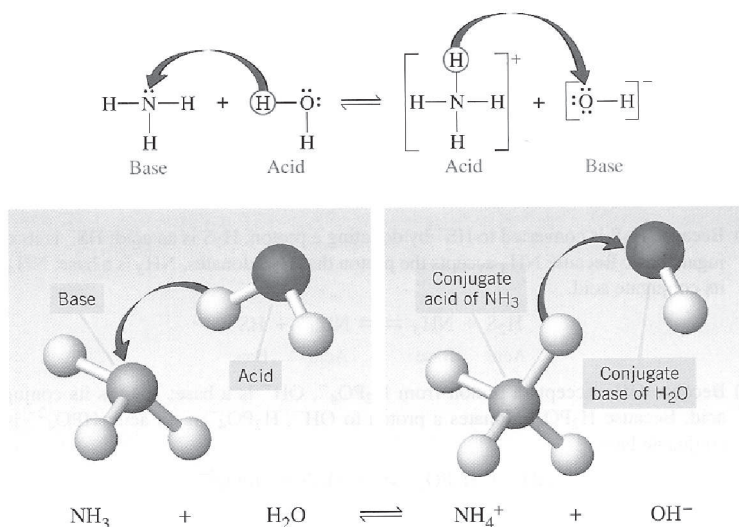
(a) Write a chemical equation showing how HOCl behaves as an acid in water.



Teaching Tips

Students need to practice writing equations for the reactions of weak acids and bases in water. Opportunities for such practice occur several times during the course. Questions on the AP Chemistry Exam commonly ask students to demonstrate their knowledge of writing these equations.

The illustration below shows the Brønsted-Lowry reaction of a weak base, ammonia, in water. Brønsted-Lowry bases are proton acceptors.



◀ **FIGURE 15.1 Ionization of NH_3 as a Brønsted-Lowry base**

Proton transfer is represented by a red-to-blue arrow. The red indicates loss of the proton by an acid and the blue, gain of the proton by a base. Because ammonium ion is a stronger acid than water and because hydroxide ion is a stronger base than ammonia, the equilibrium condition actually lies quite far to the left.

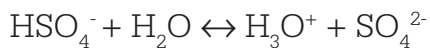
(2002)



22. In liquid ammonia, the reaction represented above occurs. In the reaction, NH_4^+ acts as

- (A) a catalyst
- (B) both an acid and a base
- * (C) the conjugate acid of NH_3
- (D) the reducing agent
- (E) the oxidizing agent

(1994)



22. In the equilibrium represented above, the species that act as bases include which of the following?

- I. HSO_4^-
- II. H_2O
- III. SO_4^{2-}
- (A) II only
- (B) III only
- (C) I and II
- (D) I and III
- * (E) II and III

(1989)

34. All of the following species can function as Brønsted-Lowry bases in solution EXCEPT

- (A) H_2O
- (B) NH_3
- (C) S^{2-}
- * (D) NH_4^+
- (E) HCO_3^-

* Proton acceptors must have a lone pair of electrons.

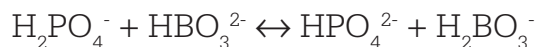
Brønsted-Lowry reactions are reversible and will establish a chemical equilibrium between the forward and reverse reactions. The position of the equilibrium depends on the strength of the acid and/or base, in aqueous solutions, in comparison to water. The relative strengths of the various weak acids can be described in different ways: the value of the acid dissociation, K_a , the $[\text{H}^+]$ compared to the initial $[\text{HA}]$, strength of the conjugate base compared to water, or the position of the dissociation.

The weaker acids have stronger conjugate bases. Stronger acids and bases tend to react with each other to produce their weaker conjugates. Since the stronger species are more likely to react, the conjugates are less likely to react and are thus weaker. The strong acids and bases are essentially totally ionized. The conjugates are very weak and less likely to react with water. Since the weaker species is less likely to react, it is in higher concentrations in the solution. The weaker species will be in greater concentration when equilibrium is established.

(1999)

62. The reaction represented above has an equilibrium constant equal to 3.7×10^4 . Which of the following can be concluded from this information?

- * (A) $\text{CN}^-(\text{aq})$ is a stronger base than $\text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$.
- (B) $\text{HCN}(\text{aq})$ is a stronger acid than $\text{HC}_2\text{H}_3\text{O}_2(\text{aq})$.
- (C) The conjugate base of $\text{CN}^-(\text{aq})$ is $\text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$.
- (D) The equilibrium constant will increase with an increase in temperature.
- (E) The pH of a solution equimolar amounts of $\text{CN}^-(\text{aq})$ and $\text{HC}_2\text{H}_3\text{O}_2(\text{aq})$ is 7.0.

(1989)

55. The equilibrium constant for the reaction represented by the equation above is greater than 1.0. Which of the following gives the correct relative strengths of the acids and bases in the reaction?

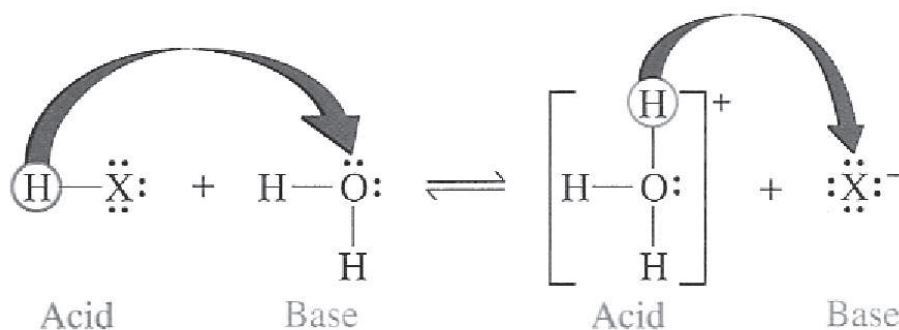
- | Acids | and | Bases |
|---|-----|---|
| * (A) $\text{H}_2\text{PO}_4^- > \text{H}_2\text{BO}_3^-$ | | $\text{HBO}_3^{2-} > \text{HPO}_4^{2-}$ |
| (B) $\text{H}_2\text{BO}_3^- > \text{H}_2\text{PO}_4^-$ | | $\text{HBO}_3^{2-} > \text{HPO}_4^{2-}$ |
| (C) $\text{H}_2\text{PO}_4^- > \text{H}_2\text{BO}_3^-$ | | $\text{HPO}_4^{2-} > \text{HBO}_3^{2-}$ |
| (D) $\text{H}_2\text{BO}_3^- > \text{H}_2\text{PO}_4^-$ | | $\text{HPO}_4^{2-} > \text{HBO}_3^{2-}$ |
| (E) $\text{H}_2\text{PO}_4^- = \text{H}_2\text{BO}_3^-$ | | $\text{HPO}_4^{2-} = \text{HBO}_3^{2-}$ |

(1984)

49. Each of the following can act as both a Brønsted acid and a Brønsted base EXCEPT

- (A) HCO_3^-
- (B) H_2PO_4^-
- * (C) NH_4^+
- (D) H_2O
- (E) HS^-

Periodic trends are observed in the relative strength of acids. Binary hydroacids—those that contain only hydrogen and a nonmetal—tend to increase in strength from left to right across the periodic table within the same period. The strength of a binary acid increases from top to bottom within the same group. The graphic below represents the reaction of a binary acid in water.



SPECIAL FOCUS: Acids and Bases

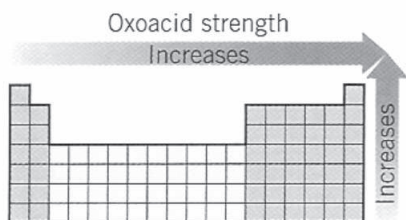
	GROUP			
	4A	5A	6A	7A
Period 2	CH ₄ No acid or base properties	NH ₃ Weak base	H ₂ O ---	HF Weak acid
Period 3	SiH ₄ No acid or base properties	PH ₃ Weak base	H ₂ S Weak acid	HCl Strong acid

◀ **Figure 16.12 Trends in acid-base properties of binary hydrides.** The acidity of the binary compounds of hydrogen and nonmetals increases moving left to right across a period and moving top to bottom down a group.

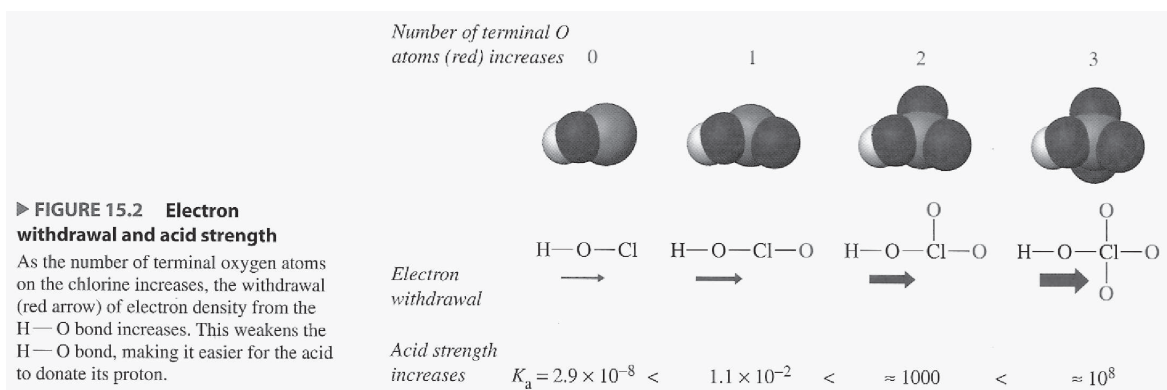
<i>Electronegativity of E increases</i>	2.5	<	2.8	<	3.0
	HOI		HOBr		HOC
<i>Acid strength increases</i>	$K_a = 2.3 \times 10^{-11}$	<	2.5×10^{-9}	<	2.9×10^{-8}

Acids composed of hydrogen, oxygen, and some other element are called oxoacids or oxyacids. Oxoacids are composed of a central atom with one or more O-H groups attached to it. The strength of an oxoacid depends upon the ease with which the hydrogen ion is released from the O-H group. The other atoms in the molecule affect the polarity of the O-H bond. As the electronegativity of the central atom increases, the electrons are pulled to the central atom and away from the O-H bond. The probability that H⁺ will be released is increased. The more readily the hydrogen ion is released, the stronger the acid. When the number of oxygens is held constant, the strength of the oxoacid increases from top to bottom within a group and from left to right across a period.

Periodic table and strengths of oxoacids



For the same central atom, the stronger acids contain more oxygen atoms.

**(2002)**

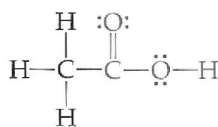
1(e). *H*OB*r* is a weaker acid than *HBrO*₃. Account for this fact in terms of molecular structure.

The H-O bond is weakened or increasingly polarized by the additional oxygen atoms bonded to the central bromine atom in <i>HBrO</i> ₃ .	1 point earned for a correct explanation.
--	--

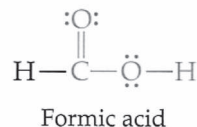
Teaching Tips

Students need to demonstrate an understanding of the strength of the O-H bond as related to the strength of the acid. The greater the number of electronegative atoms in the molecule, the weaker the O-H bond as the electrons are pulled away from the O-H bond. Many students found it helpful to draw a structural formula to help answer this question.

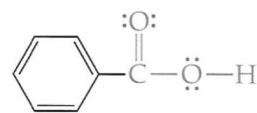
An important group of oxoacids is the carboxylic acids. These organic compounds are characterized by containing a chain of carbon atoms with one or more carboxyl groups, -COOH, attached. These compounds are weak acids called carboxylic acids. Acetic acid is an example of a simple carboxylic acid. Its reaction with water is shown on page 1. Most carboxylic acids react in a similar fashion. Only the O-H bond is polar enough so the hydrogen is readily donated as a hydrogen ion.



Acetic acid



Formic acid

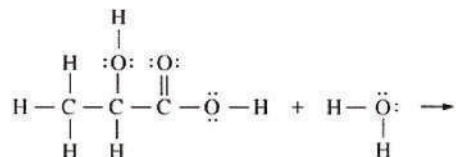


Benzoic acid

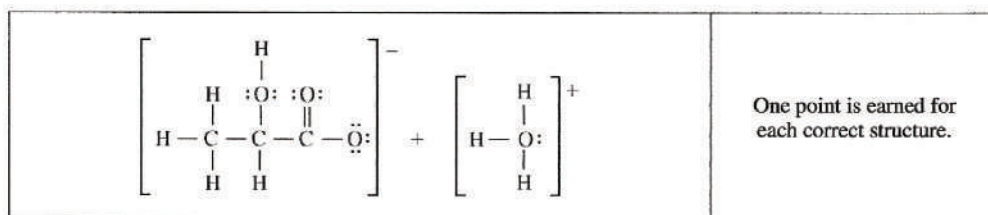
(2007 Form B)

5. Answer the following questions about laboratory solutions involving acids, bases and buffer solutions.

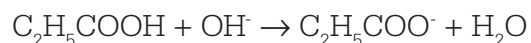
(a) Lactic acid, $\text{HC}_3\text{H}_5\text{O}_3$, reacts with water to produce an acidic solution. Show below are the complete Lewis structures of the reactants.



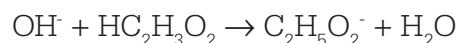
In the space provided above, complete the equation by drawing the complete Lewis structures of the reaction products.

**(2001)**

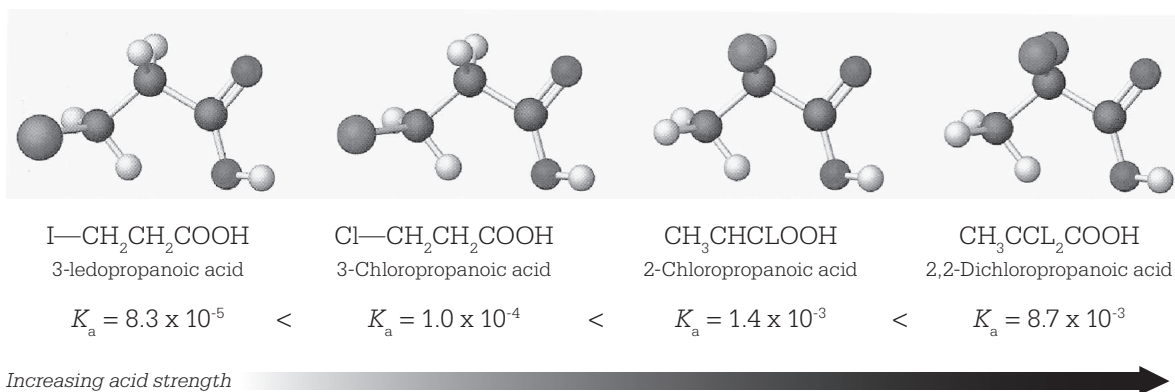
4(d). Write the net ionic equation for the following reaction: Solutions of potassium hydroxide and propanoic acid are mixed.

**(2005 Form B)**

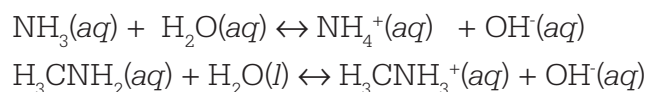
4(d). Write the net ionic equation for the following reaction: Ethanoic acid (acetic acid) is added to a solution of barium hydroxide.



The strength of the carboxylic acids is affected by the substitution of one or more hydrogen atoms with electronegative atoms. More electronegative atoms pull the electron density away from the O-H bond and cause an increase in acid strength. The closer the electronegative atoms are to the O-H bond, the greater the effect on acid strength by weakening the O-H bond.



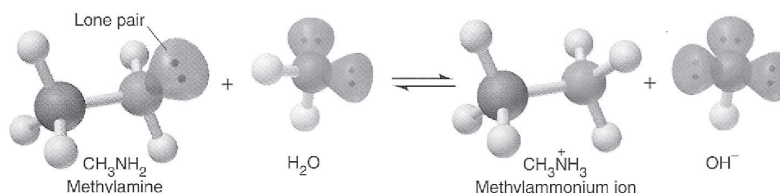
Amines are organic compounds that act as weak bases. The structure is an ammonia molecule, NH_3 , with one hydrogen substituted by a hydrocarbon group. Amines react as bases similar to reactions of NH_3 . The amines act as Brønsted-Lowry bases and are proton acceptors. The proton attaches to the nitrogen in the amine group.



Teaching Tips

The equation for the reaction of ammonia with water is compared to the equation for the reaction of methylamine with water. In each reaction the water acts as a Brønsted-Lowry acid and ammonia or methylamine as a Brønsted-Lowry base.

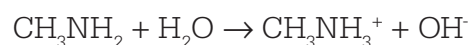
Figure 18.10 Abstraction of a proton from water by methylamine. The amines are organic derivatives of ammonia. Methylamine, the simplest amine, acts as a base in water by abstracting a proton, thereby increasing the $[\text{OH}^-]$.



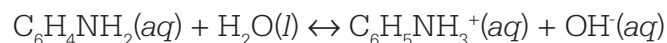
Examples of other amines.

(1999)

4(f). Write the net ionic equation for the following reaction: Methylamine gas is bubbled into distilled water.



(2003)

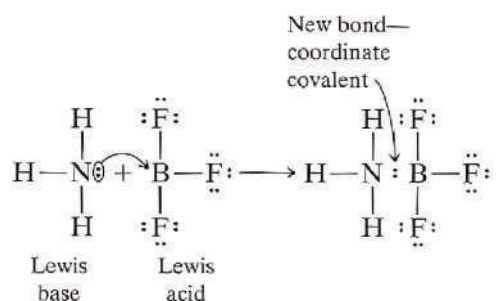


1. Aniline, a weak base, reacts with water according to the reaction represented above.

Teaching Tips

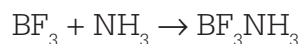
The examples above demonstrate the inclusion of amines on past AP Exams. Students need to have a background of the behavior of amines as weak bases. In question 1 from 2003, students were asked to demonstrate an understanding of the characteristics of an amine equilibrium. Students should be encouraged to develop an understanding of the similarity of amine reactions to those of ammonia. The discussion of weak acids and bases is a good time to include some organic chemistry.

Lewis acids can be described as electron-pair acceptors and Lewis bases as electron-pair donors. Sometimes the Lewis acid has fewer than eight electrons, as in compounds such as BF_3 .



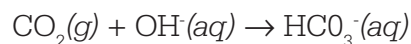
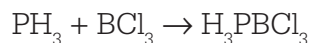
(2005)

4(f). Write the net ionic equation for the following reaction: Boron trifluoride gas is added to ammonia gas.

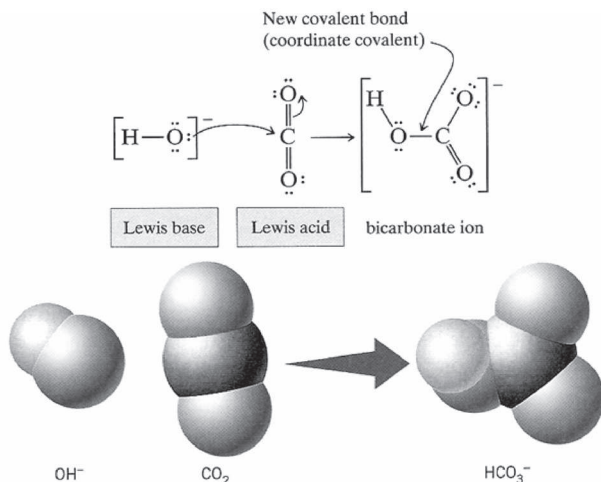


(2006)

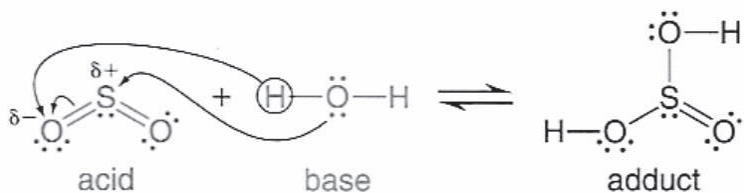
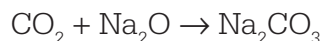
4(f). Write the net ionic equation for the following reaction: Hydrogen phosphide (phosphine) gas is added to boron trichloride gas.



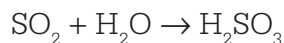
Lewis acid-base theory represents the movement of electrons in this reaction as follows.

**(1999)**

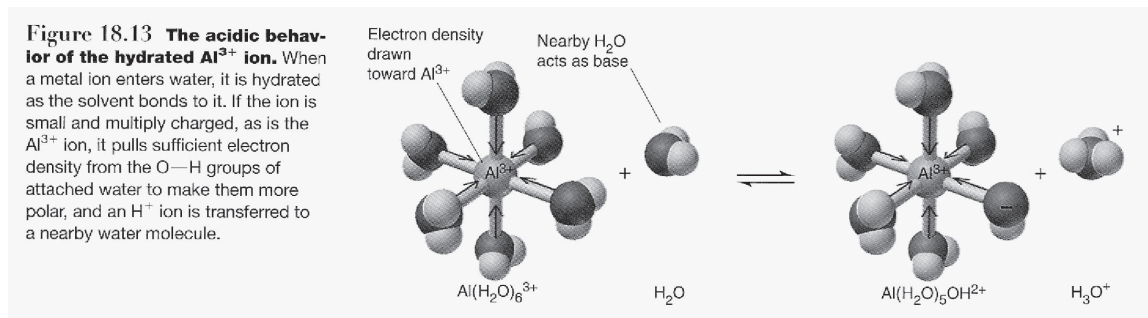
4(g). Write the net ionic equation for the following reaction: carbon dioxide gas is passed over hot, solid sodium oxide.

**(2001)**

4(a). Write the net ionic equation for the following reaction: Sulfur dioxide gas is bubbled into distilled water.

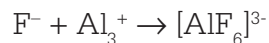


Hydrated metal ions can act as acids in water. The smaller metal ions with greater charge have a greater charge density and produce more acidic solutions.



(2004 Form B)

4(g). Write the net ionic equation for the following reaction: Excess saturated sodium fluoride solution is added to a solution of aluminum sulfate.



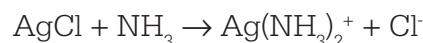
(2003 Form B)

4(g). Write the net ionic equation for the following reaction: Excess concentrated potassium hydroxide solution is added to a solution of nickel(II) chloride.



(2003)

4(e). Write the net ionic equation for the following reaction: Excess concentrated aqueous ammonia is added to solid silver chloride.



(1984)

48. Which of the following ions is the strongest Lewis acid?

- (A) Na^+
- (B) Cl^-
- (C) CH_3COO^-
- (D) Mg^{2+}
- * (E) Al^{3+}

I highly suggest using the following Web sites with simulations of weak acid and weak base behavior:

- The first is the work of Thomas Greenbowe of Iowa State University, located at: www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/animationsindex.htm.
- The second is part of a collaboration of John I. Gelder, Michael Abraham, and Kirk Haines, which can be found at: genchem1.chem.okstate.edu/CCLI/Startup.html

Bibliography

Brady, James E., and Fred Senese. *Chemistry: Matter and Its Changes*, 4th ed. Hoboken, NJ: Wiley, 2003.

Brown, Theodore E., Eugene H. LeMay, and Bruce E. Bursten. *Chemistry: The Central Science*, 10th ed. Upper Saddle River, NJ: Pearson/Prentice-Hall, 2006.

Hill, John W., Ralph H. Petrucci, Terry W. McCreary, and Scott S. Perry. *General Chemistry*, 4th ed. Upper Saddle River, NJ: Pearson/Prentice-Hall, 2005.

Silberberg, Martin S. *Chemistry: The Molecular Nature of Matter and Change*, 2nd ed. New York: McGraw-Hill Higher Education, 2000.

Whitten, Kenneth W., Raymond E. Davis, Larry M. Peck, and George G. Stanley. *Chemistry*, 8th ed. Belmont, CA: Thomson/Brooks/Cole, 2007.

Zumdahl, Steven S., and Susan A. Zumdahl. *Chemistry*, 7th ed. Boston: Houghton Mifflin, 2007.

Graphics Index

(Picture 1) Brady, James E., and Fred Senese. *Chemistry: Matter and Its Changes*, 4th ed., 738. Hoboken, NJ: Wiley, 2003.

(Picture 2) Hill, John W., Ralph H. Petrucci, Terry W. McCreary, and Scott S. Perry. *General Chemistry*, 4th ed., 617. Upper Saddle River, NJ: Pearson/Prentice-Hall, 2005.

(Picture 3) Hill, John W., Ralph H. Petrucci, Terry W. McCreary, and Scott S. Perry. *General Chemistry*, 4th ed., 617. Upper Saddle River, NJ: Pearson/Prentice-Hall, 2005.

(Picture 4) Hill, John W., Ralph H. Petrucci, Terry W. McCreary, and Scott S. Perry. *General Chemistry*, 4th ed., 621. Upper Saddle River, NJ: Pearson/Prentice-Hall, 2005.

(Picture 5) Brown, Theodore E., Eugene H. LeMay, and Bruce E. Bursten. *Chemistry: The Central Science*, 10th ed., 703. Upper Saddle River, NJ: Pearson/Prentice-Hall, 2006.

(Picture 6) Hill, John W., Ralph H. Petrucci, Terry W. McCreary, and Scott S. Perry. *General Chemistry*, 4th ed., 622. Upper Saddle River, NJ: Pearson/Prentice-Hall, 2005.

(Picture 7) Brady, James E., and Fred Senese. *Chemistry: Matter and Its Changes*, 4th ed., 748. Hoboken, NJ: Wiley, 2003.

(Picture 8) Hill, John W., Ralph H. Petrucci, Terry W. McCreary, and Scott S. Perry. *General Chemistry*, 4th ed., 622. Upper Saddle River, NJ: Pearson/Prentice-Hall, 2005.

(Picture 9) Brown, Theodore E., Eugene H. LeMay, and Bruce E. Bursten. *Chemistry: The Central Science*, 10th ed., 705. Upper Saddle River, NJ: Pearson/Prentice-Hall, 2006.

(Picture 10) Brown, Theodore E., Eugene H. LeMay, and Bruce E. Bursten. *Chemistry: The Central Science*, 10th ed., 706. Upper Saddle River, NJ: Pearson/Prentice-Hall, 2006.

- (Picture 11) Hill, John W., Ralph H. Petrucci, Terry W. McCreary, and Scott S. Perry. *General Chemistry*, 4th ed., 623. Upper Saddle River, NJ: Pearson/Prentice-Hall, 2005.
- (Picture 12) Silberberg, Martin S. *Chemistry: The Molecular Nature of Matter and Change*, 2nd ed., 780. New York: McGraw-Hill Higher Education, 2000.
- (Picture 13) Brady, James E., and Fred Senese. *Chemistry: Matter and Its Changes*, 4th ed., 751. Hoboken, NJ: Wiley, 2003.
- (Picture 14) Brady, James E., and Fred Senese. *Chemistry: Matter and Its Changes*, 4th ed., 752. Hoboken, NJ: Wiley, 2003.
- (Picture 15) Silberberg, Martin S. *Chemistry: The Molecular Nature of Matter and Change*, 2nd ed., 792. New York: McGraw-Hill Higher Education, 2000.
- (Picture 16) Silberberg, Martin S. *Chemistry: The Molecular Nature of Matter and Change*, 2nd ed., 786. New York: McGraw-Hill Higher Education, 2000.

pH and the Properties of $[H^+]$ in Aqueous Solution

Lew Acampora

St. Francis School
Louisville, Kentucky

The neutralization of a strong acid with a strong base occurs according to the net ionic equation¹:



The negative sign of ΔG°_{298K} , and experience tell us that the reaction proceeds spontaneously from standard initial concentrations of $1.0 M H^+$ and $1.0 M OH^-$. Rather than proceeding to completion, where the concentration of one or both of the reactants is completely exhausted, the reaction does attain a state of equilibrium in which small but measurable concentrations of both H^+ and OH^- are present. The state of equilibrium is quantitatively described by the equilibrium constant expression. Because the concentration of the pure water is unaffected by the progress of the reaction, it is omitted from the equilibrium constant expression, K_{eq} :

$$K_{eq} = \frac{1}{[H]^+ \cdot OH^-}$$

The value of K_{eq} can be readily calculated as:

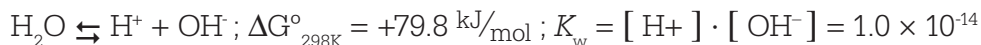
$$\begin{aligned} K_{eq} &= e^{-nG^\circ/RT} = e^{-79.8 \frac{\text{kJ}}{\text{mol}} / 0.00831 \frac{\text{kJ}}{\text{mol}\cdot\text{K}} \cdot 298 \text{ K}} \\ &= e^{32.2} = 1.0 \times 10^{14} \end{aligned}$$

1. The symbol " $H^+(aq)$ " is a shorthand representation of the hydrated proton. In aqueous solutions, the acidic proton is undoubtedly coordinated to several water molecules through and is often written as the hydronium ion, " $H_3O^+(aq)$." Because the number of water molecules coordinated to a single proton varies with time, it is probably most accurately represented as " $H_{2n+1}O_n^+(aq)$," where "n" represents the number of water molecules. In terms of calculations, when used correctly, the symbol $H^+(aq)$ is a convenient and suitable representation.

While the magnitude of the value of K_{eq} reflects the observation that the equilibrium state of this reaction lies far to the right, the equilibrium mixture will maintain small but measurable concentrations of both hydrogen ion and hydroxide ion.

Commonly, the reverse reaction of Equation 1, which represents the auto-ionization of water, is used to determine the $[H^+]$ and $[OH^-]$ in aqueous solutions. In this case:

Equation 2:

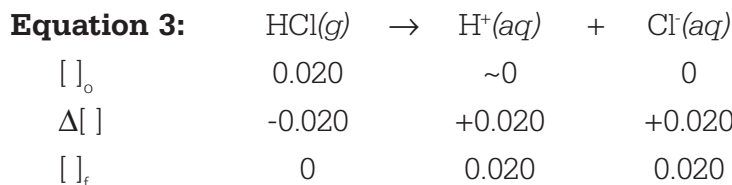


The implication of this calculation is that even in the purest sample of water at 25 °C, there are small but measurable concentrations of H^+ and OH^- ion. In pure water²:

$$[H^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} M$$

While the $[H^+] = [OH^-]$ in pure water, many solutes (acids or bases) will change the relative concentrations of these ions. In any case, the equilibrium relation, $[H^+][OH^-] = 1.0 \times 10^{-14}$, will remain applicable in any aqueous solution at 25 °C. Therefore, any substance that increases the $[H^+]$ must also decrease the $[OH^-]$ in order to satisfy the equilibrium relation. Solutes that have this effect on the relative concentrations of H^+ and OH^- are called acids. Conversely, bases are substances that will increase the $[OH^-]$ and will decrease the $[H^+]$.

In determining the $[H^+]$ and the $[OH^-]$ in an acid, base, or buffer solution containing solutes of reasonable concentration, the contribution from the auto-ionization of water can be neglected. In a solution of an acid, the $[H^+]$ can be determined directly from the concentration and strength of the acid, and the $[OH^-]$ is subsequently calculated using Equation 2. For example, the $[H^+]$ ion in a 0.020 M solution of the strong acid hydrochloric acid is readily determined as follows:



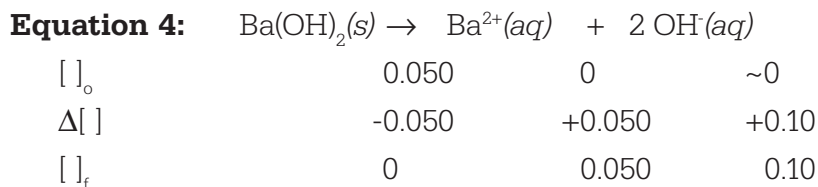
The $[H^+] = 0.020 M$. The $[OH^-]$ ion determined from Equation 2:

$$H^+ \cdot OH^- = 1.0 \times 10^{-14}$$

$$OH^- = \frac{1.0 \times 10^{-14}}{H^+} = \frac{1.0 \times 10^{-14}}{0.020} = 2.0 \times 10^{-13} M$$

2. The symbol K_w represents the specific equilibrium constant that refers to the auto-ionization of water. Like all equilibrium constants, its value is a function of the temperature. In terms of calculations expected on the AP Chemistry Examination, the value of K_w at 25°C is commonly used.

For an aqueous solution of a base, the [OH⁻] is directly calculated, and subsequently the [H⁺] can be determined. For example, the concentrations of each ion in a 0.050 M solution of barium hydroxide are determined as:



The [OH⁻] = 0.10 M. The [H⁺] ion determined from Equation 2:

$$\text{H}^+ \cdot \text{OH}^- = 1.0 \times 10^{-14}$$

$$\text{H}^+ = \frac{1.0 \times 10^{-14}}{\text{OH}^-} = \frac{1.0 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13} \text{ M}$$

The preceding examples illustrate that both the [H⁺] and the [OH⁻] in aqueous solutions vary over a range that is greater than 14 orders of magnitude. The pH scale is commonly used as an alternative expression to the [H⁺], where pH is defined as $\text{pH} = -\log_{10}[\text{H}^+]$. Algebraically, this is equivalent to $[\text{H}^+] = 10^{-\text{pH}}$, and shows that the pH value is the negative of the exponent of 10 when the concentration is expressed as a power of 10. The range of values for [H⁺] in aqueous solutions, approximately $1.0 \times 10^{-14} \text{ M} < [\text{H}^+] < 1.0 \text{ M}$, translates to a pH range from 14.00 to 0.00. Referring to the previous examples, the pH of the 0.020 M HCl(aq) solution is $\text{pH} = -\log_{10} 0.020 = 1.70$, the pH of the 0.050 M Ba(OH)₂(aq) solution is $\text{pH} = -\log_{10} 1.0 \times 10^{-13} = 13.00$, and the pH of pure, neutral water is then $\text{pH} = -\log_{10} 1.0 \times 10^{-7} = 7.00$. Analogously, the pOH of an aqueous solution is defined as $\text{pOH} = -\log_{10} [\text{OH}^-]$, and $[\text{OH}^-] = 10^{-\text{pOH}}$.

The logarithmic pH scale conveniently represents the [H⁺] over the 14 orders of magnitude, but no additional information is conveyed by the pH of the solution that is not already indicated by the [H⁺]. In fact, the above relationships among [H⁺], [OH⁻], pH, and pOH imply that the value of any one of these will fix the values of the others.³ Calculation of these values for aqueous solutions will depend on the type of solute, and five types of calculations can be identified:

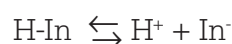
- Solutions of strong acids only.
- Solutions of strong bases only.
- Solutions of weak acids only.
- Solutions of weak bases only.

3. The value of K_w , like all equilibrium constants, is temperature dependent. While the relation: $K_w = [\text{H}^+][\text{OH}^-]$ is generally true, the value of $K_w = 1.0 \times 10^{-14}$ at standard temperature of 25 °C.

- Buffer solutions (containing appreciable concentrations of a weak acid and its conjugate base).

Examples of these calculations are described elsewhere in this manual.

The laboratory determination of the $[H^+]$ of an aqueous solution, or equivalently, its pH, can be done in two ways. The use of indicators, either in solution or adsorbed onto pH paper, affords a crude determination of the pH of a sample. An indicator is itself a weak acid whose color is different from that of its conjugate base. The indicator is intensely colored, so that a negligible concentration of the indicator is added to the solution – sufficiently dilute so that it does not have an appreciable effect on the $[H^+]$ of the solution. The indicator will then ionize according to the equation:



The acid dissociation constant of the indicator is written as $K_{a,\text{In}} = \frac{H^+ \cdot \text{In}^-}{[H\text{-In}]}$. This equation can be rearranged as $\frac{\text{In}^-}{[H\text{-In}]} = \frac{K_{a,\text{In}}}{H^+}$, showing that the ratio of the concentration of the conjugate base form to the acid form depends on the value of K_a of the indicator, and the $[H^+]$ in the solution. For $K_{a,\text{In}} \gg [H^+]$, $[\text{In}^-] \gg [H\text{-In}]$, and the solution will have the color of the base form of the indicator. Conversely, for $K_{a,\text{In}} \ll [H^+]$, $[\text{In}^-] \ll [H\text{-In}]$ and the solution will have the color of the acid form of the indicator. In practice, the pK_a of the indicator, defined as $-\log_{10} K_{a,\text{In}}$, is compared to the pH of the solution, and the color of the solution changes from that of the acid form to the color of the base form as the pH of the solution changes from $(pK_a - 1)$ to $(pK_a + 1)$. Indicators with different pK_a 's can be used to measure different ranges of pH values. A chart of commonly used indicators and their transition point (pK_a 's) can be found in most textbooks.

More precise pH measurements are made with a pH meter. Though the technical details vary by instrument, the fundamental operation of a pH meter is to measure the electrochemical potential difference between a glass membrane electrode, whose electrochemical potential is sensitive to the $[H^+]$ in the solution being measured, and an internal reference electrode.⁴ The measured potential depends on the $[H^+]$ in the external solution, and the pH meter is simply a high impedance voltmeter that is calibrated to reflect the pH of the solution. With careful calibration using standard buffer solutions, laboratory pH meters are routinely capable of making accurate pH measurements to ± 0.01 pH unit.

4. In practice, the test electrode and the reference electrode are combined into the same body, referred to as a combination electrode.

In closing, the equilibrium that exists between H^+ ions and OH^- ions in any aqueous solution determines much of the chemistry of the solutions. Because chemical properties of the solution are sensitive to variations in the concentrations of these ions, the concentrations of these ions in such solutions are often critically important. Though these equilibrium concepts are sometimes difficult for students to master, the role of pH as a measure of the concentration of not only the H^+ ion but also the OH^- ion is an important step that will allow students to go further in their mastery of the material.

Exercises

Complete the following table:

Solute and Concentration	[H ⁺]	[OH ⁻]	pH	pOH
? M HCl	0.050 M			
0.10 M CH ₃ COOH [K _a = 1.8 × 10 ⁻⁵]				
0.10 M CH ₃ COOH [K _a = 1.8 × 10 ⁻⁵] & ? M CH ₃ COO ⁻			5.12	
Pure Water				
0.10 M NH ₃ [K _b = 1.8 × 10 ⁻⁵] & 0.20 M NH ₄ ⁺				
? M NH ₃ [K _b = 1.8 × 10 ⁻⁵]		1.0 × 10 ⁻³ M		
? M Ba(OH) ₂			13.70	

Answer:

Solute and Concentration	[H ⁺]	[OH ⁻]	pH	pOH
0.050 M HCl	0.050 M	2.0 × 10 ⁻¹³ M	1.30	13.70
0.10 M CH ₃ COOH [K _a = 1.8 × 10 ⁻⁵]	1.3 × 10 ⁻³ M	7.5 × 10 ⁻¹² M	2.87	11.13
0.10 M CH ₃ COOH [K _a = 1.8 × 10 ⁻⁵] & 0.24 M CH ₃ COO ⁻	1.2 × 10 ⁻⁵ M	8.8 × 10 ⁻⁸ M	5.12	8.88
Pure Water	1.0 × 10 ⁻⁷ M	1.0 × 10 ⁻⁷ M	7.00	7.00
0.10 M NH ₃ [K _b = 1.8 × 10 ⁻⁵] & 0.20 M NH ₄ ⁺	1.1 × 10 ⁻⁹ M	9.0 × 10 ⁻⁶ M	8.95	5.05
0.056 M NH ₃ [K _b = 1.8 × 10 ⁻⁵]	1.0 × 10 ⁻¹¹ M	1.0 × 10 ⁻³ M	11.00	3.00
0.25 M Ba(OH) ₂	2.0 × 10 ⁻¹⁴ M	0.50 M	13.70	0.30

AP Exam Questions – Past Exams**(1984)**

2. The pH of 0.1-molar ammonia is approximately

- (A) 1
- (B) 4
- (C) 7
- * (D) 11
- (E) 14

Students should recognize that ammonia is a weak base and that a solution of a weak base will have a $\text{pH} > 7$. Because a 0.1-molar solution of a strong base would have a $[\text{OH}^-] = 0.1 \text{ M}$, a $[\text{H}^+]$ ion = $1 \times 10^{-13} \text{ M}$ and $\text{pH} = 13$, the same concentration of a weak base would have to have a lower pH value. Choice (D) is the only choice that matches these constraints.

3. Find the pH of each of the following:

- a. 0.10 M HCl.
- b. A solution prepared by mixing 10.0 mL of a solution of 0.10 M HCl with 990.0 mL of distilled water.
- c. A solution prepared by mixing 45.0 mL of 0.10 M HCl with 55.0 mL of 0.10 M NaOH.
- d. A solution prepared by mixing 50.0 mL of a buffer of pH 4.00 with 50.0 mL of distilled water.

3. Answers:

- a. 0.10 M HCl is a solution of a strong acid:

$$\begin{aligned} \text{H}^+_{\text{f}} &= [\text{HCl}]_{\text{o}} = 0.10 \text{ M} \\ \text{pH} &= -\log_{10} 0.10 = 1.00 \end{aligned}$$

- b. Solution of a strong acid:

$$\begin{aligned} \text{H}^+_{\text{f}} &= 0.10 \text{ M} \times \frac{10 \text{ mL}}{990 \text{ mL} + 10 \text{ mL}} = 0.0010 \text{ M} \\ \text{pH} &= -\log_{10} 0.0010 = 3.00 \end{aligned}$$

- c. The strong acid and strong base will neutralize, and there will be excess base remaining:

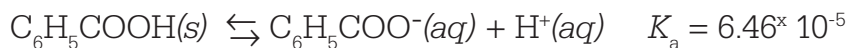
Rxn:	H ⁺	+	OH ⁻	→	H ₂ O
mol _o	0.0045		0.0055		0
Δmol	-0.0045		-0.0045		+0.0045
mol _f	0		0.0010		0.0045

$$\text{OH}^-_f = \frac{0.0010 \text{ M}}{0.10 \text{ L}} = 0.010 \text{ M}$$

$$\text{pOH} = -\log_{10} 0.010 = 2.00$$

$$\text{pH} = 14.00 - 2.00 = 12.00$$

- d. Because solution (d) is a buffer solution, the ratio $\frac{A^-}{[HA]}$ will not be affected by dilution and the pH will remain unchanged. pH = 4.00 (assuming that after dilution, [A⁻], [HA] >> [H⁺], [OH⁻]).

(2006B, Q1ai, Q1aii)

2. Benzoic acid, C₆H₅COOH, dissociates in water as shown in the equation above. A 25.0 mL sample of an aqueous solution of pure benzoic acid is titrated using standardized 0.150 M NaOH.

- (a) After addition of 15.0 mL of the 0.150 M NaOH, the pH of the resulting solution is 4.47. Calculate each of the following.
- (i) [H⁺] in the solution
- (ii) [OH⁻] in the solution

2. Answers:

Students should be able to convert among [H⁺], [OH⁻], pH, and pOH easily.

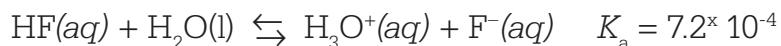
$$\text{(a)(i)} \quad \text{H}^+ = 10^{-\text{pH}} = 10^{-4.47} = 3.4 \times 10^{-5} \text{ M}$$

$$\text{(a)(ii)} \quad \text{OH}^- = \frac{K_w}{\text{H}^+} = \frac{1.0 \times 10^{-14}}{3.4 \times 10^{-5}} = 3.0 \times 10^{-10} \text{ M}$$

or

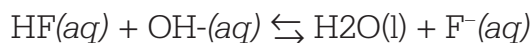
$$\text{pOH} = \text{p}K_w - \text{pH} = 14.00 - 4.47 = 9.53$$

$$\text{OH}^- = 10^{-\text{pOH}} = 10^{-9.53} = 3.0 \times 10^{-10} \text{ M}$$

(2007, Q1c - e)

Hydrofluoric acid, $\text{HF}(aq)$, dissociates in water as represented by the equation above.

$\text{HF}(aq)$ reacts with $\text{NaOH}(aq)$ according to the reaction represented below.



2. A volume of 15.0 mL of 0.40 M $\text{NaOH}(aq)$ is added to 25.0 mL of 0.40 M $\text{HF}(aq)$ solution. Assume that volumes are additive.

- (c) Calculate the number of moles of $\text{HF}(aq)$ remaining in the solution.
 (d) Calculate the molar concentration of $\text{F}^-(aq)$ in the solution.
 (e) Calculate the pH of the solution.

2. Answers:

$$\begin{aligned} \text{(c) mol HF}(aq) &= \text{initial mol HF}(aq) - \text{mol OH}^-(aq) \text{ added} \\ &= (0.025 \text{ L})(0.40 \text{ mol L}^{-1}) - (0.015 \text{ L})(0.40 \text{ mol L}^{-1}) \\ &= 0.010 \text{ mol} - 0.0060 \text{ mol} = 0.004 \text{ mol} \end{aligned}$$

$$\text{(d) } [\text{HF}] = \frac{.004 \text{ mol HF}}{.040 \text{ L}} = 0.10 \text{ M HF}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}$$

$$[\text{H}_3\text{O}^+] = \frac{[\text{HF}] \times K_a}{[\text{F}^-]} = \frac{0.10 \text{ M} \times (7.2 \times 10^{-4})}{0.15 \text{ M}} = 4.8 \times 10^{-4} \text{ M}$$

$$\text{(e) } \text{pH} = -\log_{10}(4.8 \times 10^{-4}) = 3.32$$

OR

$$\text{pH} = \text{p}K_a + \log \frac{[\text{F}^-]}{[\text{HF}]} = 3.14 + \log \frac{.15 \text{ M}}{.10 \text{ M}} = 3.32$$

Teaching Strategies

Introduce the auto-ionization of pure water as the reverse of the neutralization reaction of a strong acid and a strong base. Emphasize that both H^+ and OH^- are present in any aqueous solution, and that the concentration of either particle will fix the concentration of the other.

Emphasize the mathematical relationships among $[H^+]$, $[OH^-]$, pH, and pOH for aqueous solutions and that, given the value of any one of these data, values for the remaining are fixed and can easily be determined. Remind students that the relevant equations are provided on the insert for the free-response section of the AP Chemistry Examination, but they are not available for the multiple-choice questions.

In determining the $[H^+]$ in an aqueous solution, be sure that students can identify the type of solution that they are dealing with:

- strong acid, only
- strong base, only
- weak acid, only
- weak base, only
- buffer solution containing both a weak acid and its conjugate base

Students should understand which principles/equations are applicable to each of these instances.

Acid–Base Titrations

Cheri Smith

Yale Secondary School

Abbotsford, British Columbia

Titration is an important type of volumetric analysis usually used to determine the number of moles of solute in a certain amount of aqueous solution. Once the amount is known, other quantities may be discerned, such as the concentration of the solution or the molar mass of the solute. The titration procedure generally involves the addition of carefully measured portions of a “standard” solution of known concentration to a measured mass or volume of an unknown. In many acid–base titrations, a chemical indicator is added to signal the point at which the two reactants have been combined in just the right ratio to give a complete reaction. This is sometimes called the stoichiometric point or, more commonly, the equivalence point. Alternatively, the equivalence point may be determined using a pH meter to follow the progress of the reaction.

Approaching Titration Problems with an AP[®] Chemistry Class

AP students may or may not be already familiar with introductory titration problems such as those involving the determination of an unknown solution’s concentration or finding the volume of a solution required to react with a standard solution, from their first course in chemistry. In any event, the AP Chemistry teacher would be wise to briefly review some simple problems before using a more sophisticated lecture and laboratory approach. Simple problems should involve the idea of “matching” equivalent amounts of strong acids and strong bases in solutions, for example, how many mL of 0.25 *M* sodium hydroxide will it take to be equivalent to 20 mL of 0.50 *M* hydrochloric acid. For students who have done little lab, a good introduction may be to titrate HCl with NaOH by drop counting in a well tray using phenolphthalein indicator. (For

example, how many drops of 0.1M NaOH are equivalent to 10 drops of 0.2 M HCl?)

Examples of more sophisticated lecture topics and labs that should be done in AP Chemistry include:

- Determination of the molar mass of a unknown monoprotic acid. (KHP, KHSO_4 , and NaHSO_3 are good unknowns to use in lab as their masses vary significantly from one another.)
- Determination of the K_a value for an unknown monoprotic acid. (Approximately 0.1 mol/L acetic acid, formic acid and propanoic acids are good unknowns for lab use as their K_a values differ by a full order of magnitude.)
- Back titrations to determine the strength of antacid products.

Once the teacher has reviewed and reinforced the students' basic understanding of titration, he or she can move on to the determination of pH experimentally and mathematically at different points during a titration. Included should be titrations of a strong acid with a strong base and, more important for AP Chemistry, a strong acid or base with a weak acid or base. The teacher may elect to include diprotic titrations and should certainly consider the selection of appropriate acid–base indicators, as well as the use of pH meters or probeware.

Calculating the pH at various points during a theoretical titration is an extremely valuable exercise for AP Chemistry students, as it requires the application of virtually every type of pH problem encountered in the acid–base unit. An AP Chemistry teacher would find it beneficial to begin with strong–strong titration curves, thus reviewing the determination of the pH of strong acids and bases alone and in combination with one or the other in excess, including the applications of K_w and/or $\text{p}K_w$. Weak–strong curves are the source of a wealth of review, including weak acid and base pH problems (ICE table calculations), buffer calculations, hydrolysis problems, and strong acids or bases in excess. These should be reinforced by either student run pH meter/probe use, or at least teacher demonstration of actual variation of pH during titrations, buffer use, and hydrolysis reactions.

Calculation of pH in a Theoretical Titration Curve— Use of the ICF Table

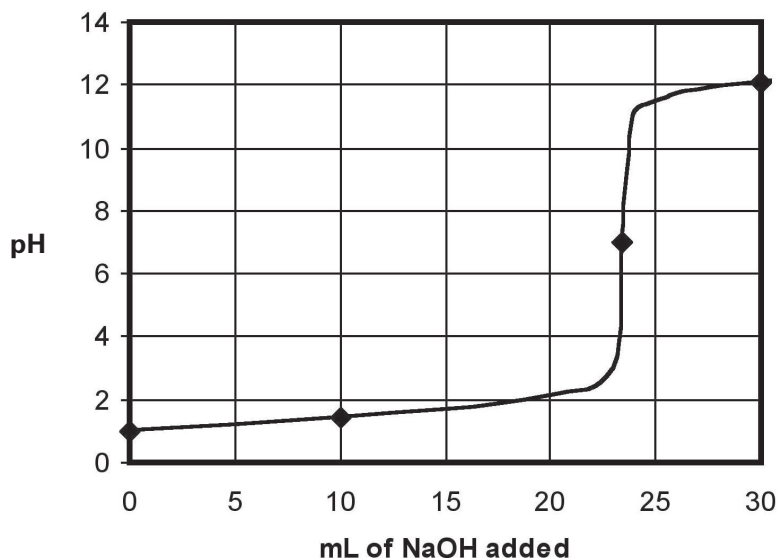
Most AP Chemistry students are able to handle the calculation of pH in a solution containing only one dissolved species. When two solutions are combined, however, they find the problem considerably more difficult. One of the biggest issues is the

organization of the increased amount of information given in such problems. The ICF table is a valuable tool for AP Chemistry teachers and students facing problems that involve chemical reactions such as neutralization with limiting and excess reactants. It is similar to the ICE chart used for equilibrium problems in that the “I” represents “initial” concentrations or numbers of moles and the “C” is the “change” in the initial quantities during the reaction. The traditional “E,” for “equilibrium” in an ICE chart, is replaced by an “F” that stands for “final” quantities following a reaction that goes to completion in one direction. Such a reaction in a titration curve calculation will involve neutralization by a strong acid or base. Because one (or both) of the reacting species is strong, the reaction goes virtually to completion, hence “F” replaces “E.” Such a reaction is said to be quantitative and is useful for analytic calculations.

Strong Acid–Strong Base Titrations

Though the pH at various points during the titration of a strong acid with a strong base (or vice versa) is relatively easy to determine, pre-AP and AP Chemistry teachers alike would be wise to apply the ICF technique early as it will build student confidence for its application to more difficult problems later. Consider the curve that describes the titration of 25.0 mL of 0.100 mol/L HCl with NaOH.

FIGURE 1



Providing such a curve for the titration of 25 mL of 0.100 mol/L HCl, with no further information, the AP Chemistry teacher might ask the class members to take several minutes, working alone or collaboratively, to list any information they can

determine about the titration from the pH profile. Sample student responses might include:

- Base is being added to acid.
- The reaction is represented by: $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$
- The initial pH = 1.0
- The initial $[\text{HCl}] = [\text{H}^+] = 10^{-\text{pH}} = 10^{-1.0} = 0.1 \text{ mol/L}$
- The acid is strong as the initial $[\text{H}^+] =$ the initial $[\text{HCl}]$ indicates 100% ionization.
- The pH at equivalence = 7.0
- The volume of base required to reach equivalence = 23.5 mL.
- The moles NaOH = moles $\text{OH}^- = 25.0 \text{ mL} \times \frac{0.100 \text{ mol HCl}}{1000 \text{ mL}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol HCl}} = 0.00250 \text{ mol NaOH}$ are required to reach equivalence.
- The $[\text{NaOH}] = \frac{0.00250 \text{ mol}}{23.5 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.106 \text{ mol/L}$

AP Chemistry teachers should reinforce the importance of beginning titration calculations with a balanced chemical equation, ideally in molecular form. This leads to a proper mole ratio that is most likely to be correct when units include the formula of the species they refer to. Any AP Chemistry text will contain a sample curve to which teachers can refer; however, the teacher might prefer to produce a curve using probeware (such as that available from Vernier or Pasco) or to use a variety of simulations available commercially or on the Internet (see suggestions in the laboratory section at the end of this chapter). Production of the curve could be done after, during, or even before the calculations.

Once students have examined a pH profile, or a titration curve for a strong monoprotic acid being titrated with a strong base, the AP Chemistry teacher can discuss the calculation of pH at various points throughout the curve.

Example 1

Calculate the pH of the 25.0 mL sample of 0.100 mol/L solution of HCl being titrated in the profile above.

Strategy:

The student should recognize that $\text{pH} = -\log [\text{H}^+]$ and that *the concentration of a solution is independent of its volume*. Hence, 25.0 mL is irrelevant to the problem at this point. Strong acids such as HCl, ionize completely, hence, $[\text{H}^+] = [\text{HCl}]$.

(AP Chemistry students must be aware of the “BIG 6” strong acids: HCl, HBr, HI, HClO_4 , HNO_3 , and H_2SO_4 (HClO_3 is included in some texts, although it ionizes less than 100%); H_2SO_4 is only nearly completely ionized for its first ionization) as there is no table of acid ionization constants included with the AP Chemistry Exam.)

Solution:

$$\text{pH} = -\log [\text{H}^+] = -\log [\text{HCl}] = -\log (0.100 \text{ mol/L}) = 1.000$$

Example 2

Calculate the pH of the 25.0 mL sample of HCl following the addition of 10.0 mL of 0.106 mol/L NaOH. Note that a “rounder” concentration of base might be used for introduction; however, this is what we’ve determined for our example.

Strategy:

The ICF table is very useful for helping students keep track of everything necessary to solve this problem. If concentrations are to be used (which may be preferable because pH depends upon concentration rather than moles), students must recognize that the concentration of a solution *is* affected by the addition of water or another solution as both of these cause *dilution*.

Step one is to *dilute*. The dilution factors are 25/35ths and 10/35ths, respectively. Step two is to neutralize by applying the ICF table. Step three is to examine the bottom line of the ICF table to determine what affects the pH.

Solution:

$$[\text{HCl}]_{\text{in}} = 0.100 \text{ mol/L} \frac{(25.0 \text{ mL})}{(35.0 \text{ mL})} \quad [\text{NaOH}]_{\text{in}} = 0.106 \text{ mol/L} \frac{(10.0 \text{ mL})}{(35.0 \text{ mL})}$$

$$= 0.0714 \text{ mol/L} \quad = 0.0303 \text{ mol/L}$$

Neutralization in ICF shows: $\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$

I:	0.0714 M	0.0303 M	0 M
C:	-0.0303	-0.0303	+0.0303
F:	0.0411	0	0.0303

The bottom line indicates a $[\text{HCl}] = [\text{H}^+] = 0.0411 \text{ mol/L}$, hence, $\text{pH} = -\log [\text{H}^+] = -\log (0.0411) = 1.386$

(Note that *moles* might have been used by multiplying the molarity of each reactant by its volume and using the moles in the "I" line. The changes would then have been 0.00106 moles. The final moles of acid divided by a total volume of 0.0350 L would give the same concentration and consequently, the same pH as shown.)

One final note that should be mentioned is that the ICF table indicates that the $[\text{NaOH}]_{\text{final}} = 0 \text{ mol/L}$, following the neutralization. This is, of course, impossible, as $[\text{H}^+][\text{OH}^-]$ must always $= 10^{-14} = K_w$ (at 25°C). Hence, $[\text{OH}^-] = [\text{NaOH}]$ at equivalence is negligible and approaches 0, though it can never actually equal 0. If $[\text{H}^+] = [\text{OH}^-]$, then each $= \sqrt{10^{-14}} = 10^{-7}$, which is very small compared to the molarity numbers on the problem, and so ≈ 0 .

Example 3

Calculate the pH of the 25.0 mL sample of HCl following the addition of 23.5 mL of 0.106 mol/L NaOH.

Strategy:

As in example 2, dilute and neutralize, then examine the bottom line of the ICF table.

Solution:

$$[\text{HCl}]_{\text{in}} = 0.100 \text{ mol/L} \frac{(25.0 \text{ mL})}{(48.5 \text{ mL})} \quad [\text{NaOH}]_{\text{in}} = 0.10638 \text{ mol/L} \frac{(23.5 \text{ mL})}{(48.5 \text{ mL})}$$

$$= 0.0515 \text{ mol/L} \qquad \qquad \qquad = 0.0515 \text{ mol/L}$$

Neutralization in ICF shows: $\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$

I:	0.0515 M	0.0515 M	0 M-
C:	-0.0515	-0.0515	+0.0515
F:	0	0	0.0515

This process shows that the pH of 7 at the equivalence point is due to the formation of 48.5 mL of a 0.0515 mol/L solution of NaCl, which dissociates to form the neutral cation, Na^+ and an anion, Cl^- . As the conjugate base of the strong acid, HCl, Cl^- is too weak to accept any appreciable quantity of protons from the water it is dissolved in and hence, it too is neutral. Determination of the pH at some point beyond

equivalence in the same fashion is helpful as it involves the application of K_w and/or pK_w along with the ICF table.

Example 4

Calculate the pH of the 25.0 mL sample of HCl following the addition of 30.0 mL of 0.106 mol/L NaOH solution.

Strategy:

As in example 2, dilute and neutralize, then examine the bottom line of the ICF table. The application of K_w and/or pK_w will be required to convert the $[\text{OH}^-]$.

Solution:

$$\begin{aligned} [\text{HCl}]_{\text{in}} &= 0.100 \text{ mol/L} \frac{(25.0 \text{ mL})}{(55.0 \text{ mL})} & [\text{NaOH}]_{\text{in}} &= 0.10638 \text{ mol/L} \frac{(30.0 \text{ mL})}{(55.0 \text{ mL})} \\ &= 0.0455 \text{ mol/L} & &= 0.0580 \text{ mol/L} \end{aligned}$$

Neutralization in ICF shows: $\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$

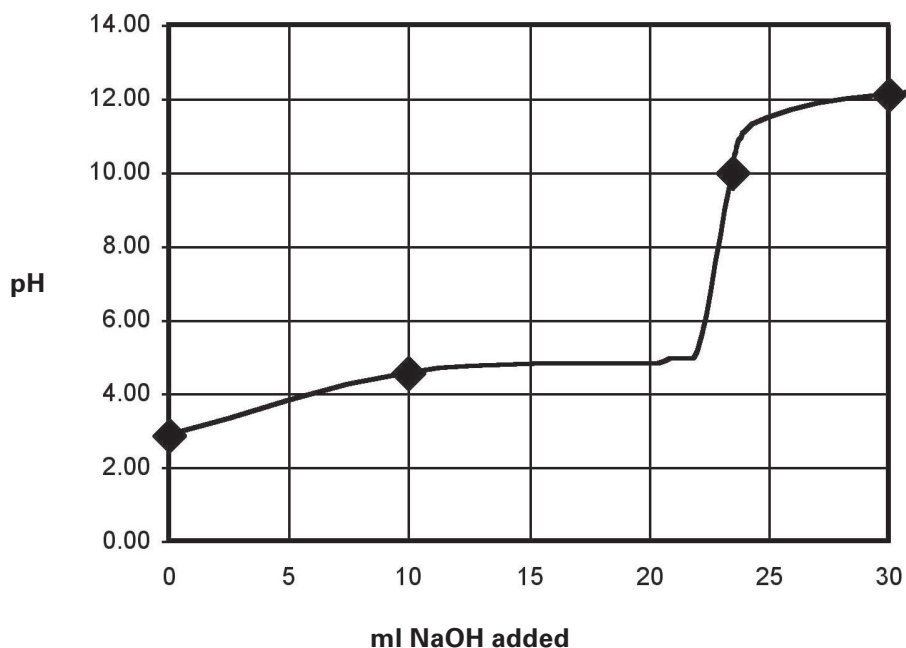
<i>I:</i>	0.0455 M	0.0580 M	0 M-
<i>C:</i>	-0.0455	-0.0455	+0.0455
<i>F:</i>	0	0.0125	0.0455

As explained in example 3, the salt, NaCl, is completely neutral and does not affect the pH at all. However, the $[\text{NaOH}]_{\text{excess}}$ is very significant. From this number, it becomes evident that the $p\text{OH} = -\log [\text{OH}^-] = -\log[\text{NaOH}] = -\log (0.0125) = 1.90$. Consequently, as $pK_w = \text{pH} + p\text{OH} = 14.00$ at 25°C , the $\text{pH} = 14.00 - 1.90 = 12.10$. The alternative approach would be to recognize that $[\text{H}^+] = K_w/[\text{OH}^-] = 10^{-14}/0.0125 = 8.0 \times 10^{-13}$ M. Hence, $\text{pH} = -\log (8.0 \times 10^{-13}) = 12.10$.

Weak–Strong Titrations

A classic weak–strong titration involves the titration of a weak carboxylic acid, such as ethanoic (acetic) acid or methanoic (formic) acid, with a strong base. Once students have examined a pH profile, or titration curve for a weak monoprotic acid being titrated with a strong base, the AP Chemistry teacher can compare the calculation of pH at various points throughout the curve with that of a strong–strong titration.

FIGURE 2



Providing such a curve, for the titration of 25 mL of 0.100 mol/L acetic acid, with no further information, the AP Chemistry teacher might ask the class to take several minutes, working collaboratively with a partner, to list any information they can determine about the titration from the pH profile, with emphasis on any obvious differences they notice between this curve and the earlier strong–strong one. Sample student responses might include:

- Base is being added to acid.
- The reaction is represented by: $\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$.
- The net ionic reaction is $\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{COO}^-$.
- The initial pH approximates 2.9 (higher than the strong acid).
- The initial $[\text{H}^+] = 10^{-\text{pH}} = 10^{-2.9} = 0.0013 \text{ mol/L}$.
- The acid is *not* as strong as the initial $[\text{H}^+] \ll$ the initial $[\text{CH}_3\text{COOH}]$ indicates less than 100% ionization.
- The % ionization = $\frac{0.0013 \times 100\%}{0.100} = 1.3\%$. This is typical of a weak acid.
- The pH rises more quickly during a weak–strong titration.
- The pH at equivalence is between 8 and 9 (above the neutral value of 7).
- The volume of base required to reach equivalence = 23.5 mL (same value).
- This is a particularly significant point for students to recognize and it should be emphasized that the *strength* of an acid has *no bearing* on the volume

of base required to neutralize it. One mole of monoprotic acid requires one mole of base to neutralize it completely whether the acid is strong or weak.

- The moles NaOH = $25.0 \text{ mL} \times \frac{0.100 \text{ mol HA}}{1000 \text{ mL}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol HA}} = 0.00250 \text{ mol}$ required to reach equivalence.
- The $[\text{NaOH}] = \frac{0.00250 \text{ mol}}{23.5 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.106 \text{ mol/L}$.

The same sources suggested for strong–strong curves may be relied upon for weak–strong curves. Once students have examined a pH profile, or titration curve for a weak monoprotic acid being titrated with a strong base, the AP Chemistry teacher can discuss the calculation of pH at various points throughout the curve. The ICF table is particularly useful for students attempting to deal with the additional complexity of these problems. AP Chemistry teachers should stress the review of weak acid, weak base, buffer, and hydrolysis calculations as they arise. It is important for students to consider the chemical composition of the solution being titrated as well as the process for calculating its pH at any particular point.

Example 5

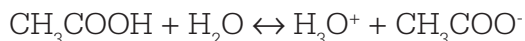
Calculate the pH of the 25.0 mL sample of a 0.100 mol/L solution of CH_3COOH being titrated in the profile above. (Given the K_a of acetic acid = 1.8×10^{-5} .)

Strategy:

The student should recognize that acetic acid is a *weak* acid, hence an ICE table type of calculation is required to determine the $[\text{H}_3\text{O}^+]$.

Solution:

According to the Brønsted-Lowry definition, an acid will donate a proton to the base it is dissolved in. Because this acid is weak, only a small percentage of the molecules will donate protons, resulting in the following equilibrium:



$$I: \quad 0.100 \text{ M} \quad - \quad 0 \text{ M} \quad 0 \text{ M}$$

$$C: \quad -x \quad \quad \quad +x \quad +x \quad [\text{H}^+] \text{ formed is defined as } x$$

$$E: \quad \sim 0.100 \quad \quad \quad x \quad x \quad \text{For weak acids that ionize less than 5\%, } x \text{ may be considered negligible compared with the initial concentration.}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{x^2}{0.100} = 1.8 \times 10^{-5}$$

Simple algebra reveals $x = [\text{H}_3\text{O}^+] = 1.3 \times 10^{-3}$ mol/L and $\text{pH} = -\log [\text{H}_3\text{O}^+]$
 $= -\log (1.3 \times 10^{-3}) = 2.87$.

Example 6

Calculate the pH of the 25.0 mL sample of CH_3COOH following the addition of 10.0 mL of 0.106 mol/L NaOH.

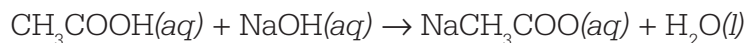
Strategy:

The ICF table may be used in an identical series of steps to those used for example 2 for the strong–strong titration shown previously.

Solution:

$$\begin{aligned} [\text{CH}_3\text{COOH}]_{\text{in}} &= 0.100 \text{ M} \left(\frac{25.0 \text{ mL}}{35.0 \text{ mL}} \right) & [\text{NaOH}]_{\text{in}} &= 0.106 \text{ M} \left(\frac{10.0 \text{ mL}}{35.0 \text{ mL}} \right) \\ &= 0.0714 \text{ mol/L} & &= 0.0303 \text{ mol/L} \end{aligned}$$

Neutralization in ICF shows:



<i>I:</i>	0.0714 M	0.0303 M	0 M	-
<i>C:</i>	-0.0303	-0.0303	+0.0303	
<i>F:</i>	0.0411	0	0.0303	

The bottom line indicates a $[\text{CH}_3\text{COOH}] = 0.0411 \text{ M}$ and a $[\text{CH}_3\text{COO}^-] = 0.0303 \text{ M}$. The student should recognize the presence of a weak conjugate pair with significant quantities of both the conjugate acid and base present. The AP Chemistry teacher should point out that such a solution constitutes a buffer. The pH of this solution may be calculated as a weak acid with conjugate base present as a common ion:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{[\text{H}_3\text{O}^+](0.0303)}{0.0411} = 1.8 \times 10^{-5}$$

Since $[\text{H}_3\text{O}^+] = 2.4 \times 10^{-5}$ mol/L, $\text{pH} = -\log (2.4 \times 10^{-5}) = 4.61$.

The pH of a buffer may also be calculated using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 4.74 + \log \frac{(0.0303)}{(0.0411)} = 4.61$$

This portion of the curve is referred to as the “buffer zone.” It is particularly instructive for the AP Chemistry teacher to point out that exactly half way to equivalence, the quantity of excess weak acid *exactly equals* the quantity of conjugate base formed by the neutralization. Substitution into each of the equations above, in turn, shows:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = [\text{H}_3\text{O}^+] \text{ and } \text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \text{p}K_a + \log(1) = \text{p}K_a$$

The teacher should encourage AP Chemistry students to use either or both of these equations to recognize and to verify the changes that occur during the buffer zone portion of a weak-strong titration curve:

- halfway to equivalence, $[\text{H}^+] = K_a$ and $\text{pH} = \text{p}K_a$.
- prior to halfway, $[\text{H}^+]$ exceeds K_a and so $\text{pH} < \text{p}K_a$.
- past halfway and before equivalence, $[\text{H}^+] < K_a$ and so pH exceeds $\text{p}K_a$.

Example 7

Calculate the pH of the 25.0 mL sample of CH_3COOH following the addition of 23.5 mL of 0.106 mol/L NaOH.

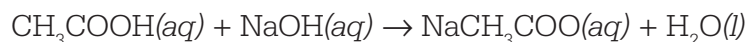
Strategy:

As in example 6, dilute and neutralize, then examine the bottom line of the ICF table.

Solution:

$$\begin{aligned} [\text{CH}_3\text{COOH}]_{\text{in}} &= 0.100 \text{ M} \quad \frac{(25.0 \text{ mL})}{(48.5 \text{ mL})} & [\text{NaOH}]_{\text{in}} &= 0.10638 \text{ M} \quad \frac{(23.5 \text{ mL})}{(48.5 \text{ mL})} \\ &= 0.0515 \text{ mol/L} & & = 0.0515 \text{ mol/L} \end{aligned}$$

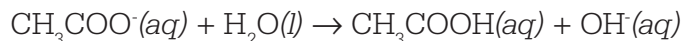
Neutralization in ICF shows:



<i>I:</i>	0.0515 M	0.0515 M	0 M	-
<i>C:</i>	-0.0515	-0.0515	+0.0515	
<i>F:</i>	0	0	0.0515	

The bottom line shows that the basic pH at the equivalence point is due to the formation of 48.5 mL of a 0.0515 mol/L solution of the salt, NaCH_3COO ,

which dissociates to form the neutral cation, Na^+ and the weakly basic anion, CH_3COO^- . As the conjugate base of the weak acid, CH_3COOH , CH_3COO^- is strong enough to accept an appreciable quantity of protons from the water it is dissolved in and hence, it forms hydroxide ions by hydrolysis.



<i>I:</i>	0.0515 M	- 0 M	0 M	
<i>C:</i>	-x	+ x	+ x	[OH ⁻] formed is
<i>E:</i>	<u>≈ 0.0515</u>	x	x	defined as x

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{K_w}{K_a} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = \frac{x^2}{0.0515} \text{ hence,}$$

$$x = [\text{OH}^-] = 5.3 \times 10^{-6} \text{ mol/L and pOH} = -\log(5.3 \times 10^{-6}) = 5.27, \\ \text{and pH} = 14 - 5.27 = 8.73$$

Example 8

Calculate the pH of the 25.0 mL sample of CH_3COOH following the addition of 30.0 mL of 0.106 mol/L NaOH solution.

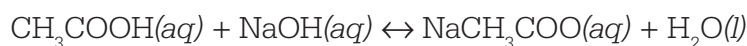
Strategy:

As in example 7, dilute and neutralize, then examine the bottom line of the ICF table. As in the strong-strong example 4 shown previously, the application of K_w and/or $\text{p}K_w$ will be required to convert the [OH⁻].

Solution:

$$\begin{aligned} [\text{CH}_3\text{COOH}]_{\text{in}} &= 0.100 \text{ M} \quad \frac{(25.0 \text{ mL})}{(55.0 \text{ mL})} \quad [\text{NaOH}]_{\text{in}} &= 0.10638 \text{ M} \quad \frac{(30.0 \text{ mL})}{(55.0 \text{ mL})} \\ &= 0.0455 \text{ mol/L} & &= 0.0580 \text{ mol/L} \end{aligned}$$

Neutralization in ICF shows:



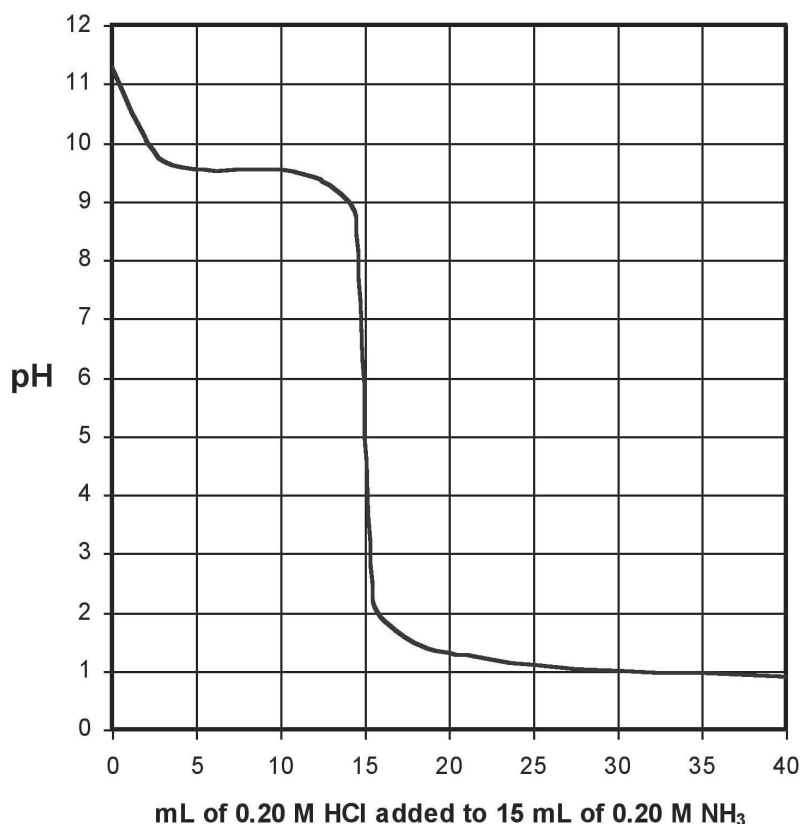
<i>I:</i>	0.0455 M	0.0580 M	0 M	-
<i>C:</i>	-0.0455	-0.0455	+0.0455	
<i>F:</i>	0	0.0125	0.0455	

As explained in example 7, the salt, NaCH_3COO , is weakly basic due to hydrolysis. However, the $[\text{NaOH}]_{\text{excess}}$ is much more significant. In fact, the hydroxide

ion from the NaOH forces the hydrolysis reaction so far left that its contribution to the $[\text{OH}^-]$ may be completely ignored. The $[\text{OH}^-] = [\text{NaOH}]_{\text{excess}}$ for all intents and purposes. Consequently, the $\text{pOH} = -\log [\text{OH}^-] = -\log (0.0125) = 1.90$. Hence, as $\text{p}K_{\text{w}} = \text{pH} + \text{pOH} = 14.00$ at 25°C , the $\text{pH} = 14.00 - 1.90 = 12.10$. The alternative approach would be to recognize that $[\text{H}_3\text{O}^+] = K_{\text{w}}/[\text{OH}^-] = 10^{-14}/0.0125 = 8.0 \times 10^{-13} \text{ M}$. Hence, $\text{pH} = -\log (8.0 \times 10^{-13}) = 12.10$.

The alternative to titrating a weak acid with a strong base is, of course, the titration of a weak base with a strong acid. A classic example might be the titration of ammonia with hydrochloric acid.

FIGURE 3



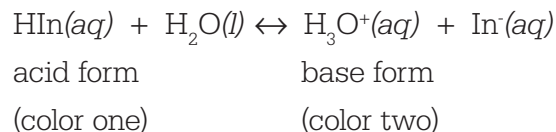
Such a titration would include the calculation of pH by:

- The use of the ionization constant of a weak base, K_{b} . Initially one is determining the pH of a solution of ammonia.
- The use of a K_{b} expression or Henderson-Hasselbalch during the buffer zone. In this portion of the curve the solution contains the weak conjugate pair ammonia and ammonium ion, therefore it is a basic buffer.

- The use of the acid ionization constant of a weak acid, K_a at equivalence due to the formation of an acidic salt, in this case, ammonium chloride, which undergoes cationic hydrolysis.
- The application of the standard definition of pH applied to the excess $[H_3O^+]$ present in a solution of ammonium chloride once excess strong acid has been added and the titration proceeds beyond equivalence.

Selection of an Appropriate Acid-Base Indicator

An acid–base indicator is a chemical species that has *an acid and a base form with one or both forms being visibly colored*. Many indicators were originally isolated from organic plants or foods. Some have been used as dyes. The general form for the equation that represents the equilibrium for an indicator is:



If the indicator is placed in a stronger acid, the acid will donate protons to the indicator, producing the HIn form (and color). A stronger base will pull protons from the indicator, producing the In^- form (and color). When indicators are in the middle of their color change, the $[\text{HIn}] = [\text{In}^-]$ and the color shown will be a combination of the acid and base form colors. This is called the *endpoint* or *transition point* for the indicator.

Since indicators are actually weak acids, they do have K_a and consequently $\text{p}K_a$ values. Substitution into familiar equations shows:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} = [\text{H}_3\text{O}^+] \text{ and } \text{pH} = \text{p}K_a + \log \frac{[\text{In}^-]}{[\text{HIn}]} = \text{p}K_a + \log(1) = \text{p}K_a$$

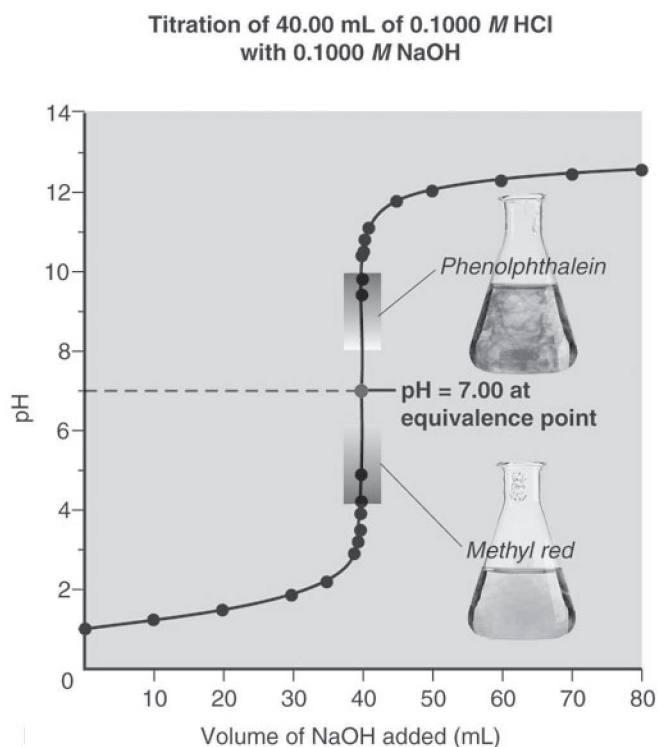
Hence, an indicator will reach its endpoint and change color when the $[\text{H}_3\text{O}^+]$ in the system equals the indicator's K_a . Similarly, during the color change (at the indicator's endpoint), the pH of the system will equal the indicator's $\text{p}K_a$.

Ideally, endpoints should occur exactly at equivalence. Thus, different types of titrations will require different indicators. Phenolphthalein changes color between pH 8.2 and 10.0. It has a $\text{p}K_a$ of approximately 9.1, hence it would be quite appropriate for the acetic acid titration because example 7's calculated equivalence point was pH 8.73. On the other hand, it would be absolutely wrong for use in the titration of ammonia with hydrochloric acid because the pH at equivalence for that titration

would be around 5.4, as shown in the third curve (Figure 3). One significant point demonstrated by each of the curves we've studied is the rapid change in pH that suddenly occurs at equivalence. AP Chemistry teachers can demonstrate this dramatically through the use of a pH meter or probe ware (such as that available from Vernier or Pasco) or a variety of simulations available commercially or on the Internet (see suggestions in the laboratory section at the end of this chapter). Because of this rapid change, an indicator's pK_a need not exactly match the pH expected at equivalence. Rather, the indicator must simply complete its entire color change during the *vertical part* of the titration curve. This means that phenolphthalein might be selected ahead of an indicator having a pK_a closer to the pH at equivalence simply because its change from colorless to pink is so clearly visible and easy to detect.

The titration curve below shows that phenolphthalein or methyl red along with many other indicators would be appropriate for determining the equivalence point for a strong–strong titration.

FIGURE 4

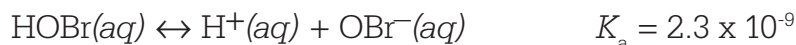


Sample Questions from Previous AP Chemistry Exams

The topic of titration appears on virtually every AP Chemistry exam. It is often a significant topic in the free-response portion of the examination. Problem number

one of the three required problems is always an equilibrium problem. This problem centers on an acid–base equilibrium nearly every other year. Such problems require student confidence with acid–base calculations of the sort discussed in this chapter.

2002 Operational Exam



1. Hypobromous acid, HOBr, is a weak acid that dissociates in water, as represented by the equation above.

- (a) Calculate the value of $[\text{H}^+]$ in an HOBr solution that has a pH of 4.95.
- (b) Write the equilibrium constant expression for the ionization of HOBr in water, then calculate the concentration of HOBr(*aq*) in an HOBr solution that has $[\text{H}^+]$ equal to $1.8 \times 10^{-5} \text{ M}$.
- (c) A solution of Ba(OH)₂ is titrated into a solution of HOBr.
 - (i) Calculate the volume of 0.115 M Ba(OH)₂(*aq*) needed to reach the equivalence point when titrated into a 65.0 mL sample of 0.146 M HOBr(*aq*).
 - (ii) Indicate whether the pH at the equivalence point is less than 7, equal to 7, or greater than 7. Explain.
- (d) Calculate the number of moles of NaOBr(*s*) that would have to be added to 125 mL of 0.160 M HOBr to produce a buffer solution with $[\text{H}^+] = 5.00 \times 10^{-9} \text{ M}$.
Assume that volume change is negligible.
- (e) HOBr is a weaker acid than HBrO₃. Account for this fact in terms of molecular structure.

Solution:

(a) $\text{pH} = -\log[\text{H}^+]$; $[\text{H}^+] = 10^{-4.95} = 1.1 \times 10^{-5} \text{ mol/L}$

(b) $K_a = \frac{[\text{H}^+][\text{OBr}^-]}{[\text{HOBr}]} = 2.3 \times 10^{-9}$

$$[\text{H}^+] = [\text{OBr}^-] = 1.8 \times 10^{-5} \text{ M}$$

$$\frac{(1.8 \times 10^{-5})^2}{x} = 2.3 \times 10^{-9}$$

$$x = [\text{HOBr}] = 0.14 \text{ M}$$

$$(c) \text{ (i) } 65.0 \text{ mL} \times \frac{0.146 \text{ mol HOBr}}{1000 \text{ mL}} \times \frac{1 \text{ mol H}^+}{1 \text{ mol HOBr}} \times \frac{1 \text{ mol OH}^-}{1 \text{ mol H}^+} \times \frac{1 \text{ mol Ba(OH)}_2}{2 \text{ mol OH}^-}$$

$$\times \frac{1000 \text{ mL}}{0.115 \text{ mol Ba(OH)}_2} = 41.3 \text{ mL}$$

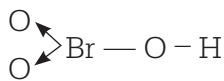
(ii) $\text{pH} > 7$; salt of a weak acid is a weak base (hydrolysis of OBr^-)

$$(d) \text{ pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \quad \text{or} \quad [\text{A}^-] = \frac{[\text{HA}]K_a}{[\text{H}^+]}$$

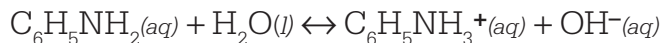
$$[\text{OBr}^-] = \frac{(0.160)(2.3 \times 10^{-9})}{5.00 \times 10^{-9}} = 0.0736 \text{ M}$$

$$125 \text{ mL} \times \frac{0.736 \text{ mol OBr}^-}{1000 \text{ mL}} \times \frac{1 \text{ mol NaOBr}}{1 \text{ mol OBr}^-} = 0.00920 \text{ mol NaOBr}$$

(e) very electronegative oxygen is able to draw electrons away from the bromine and weaken the O-H bond, making it easier for the hydrogen ion to be donated.



2003 Operational Exam



1. Aniline, a weak base, reacts with water according to the reaction represented above.

- Write the equilibrium constant expression, K_b , for the reaction represented above.
- A sample of aniline is dissolved in water to produce 25.0 mL of 0.10 M solution. The pH of the solution is 8.82. Calculate the equilibrium constant, K_b , for this reaction.
- The solution prepared in part (b) is titrated with 0.10 M HCl. Calculate the pH of the solution when 5.0 mL of the acid has been titrated.
- Calculate the pH at the equivalence point of the titration in part (c).
- The $\text{p}K_a$ values for several indicators are given below. Which of the indicators listed is most suitable for this titration? Justify your answer.

Indicator	p <i>K</i> _a
Erythrosine	3
Litmus	7
Thymolphthalein	10

Solution

$$(a) K_b = \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]}$$

$$(b) pOH = 14 - pH = 14 - 8.82 = 5.18$$

$$-\log[OH^-] = 5.18; [OH^-] = 6.61 \times 10^{-6} M$$

$$[OH^-] = [C_6H_5NH_3^+]$$

$$K_b = \frac{(6.61 \times 10^{-6})^2}{0.10 - 6.61 \times 10^{-6}} = 4.4 \times 10^{-10}$$

$$(c) 25 \text{ mL} \times \frac{0.1 \text{ mol}}{1 L} = 2.5 \text{ mmol } C_6H_5NH_2$$

$$5 \text{ mL} \times \frac{0.1 \text{ mol}}{1 L} = 0.5 \text{ mmol } H^+ \text{ added}$$

2.0 mmol base remains in 30.0 mL solution (*may determine from ICF*)

$$4.4 \times 10^{-10} = \frac{[X] \left[X + \frac{0.50 \text{ mmol}}{30.0 \text{ mL}} \right]}{\left[\frac{2.0 \text{ mmol}}{30.0 \text{ mL}} \right]}$$

$$X = 1.80 \times 10^{-9} = [OH^-]$$

$$[H^+] = \frac{1 \times 10^{-14}}{1.8 \times 10^{-9}} = 5.6 \times 10^{-6}; \text{ pH} = 5.26$$

(d) When neutralized, there are 2.5 mmol of $C_6H_5NH_3^+$ in 50.0 mL of solution, giving a $[C_6H_5NH_3^+] = 0.050 M$ (*may determine from ICF*)

This cation will partially ionize according to the following equilibrium:



at equilibrium, $[C_6H_5NH_2] = [H^+] = X$

$$[C_6H_5NH_3^+] = (0.050 - X)$$

$$\frac{X^2}{(0.050 - X)} = K_a = 2.3 \times 10^{-5}$$

$$X = 1.06 \times 10^{-3} = [H^+]$$

$$\text{pH} = -\log[H^+] = 2.98$$

- (e) Erythrosine; the indicator will change color when the pH is near its pK_a , since the equivalence point is near pH 3, the indicator must have a pK_a near this value.

The lab-based essay question has focused on acid-base titrations. Occasionally, the core concepts of titrimetry will be tested in an essay question that is not lab based. The following is an example of a lab-based acid–base essay question:

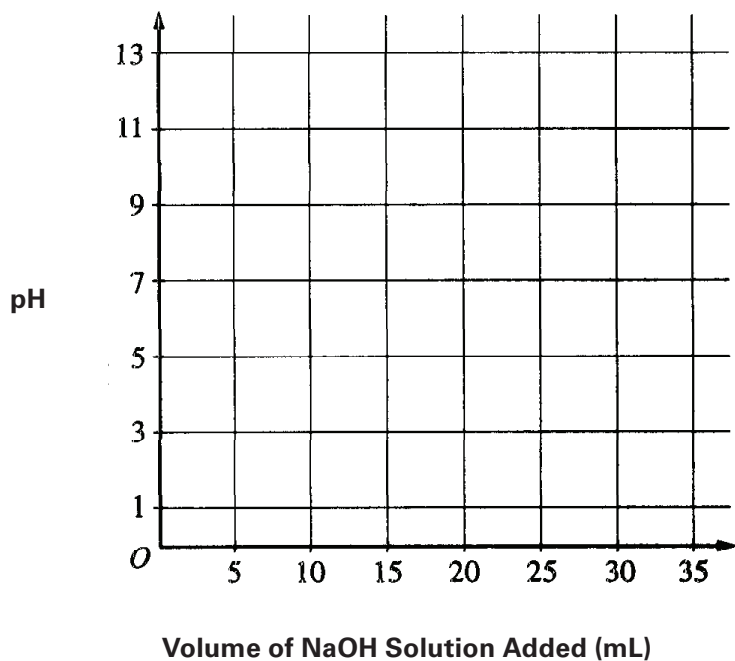
1998 Operational Exam

Lab-Based Question

An approximately 0.1–molar solution of NaOH is to be standardized by titration. Assume that the following materials are available.

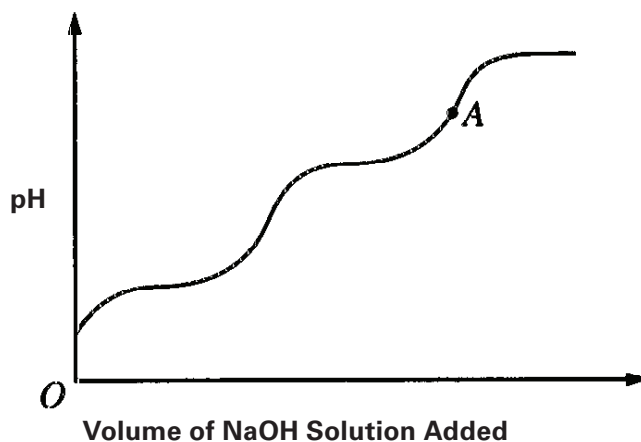
- Clean, dry 50 mL buret
 - 250 mL Erlenmeyer flask
 - Wash bottle filled with distilled water
 - Analytical balance
 - Phenolphthalein indicator solution
 - Potassium hydrogen phthalate, KHP, a pure solid monoprotic acid (to be used as the primary standard)
- (a) Briefly describe the steps you would take, using the materials listed above, to standardize the NaOH solution.
- (b) Describe (i.e., set up) the calculations necessary to determine the concentration of the NaOH solution.
- (c) After the NaOH solution has been standardized, it is used to titrate a weak monoprotic acid, HX. The equivalence point is reached when 25.0 mL of NaOH solution has been added. In the space provided at the right, sketch the titration curve, showing the pH changes that occur as the volume of NaOH solution added increases from 0 to 35.0 mL. Clearly label the equivalence point on the curve.

FIGURE 5



- (d) Describe how the value of the acid-dissociation constant, K_a , for the weak acid HX could be determined from the titration curve in part (c).
- (e) The graph below shows the results obtained by titrating a different weak acid, H_2Y , with the standardized NaOH solution. Identify the negative ion that is present in the highest concentration at the point in the titration represented by the letter A on the curve.

FIGURE 6



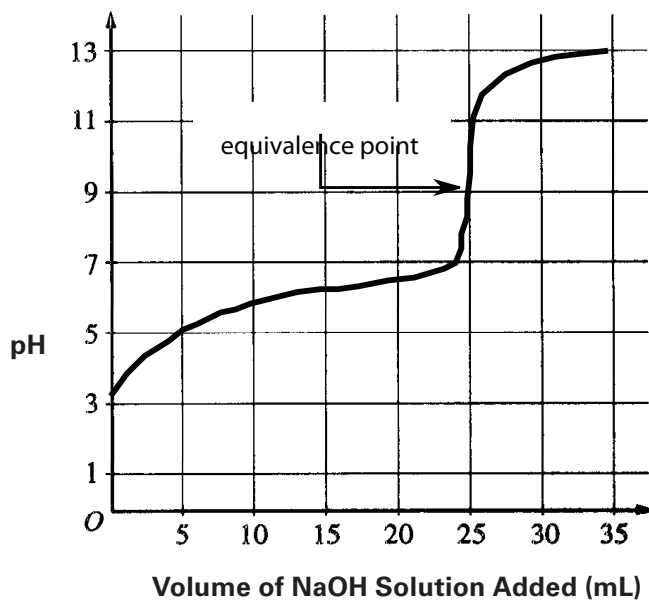
Solution:

- (a)
- Exactly mass a sample of KHP in the Erlenmeyer flask and add distilled water to dissolve the solid.
 - Add a few drops of phenolphthalein to the flask.
 - Rinse the buret with the NaOH solution and fill.
 - Record starting volume of base in buret.
 - With mixing, titrate the KHP with the NaOH solution until it just turns slightly pink.
 - Record end volume of buret.
 - Repeat to check your results.

(b)
$$\frac{\text{mass of KHP}}{\text{molar mass KHP}} = \text{moles of KHP};$$

since KHP is monoprotic, this is the number of moles of NaOH.

$$\frac{\text{moles of NaOH}}{\text{L of titrant}} = \text{molarity of NaOH}$$

FIGURE 7

- (d) From the titration curve, at the 12.5 mL volume point, the acid is half-neutralized and the $\text{pH} = \text{p}K_a$. $K_a = 10^{-\text{p}K_a}$

- (e) Y^{2-}

Recommended Laboratory Exercises Related to Acid–Base Titration

Wet Labs

Of the 22 recommended laboratory experiments for AP Chemistry, three involve acid–base titrimetry. As suggested earlier, the first experiment should involve the preparation of a primary standard that could be used to standardize a base that might be used to determine a molar mass, a K_a value, the moles of water of hydration, the efficiency of an antacid or the concentration of a diprotic acid, to list a few possibilities. An even simpler experiment (titration by drops) may be useful for students who have not encountered any form of titration in a previous class. Such an experiment will help bridge students' pre-AP or general chemistry skills to those required for AP Chemistry.

The second experiment should involve the development of experimental titration curves to be graphed and interpreted by the students. The classic two curves are, of course, the titration of first, HCl and second, CH_3COOH with NaOH as examples of strong acid–strong base and weak acid–strong base curves. Other possibilities include the titration of a weak base such as NH_3 with HCl or a polyprotic acid, such as H_3PO_4 with NaOH. A *potentiometric* titration, based on conductivity of, for example, $\text{Ba}(\text{OH})_2$ with H_2SO_4 is another possibility.

The third experiment involves the determination of appropriate indicators for different acid–base titrations.

There are a number of excellent resources for laboratories such as these. *Essential Experiments in Chemistry* by Morrison and Scodellaro, SMG Lab Books, 2005, includes all three of these labs (14A, 14G and 14 H). *Laboratory Investigations: AP Chemistry* by Hostage and Fossett, Peoples Publishing Group, 2005, contains two of them (#8 and #10). Additionally *Chemistry and Computers* by Holmquist and Volz, 2003, contains five of these labs (#23–#27) each with specific direction for use of probe ware.

Virtual Labs

There are a number of laboratory exercises that may be done virtually. Some of them are commercially available on DVD or CD. One of the more popular is the *Virtual Chemlab* disc provided with the text, *Chemistry, the Central Science, 10th edition*, by Brown, LeMay and Bursten (Prentice Hall, 2006). This disc includes several lab exercises that students may perform virtually, on the computer, including a titration

lab that allows them to select various reagents to use in a variety of titrations. The data they collect may be presented in tabular and/or graphic form.

Bridging to the Lab by Jones and Tasker, W.H. Freeman and Company, 2002, includes 11 different virtual lab exercises, one of which uses an acid-base titration to determine the pK_a of a food preservative. Students produce a titration curve and use it to determine the pK_a of a weak acid as well as its concentration and finally its molar mass.

In addition to the commercial lab exercises, there are some Web sites whose authors have graciously provided their lab exercises free of charge. A fantastic source of Flash-based chemistry simulations has been prepared by Tom Greenbowe from Iowa State. Start at www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/flashfiles/ to select a titration simulation that is very easy to use. Students may select from several weak or strong acids, one of two possible indicators, and four different bases that may be placed in the buret.

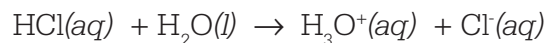
Another great Web site for curves was prepared by Yue-Wing Long from Wake Forest University. Visit www.wfu.edu/~ylwong/chem/titrationsimulator/index.html to actually plot a titration curve that may be used to determine the concentration and/or the pK_a of a variety of weak acids. This site is particularly useful as it allows students to alter the strength of the acid they use by selecting various K_a or concentration values for the acids they titrate.

Polyprotic Acids

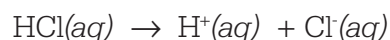
Lew Acampora

St. Francis School
Louisville, Kentucky

According to Brønsted-Lowry formalism, an acid is defined as a proton donor.⁵ The common and unique reactivity of the proton, also represented as the H^+ ion, imbues acids with their familiar properties. Though all Brønsted-Lowry acids contain hydrogen, the converse statement—that all hydrogen-containing compounds act as acids—is not generally true. The extent to which a species donates a proton is a measure of the acidity of the species and is ultimately determined by the electronic structure of the particle. For example, because gaseous hydrogen chloride dissolves and ionizes completely in aqueous solutions, it is classified as a strong acid:



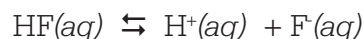
or



Hydrogen fluoride, however, dissolves into water and reaches a state of dynamic equilibrium in which a fraction of the HF molecules will be ionized at any instant. This state of equilibrium is indicated by the double arrows and leads to the classification of hydrofluoric acid as a weak acid:



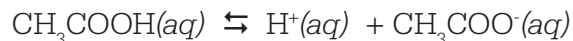
or



The difference in the behavior of HCl and HF can be traced to such factors as the relative strength of the H-X bond, the strength of the intermolecular forces between the HX molecule and the water molecules, and the energy of hydration of the X^- ion.

5. The more general definition of acids, attributed to G. N. Lewis, defines acids and bases in terms of their capacity to accept or donate pairs of electron. A Lewis acid is an electron-pair acceptor. Though this definition is more general, most quantitative problems in AP Chemistry can be approached using the Brønsted-Lowry formalism.

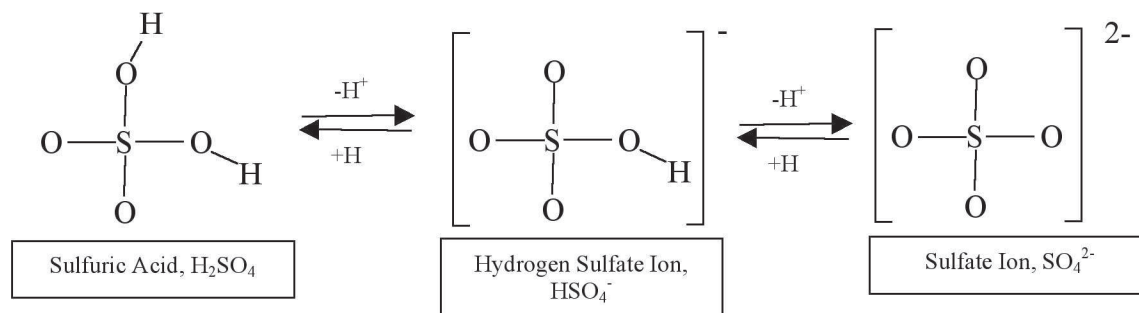
Hydrochloric acid and hydrofluoric acid are examples of monoprotic acids because each molecule contains only one ionizable hydrogen. Acetic Acid, CH_3COOH , is another example of a monoprotic acid because, though each molecule contains four hydrogen atoms, it is only the carboxylic hydrogen that is ionized in aqueous solution:



Because of the covalent character of the C – H bond, the hydrogen atoms that are directly bonded to carbon are not ionized in aqueous solution.

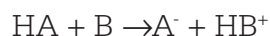
Many substances contain more than one ionizable hydrogen atom, and such substances are generally referred to as polyprotic acids, with subsets including diprotic, triprotic, etc. In these substances, each acidic hydrogen can be donated. For example, one of the most common diprotic acids is sulfuric acid, H_2SO_4 . A structural diagram for sulfuric acid shows that both hydrogen atoms are directly bonded to oxygen atoms, and the character of these O-H bonds leads to the acidity of both hydrogen atoms. Thus, the sulfuric acid molecule can lose both protons sequentially to become, first, the hydrogen sulfate ion, HSO_4^- , and finally the sulfate ion, SO_4^{2-} .

FIGURE 1

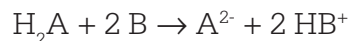


The underlying principles of reactivity that govern the behavior of monoprotic acids are generally true for polyprotic acids; however, there are two additional factors or considerations that should be noted. The presence of more than one acidic hydrogen per molecule will affect the stoichiometry of reactions of those polyprotic acids. Additionally, the tendency to donate each proton will be different, and will have ramifications in terms of the acid strength.

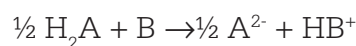
The Brønsted-Lowry formalism considers an acid–base reaction as simply a proton transfer reaction between a proton donor (the acid) and a proton acceptor (the base). A general schema for such a reaction with a monoprotic acid is:



The stoichiometry of the reaction shows that acid and base are consumed in equimolar quantities. If the reactant is a diprotic acid, then each mole of acid will contribute two moles of protons. In order to neutralize a given quantity of base, then, only half as many moles of the diprotic acid are required:



or



While 1 mole of hydrochloric acid will completely neutralize 1 mole of sodium hydroxide, the same neutralization would require only $\frac{1}{2}$ mole of sulfuric acid.⁶

The tendency of a particular species to donate a proton—the acid strength—is ultimately traced to the electronic structure of the acid and its conjugate base. For this reason, successive ionizations of a polyprotic acid are generally weaker. As protons are removed from the substance, any remaining ionizable protons are more strongly bonded because a positively charged proton will be more strongly attracted to the more negatively charged particle. The resulting species is a weaker acid than the original particle. This is reflected in the values of the acid dissociation constants,⁷ K_{an} , for polyprotic acids, which decrease in value for successive ionizations. Consider, for example, the triprotic weak phosphoric acid, H_3PO_4 . Steps in the complete ionization of phosphoric acid and the values of the acid dissociation constants are shown here:

Reaction Equation	Equilibrium Constant Expression	Equilibrium Constant Value
$\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^-$	$K_{a1} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$	7.3×10^{-3}
$\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-}$	$K_{a2} = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$	6.2×10^{-8}
$\text{HPO}_4^{2-} \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-}$	$K_{a3} = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}$	4.8×10^{-13}

6. The concept of “normality” has fallen somewhat out of favor and can be omitted from the AP Chemistry course, but it still may be useful in describing the stoichiometry of acid–base reactions. Normality in this context is defined as “moles of ionizable protons per liter of solution.” For a diprotic acid, the normality is simply twice the molarity. Thus, a 0.10 M H_2SO_4 solution would be considered 0.20 N, or 0.20 normal. Similarly, a 0.10 M solution of the triprotic phosphoric acid, H_3PO_4 , would be 0.30 N.

7. The acid dissociation constants for polyprotic acids are generally denoted as K_{an} , where the “n” refers to the nth proton donated by the molecular species. A diprotic acid would have different values of K_{a1} and K_{a2} , a triprotic acid would have K_{a1} , K_{a2} , and K_{a3} .

SPECIAL FOCUS: Acids and Bases

The phosphoric acid molecule H_3PO_4 is the strongest acid among the substances listed. Its conjugate base, the dihydrogen phosphate ion H_2PO_4^- , still contains two ionizable protons and is itself an acid.⁸ Because of its overall negative charge and the bond electron density, the H-O bonds in H_2PO_4^- are stronger than those in H_3PO_4 , and H_2PO_4^- is a weaker acid.

The observation that successive protons are increasingly difficult to remove from polyprotic acids implies that these polyprotic acids ionize stepwise when reacting with strong bases. For phosphoric acids, the following net ionic equations apply:

Reaction Description	Net Ionic Equation
Equal volumes of 0.10 M phosphoric acid and 0.10 M sodium hydroxide are mixed.	$\text{H}_3\text{PO}_4 + \text{OH}^- \rightarrow \text{H}_2\text{PO}_4^- + \text{H}_2\text{O}$
Equal volumes of 0.10 M phosphoric acid and 0.20 M sodium hydroxide are mixed.	$\text{H}_3\text{PO}_4 + 2 \text{OH}^- \rightarrow \text{HPO}_4^{2-} + 2 \text{H}_2\text{O}$
Equal volumes of 0.10 M phosphoric acid and 0.30 M sodium hydroxide are mixed.	$\text{H}_3\text{PO}_4 + 3 \text{OH}^- \rightarrow \text{PO}_4^{3-} + 3 \text{H}_2\text{O}$
Equal volumes of 0.10 M sodium dihydrogen phosphate and 0.20 M sodium hydroxide are mixed.	$\text{H}_2\text{PO}_4^- + 2 \text{OH}^- \rightarrow \text{PO}_4^{3-} + 2 \text{H}_2\text{O}$

Since phosphoric acid, dihydrogen phosphate ion, and monohydrogen phosphate ion can each act as acids, their respective conjugate bases are dihydrogen phosphate, monohydrogen phosphate, and phosphate ion. These bases are listed in order of increasing base strength, and the values of the respective base dissociation constants reflect this:

Reaction Equation	Equilibrium Constant Expression	Equilibrium Constant Value
$\text{PO}_4^{3-} + \text{H}_2\text{O} \rightleftharpoons \text{HPO}_4^{2-} + \text{OH}^-$	$K_{b3} = \frac{[\text{HPO}_4^{2-}] \cdot [\text{OH}^-]}{[\text{PO}_4^{3-}]}$	2.1×10^{-2}
$\text{HPO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{OH}^-$	$K_{b2} = \frac{[\text{H}_2\text{PO}_4^-] \cdot [\text{OH}^-]}{[\text{HPO}_4^{2-}]}$	1.6×10^{-7}
$\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{PO}_4 + \text{OH}^-$	$K_{b1} = \frac{[\text{H}_3\text{PO}_4] \cdot [\text{OH}^-]}{[\text{H}_2\text{PO}_4^-]}$	1.3×10^{-12}

Again, since the bases will accept protons stepwise, the following net ionic equations can be written:

8. A species such as H_2PO_4^- , which can either donate a proton, acting as an acid, or accept a proton, acting as a base, is termed amphiprotic or amphoteric. Though these terms are not strictly synonymous, for the purposes of the AP Chemistry curriculum, they can be considered interchangeable. Other examples of such species include the monohydrogen phosphate ion, HPO_4^{2-} , and the hydrogen carbonate or bicarbonate ion, HCO_3^- .

Reaction Description	Net Ionic Equation
Equal volumes of 0.10 M hydrochloric acid and 0.10 M sodium phosphate are mixed.	$\text{PO}_4^{3-} + \text{H}^+ \rightarrow \text{HPO}_4^{2-}$
Equal volumes of 0.20 M hydrochloric acid and 0.10 M sodium phosphate are mixed.	$\text{PO}_4^{3-} + 2 \text{H}^+ \rightarrow \text{H}_2\text{PO}_4^-$
Equal volumes of 0.30 M hydrochloric acid and 0.10 M sodium phosphate are mixed.	$\text{PO}_4^{3-} + 3 \text{H}^+ \rightarrow \text{H}_3\text{PO}_4$
Equal volumes of 0.10 M hydrochloric acid and 0.10 M sodium monohydrogen phosphate are mixed.	$\text{HPO}_4^{2-} + \text{H}^+ \rightarrow \text{H}_2\text{PO}_4^-$

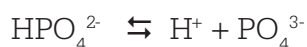
Because a solution of a polyprotic acid or its conjugate base(s) may contain several species related by different equilibrium reactions and constants, calculations to determine the concentration of each species may seem intractable. Fortunately, the values of the relevant acid dissociation constants are sufficiently diverse that the solution chemistry is usually dominated by one ionization, and the concentrations of each species can be determined from straightforward calculation. Consider, for example, a solution of 0.10 M phosphoric acid. In principle, the solution contains the species H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} , in addition to the H^+ and OH^- ions. In practice, the chemistry of the solution is dominated by the ionization reaction of the first proton:



Ionization of subsequent protons:



and



will have a negligible effect on the $[\text{H}^+]$ in the solution. The $[\text{H}^+]$ of the resulting solution can be determined from the ionization of the first proton:

	H_3PO_4	\rightleftharpoons	H^+	+	H_2PO_4^-
$[\]_o$	0.10 M		~ 0		0
$\Delta[\]$	-x		+x		+x
$[\]_{\text{eq}}$	0.10 - x		x		x

$$K_{a1} = \frac{[\text{H}^+] \cdot [\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$$

$$7.5 \times 10^{-3} = \frac{x \cdot x}{0.10 - x}$$

$$[\text{H}^+] = [\text{H}_2\text{PO}_4^-] = x = 0.024 \text{ M}$$

The resulting $[H^+]$ and $[H_2PO_4^-]$ can be used to determine the $[HPO_4^{2-}]$:

$$K_{a2} = \frac{H^+ \cdot HPO_4^{2-}}{H_2PO_4^-}$$

$$6.2 \times 10^{-8} = \frac{(0.024 \text{ M}) \cdot x}{(0.024 \text{ M})}$$

$$HPO_4^{2-} = x = 6.2 \times 10^{-8} \text{ M}$$

As expected, the relatively small $[HPO_4^{2-}]$ implies that the second ionization occurs to a negligible extent and has no measurable effect on the $[H^+]$ or the $[H_2PO_4^-]$. Similarly, the $[PO_4^{3-}]$ can be determined using previously calculated concentrations:

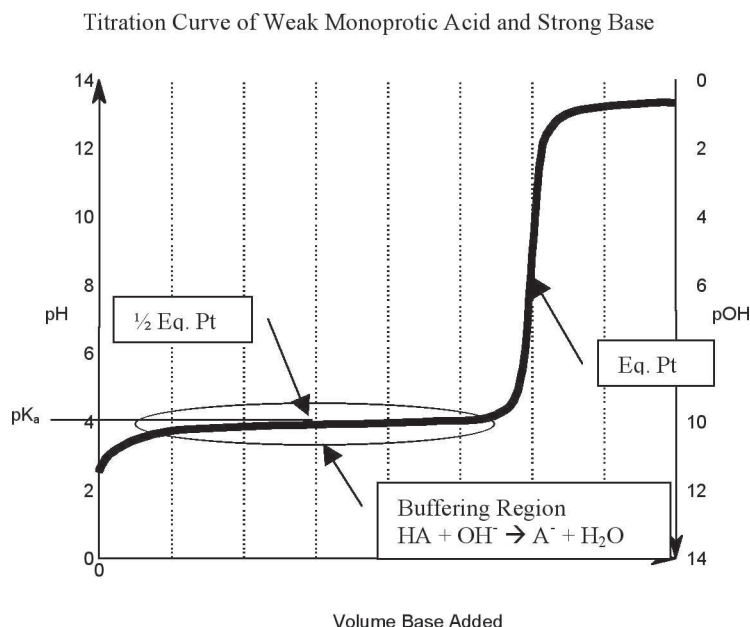
$$K_{a3} = \frac{H^+ \cdot PO_4^{3-}}{HPO_4^{2-}}$$

$$4.8 \times 10^{-13} = \frac{(0.024 \text{ M}) \cdot x}{(6.2 \times 10^{-8} \text{ M})}$$

$$PO_4^{3-} = x = 1.2 \times 10^{-18} \text{ M}$$

Not surprisingly, the calculated $[PO_4^{3-}]$ is extremely small.

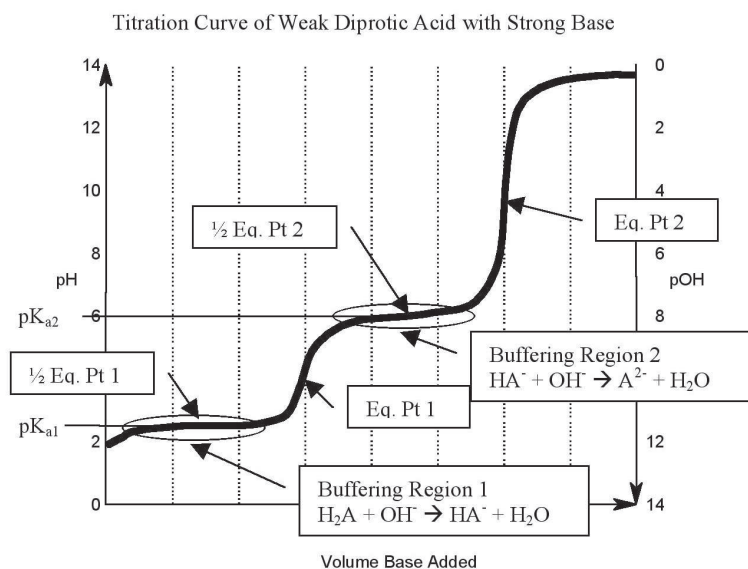
FIGURE 2



The behavior of polyprotic acids in acid–base titrations reflects the same considerations. Each of the ionizable protons is lost from the acid sequentially with increasing pK_a values. The graph of **pH vs. volume base added**, above, illustrates

what happens when a solution of a weak, monoprotic acid is titrated with a strong base. Important points on the graph are the equivalence point, where the moles of added OH^- are equal to the moles of HA initially present, and the half-equivalence point. At the half-equivalence point, half of the initial moles of weak acid remain, and half have been converted to the conjugate base. At this point in the titration, $[\text{HA}] = [\text{A}^-]$, and $K_a = \frac{\text{H}^+ \cdot \text{A}^-}{[\text{HA}]} = \text{H}^+$, so $\text{p}K_a = \text{pH}_{\frac{1}{2} \text{ Eq. Pt.}}$ and $K_a = 10^{-\text{p}K_a}$.

FIGURE 3



The graph of **pH vs. volume base** shows two buffering regions corresponding to the sequential ionization of each proton from the acid when a solution of a weak diprotic acid is titrated with a strong base. As in the case of the monoprotic acid, the equilibrium constants for each ionization may be determined from the pH values at *each* half-equivalence point. At the first half-equivalence point in the titration curve, $[\text{H}_2\text{A}] = [\text{HA}^-]$ and:

$$K_{a1} = \frac{\text{H}^+ \cdot \text{HA}^-}{[\text{H}_2\text{A}]} = \text{H}^+, \text{ so } \text{p}K_{a1} = \text{pH}_{\frac{1}{2} \text{ Eq. Pt. 1}}, \text{ and } K_{a1} = 10^{-\text{p}K_{a1}}.$$

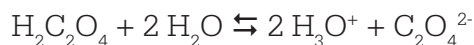
At the half-equivalence point corresponding to the second ionization, $[\text{HA}^-] = [\text{A}^{2-}]$ and

$$K_{a2} = \frac{\text{H}^+ \cdot \text{A}^{2-}}{[\text{HA}^-]} = \text{H}^+, \text{ so } \text{p}K_{a2} = \text{pH}_{\frac{1}{2} \text{ Eq. Pt. 2}}, \text{ and } K_{a2} = 10^{-\text{p}K_{a2}}.$$

The fundamental principles of acid–base chemistry remain valid for acids that have many ionizable protons, and a solid understanding of the chemistry of monoprotic acids and bases is essential for students before they can grasp the details of the chemistry of polyprotic species.

Examples from Prior AP Chemistry Examinations

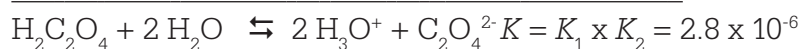
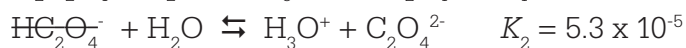
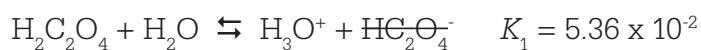
(1994)



31. Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, is a diprotic acid with $K_1 = 5.36 \times 10^{-2}$ and $K_2 = 5.3 \times 10^{-5}$. For the reaction above, what is the equilibrium constant?

- (A) 5.36×10^{-2}
- (B) 5.3×10^{-5}
- (C) 2.8×10^{-6}
- (D) 1.9×10^{-10}
- (E) 1.9×10^{-13}

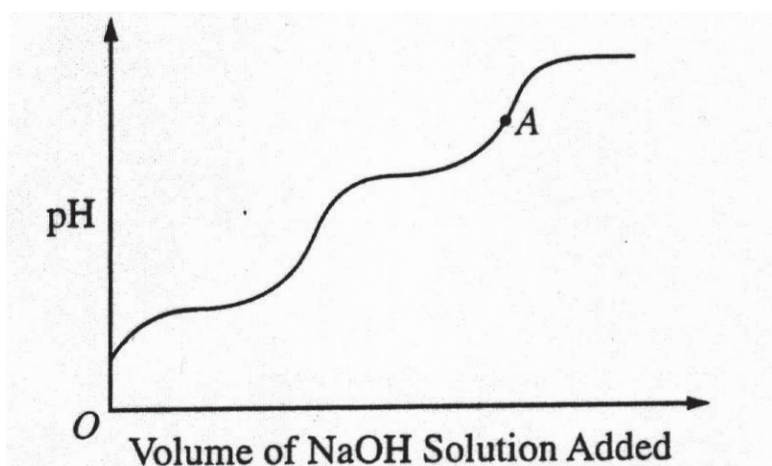
31. Answer: (C) From Hess's Law



(1998)

5(e). The graph below shows the results obtained by titrating a different weak acid, H_2Y , with the standardized NaOH solution. Identify the negative ion that is present in the highest concentration at the point in the titration represented by the letter "A" on the curve.

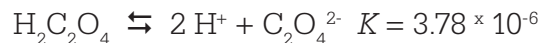
FIGURE 4



5(e). Answer: A^{2-}

(1997)

1. The overall dissociation of oxalic acid, $H_2C_2O_4$, is represented below. The overall dissociation constant is also indicated.



- (a) What volume of 0.400-molar NaOH is required to neutralize completely a 5.00×10^{-3} -mole sample of pure oxalic acid?
- (b) Give the equations representing the first and second dissociations of oxalic acid. Calculate the value of the first dissociation constant, K_1 , for oxalic acid if the value of the second dissociation constant, K_2 , is 6.40×10^{-5} .
- (c) To a 0.015-molar solution of oxalic acid, a strong acid is added until the pH is 0.5. Calculate the $[C_2O_4^{2-}]$ in the resulting solution. (Assume the change in volume is negligible.)
- (d) Calculate the value of the equilibrium constant, K_b , for the reaction that occurs when solid $Na_2C_2O_4$ is dissolved in water.

Answers:

(a) $5.00 \times 10^{-3} \text{ mol } H_2C_2O_4 = 2 \times (5.00 \times 10^{-3} \text{ mol}) H^+ = 1.00 \times 10^{-2} \text{ mol } H^+ = 1.00 \times 10^{-2} \text{ mol } OH^-$
 $\frac{1.00 \times 10^{-2} \text{ mol } OH^-}{0.400 \text{ M}} = 0.0250 \text{ L} = 25.0 \text{ mL}$

(b) There are two successive dissociations:



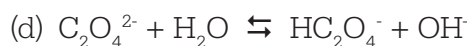
$$K = K_1 \times K_2$$

$$K_1 = \frac{K}{K_2} = \frac{3.78 \times 10^{-6}}{6.40 \times 10^{-5}} = 5.91$$

(c) $\text{pH} = 0.5 \quad H^+ = 10^{-0.5} =$

Because $K \ll 1$, $[H_2C_2O_4]_{\text{eq}} \approx 0.015 \text{ M}$

$$K = \frac{H^+{}^2 \cdot C_2O_4^{2-}}{[H_2C_2O_4]} \quad C_2O_4^{2-} = \frac{K \cdot [H_2C_2O_4]}{H^+{}^2} = \frac{(3.78 \times 10^{-6}) \times (0.015)}{(0.32)^2} = 6.0 \times 10^{-7}$$

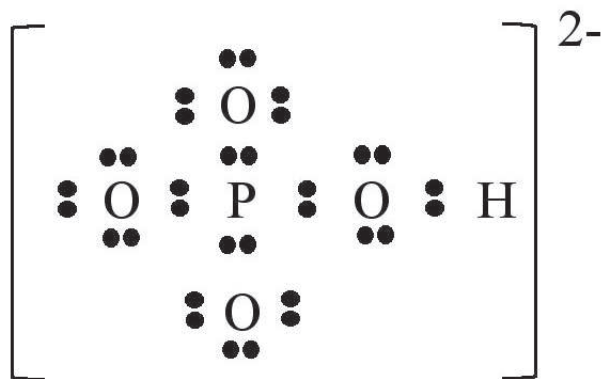
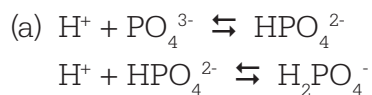


$$K_b = \frac{K_w}{K_{a2}} = \frac{1.00 \times 10^{-14}}{6.40 \times 10^{-5}} = 1.56$$

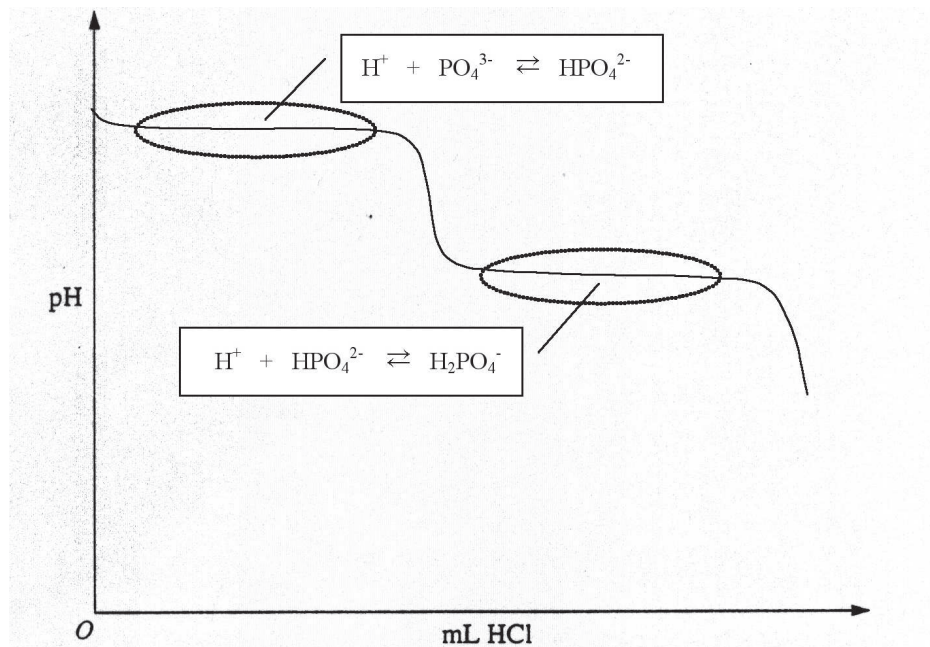
(1994)

7. A chemical reaction occurs when 100. milliliters of 0.2000-molar HCl is added dropwise to 100. milliliters of 0.100-molar Na₃PO₄ solution.

- Write the two net ionic equations for the formation of the major species.
- Identify the species that acts as both a Brønsted acid and as a Brønsted base in the equations in (a). Draw the Lewis electron-dot diagram for this species.
- Sketch a graph using the axis provided, showing the shape of the titration curve that results when 100. milliliters of the HCl solution is added slowly from a buret to the Na₃PO₄ solution. Account for the shape of the curve.
- Write the equation for the reaction that occurs if a few additional milliliters of HCl solution are added to the solution resulting from the titration in (c).

7. Answers:

(c)

(d) $\text{H}^+ + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}_3\text{PO}_4$

Salts and Buffers

Adele Mouakad

St. John's School

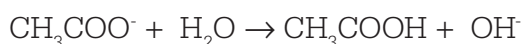
San Juan, Puerto Rico

Acid–Base Properties of Salt Solutions

A salt is an ionic compound that can be considered to be the product of the reaction between an acid and a base. The salt that is produced is sometimes neutral, but in many instances it dissolves in water to form a solution that is acidic or basic. This can be clearly explained from the Brønsted-Lowry theory, which shows that some ions can act as acids or bases. These ions can act as acids or bases because they react with water. This reaction with water is called *hydrolysis*. Hydrolysis is the reaction of an ion with water to produce the conjugate acid and hydroxide ion or the conjugate base and hydronium ion.

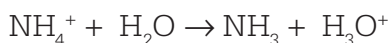
Notable examples are:

- (i) The reaction of the acetate ion with water.



This resulting solution would be basic due to the presence of the hydroxide ion. Since this solution has the form of a base ionization, you can write an expression for K_b . $K_b = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$

- (ii) The reaction of the ammonium ion with water.



This resulting solution would be acidic due to the presence of the hydronium ion. Since the resulting solution has the form of an acid ionization, the expression for K_a is: $K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]}$

How can you predict whether a salt will be acidic, basic or neutral?

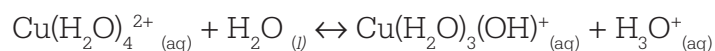
When the acetate ion hydrolyzes, it produces acetic acid, which is a weak acid. This means that the acetate ion holds fairly strongly to the proton (i.e., it does not ionize readily). So we can say that the acetate ion acts as a base. In general, we can say that anions of weak acids will be basic. On the other hand, the anions of strong acids (e.g., Cl⁻ from HCl) have very little basic character. In other words, these anions do not hydrolyze.

Let us examine the cation conjugate to a weak base, such as the ammonium (NH₄⁺) ion, which we used in our example above. It is clearly seen that it behaves like an acid. So we can generalize that the cations of weak bases are acidic. On the other hand, the cations of strong bases (alkali metal cations and alkaline earth metal cations) have hardly any acidic character.

Aqueous metal ions, that are not those of the alkali or alkaline earth metals, usually hydrolyze by acting as acids. Many of these ions form hydrated metal ions.

For example, copper (II) ion forms the Cu(H₂O)₄²⁺ ion. The Cu²⁺ ion acts as a Lewis acid, forming bonds with a lone pair of electrons in the O atoms of H₂O. Because the electrons are drawn away from the oxygen atoms by the Cu atom, the O atoms, in turn, tend to draw electrons from the O – H bonds, making them increasingly polar and weaker. As a result, the H₂O molecules in Cu(H₂O)₄²⁺ are acidic. Copper (II) salts tend to have a pH around 3.5.

Cu(H₂O)₄²⁺ hydrolyzes by donating a proton to a free water molecule. One of the water molecules loses a proton, reducing the charge of the ion by 1, and the water molecule becomes a hydroxide as shown in the reaction below.



We can summarize this in the following tables:

IONS OF NEUTRAL SALTS	
Cations	Na ⁺ , K ⁺ , Rb ⁺ , Cs ⁺ Mg ²⁺ , Ca ²⁺ , Sr ²⁺ , Ba ²⁺
Anions	Cl ⁻ , Br ⁻ , I ⁻ , ClO ₄ ⁻ , BrO ₄ ⁻ , ClO ₃ ⁻ , NO ₃ ⁻

Some Common Basic Ions			
F ⁻	CH ₃ COO ⁻	NO ₂ ⁻	CN ⁻
HCO ₃ ⁻	CO ₃ ²⁻	S ²⁻	HS ⁻
SO ₄ ²⁻	HPO ₄ ²⁻	PO ₄ ³⁻	ClO ⁻
ClO ₂ ⁻			

Some Common Acidic Ions			
NH_4^+	CH_3NH_3^+	Al^{3+}	Pb^{2+}
Transition metal ions (e.g., Cu^{2+})			
HSO_4^-	H_2PO_4^-		

To predict whether the salt solution is acidic, basic, or neutral you need to know whether the ions comprising the salt are acidic or basic or do not hydrolyze. In other words, you have to determine the acidity or basicity of the ions comprising the salt. Consider sodium cyanide, NaCN. This salt is composed of the potassium ion, Na^+ and the cyanide ion, CN^- . Sodium is an alkali metal, so Na^+ does not hydrolyze. However, the CN^- is the conjugate base of a weak acid, hydrocyanic acid, a weak acid. Therefore, the cyanide ion, CN^- , is basic. A salt of sodium cyanide is expected to be basic. Conclusions regarding acid or basic hydrolysis can be made by examining the K_a or K_b values in the literature for the species involved.

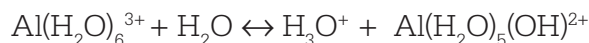
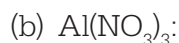
Let us examine the following exercise from the 1981 AP Exam.

Exercise 1

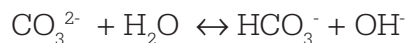
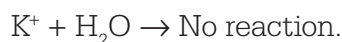


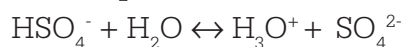
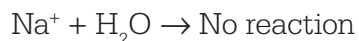
- (a) Predict whether a 0.10 molar solution of each of the salts above is acidic, neutral, or basic.
- (b) For each of the solutions that is not neutral, write a balanced chemical equation for a reaction occurring with water that supports your prediction.

Solution:



$\text{NO}_3^- + \text{H}_2\text{O} \rightarrow \text{No reaction}$ (conjugate base of a strong acid; it does not hydrolyze)





$\text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{No reaction}$ (conjugate base of strong acid; it does not hydrolyze)



One of the things to note from the above exercise is that students need to be aware that the transition metal ions and other metallic ions mentioned above do form complex ions with water. Students need to know the coordination number for the more common ions, such as Al^{3+} , Cu^{2+} , Zn^{2+} , etc.

A few basic rules would be:

1. A salt of a strong acid and a strong base. (e.g. NaCl). The salt does not have any ions that will hydrolyze, so it will be neutral.
2. A salt of a strong base and a weak acid. The anion is the conjugate base of a weak acid, so it hydrolyzes giving a basic solution.
3. A salt of a weak acid and a strong base. The cation of this salt is the conjugate of a weak base, so it hydrolyzes producing an acidic solution.
4. A salt of a weak acid and weak base. In this case both ions hydrolyze, the acidity or basicity depends on the K_a and K_b of the conjugate acids and bases respectively. If the $K_a > K_b$, the solution will be acidic. If the $K_b > K_a$, the solution will be basic.

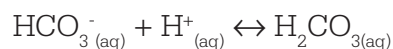
Buffers

Definition: A buffer solution is one that resists changes in pH when small quantities of an acid or a base are added to it. If 0.01 mol of HCl is added to 1.0 L of sodium chloride solution, the pH changes from 7.0 to 2.0. On the other hand, if this same amount of hydrochloric acid is added to 1.0 L of ocean or sea water, the pH changes by only 0.1 unit. Obviously, sea water has other substances present that maintain the pH of sea water at a fairly constant level. The pH of sea water ranges from 7.5 to 8.4. This is very important because many aquatic organisms are very sensitive to changes in pH. The pH of mammalian blood is also maintained at a pH of close to 7.38.

Composition: A buffer contains a weak acid and its conjugate base or a weak base and its conjugate acid. Thus a buffer solution contains both an acid species and a

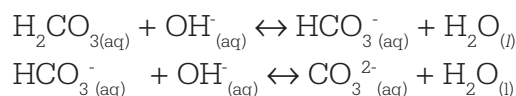
base species. The buffer in sea water is mostly due to the presence of carbonic acid, H_2CO_3 , and its conjugate base, the bicarbonate ion HCO_3^- . In blood, both the carbonate and phosphate buffers are present.

Adding an acid to the buffer: The buffer solution must remove most of the new hydrogen ions otherwise the pH would drop markedly. The hydrogen ions will combine with the bicarbonate ion to make carbonic acid:



Even though the reaction is reversible, most of the new hydrogen ions have been removed, so the pH won't change very much. But *because* the reaction is reversible, the pH will decrease a very small amount.

Adding a base to the buffer solution: Bases contain hydroxide ions or react to form them, so the buffer solution must remove most of these ions. There are two ways in which the carbonic/bicarbonate buffer can remove the hydroxide ion. Either carbonic acid or bicarbonate ion reacts:



Since most of the hydroxide has been removed, the pH of the buffer changes very little.

The pH of a buffer: The pH of buffers can vary from being in the acid range of the pH scale all the way to the basic range. The pH of a buffer is determined by the relative amounts of acid and conjugate base that are present in the solution and the K_a of the acid. Let us examine a buffer made of acetic acid and sodium acetate. This is similar to one of citric acid and sodium citrate that is often found in commercial fruit juices, to maintain the pH of the juice.

Let us compare the pH of two different buffer solutions.

1.(a) A buffer made of 50.0 mL of a 0.10 M solution of acetic acid, CH_3COOH , and 50.0 mL of a 0.10 M sodium acetate, CH_3COONa .

- The K_a of acetic acid is 1.7×10^{-5} .
- The equilibrium reaction is $\text{CH}_3\text{COOH}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \leftrightarrow \text{CH}_3\text{COO}^-{}_{(\text{aq})} + \text{H}_3\text{O}^+{}_{(\text{aq})}$.
- The total volume of the buffer is 100.0 mL.
- The concentration of acetic acid is 0.0050 moles of acid/0.100L = 0.050 M.
- The concentration of the acetate ion is 0.0050 moles of acetate ion/0.100 L = 0.050 M.

Filling in the ICE concentration table:

	CH₃COOH	H₂O	CH₃COO⁻	H₃O⁺
Initial	0.050 M		0.050 M	0
Change	-X		+X	+X
Equilibrium	0.050 M - X		0.050 M + X	X

In this solution

$$K_a = [\text{H}_3\text{O}^+] [\text{CH}_3\text{COO}^-] / [\text{CH}_3\text{COOH}].$$

We substitute the equilibrium concentrations in the above equation. In doing so we can assume that X is small compared with 0.050 M.

So the net equation is:

$$1.7 \times 10^{-5} = [X] [0.050 M] / [0.050 M]$$

After rearranging, we get

$$[\text{H}_3\text{O}^+] = (1.7 \times 10^{-5}) (0.050 M) / (0.050 M)$$

$$[\text{H}_3\text{O}^+] = 1.7 \times 10^{-5} M$$

$$\text{pH} = -\log [1.7 \times 10^{-5} M] = 4.76 \text{ which is in the acid range}$$

Now in this example the concentrations of the acid and the conjugate base are equal and the concentration of the hydronium ion is equal to K_a . The pH of this buffer can be altered by adjusting the relative concentrations of the acid and the conjugate base.

- (b) For example, if the equilibrium concentration of the acetate ion is 0.070 M and the equilibrium concentration of the acetic acid is 0.025 M, the concentration of hydronium ion is

$$[\text{H}_3\text{O}^+] = K_a [\text{HA}] / [\text{A}^-].$$

Substituting in the above equation we can see that the ratio $[\text{HA}]/[\text{A}^-] = 0.025/0.070$, is less than 1, and the resulting $[\text{H}_3\text{O}^+] = 5.67 \times 10^{-5}$ has a pH of 5.25. It is slightly more basic than the previous solution, but still well within the acid range.

A conclusion from the above problem:

If the ratio $[\text{HA}]/[\text{A}^-] = 1$ then the pH of the resulting solution will be equal to

$$\text{p}K_a$$

If the ratio $[\text{HA}]/[\text{A}^-] > 1$ then the resulting solution will be more acidic than

$$\text{p}K_a.$$

If the ratio $[\text{HA}]/[\text{A}^-] < 1$ then the resulting solution will be more basic than

$$\text{p}K_a.$$

2. A buffer solution is made up of 50.0 mL of 0.10 M NH_4^+ and 50.0 mL of 0.10 M NH_3 . The K_a of ammonium ion is K_w / K_b

$$K_a = 1 \times 10^{-14} / 1.8 \times 10^{-5}$$

$$K_a = 5.56 \times 10^{-10}$$

The equilibrium reaction is $\text{NH}_4^+_{(aq)} + \text{H}_2\text{O}_{(l)} \leftrightarrow \text{NH}_3_{(aq)} + \text{H}_3\text{O}^+$.

The final volume is 100 mL, so the final concentration of $[\text{NH}_4^+] = 0.050 \text{ M}$.

The final concentration of $[\text{NH}_3] = 0.050 \text{ M}$.

Filling in the ICE concentration table:

	NH_4^+	H_2O	NH_3	H_3O^+
Initial	0.050 M		0.050 M	0
Change	-X		+X	+X
Equilibrium	0.050 M - X		0.050 M + X	X

Now $K_a = [\text{H}_3\text{O}^+] [\text{NH}_3] / [\text{NH}_4^+]$.

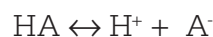
We can assume that X is small compared to 0.050 M.

Substituting we get:

- $5.56 \times 10^{-10} = (X) (0.050 \text{ M}) / (0.050 \text{ M})$
- We can see that $X = [\text{H}_3\text{O}^+] = 5.56 \times 10^{-10} \text{ M}$
- $\text{pH} = -\log [5.56 \times 10^{-10}]$

This gives a pH of 9.3, which is in the basic range.

3. From studying the two different buffers, we can clearly see that the pH of the buffer will be determined mainly by the value of K_a .
- For a buffer with pH 3, we choose an acid/conjugate base combination that has a $\text{p}K_a$ close to 3.
 - For a buffer with a pH of 9, we choose an acid/conjugate base combination that has a $\text{p}K_a$ close to 9.
4. The addition of water affects a buffer solution (dilutes of a buffer). When water is added to a buffer solution, the pH remains unchanged. Let us examine this.



$$K_a = [\text{H}^+] [\text{A}^-] / [\text{HA}]$$

Rearranging this, we can see that:

$$[\text{H}^+] = K_a [\text{HA}] / [\text{A}^-].$$

The addition of more water to the buffer does not change the ratio $[\text{HA}]/[\text{A}^-]$, since the same amount of water is being added to both. If this ratio remains unchanged, the pH stays the same. This analysis does not consider new effects that appear if the solution becomes extremely dilute.

5. A buffer resists change to pH when small amounts of acid or base are added. We are now going to examine this quantitatively.

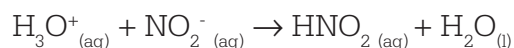
Suppose we have a buffer consisting of 0.10 *M* nitrous acid and 0.20 *M* sodium nitrite. The K_a of nitrous acid is 4.5×10^{-4} . To 95.0 mL of this buffer solution we add 5.0 mL of 0.10 *M* hydrochloric acid. This type of problem becomes a two-part problem.

This first part is a stoichiometric calculation where we assume that all the H_3O^+ from the strong acid reacts with the nitrite ion forming nitrous acid. The second part is an equilibrium problem where the concentrations from the first part are used.

Solution

Part 1—Stoichiometric Calculation

When a hydronium ion is added to the buffer it reacts with the nitrite ion:



Because the nitrous acid is a weak acid, we assume that the reaction goes to completion.

First, we must calculate amounts of hydrogen ions, nitrous acid and nitrite ions in the solution before the reaction. Because HCl is a strong acid, the hydrogen ion concentration is equal to the molarity of the acid.

- HCl is 0.10 *M*, therefore the concentration of H_3O^+ is 0.10 *M*.
- The moles of H_3O^+ = (0.10 moles/L) (0.005L) = 0.00050 moles.
- The moles of HNO_2 = (0.10 moles/L) (0.095L) = 0.0095 moles.
- The moles of NO_2^- = (0.20 moles/L) (0.095L) = 0.019 moles.

We assume that all the H_3O^+ added reacts with the nitrite ion. Therefore, 0.00050 moles of acid is produced and 0.00050 moles of nitrite ion is used up.

- Moles of nitrite ion remaining = (0.019 – 0.00050) mol = 0.0185 mol.

- Moles of nitrous acid after reaction = $(0.0095 + 0.00050) \text{ mol} = 0.010 \text{ mol}$.
- $[\text{HNO}_2] = 0.010 \text{ mol}/0.10 \text{ L} = 0.10 \text{ M}$.
- $[\text{NO}_2^-] = 0.0185 \text{ moles}/0.10\text{L} = 0.185\text{M}$.

Part 2—Equilibrium Problem

Using the concentration found in Part 1, you construct the following ICE table:

	HNO_2 (mol/L)	H_3O^+ (mol/L)	NO_2^- (mol/L)
Initial	0.10 M	0	0.185 M
Change	- X	+ X	+ X
Equilibrium	0.10 - X	X	0.185 + X

The equilibrium constant equation is:

$$K_a = [\text{H}_3\text{O}^+] [\text{NO}_2^-] / [\text{HNO}_2]$$

Substituting, you get:

$$4.5 \times 10^{-4} = [X] [0.185 + X] / [0.10 - X]$$

Assuming that X is small enough that $0.1855 + x \approx 0.185$ and $0.10 - X \approx 0.10$,

$$x \times 10^{-4} = (X) (0.185) / 0.10$$

$$[\text{H}_3\text{O}^+] = X = 2.43 \times 10^{-4}$$

The pH of the original buffer was 3.65, the pH after the addition of the 5.0 mL of 0.10 M $\text{HCl}_{(\text{aq})}$ is 3.61. So the pH changed by only 0.04 units. The buffer pH changed much less than 0.5 units, which is considered the maximum change that a buffer should have and continue to be effective at pH control.

Examples from Prior AP Chemistry Examinations

(1983)

- 2(a). Specify the properties of a buffer solution. Describe the components and the composition of effective buffer solutions.
- 2(b). An employer is interviewing four applicants for a job as a laboratory technician and asks each how to prepare a buffer solution with a pH close to 9.

Archie A. says he would mix acetic acid and sodium acetate solutions.

Beula B. says she would mix NH_4Cl and HCl solutions.

Carla C. says she would mix NH_4Cl and NH_3 solutions.

Dexter D. says he would mix NH_3 and NaOH solutions.

Which of these applicants has given an appropriate procedure? Explain your answer, referring to your discussion in part (a). Explain what is wrong with the erroneous procedures.

(No calculations are necessary, but the following acidity constants may be helpful: acetic acid, $K_a = 1.8 \times 10^{-5}$; NH_4^+ , $K_a = 5.6 \times 10^{-10}$)

Answer:

2(a). A buffer solution resists changes in pH when small amounts of an acid or a base are added. Preparation of a buffer: Mix a weak acid with the conjugate base of the acid.

2(b). Archie has a buffer solution: he has a weak acid and its conjugate base, but it does not have the correct pH since the $\text{p}K_a$ is close to 5. So he does not have the correct buffer.

- Beula does not have a buffer, since she has a weak acid (NH_4^+) and a strong acid (HCl).
- Carla has the correct buffer. She has a weak acid, (NH_4^+) and its conjugate base (NH_3). She also has the correct pH, since the $\text{p}K_a$ is close to 9.
- Dexter does not have a buffer since he has mixed a weak base and a strong base.

(1977A)

3. The value of the ionization constant, K_a , for hypochlorous acid, HOCl, is 3.1×10^{-8} .

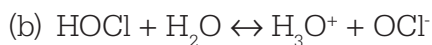
- (a) Calculate the hydronium ion concentration of a 0.050 molar solution of HOCl.
- (b) Calculate the concentration of hydronium ion in a solution prepared by mixing equal volumes of 0.050 molar HOCl and 0.020 molar sodium hypochlorite, NaOCl.

Answer:



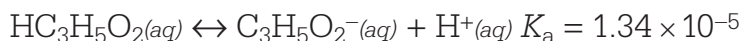
$$X \ll 0.050$$

$$X = [\text{H}_3\text{O}^+] = 4.0 \times 10^{-5}M$$



$$X \ll 0.010$$

$$X = [\text{H}_3\text{O}^+] = 8.0 \times 10^{-8}M$$

(2005A)

Propanoic acid, $\text{HC}_3\text{H}_5\text{O}_2$, ionizes in water according to the equation above.

- Write the equilibrium constant expression for the reaction.
- Calculate the pH of a 0.265 M solution of propanoic acid.
- A 0.496 g sample of sodium propanoate, $\text{NaC}_3\text{H}_5\text{O}_2$, is added to a 50.0 mL sample of a 0.265 M solution of propanoic acid. Assuming that no change in the volume of the solution occurs, calculate each of the following.
 - The concentration of the propanoate ion, $\text{C}_3\text{H}_5\text{O}_2^-(\text{aq})$ in the solution
 - The concentration of the $\text{H}^+(\text{aq})$ ion in the solution

Answer:

$$(a) \frac{[\text{C}_3\text{H}_5\text{O}_2^-][\text{H}^+]}{[\text{HC}_3\text{H}_5\text{O}_2]} = K_a$$

- (b) let X be the amount of acid that ionizes, then

$$X = [\text{C}_3\text{H}_5\text{O}_2^-] = [\text{H}^+]$$

$$0.265 - X = [\text{HC}_3\text{H}_5\text{O}_2]$$

$$\frac{X^2}{0.265 - X} = K_a = 1.34 \times 10^{-5}$$

$$X = 0.00188 \text{ M} = [\text{H}^+]$$

[you can assume that $0.265 - X \approx 0.265$ in order to simplify your calculations]

$$\text{pH} = -\log[\text{H}^+] = 2.73$$

$$(c) (i) \frac{0.496\text{g} \times \frac{1\text{mol}}{96.0\text{g}}}{0.50\text{L}} = 0.103 \text{ M}$$

since each sodium propanoate dissociates completely when dissolved, producing 1 propanoate ion for every sodium propanoate, and this is more than thousands of times larger than the propanoate ions from the acid, then $[\text{C}_3\text{H}_5\text{O}_2^-] = 0.103 \text{ M}$

- (ii) let X be the amount that ionizes, then:

$$X = [\text{H}^+]$$

$$X + 0.103 = [\text{C}_3\text{H}_5\text{O}_2^-]$$

$$0.265 - X = [\text{HC}_3\text{H}_5\text{O}_2]$$

$$\frac{(X)(0.103 + X)}{0.265 - X} = K_a = 1.34 \times 10^{-5}$$

$$X = 3.43 \times 10^{-5} \text{ M} = [\text{H}^+]$$

[We can assume that $0.265 - X \approx 0.265$ and $X + 0.103 \approx 0.103$, in order to simplify calculations.]

Buffer capacity is the amount of acid or base that can be added to a buffer solution before a major pH change (more than ± 0.5 units) occurs. All buffers have a buffer capacity. They will resist change to pH when only small amounts of acid or base added. If large amounts of acid or base are added, then the buffer's capacity is exceeded and a major pH change will occur. The buffer's capacity is determined by the amount of acid and conjugate base. A buffer with a large capacity has a large concentration of HA and of A⁻, so that it can absorb a relatively large amount of H₃O⁺ or OH⁻. The pH of a buffered solution is determined by the ratio [HA]/[A⁻]. The capacity of a buffer is determined by the magnitude of [HA] and [A⁻].

A good laboratory activity to do with the students is to study the buffering capacity of seawater as compared to that of a 0.50 M NaCl solution. (This concentration \approx the concentration of NaCl in seawater.) The students can see the importance of a natural buffer such as is present in seawater and also study the buffering capacity of seawater.

Bibliography

Cyberspace Chemistry. "Hydrolysis of Metal Salts." University of Waterloo. <http://www.science.uwaterloo.ca/~cchieh/cact/c123/salts.html> (accessed January 2008).

Mitchell, Philip, and Norris Rakestraw. "The Buffer Capacity of Sea Water", *The Biological Bulletin* 65 (December 1933): 437–451.

Ebbing, Darrell, and Steve Gammon. *General Chemistry*, 8th ed. Boston: Houghton Mifflin Company, 2005.

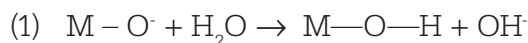
Acidic and Basic Reactions of Oxides

Marian DeWane

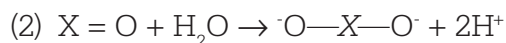
Centennial High School
Boise, Idaho

The oxides of the elements form an interesting group of acidic and basic compounds. The combination of element X with the highly electronegative oxygen results in a polarized bond (in every instance except two oxygen atoms bonding to form O_2), which then can be a reaction site when the oxide is added to water to form an aqueous solution, or when the oxide is reacted directly with an acid or a base.

Two types of reactions can result:



Here the oxide is a proton acceptor from water leaving an excess of hydroxide ion in solution, hence forming a *basic* solution. In this case the oxides are classified as basic oxides. Oxides behaving in this way include those of lithium, sodium, potassium, cesium, calcium, strontium, and barium. These are among the least electronegative elements or metals group.



Here the oxide is an oxygen acceptor from water, which releases hydrogen ions into the solution, hence forming an *acidic* solution and in effect acting as a proton donor. Such oxides are classified as acidic oxides. Oxides behaving in this way include those of carbon, nitrogen, sulfur, phosphorous, and the halogens. These are among the most electronegative elements or nonmetals group.

These reactions are obviously oversimplified, and can be studied more closely as follows:

- (1) An alternative view of the basic oxides is that these are mostly ionic compounds (with a high degree of ionic character) and can be thought of as

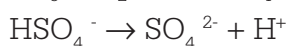
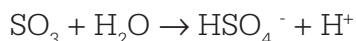
containing ions in the solid state. When added to water, it is these ions that act as proton acceptors as follows:

$O^{2-} + H_2O \rightarrow 2 OH^-$, each O^{2-} ion reacting to form two hydroxide ions, hence the highly basic nature of the resulting solution.

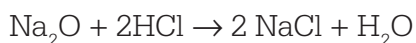
Thus it is the ionic structure of the metal oxides that best explains their reaction in aqueous solution. The combination of the highly electronegative oxygen atom with the low electronegativity atom of a typical metal produces the ionic bond in metal oxides. The electronegative oxygen is easily able to attract the most weakly bonded electron away from a metal atom to form the ionic bond. Two electrons can be taken from an alkaline earth element such as magnesium to form $Mg^{2+}O^{2-}$. Typical oxides are Na_2O , K_2O , MgO , CaO , etc.

- (2) In the acidic oxides, the nonmetal atom readily forms covalent bonding with the oxygen, as in common examples such as CO_2 , SO_3 , NO_2 , Cl_2O , for example. While this uses some electron density of the central atom, the more electronegative atoms in the nonmetals still have sufficient remaining electron density to form additional bonding with oxygen atoms in water molecules. This weakens the O-H bond in water, releasing H^+ ion. The complete reaction may take place in two steps to release two H^+ ions.

For example:



Direct reactions of oxides can occur without water being an obvious reagent. So, for example, sodium oxide can react with hydrochloric acid to form sodium chloride and water in a typical acid–base reaction forming a salt and water:



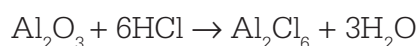
However, when an acidic oxide reacts with some bases water must be present to provide the oxygen transferred to the central atom. For example, sulfur trioxide can react with ammonia to form ammonium sulfate. Water has to be included as a reagent to provide the oxygen transferred.



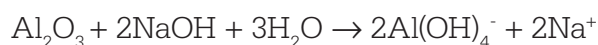
Amphoteric Oxides

As in all other areas of chemistry, there are chemical behaviors that fall in between two extremes, and oxides are no exception. Amphoteric oxides can act as acids or bases, depending on the circumstances. With hydrogen as an exception (water is clearly an example of an amphoteric oxide), metals in the center of periods and semimetals tend to form such oxides. For example aluminum oxide, Al_2O_3 , can act as an acid or a base, as can SiO_2 .

Aluminum oxide is a compact strong structure relatively insoluble in water, but it can be dissolved by reacting in strong HCl. Here the aluminum oxide is acting as a base, neutralizing the hydrochloric acid, as represented in the reaction below:



However, aluminum oxide also dissolves in strong sodium hydroxide solution acting as an acid neutralizing the sodium hydroxide. This reaction can be represented by the equation:

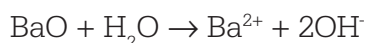


AP Exam Examples of Free-Response Questions:

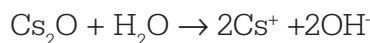
Free-response questions about oxides are usually in the equations section, question 4. The question now requires students to provide a balanced net equation and answer a question about the reaction. The year these questions were given, no additional questions were asked.

Metal oxide plus water examples:

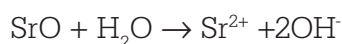
2004 Form B Question 4 (f): Powdered barium oxide is mixed with water.



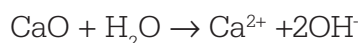
2002 Question 4 (c): Solid cesium oxide is added to water.



2000 Question 4 (g): Powdered strontium oxide is added to distilled water.

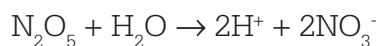


1999 Question 4 (a) Calcium oxide powder is added to distilled water.

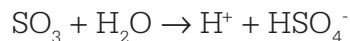


Nonmetal oxide plus water examples:

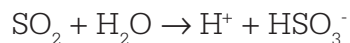
2003 Question 4 (h): Solid dinitrogen pentoxide is added to water.



2003 Form B Question 4 (f): Sulfur trioxide gas is bubbled into water.

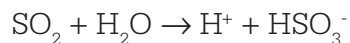


2002 Form B Question 4 (e): Sulfur dioxide gas is bubbled into a beaker of water.



$\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$ was also accepted.

2001 Question 4 (a): Sulfur dioxide gas is bubbled into distilled water.



$\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$ was also accepted.

Bibliography

Brady, J., and F. Senese. *Chemistry: Matter and Its Changes*, 4th ed. New York: John Wiley and Sons, 2004.

Cotton, F. A., G. Wilkinson, Carlos Murillo, and M. Bochmann. *Advanced Inorganic Chemistry*, 6th ed. New York: John Wiley and Sons, 1999.

Oxtoby, D. W., and N. H. Nachtrieb. *Principles of Modern Chemistry*, 2nd ed. New York: Saunders, 1990.

Rayner-Canham, G. *Descriptive Inorganic Chemistry*, 2nd ed. New York: Freeman, 1998.

Misconceptions in Chemistry Demonstrated on AP Chemistry Examinations

George E. Miller

University of California, Irvine
Irvine, California

Misconceptions and misunderstandings are often demonstrated by students on both multiple-choice and free-response portions of the AP Chemistry Examination. Many may reflect prior thinking brought to the AP class. These are often termed “preconceptions.” Others reflect misunderstanding of material presented within the AP class or read from the textbook. Frequently, misunderstandings arise from a lack of depth and/or accuracy of thinking about a topic or question.

On multiple-choice questions, frequent misconceptions are often included by the item writers as possible wrong answers, or distracters. Students who select these answers are showing they have that misconception. Teachers should always ask students to explain why they selected a particular distracter. The teacher can then proceed to help the student correct the misconception in their thinking, which will help the student make the correct selection.

In free-response questions, perhaps the most common misconception demonstrated is a lack of understanding of the words “explain,” or “justify.” This persists even when the examination question tries to provide guidance as to what is expected. Use of familiar examples is helpful. If a sportswriter or commentator explained why team X won the game against team Y by stating, “It was because team X scored more points,” they would not survive long in their jobs. Yet that is the format a considerable number of students exhibit when providing an explanation on the AP Chemistry Exam. Restating the question also does not answer the question.

For example, the following question and answer might have appeared in AP:
Using the information given in the following table, explain the difference in K_a values for HClO and HBrO.

Acid	K_a	Electronegativity of halogen
HClO	3.0×10^{-8}	3.0
HBrO	2.8×10^{-9}	2.8

Incorrect response (1):

The table shows there is a difference between the K_a values of HClO and HBrO.

Incorrect response (2):

HBrO has a larger K_a because 2.8×10^{-9} is larger than 3×10^{-8} .

Mathematical errors even creep in as a result of carelessness or real misunderstandings of conceptual algebra, or exponential notation (as seen above).

For example, students may transcribe $K = \frac{[H][A]}{[HA]} \cong \frac{[H]^2}{[HA]}$ incorrectly as $[H] = \sqrt{K/[HA]}$. Reflective conceptual thinking would always look for responses where numerator and denominator values moved in the same direction. To foster correct thinking, teachers should encourage students to always answer the question qualitatively *before* plugging in any numbers.

The remaining document addresses selected topics where frequent misunderstandings are demonstrated, together with some hints for instructors.

Misconceptions Regarding Acids, Bases, and Aqueous Equilibria

There is confusion on a number of issues relating to acids and bases, as noted below. Student and teacher dialogue (almost more than demonstrations, which also can easily be misconstrued) is key. The answer is to start with basic principles, arguing somewhat as follows:

1. Reactions of acids and bases occur in water. (No nonaqueous systems are dealt with in AP Chemistry.) Lewis acids are barely mentioned, so master Brønsted-Lowry or proton transfer systems before even thinking about anything else.
2. The largest numbers of molecules present in solutions are therefore water molecules.

3. The obvious species for anything to react with is, therefore, water. If you jump into a crowded swimming pool, the chances are that you will hit water molecules first!
4. Thus, first-cut reactions are water reactions.
5. Water is amphiprotic and amphoteric, so its reactions are to accept a proton or donate a proton. Free protons do not exist in water solutions—they must be attached to something. *Most* will be attached to water molecules in the form of $\text{H}(\text{H}_2\text{O})_n^+$ where n is 1-4. In most texts, this is abbreviated to H^+ .
6. Thus, acid–base chemistry is almost exclusively (>99%!) the study of proton transfer reactions all of which are equilibrium reactions and each of which has a well-defined equilibrium constant that only varies with temperature.
7. So we simply must list all possible reactions of any given system in water and ask: “Is the system at equilibrium?” If not, then consider reactions that happen as they go to equilibrium; if it is at equilibrium, then what do we know about all the possible equilibrium constants?
8. In one system at equilibrium, all possible equilibria and the corresponding equilibrium constant expressions must be simultaneously satisfied. One cannot have some OK, and some not OK.
9. Correspondingly, there can only be ONE value of a species concentration (e.g., one value of $[\text{H}^+]$ or $[\text{OH}^-]$). The solution cannot track what H^+ came from what source to create separate values.

So what are the misconceptions, and why do they exist? The following examples are given mostly for an acid, but the corresponding idea for a base also exists.

1. Acid–base “strength” is related to acid–base concentration.

This is a semantic problem caused by the unfortunate choice of terms by chemists. To the lay public, putting a lot of any chemical in water makes it “strong.” Strong coffee or strong lemonade has a high concentration of those chemicals.

However, acids and bases are defined as strong or weak solely on the basis of their equilibrium constants in reaction with water. An acid with a high K value (K value $> 10^1$) for the reaction $\text{HA} + \text{H}_2\text{O} \leftrightarrow \text{A}^- + \text{H}_3\text{O}^+$ is a strong acid. This is often stated in terminology regarding the “degree of ionization.” Conversely, strong bases have a high K value for the reaction $\text{B} + \text{H}_2\text{O} \leftrightarrow \text{B}^+ + \text{OH}^-$.

Some texts still may use the term “dissociation” based on the idea that HA becomes H^+ and A^- by simple dissociation. Generally, it is now recognized that proton

transfer reactions to water are what actually takes place. It is the K value for the transfer to water that determines whether an acid is classified as strong or weak.

The “concentration” of a solution of an acid in water strictly refers to the *formal concentration* which is the same as $[HA] + [A^-]$, or the corresponding values for a base. This concentration expression is *the same* for either a strong or a weak acid.

Thus, one can have a high concentration of a weak acid, or a small concentration of a strong acid, and vice versa. Weaker students find this quite difficult.

A class of one strong student is a strong class, but a class of 40 weak students is still a weak class.

2. “Reaction to completion can only occur as the K value will allow.”

So a weak acid cannot react to neutralize a strong base. For example: 5 mL of 0.1 M NaOH is added to 10 mL of 0.1 M acetic acid. What is the end result? Beginning students who have learned to correctly write an equilibrium constant for the weak acid in water as $HAc + H_2O \leftrightarrow H^+ + Ac^-$ with $K_a = 1.8 \times 10^{-5}$ frequently will argue that since $[H^+] = [Ac^-]$, now $1.8 \times 10^{-5} = [H^+]^2 / (0.1)$ and the concentration of hydrogen ion is now only $\sqrt{1.8 \times 10^{-6}}$ or $1.3 \times 10^{-3} M$.

Thus the reaction can only consume 1.3×10^{-3} moles of OH^- , leaving the remainder in solution, so the result is strongly basic.

When the solution is mixed, it is not at equilibrium. All reactions must be allowed to proceed to equilibrium before the equilibrium mixture is analyzed. With this in mind, the ICE tabulation method can be used to obtain a result.

3. “Acids are the only source of protons in water.”

In many problems with high or medium concentrations of acids, this is approximately true, so often neglecting water as a source works. The full treatment of this, which leads to a third order equation for $[H^+]$, is usually given in college analytical chemistry courses. However, there are circumstances where the contribution of the “auto-ionization” or “autoprotolysis” of water according to $H_2O + H_2O \leftrightarrow H(H_2O)^+ + OH^-$ cannot be ignored. The classic catch question is:

What is the $[H^+]$ of a $1 \times 10^{-10} M$ solution of HCl in water? Since HCl is a strong acid, we assume complete transfer, so $[H^+]$ from HCl is $1 \times 10^{-10} M$. (pH = 10). A good student will recognize this as nonsense since this is a basic solution. The water is contribution 1×10^{-7} , so the true value is close to $1 \times 10^{-7} + 1 \times 10^{-10}$ or $1 \times 10^{-7} M$, a “neutral” solution of pH = 7.

Usually the examination committee for AP has tried to set problems on the free-response section where the water contribution can be ignored and approximations are simple.

4. [H⁺] and [OH⁻] values are independent of each other.

A small but significant number of students fail to apply the water equilibrium in acid–base solutions. Thus they are comfortable to report a pH of 4 and a pOH of 4 (or the equivalent concentrations values) in the *same* solution. Perhaps a focus during discussions on the need to satisfy the water equilibrium, or at least a frequent repetition of the mantra pH + pOH ALWAYS = 14 (at normal room temperature) could help.

5. Acids are compounds containing H atoms, bases are compounds containing OH.

Unfortunately, this defines NH₃ as an acid. Acids and bases are defined according to their ability to donate or accept protons, almost exclusively (for AP) in reaction with water. Accepting a proton from water creates a basic solution (larger [OH⁻] than [H⁺]).

This enables reactions such as $\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^-$ to be written to correctly identify ammonia as a (weak) base. Much practice in writing reaction equations with water as reagent and seeking the *K* values for the reactions in tables will help students learn how to classify more correctly. Of course there are nonaqueous systems, but these are rarely dealt with in any significant way in AP or first-year college chemistry courses.

Acid–Base Chemistry Beyond AP[®]

Arden P. Zipp

SUNY Cortland

Cortland, New York

Most of the acid–base behavior discussed in AP Chemistry occurs in water. However, the use of water as a solvent limits the species that can act as acids or bases and restricts the range of reactions that can be legitimately considered as acid–base reactions. This article will address acid–base chemistry beyond water and, thus, beyond the usual considerations of AP. A further extension is provided by acidity and basicity measurements in the gas phase, where the relative tendency of a molecule to donate or accept a proton can be measured. Trends in acidity as a function of molecular structure in the gas phase can often be more easily understood, as many trends in solution depend on solvation energy considerations, which are absent in the gas phase (Barntmess, Scott, McIver 1979).

Leveling Effect of Water

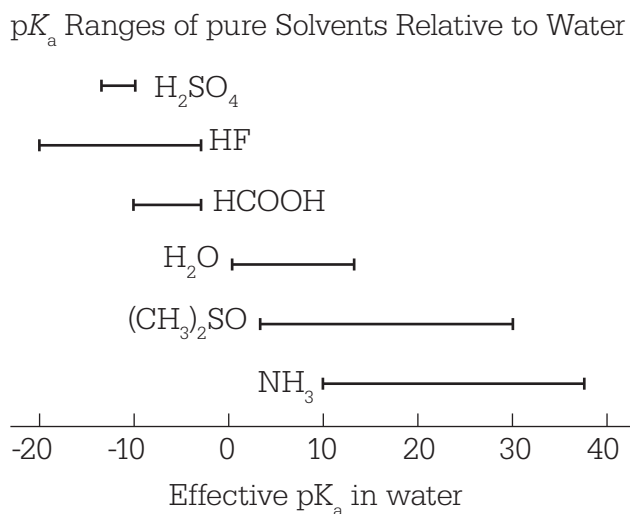
It is well known that H_2O ionizes into H^+ (or H_3O^+) and OH^- . Acids that are stronger than H_3O^+ will donate protons to H_2O to form H_3O^+ ions, while bases that are stronger than OH^- will abstract protons from H_2O to leave OH^- ions. As a consequence, all stronger acids (or bases) are made to appear as if they are of equal strength. This is the situation with HCl , HBr , HI , HNO_3 , HClO_4 , and H_2SO_4 (first proton), which appear equally strong in water. Although the K_a of these substances actually varies from 10^1 to 10^{11} , these differences are not apparent in water because H_2O molecules attract the H^+ from the various anions so strongly that all the acid is converted into H_3O^+ and the corresponding anion. This occurs because H_2O molecules are stronger bases toward H^+ than any of the anions in these acids, so the differences in anion attraction for the H^+ are not apparent. (Recall from the discussion of Brønsted-Lowry acids and bases that reactions with H^+ ions involve competitions

between two bases.) The same “leveling” phenomenon occurs with bases that are stronger than OH^- (e.g., H^- , $\text{C}_2\text{H}_5\text{O}^-$ or S^{2-}) because they react with an H^+ from water to form H_2 , $\text{C}_2\text{H}_5\text{OH}$, or HS^- , respectively, leaving OH^- as the predominant anion in solution.

The opposite effect occurs for very weak acids (or bases), which are not strong enough to exhibit their acid or base properties in water. As an example of this behavior, alcohols (ROH) contain hydroxyl ($-\text{OH}$) groups but exhibit neither acidic nor basic properties in H_2O . The K_a for a typical alcohol is about 10^{-18} ($\text{p}K_a = 18$).

Note: Saying that alcohols are very weak acids is equivalent to stating that their conjugate bases (RO^-) are very strong, which would lead to them being leveled in water as discussed above. (There is virtually no tendency for an alcohol to behave as a base by either gaining an H^+ or losing an OH^- in water.)

Nominally, acids with K_a values that range from 10^0 to 10^{-14} ($\text{p}K_a$ s from 0 to 14) can be studied in water and substances with values outside this range must be investigated in other solvents. One way to compare the useful ranges of different solvents is to graph their effective $\text{p}K_a$ ranges relative to H_2O as depicted below (Atkins, Overton, Rourke, Weller, and Armstrong 2006, 117).



In order to discriminate among the acidities of the six strong acids mentioned above, a less basic solvent than water (one with a more negative $\text{p}K_a$ value) can be used. Two examples of such solvents are liquid methanoic (formic) acid, HCOOH, and liquid HF. Because these solvent molecules have less attraction for H^+ than does H_2O , the acids do not ionize completely. Thus, it is possible to measure the relative amounts of the ionized and un-ionized acids, to calculate their ionization constants, and to relate these values to aqueous solutions. In this way, the K_a values of HNO_3 , H_2SO_4 , HCl, HBr, HClO_4 and HI have been found to be 10^1 , 10^2 , 10^7 , 10^9 , 10^{10} , and 10^{11} , respectively.

On the other hand, bases stronger than OH^- can be distinguished by using solvents such as liquid dimethyl sulfoxide, $(\text{CH}_3)_2\text{SO}$, or liquid NH_3 , which have $\text{p}K_a$ values greater than 14.

The opposite strategy applies to the task of distinguishing among very weak acids (or bases). In the case of very weak bases a more acidic solvent than H_2O is needed in order to protonate the basic site more effectively and for very weak acids a more basic solvent must be employed to help remove H^+ . For a series of alcohols their relative strengths could potentially be determined by studying them in either dimethylsulfoxide or ammonia.

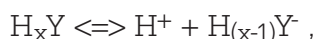
Once the constraints of an aqueous solution have been eliminated, a variety of other acid–base reactions can be observed. Chemists have developed “super acids,” i.e., acids that are stronger than 100% sulfuric acid, which can even protonate hydrocarbons! At the other extreme are super bases, such as butyllithium— LiC_4H_9 , which can remove H^+ ions from virtually anything including many hydrocarbons, which do not show acidic properties under other circumstances.

Relative Acid Strengths

Although it is common to classify acids as *either* strong or weak, there is a great deal of variation among the species in each category. These variations can be accounted for on the basis of the structures of the molecules involved. Although the specific structural factors depend on the acid category (hydroacids vs. oxoacids), the fact that acid strengths can be correlated with structures for a given category of acids provides a very powerful organizational tool. Consideration of acid strength from gas phase species, which can be done both theoretically and experimentally, can lead to interestingly different results as solvation effects are removed (Bartmess and Hinde 2005).

Hydroacids

These acids can be represented by the general formula H_xY and include species in which an atom of a nonmetal is attached directly to one or more hydrogen atoms. Such substances ionize according to the equation:



with the extent of this reaction dependent on the ease with which the bond between H^+ and $\text{H}_{(x-1)}\text{Y}^-$ can be broken. The K_a values for the compounds in groups 14 to 17,

most of which had to be measured in solvents other than water, cover a range of 10^{60} (from 10^{-49} to 10^{11}) as reflected in the pK_a s given in the table below (Bowser 1993, 314).

pK_a for Hydroacids

CH_4	49	NH_3	39	H_2O	15.74	HF	3.45
SiH_4	35	PH_3	27	H_2S	7.05	HCl	-7
GeH_4	25	AsH_3	23	H_2Se	3.8	HBr	-9
				H_2Te	2.6	HI	-11

The pK_a values of these substances decrease down the periodic table and from left to right, reflecting an increase in K_a values and, therefore, acid strength in the same directions.

There are two factors that influence the ease with which the H-Y bond can be broken. These are the electronegativity (EN) and the size of the atom Y. The increase in acidity going across the periodic table can be accounted for by the change in EN. As the EN of Y increases across the period, the electron pair in the H-Y bond will be drawn closer to Y, increasing the polarity of the bond. Because the atomic size does not vary appreciably across a period, the change in EN is the major factor affecting the acidity.

The increase in the acidity down the table cannot be explained in terms of the EN, however, because the EN changes in the wrong direction, decreasing down the table. However, there is a large increase in atomic size descending in any group. As the size of an anion increases, its electrostatic attraction for H^+ decreases, which would increase the acidity.

Oxoacids

This group of acids is more extensive and diverse than the hydroacids discussed above, with changes in both the central atom and the number of oxygen and/or hydrogen atoms as shown in the list of several of the more common oxoacids: HClO , HClO_2 , HClO_3 , HClO_4 , HNO_2 , HNO_3 , H_2CO_3 , H_2SO_3 , H_2SO_4 , and H_3PO_4 . Despite this variability in formula, all of the acids in this group can be represented by the general formula $(\text{HO})_m\text{YO}_n$, which emphasizes the fact that the ionizable protons are bonded to oxygen atoms, which, in turn, are bonded to the central atom Y. Thus, the structure of HClO is actually HOCl , while that of HClO_2 is HOClO and that of H_2SO_4 is $(\text{HO})_2\text{SO}_2$. When these species are compared in this manner, their strengths as represented by their K_a (or pK_a) values are found to fall into different categories depending on the number of unprotonated oxygen atoms, regardless of the number of ionizable H's in the molecule. This is shown in the table below (Bowser 1993, 314).

pK_a Table for Oxoacids

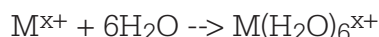
(HO) _m Y Very weak pK _a > 7	(HO) _m YO Weak pK _a 2 – 5	(HO) _m YO ₂ Strong pK _a < 1	(HO) _m YO ₃ Very Strong pK _a < 5
HOCl 7.54	HOCIO 1.94	HOCIO ₂ -2.0	HOCIO ₃ -7.3
HOBr 8.49	HONO 3.20	HONO ₂ -1.44	
(HO) ₃ As 9.18	(HO) ₂ CO 3.60	(HO) ₂ SO ₂ -3	
(HO) ₄ Si 9.77	(HO) ₂ SO 1.89	(HO) ₂ SeO ₂ 1.66	
	(HO) ₂ SeO 2.62		
	(HO) ₃ PO 2.15		
	(HO) ₃ AsO 2.21		

Several points are notable about the data in this table. First, the acid strength increases with the number of unprotonated oxygen atoms in the molecule. An increase in the number of such electron-attracting oxygen atoms will withdraw electrons more effectively from the H in the O-H bond. This increases the polarity of the bond and makes the H atom more H⁺-like. Second, the acid strength changes little with variations in atomic size or electronegativity in contrast to the behavior observed for the hydroacids discussed above. This can be accounted for by the fact that the ionizable H⁺ is always attached to an oxygen atom whose size doesn't change and, further, any change in the size of the central atom has little effect on the size of the anion as a whole. Similarly, changes in the electronegativity of the central atom represent a small effect on the attraction for the H⁺ compared to the influence of the greater EN effects of one or more (more electronegative) oxygen atoms.

Acidity of Metal Ions

Metal ions behave as Lewis acids, accepting a share of a pair of electrons from appropriate donors.

One of the most common electron pair donors is the H₂O molecule, especially in aqueous solutions, where most metal ions exist as octahedral species as shown by the equation:



The interaction of some metal ions (most notably alkali metal ions and larger alkaline earth metal ions such as Ca²⁺, Sr²⁺ and Ba²⁺) with H₂O goes no further. However, many metal ions attract the electron pairs of the coordinated H₂O molecules so strongly that one or more molecules may actually be torn apart, releasing H⁺ and making the solution acidic as represented in the equation:

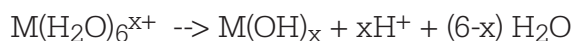


The tendency of metal ions to behave in this manner depends primarily on two factors: charge and size, as shown in the table below where the pK_a values for several metal ions participating in this reaction are given along with their radii (Wulfsberg 1991, 25).

pKa values and Radii of Common Metal Ions						
Ion	Na ⁺	Ca ²⁺	Pu ³⁺	Mg ²⁺	Ca ²⁺	Ba ²⁺
pK	14.2	12.8	7.0	11.4	12.8	13.5
Radius (nm)	0.116	0.114	0.114	0.086	0.114	0.149

The radius and charge can be combined into a single quantity called the charge density. (It is not necessary to consider the details of calculating this quantity but only to deal with it qualitatively, where it increases with an increase in charge and/or a decrease in ionic radius.) As a first approximation, solutions containing metal ions become more acidic as the charge density of the metal ion increases.

As the charge density of metal ions increases, this reaction may proceed further, to the precipitation of metal hydroxides:



The pH at which this reaction is initiated decreases as the charge density of the metal ion increases, as shown by the pH values for the formation of the following hydroxides, which are characterized by a decrease in size and/or an increase in the charge of the cation (Masterton and Hurley 2006, 427).



For species with extremely high charge densities, the potential cations may exist as oxoanions. This is illustrated by the ions VO_4^{3-} , CrO_4^{2-} and MnO_4^- , in which the charges on the nonexistent cations would be +5, +6, and +7, respectively.

Hard and Soft Acids and Bases (HSAB)

This concept represents one of the most significant developments in acid–base theory in recent years. It represents an extension of the Lewis theory and was developed to account for the results obtained when a variety of electron-pair acceptors were reacted with several electron pair donors.

Specifically, it was found that a cation such as Ag^+ reacts with halide ions in the order $I^- > Br^- > Cl^- > F^-$, whereas (as was pointed out above) H^+ reacts with this same series of ions in the opposite order: $F^- > Cl^- > Br^- > I^-$.

To account for this difference in behavior, the electron-pair acceptors (Lewis acids) H^+ and Ag^+ were labeled as hard and soft, respectively, while the halide ions F^- , Cl^- , Br^- , and I^- were assumed to progress from hard to soft. Hard acids and bases are species that interact in an electrostatic manner, whereas soft acids and bases exhibit covalent interactions. A fundamental principle of this theory is that hard acids interact preferentially with hard bases. Thus, hard H^+ reacts more strongly with hard F^- (to form the weak acid HF) than with the soft I^- (since HI is a strong acid) and the soft Ag^+ interacts more strongly with soft I^- (to form the less soluble AgI) than with harder F^- (AgF is more soluble).

The HSAB theory has provided the basis to account for a wide range of chemical phenomena. For example, it offers explanations for the strengths of the hydrohalic acids and the solubilities of the silver halides as described above. Further, however, it provides the basis to understand the distribution of metal ions in nature between sulfides (soft species such as Ag^+ , Hg^{2+} , Pt^{2+}) and oxides (hard species $\text{Fe}^{2+/3+}$, Cu^{2+}).

Activities

- Determine the $\text{p}K_{\text{a}}$ value of an acid with a $K_{\text{a}} = 1.2 \times 10^2$.
- Give the formula for the acidic and basic species in CH_3COOH .
- Organic amines behave as weak bases in aqueous solutions when an H^+ ion reacts with the lone pair of electrons on the N atom.
 - Predict the relative strength of an organic amide (RCONH_2) behaving as a weak base.
 - Give the formula of an appropriate solvent in which an amide would behave this way.
- Give an approximate $\text{p}K$ for the hydroacid stibine (SbH_3).
- The oxoacid pyrosulfuric acid ($\text{H}_2\text{S}_2\text{O}_7$) is produced when SO_3 is bubbled into H_2SO_4 . Write the formula in the $(\text{HO})_m\text{EO}_n$ style, determine the number of free O atoms per S atom and predict its strength relative to that of H_2SO_4 .
- Use the charge density to
 - Account for the fact that the reaction of alkali metal ions and H_2O goes only to $\text{M}(\text{H}_2\text{O})_6^+$.
 - Identify the alkali metal ion that would be most likely to go beyond this stage.

- (7) Copper can form the ions Cu^+ and Cu^{2+} . State and explain which of these is more likely to react with the hard base F^- .

Conclusion

This essay has attempted to present several aspects of acid–base theory beyond those discussed in earlier selections (or in the average AP Chemistry course). The topics covered here were chosen in the hope that they would further the understanding and appreciation of the topics usually found in AP courses.

Bibliography

- Atkins, P. W., T.L. Overton, J.P. Rourke, M.T. Weller, and F.A. Armstrong. *Inorganic Chemistry*, 4th ed., Oxford, UK: Oxford University Press, 2006, 117.
- Bartmess, J. E., J. A. Scott, and R. T. McIver Jr. "Scale Of Acidities in the Gas Phase from Methanol to Phenol." *Journal of American Chemistry Society* 101 (1979): 6046–56.
- Bartmess, J. E., and Robert J. Hinde. "The Gas-Phase Acidities of the Elemental Hydrides are Functions of Electronegativity and Bond Length." *Canadian Journal of Chemistry* 83(11) (2005): 2005–12.
- Bowser, J. R. *Inorganic Chemistry*. Pacific Grove, CA: Brooks/Cole Publishing, 1993, 312–14.
- Masterton, W. L., and C. N. Hurley. *Chemistry: Principles and Reactions*, 5th ed. Pacific Grove, CA: Brooks/Cole Publishing, 2006, 427.
- Wulfsberg, G. *Principles of Descriptive Inorganic Chemistry*. Mill Valley, CA: University Science Books, 1991, 25.

Acid–Base Lesson Plans

Heather Hattori

John H. Guyer High School
Denton, Texas

This is one of my favorite units of the year. It brings back familiar concepts and calculations to second-year students, as well as a wealth of laboratory activities to keep them engaged. I teach on an A/B day 90-minute block schedule so some activities are done during class while others are done outside (either after school or on Saturdays). Tenth-, eleventh-, and twelfth-grade students enroll in AP Chemistry with an Algebra II minimum math co-requisite, since we teach the first year of chemistry to freshmen. The text provided to students is Zumdahl's *Chemistry*, 5th edition, from the Houghton Mifflin Company.

You may find my problem selections in the study guide odd, but that would be dependent on when I teach acids and bases. This past year, we as a district moved equilibrium into the first semester with the acid–base unit following directly after it. This may be disconcerting to some who would prefer to follow the textbook in the order it is presented. It works for us, but may not work for you. Be that as it may, here is a basic outline of what I would cover in my acid–base unit in years where I did not teach the pre-AP class and was unsure of the students' background.

General Outline

Day 1:

- Review characteristics and examples of acids and bases
- Review acid/base theories (Arrhenius, Brønsted-Lowry, and Lewis) and associated concepts
- Review strong/weak acids and bases as well as additional classifications of acids (monoprotic, diprotic, polyprotic, ternary, oxy acids, etc.)

SPECIAL FOCUS: Acids and Bases

- Review concentration terms (concentrated, dilute) and calculations (molarity)
- Review acid–base reactions including acid–base formation from acid–base anhydrides
- Review pH scale, logarithms, and associated strong acid–base calculations ($[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, pH, and pOH)
- Pre-lab: *Determining the pH of a Substance* (fits AP suggested lab topic: Determination of Appropriate Indicators for Various Acid–Base Titrations; pH Determination)
- Assign Study Guides for Chapters 14 and 15.

Day 2:

- Determining the pH of a substance lab
- Discussion of titration curves
- Pre-lab: *Titration Curves of Weak and Strong Acids and Bases*

Day 3:

- *Titration Curves of Weak and Strong Acids and Bases* Lab
- Review titration problems
- Pre-lab: *% Acetic Acid in Vinegar* (fits AP suggested lab topic: Determination of Concentration by Acid–Base Titration, Including a Weak Acid or Weak Base)

Day 4: (*this lab has been done outside the school day*)

- *% Acetic Acid in Vinegar* Lab

Day 5:

- Weak acid–base equilibria—revisiting K
- Calculating the pH of a weak acid or base
- Use past AP free-response questions for practice

Day 6:

- Common-ion Effect
- Buffers

- Pre-lab: *Preparation of a Buffer Solution at a Given pH or A Resistance to Change* (fits AP suggested lab topic: Preparation and Properties of Buffer Solutions)

Day 7: (*this lab has been done outside the school day*)

- *Preparation of a Buffer Solution at a Given pH Lab*

Day 8: (*If time permits. If not, then skip to Day 9*)

- Complex Ion Equilibria

Day 9:

- Unit Assessment

Additional Attachments:

- Study Guides to Accompany Zumdahl's *Chemistry, 5th edition*. Hattori, Heather R. 2001.
- Acids and Bases Introduction-Review Notes
- Titration Notes
- Calculating the pH of a Weak Acid or Base Notes
- Common Ion Effect and Buffers Notes
- *Determining the pH of a Substance*. Hattori, Heather R. 1995.
- *Acid-Bases, Reactions, and Titration Calculation Review Worksheet*. Hattori, Heather R. 2007.
- *Dissociation and pH Practice*. Hattori, Heather R. 2005.

Bibliography

Holmquist Dan D., Jack Randall, and Don Volz. In *Chemistry with Calculators*, Beaverton, OR: Vernier Software & Technology, 2000.

Hostage, David, and Martin Fossett. "Finding the Mass Percent of Acetic Acid in Vinegar," in *Laboratory Investigations: AP Chemistry*, Saddle Brook, NJ: The Peoples Publishing Group, Inc., 2006.

SPECIAL FOCUS: Acids and Bases

Hostage, David, and Martin Fossett. *Laboratory Investigations: AP Chemistry*, Saddle Brook, NJ: The Peoples Publishing Group, 2006.

Moore, John T., and Richard Langley. *5 Steps to a 5 AP Chemistry*, McGraw-Hill, 2004.

Pasco Scientific. "A Resistance to Change," in *PasPort Explorations in Chemistry*. Roseville, CA: PASCO Scientific, 2003.

Zumdahl, Steven S., and Zumdahl. *Chemistry*, 5th ed. Houghton Mifflin Company, 2000.

Appendix A

Review Notes on Acids and Bases Introduction

Common Acids and Bases

Where do I find acids?

- Fruits (lemons, oranges, etc.) contain citric acid.
- Vinegar contains acetic acid.
- Rain water contains sulfuric acid.
- Soft drinks contain carbonic and phosphoric acids.

Where do I find bases?

- Cleaners contain ammonia.
- Milk of magnesia contains magnesium hydroxide.
- Drano contains sodium hydroxide.

Characteristics of Acids and Bases

- Acids
 - Taste sour
 - Turn blue litmus paper red
 - Have a $\text{pH} < 7.0$
 - Are corrosive
- Bases
 - Taste bitter
 - Turn red litmus paper blue
 - Have a $\text{pH} > 7.0$
 - Are caustic

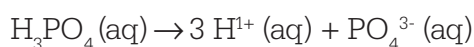
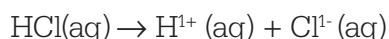
Three Acid–Base Theories

The following theories are where we get our definitions of what acids and bases are:

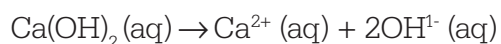
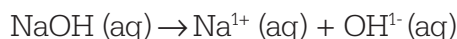
- Arrhenius Concept
- Brønsted-Lowry Model
- Lewis Theory

Arrhenius Concept

Acids produce H^+ (hydrogen ions) in solution.

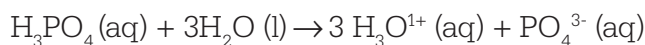
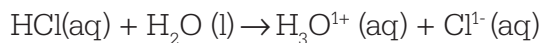


Bases produce OH^- (hydroxide ions) in solution.

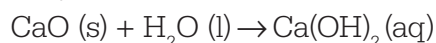
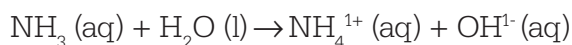


Brønsted-Lowry Model

Acids are proton donors. In other words, acids *donate* H^+ (hydrogen ions) in solution.



Bases are proton acceptors. In other words, bases *accept* H^+ (hydrogen ions) in solution.

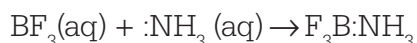


The first equation sets up two interesting relationships. Not only does the ammonia accept a hydrogen ion to become the ammonium ion, the hydroxide ion could accept a hydrogen ion from the ammonium and become water. These two relationships make the ammonia/ammonium ion and the water/hydroxide ion **conjugate acid/base pairs**.

Lewis Theory

Acids are electron-pair *acceptors* in solution.

Bases are electron-pair *donors* in solution.



The pH Concept

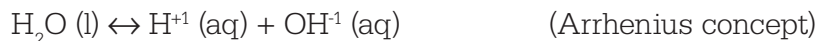
pH represents the relative acidity of a solution based on hydrogen ion or hydronium ion concentration and can be found using either of the following equations:

$$\text{pH} = -\log[\text{H}^+] \quad \text{or} \quad \text{pH} = -\log[\text{H}_3\text{O}^+]$$

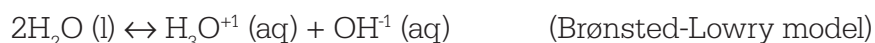
Since concentrations can be large or small, such as 12 M or 4.2×10^{-13} M, sometimes it is hard to compare the $[\text{H}_3\text{O}^+]$. The pH scale was developed to make it easier to recognize if a substance was acidic or basic.

The *amphoteric* nature of pure water contributes to its neutral nature. This means that water can act as an acid or a base due to the concept known as auto-ionization shown in the following two examples.

Remember that:



According to the Arrhenius concept water (in the equation above) is acting as an acid by producing hydrogen ions as well as a base by producing hydroxide ions.



According to the Brønsted-Lowry model one water molecule (in the equation above) is acting as an acid by donating a hydrogen ion to the other molecule of water forming a hydronium ion. The water molecule that is accepting the hydrogen ion is acting as the base.

If we write the equilibrium expression for this we get:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ always at } 25^\circ\text{C}$$

We can solve for the $[\text{H}_3\text{O}^+]$ or $[\text{OH}^-]$ based on the above equation.

For every H_3O^+ produced, one OH^- is made, so:

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ becomes}$$

$$[x][x] = 1.0 \times 10^{-14}$$

$$x^2 = 1.0 \times 10^{-14}$$

$$x = 1.0 \times 10^{-7}$$

$$\therefore [\text{H}_3\text{O}^+] = 1.0 \times 10^{-7} \text{ M} = [\text{OH}^-]$$

In solutions when the:

$[\text{H}^+] > [\text{OH}^-]$, then the solution is acidic

$[\text{H}^+] < [\text{OH}^-]$, then the solution is basic

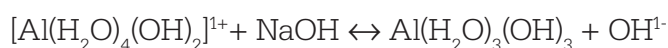
$[\text{H}^+] = [\text{OH}^-]$, then the solution is neutral

Based on this and the fact that $[H^+]$ and $[OH^-]$ can be calculated if you know one or the other, it's time to solve some problems.

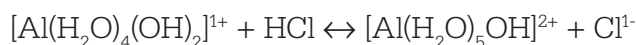
Examples

1. Given the $[OH^-] = 1.0 \times 10^{-5}M$, solve for the $[H_3O^{1+}]$ and determine the solution's nature (acidic, basic, or neutral).
2. Given the $[H_3O^{1+}] = 1.0 \times 10^{-2}M$, solve for the $[OH^-]$ and determine the solution's nature (acidic, basic, or neutral).

Substances other than water can also be amphoteric. Let's look at a hydrated aluminum hydroxide ion as an example.



When a water of hydration from $[Al(H_2O)_4(OH)_2]^{1+}$ donates the hydrogen ion to become the third hydroxide ion, it is acting as a Brønsted-Lowry acid.



When a hydroxide from $[Al(H_2O)_4(OH)_2]^{1+}$ accepts the hydrogen ion to create the fifth water of hydration, it is acting as a Brønsted-Lowry base.

pH scale

Based on logarithms, the pH scale was developed.



$$pH = -\log[H^+] \quad \text{or} \quad pH = -\log [H_3O^+]$$

3. What is the pH of a solution with a $[H^+] = 1.0 \times 10^{-9}M$?

A similar formula can be used to calculate the pOH (relative basicity) if you know the $[OH^-]$.

$$pOH = -\log [OH^-]$$

4. What is the pOH of a solution with a $[OH^-] = 2.4 \times 10^{-7}M$?

By combining all three of the previous formulas:

$$K_w = [H_3O^{1+}][OH^-] = 1.0 \times 10^{-14}$$

$$pH = -\log [H_3O^{1+}]$$

$$\text{pOH} = -\log [\text{OH}^{1-}],$$

we can derive the formula:

$$\text{pH} + \text{pOH} = 14.$$

5. *What is the pOH of a solution that has a pH of 10.0?*

Vinegar has a pH of 2.8. What are the pOH, $[\text{H}_3\text{O}^{1+}]$, and $[\text{OH}^{1-}]$ of a vinegar solution?

Relative Strengths of Acids and Bases

Acids and bases can be concentrated or dilute, weak or strong. Do not confuse the first two, which describe the solution concentration, with the last two, which describe the amount of dissociation. A strong acid or base is one that completely dissociates in water or has 100% ionization. A weak acid or base is one in which only a small portion of the particles dissociate or one that only partially ionizes.

- **Strong acids include:** HCl, HBr, HI, HNO_3 , H_2SO_4 , and HClO_4 . All others are considered weak.
- **Strong bases include:** LiOH, NaOH, KOH, $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, and $\text{Ba}(\text{OH})_2$. All others are considered weak.

Appendix B

Review Notes on Acids and Bases— Teacher's Edition

Common Acids and Bases

Where do I find acids?

- Fruits (lemons, oranges, etc.) contain citric acid.
- Vinegar contains acetic acid.
- Rain water contains sulfuric acid.
- Soft drinks contain carbonic and phosphoric acids.

Where do I find bases?

- Cleaners contain ammonia.
- Milk of magnesia contains magnesium hydroxide.
- Drano contains sodium hydroxide.

Characteristics of Acids and Bases

Acids:

- taste sour
- turn blue litmus paper red
- have a $\text{pH} < 7.0$
- are corrosive

Bases:

- taste bitter
- turn red litmus paper blue
- have a $\text{pH} > 7.0$
- are caustic

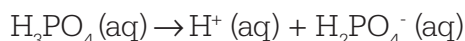
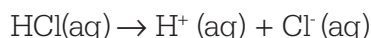
Three Acid–Base Theories

The following theories are where we get our definitions of what acids and bases are:

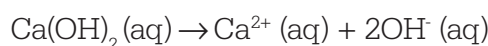
- Arrhenius Concept
- Brønsted-Lowry Model
- Lewis Theory

Arrhenius Concept

Acids produce H^+ (hydrogen ions) in solution.

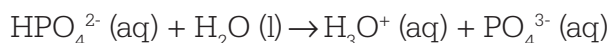
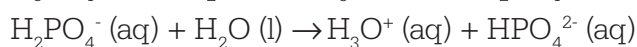
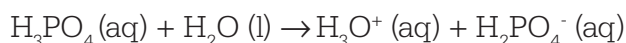
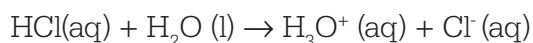


Bases produce OH^- (hydroxide ions) in solution.

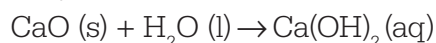
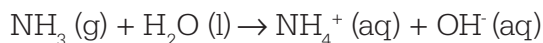


Brønsted-Lowry Model

Acids are proton donors. In other words, acids *donate* H^+ (hydrogen ions) in solution, usually to water. These are hydrated to form $\text{H}(\text{H}_2\text{O})_n^+$, where n may be 1–6. For convenience, this species is usually abbreviated to H^+ except when a balanced equation is desired, as shown in some of the examples below.



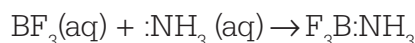
Bases are proton acceptors. In other words, bases *accept* H^+ (hydrogen ions) in solution.



The first equation sets up two interesting relationships. Not only does the ammonia accept a hydrogen ion to become the ammonium ion, the hydroxide ion could accept a hydrogen ion from the ammonium ion and become water. These two relationships make the ammonia/ammonium ion and the water/hydroxide ion **conjugate acid–base pairs**. The reaction goes both ways and so reaches equilibrium.

Lewis Theory

Acids are electron pair *acceptors* in solution. Bases are electron pair *donors* in solution.



The pH Concept

Conventionally, the symbol $[\text{H}^+]$ is used to represent the concentration of H^+ ions in moles per liter. Since concentrations can be large or small, such as 12 M or 4.2×10^{-13} M, sometimes it is hard to compare the $[\text{H}^+]$. The pH scale was developed to make it easier to recognize if a substance was acidic or basic.

pH represents the relative acidity of a solution based on hydrogen ion or hydronium ion concentration and can be found using either of the following equations:

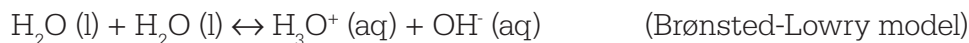
$$\text{pH} = -\log[\text{H}^+] \quad \text{or} \quad \text{pH} = -\log[\text{H}_3\text{O}^+]$$

The *amphoteric* nature of pure water contributes to its neutral nature. This means that water can act as an acid or a base by accepting or donating protons. Water also undergoes a process called auto-ionization, which is shown in the following two examples.

Remember that:



According to the Arrhenius concept, water, in the equation above, is acting as an acid by producing hydrogen ions as well as a base by producing hydroxide ions.



According to the Brønsted-Lowry model, one water molecule in the equation above is acting as an acid by donating a hydrogen ion to the other molecule of water forming a hydronium ion. The water molecule that is accepting the hydrogen ion is acting as the base.

If we write the equilibrium expression for this we get:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

We can solve for the $[\text{H}_3\text{O}^+]$ or $[\text{OH}^-]$ based on the above equation.

In pure water, with *no* other substances present, for every H_3O^+ produced, one OH^- is made so $[\text{H}_3\text{O}^+] = [\text{OH}^-] = x$

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ becomes}$$

$$[x][x] = 1.0 \times 10^{-14}$$

$$x^2 = 1.0 \times 10^{-14}$$

$$x = 1.0 \times 10^{-7}$$

$$\therefore [\text{H}_3\text{O}^+] = 1.0 \times 10^{-7} \text{ M} = [\text{OH}^-]$$

In solutions when the:

$[\text{H}^+] > [\text{OH}^-]$, then the solution is acidic.

$[\text{H}^+] < [\text{OH}^-]$, then the solution is basic.

$[\text{H}^+] = [\text{OH}^-]$, then the solution is neutral.

Based on this and the fact that $[\text{H}^+]$ and $[\text{OH}^-]$ can be calculated using K_w if you know one or the other, it's time to solve some problems.

Examples

1. Given the $[\text{OH}^-] = 1.0 \times 10^{-5} \text{ M}$, solve for the $[\text{H}_3\text{O}^+]$ and determine the solution's nature (acidic, basic, or neutral).

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \qquad [\text{H}_3\text{O}^+] [1.0 \times 10^{-5}] = 1.0 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14} \text{ M}^2}{1.0 \times 10^{-5} \text{ M}} = 1.0 \times 10^{-9} \text{ M} \quad \text{which is less than the } [\text{OH}^-] \text{ so the solution is basic.}$$

2. Given the $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-2} \text{ M}$, solve for the $[\text{OH}^-]$ and determine the solution's nature (acidic, basic, or neutral).

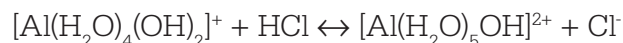
$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \qquad [1.0 \times 10^{-2} \text{ M}][\text{OH}^-] = 1.0 \times 10^{-14}$$

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14} \text{ M}^2}{1.0 \times 10^{-2} \text{ M}} = 1.0 \times 10^{-12} \text{ M} \quad \text{which is less than the } [\text{H}_3\text{O}^+] \text{ so the solution is basic.}$$

Substances other than water can also be amphoteric. Let's look at a hydrated aluminum hydroxide ion as an example.



When a water of hydration from $[\text{Al}(\text{H}_2\text{O})_4(\text{OH})_2]^+$ donates the hydrogen ion to become the third hydroxide ion it is acting as a Brønsted-Lowry acid.



When a hydroxide from $[\text{Al}(\text{H}_2\text{O})_4(\text{OH})_2]^+$ accepts the hydrogen ion to create the fifth water of hydration, it is acting as a Brønsted-Lowry base.

pH scale

Based on logarithms, the pH scale was developed.



$$\text{pH} = -\log[\text{H}^+] \quad \text{or} \quad \text{pH} = -\log [\text{H}_3\text{O}^+]$$

3. What is the pH of a solution with a $[\text{H}^+] = 1.0 \times 10^{-9} \text{ M}$?

$$\text{pH} = -\log[\text{H}^+] \quad \text{pH} = -\log(1.0 \times 10^{-9} \text{ M}) \quad \text{pH} = 9.00$$

A similar formula can be used to calculate the pOH (relative basicity) if you know the $[\text{OH}^-]$.

$$\text{pOH} = -\log [\text{OH}^-]$$

What is the pOH of a solution with a $[\text{OH}^-] = 2.4 \times 10^{-7} \text{ M}$?

$$\text{pOH} = -\log [\text{OH}^-] \quad \text{pOH} = -\log(2.4 \times 10^{-7} \text{ M}) \quad \text{pOH} = 6.62$$

By combining all three of the previous formulas:

$$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

$$\text{pH} = -\log [\text{H}^+]$$

$$\text{pOH} = -\log [\text{OH}^-],$$

we can derive the formula:

$$\text{pH} + \text{pOH} = 14$$

4. What is the pOH of a solution that has a pH of 10.0?

$$\text{pH} + \text{pOH} = 14 \quad 10.0 + \text{pOH} = 14 \quad \text{pOH} = 4.0$$

Vinegar has a pH = 2.8. What are the pOH, $[\text{H}^+]$, and $[\text{OH}^-]$ of a vinegar solution?

$$\begin{array}{lll} \text{pH} + \text{pOH} = 14 & 2.8 + \text{pOH} = 14 & \text{pOH} = 11.2 \\ \text{pH} = -\log[\text{H}^+] & 2.8 = -\log[\text{H}^+] & [\text{H}^+] = 2 \times 10^{-3} \text{ M} \\ \text{pOH} = -\log[\text{OH}^-] & 11.2 = -\log[\text{OH}^-] & [\text{OH}^-] = 6 \times 10^{-12} \text{ M} \end{array}$$

Relative Strengths of Acids and Bases

Acids and bases can be concentrated or dilute, weak or strong. Do not confuse the first two, which describe the solution concentration, with the last two, which describe the amount of dissociation. A strong acid or base is one that completely dissociates in water or has 100% ionization. A weak acid or base is one in which only a small portion of the particles dissociate, or one that only partially ionizes.

Strong acids include:

HCl, HBr, HI, HNO₃, H₂SO₄, H₃PO₄, and HClO₄.

All others are considered weak.

Strong bases include:

LiOH, NaOH, KOH, Mg(OH)₂, Ca(OH)₂, Sr(OH)₂, and Ba(OH)₂.

All others are considered weak.

Appendix C

Titration Notes

A titration is the experimental procedure used to determine the concentration of an unknown acid or base. The necessary chemical components of a titration include a **standard solution**, and solution of unknown concentration, and an **indicator**.

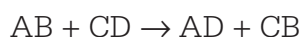
Titration curves are a way to visually represent the change in pH during a titration.

Titration curves tell you many things about a reaction. During a titration, the indicator experiences a color change at the **endpoint** of the titration. If the best indicator is chosen, the endpoint and the **equivalence point** (when there are equal amounts of acid and base) occur at nearly the same time. Common indicators used in acid–base titrations include phenolphthalein (clear to pink pH = 8-10) and bromothymol blue (yellow to blue pH = 6-8). The equivalence point can be visually determined from the titration curve. It is the area in which the slope of the line approaches infinity (or is nearly vertical).

Acid–Base Reactions

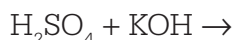
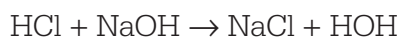
When an acid reacts with a base a neutralization reaction occurs. The same thing happens when a base reacts with an acid.

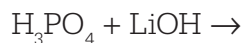
An acid–base reaction is a double displacement reaction.



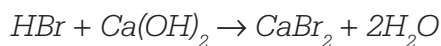
The products of an acid–base reaction are a salt (metal/nonmetal compound) and water.

Examples

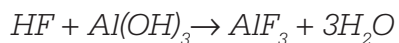




Hydrobromic acid + calcium hydroxide



Hydrofluoric acid + aluminum hydroxide



Titration Problems

Often, the goal of a titration is to calculate the concentration of one of the reactants.

This can be done using a balanced equation and stoichiometry.

1. A 25.0 mL sample of HCl was titrated to the endpoint with 15.0 mL of 2.0 M NaOH. What was the molarity of the acid?
2. A 10.0 mL sample of H_2SO_4 was neutralized by 13.5 mL of 1.0 M KOH. What was the molarity of the acid?
3. What volume of 1.50 M NaOH is necessary to neutralize 20.0 mL of 2.5M H_3PO_4 ?
4. How much 0.5M HNO_3 is necessary to titrate 25.0 mL of 0.05M $\text{Ca}(\text{OH})_2$ solution to the endpoint?

Appendix D

Titration Notes – Teacher's Edition

A titration is the experimental procedure used to determine the concentration of an unknown acid or base. The necessary chemical components of a titration include a *standard solution*, a solution of unknown concentration, and may include a colored *indicator*.

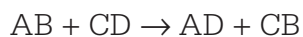
Titration curves are a way to visually represent the change in pH during a titration.

Titration curves tell you many things about a reaction. During a titration, the indicator experiences a color change at the *endpoint* of the titration. If the best indicator is chosen, the endpoint and the *equivalence point* (when equivalent amounts of acid and base have been added) occur at nearly the same time. Common indicators used in acid–base titrations include phenolphthalein (clear to pink pH = 8–10) and bromothymol blue (yellow to blue pH = 6–8). The equivalence point can be visually determined from the titration curve. It is the area where the slope of the line approaches infinity (or is nearly vertical). Titration curves and the progress of titrations can also be followed by using a pH meter or probe.

Acid–Base Reactions

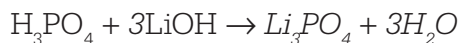
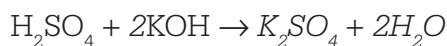
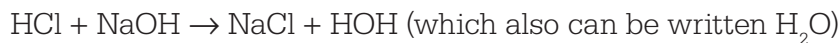
When an acid reacts with a base, a neutralization reaction occurs. The same thing happens when a base reacts with an acid.

An acid–base reaction is a double displacement reaction.

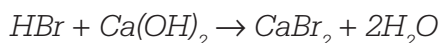


The overall products of an acid–base reaction are a salt (metal/nonmetal compound) and water.

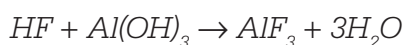
Examples



Hydrobromic acid + calcium hydroxide



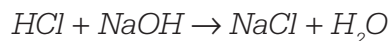
Hydrofluoric acid + aluminum hydroxide



Titration Problems

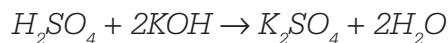
Often, the goal of a titration is to calculate the concentration of one of the reactants. This can be done using a balanced equation and stoichiometry.

1. A 25.0 mL sample of HCl was titrated to the equivalence point with 15.0 mL of 2.0 M NaOH. What was the molarity of the acid?



$$15.0 \text{ mL NaOH} \times \frac{1 \text{ L NaOH}}{1000 \text{ mL NaOH}} \times \frac{2.0 \text{ mol NaOH}}{1 \text{ L NaOH}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} \times \frac{1}{25.0 \text{ mL HCl}} \times \frac{1000 \text{ mL}}{1 \text{ L HCl}} = 1.2 \text{ M HCl}$$

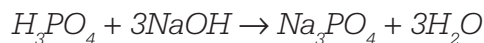
2. A 10.0 mL sample of H₂SO₄ was completely reacted by 13.5 mL of 1.0 M KOH. What was the molarity of the acid?



$$13.5 \text{ mL KOH} \times \frac{1 \text{ L KOH}}{1000 \text{ mL}} \times \frac{1.0 \text{ mol KOH}}{1 \text{ L}} \times \frac{1 \text{ mol H}_2\text{SO}_4}{2 \text{ mol KOH}} \times \frac{1000 \text{ mL H}_2\text{SO}_4}{1 \text{ L H}_2\text{SO}_4} \times \frac{1}{10.0 \text{ mL H}_2\text{SO}_4} = 0.68 \text{ M H}_2\text{SO}_4$$

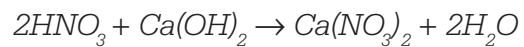
3. What volume of 1.50 M NaOH is necessary to completely react with 20.0 mL of 2.5M H₃PO₄?

Note: M is molarity, which can be mol/L or millimoles/mL.



$$20.0 \text{ mL H}_3\text{PO}_4 \times \frac{2.5 \text{ mmol H}_3\text{PO}_4}{1.0 \text{ mL H}_3\text{PO}_4} \times \frac{3 \text{ mmol NaOH}}{1 \text{ mmol H}_3\text{PO}_4} \times \frac{1 \text{ mL NaOH}}{1.50 \text{ mmol NaOH}} = 1.00 \times 10^2 \text{ mL NaOH}$$

4. How much 0.5M HNO₃ is necessary to titrate 25.0 mL of 0.05M Ca(OH)₂ solution to the equivalence point?



$$25.0 \text{ mL Ca}(\text{OH})_2 \times \frac{0.05 \text{ mmol Ca}(\text{OH})_2}{1 \text{ mL Ca}(\text{OH})_2} \times \frac{2 \text{ mmol HNO}_3}{1 \text{ mmol Ca}(\text{OH})_2} \times \frac{1 \text{ mL HNO}_3}{0.5 \text{ mmol HNO}_3} = 5.00 \text{ mL HNO}_3$$

Appendix E

Calculating the pH of a Weak Acid or Base

When working with weak acids, weak bases, or **buffer** systems, one must take into account the fact that many species exist in the reaction vessel. Take, for example, the case of calculating the pH of a 0.100 M acetic acid solution whose $K_a = 1.8 \times 10^{-5}$.



Acetic acid is a weak acid and thus, only a small percentage of it dissociates. This becomes an equilibrium problem instead of a simple stoichiometry problem (like it would if it were a strong acid).

We begin by writing the equilibrium expression:

$$K_a = \frac{[\text{H}_3\text{O}^{1+}][\text{C}_2\text{H}_3\text{O}_2^{1-}]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

Next we need to look at the conditions during the reaction:

	$\text{HC}_2\text{H}_3\text{O}_2$	H_3O^{1+}	$\text{C}_2\text{H}_3\text{O}_2^{1-}$
Initial	0.100M	0	0
Change	-x	+x	+x
Equilibrium	0.100M - x	x	x

Substituting into the equilibrium expression we get:

$$K_a = \frac{[x][x]}{[0.100\text{M} - x]} = 1.8 \times 10^{-5}$$

Assuming the effect of x on 0.100M is negligible because of the large difference (power difference $> 10^{-3}$ units) in concentration and K_a , solving for x we get:

$$x^2 = 1.8 \times 10^{-6} \quad x = 1.34 \times 10^{-3} = [\text{H}_3\text{O}^{1+}]$$

Now we can solve for pH using the equation: $\text{pH} = -\log[\text{H}_3\text{O}^{1+}]$ and find the pH to be 2.87.

Example 1

Calculate the pH of a 2.00M ammonia solution with a $K_a = 5.71 \times 10^{-10}$ @ 25°C.

- A. -0.30
- B. 2.22
- C. 8.94
- D. 11.78

Solution:

The correct answer is D. The reaction is $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$

Since $K_w = K_a K_b = 1.0 \times 10^{-14}$ so $K_b = \frac{K_w}{K_a}$ substituting in values we get:

$$K_b = \frac{1.0 \times 10^{-14}}{5.71 \times 10^{-10}} = 1.8 \times 10^{-5} \text{ M}$$

	NH_3	NH_4^{1+}	OH^{1-}
Initial	2.00 M	0	0
Change	- x	+x	+x
Equilibrium	2.00 - x	x	x

Substituting into the equilibrium expression we get:

$$K_b = \frac{[x][x]}{[2.00\text{M} - x]} = 1.8 \times 10^{-5}$$

Assuming the effect of x on 2.00M is negligible because of the large difference (power difference > 10^{-3} units) in concentration and K_b , solving for x we get:

$$x^2 = 3.6 \times 10^{-6} \quad x = 6.0 \times 10^{-3} = [\text{OH}^{1-}]$$

Now we can solve for pOH using the equation: $\text{pOH} = -\log[\text{OH}^{1-}]$ and find the pOH to be 2.22.

Since $\text{pH} + \text{pOH} = 14$, $\text{pH} = 14 - 2.22$, and the $\text{pH} = 11.78$.

If you chose answer A, you only used the initial concentration of ammonia and substituted it into the $\text{pH} = -\log[\text{H}_3\text{O}^{1+}]$ assuming that the concentration of ammonia was equal to the hydronium ion concentration. If you chose answer B, you selected the value that was equal to the pOH. If you chose answer C, you used 5.71×10^{-10} for your K_b value instead of 1.8×10^{-5} .

Appendix F

Applications of Aqueous Equilibria Notes

Different Constants (to hopefully clear confusion)

K_b	molal boiling point constant	$\Delta t_b = K_b m$
K_f	molal freezing point constant	$\Delta t_f = K_f m$
k	rate constant	Rate = k [reactants]
K_w	ionization constant for water	$K_w = K_a K_b = 1.0 \times 10^{-14}$ @ 25°C
K_a	acid dissociation constant	$K_a = \frac{[H^+][A^-]}{[HA]}$
K_b	base dissociation constant	$K_b = \frac{[X^-][OH^-]}{[XOH]}$
K_c	equilibrium constant for concentrations	
K_p	equilibrium constant based on pressures	
K_{sp}	equilibrium constant for solubility product	
K_d	equilibrium constant for decomposition reactions	
K_f	equilibrium constant for formation reactions	

The Effect of Common Ions

When a salt is added to an acid or base containing similar ions, the equilibrium shifts to relieve the stress this is an application of _____.

If NaF is added to HF:	If NH ₄ Cl is added to NH ₃ :
$HF \leftrightarrow H^+ + F^-$	$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$
$NaF \leftrightarrow Na^+ + F^-$	$NH_4Cl \leftrightarrow NH_4^+ + Cl^-$
More fluoride ions are added to the solution.	More ammonium ions are added to the solution.
The equilibrium shifts to the left.	The equilibrium shifts to the left.

This shifting process is called the *common ion effect*. This complicates the equilibrium by providing an additional source for ions.

Example 1

Calculate the pH of a mixture containing 0.100 M $\text{HC}_3\text{H}_5\text{O}_2$ and 0.100 M $\text{NaC}_3\text{H}_5\text{O}_2$. $K_a = 1.3 \times 10^{-5}$

Buffers

Combinations of weak acids or weak bases with their salts form buffers. Buffers are solutions that resist changes in pH when hydrogen or hydroxide ions are added. When working with buffers, be sure to look at the stoichiometry before setting up the equilibrium.

Example 2

What is the difference in pH of a solution containing 2.00 mol of ammonia and 3.00 mol of ammonium chloride in 1.00 L of solution versus the pH of the ammonia alone?

$$K_b = 1.81 \times 10^{-5}$$

The Henderson-Hasselbalch equation can also be used to solve for pH.

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]} \right) \quad \text{pOH} = \text{p}K_b + \log \left(\frac{[\text{X}^-]}{[\text{WB}]} \right)$$

Solution:

Titration is a laboratory procedure used to determine the concentration of acids or bases. Along the way, the pH of the mixture can be calculated. Problems like this have appeared in the past on the AP Exam.

A 100.0 mL sample of 0.150 M HNO_2 ($\text{p}K_a = 3.35$) was titrated with 0.300 M NaOH. Determine the pH after the following quantities of base have been added to the acid solution and draw the resulting titration curve.

- 0.00 mL
- 25.00 mL
- 49.50 mL
- 50.00 mL
- 55.00 mL
- 75.00 mL

Indicators and Titrations

Common indicators used in acid base titrations are:

phenolphthalein (clear to pink pH = 8-10)

bromothymol blue (yellow to blue pH = 6-8)

universal indicator (red to purple pH = 1-13)

To prepare a buffer with a specific pH (part of pre-lab discussion):

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$6.0 = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Acids to choose from:	Their K_a values		
H_2SO_3	1.5×10^{-2}	1.0×10^{-7}	
HOAc	1.8×10^{-5}		
H_3PO_4	7.3×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
HSO_4^{1-}	1.2×10^{-2}		
H_2SO_4	Large	1.2×10^{-2}	

So if I am not mistaken, for a buffer with pH = 6, you would choose HOAc and NaOAc since the $\text{p}K_a$ of HOAc is closest to 6.

$$6.0 = \text{p}(1.8 \times 10^{-5}) + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$6.0 = 4.74 + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$1.26 = \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$10^{-1.26} = \frac{[\text{A}^-]}{[\text{HA}]}$$

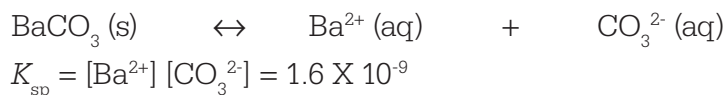
$$0.055 = \frac{[\text{A}^-]}{[\text{HA}]}$$

If $[\text{HA}] = 0.1 \text{ M}$, then $[\text{A}^-] = 0.0055 \text{ M}$.

Solubility Equilibria

When solids dissolve to form aqueous solutions, the equilibrium involved is the solubility equilibria. When a salt is added to water at first, none is dissolved, then as the water molecules collide with the salt and interact with the intermolecular forces, the formula units of the salt begin to dissolve. Eventually the maximum amount of

solid that can dissolve at that particular temperature does dissolve and equilibrium is reached.



Why is the BaCO_3 not included in the K_{sp} expression?

Notice that the K value is very small. We would expect this since barium carbonate is not considered soluble in water based on what we have learned from solubility rules. Do realize, however, that solubility and the solubility product are not the same. Solubility is a position that changes with temperature and the concentration of common ions present in the solution. The solubility product is a constant value for a particular temperature (usually room temperature when you look it up in a chart).

K_{sp} problems are much like K_{a} and K_{b} problems.

Calculating K_{sp} from solubility

Calculating solubility from K_{sp}

PbSO_4 has a measured solubility of 1.14×10^{-4} mol/L

$\text{Al}(\text{OH})_3$ has a K_{sp} of 2×10^{-32} at 25°C .

At 25°C , what is the K_{sp} of PbSO_4 ?

What is its solubility of PbSO_4 at 25°C ?

Relative Solubilities

If salts produce the same number of ions when they dissolve, then their K_{sp} values can be used to determine their solubilities relative to each other. The smaller the K_{sp} , the less soluble it is.

If the salts produce different numbers of ions when they dissolve, then you have to calculate the solubilities from the K_{sp} values, as in the previous example.

The Common Ion Effect on Solubility

A common ion affects the solubility of a solid, generally reducing the amount that dissolves by providing an initial concentration of one of the ions. RICE diagrams are very useful in demonstrating this affect.

Example 3

The K_{sp} of silver sulfate is 1.2×10^{-5} . Calculate the solubility of silver sulfate in a 0.20 M solution of potassium sulfate.

Appendix G

Applications of Aqueous Equilibria Notes – Teacher's Edition

Different Constants (to hopefully clear confusion)

K_b	molal boiling point constant	$\Delta t_b = K_b m$
K_f	molal freezing point constant	$\Delta t_f = K_f m$
k	rate constant	Rate = k [reactants]
K_w	ionization constant for water	$K_w = K_a K_b = 1.0 \times 10^{-14}$ @ 25°C
K_a	acid dissociation constant	$K_a = \frac{[H^+][A^-]}{[HA]}$
K_b	base dissociation constant	$K_b = \frac{[X^+][OH^-]}{[XOH]}$
K_c	equilibrium constant for concentrations	
K_p	equilibrium constant based on pressures	
K_{sp}	equilibrium constant for solubility product	
K_d	equilibrium constant for decomposition reactions	
K_f	equilibrium constant for formation reactions	

The Effect of Common Ions

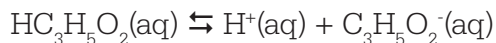
When a salt is added to an acid or base containing similar ions, the equilibrium shifts to relieve the stress this is an application of *LeChatlier's Principle*

If NaF is added to HF:	If NH ₄ Cl is added to NH ₃ :
$HF \leftrightarrow H^+ + F^-$	$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$
$NaF \leftrightarrow Na^+ + F^-$	$NH_4Cl \leftrightarrow NH_4^+ + Cl^-$
More fluoride ions are added to the solution.	More ammonium ions are added to the solution.
The equilibrium shifts to the left.	The equilibrium shifts to the left.

This shifting process is called the *common ion effect*. This complicates the equilibrium by providing an additional source for ions.

Example 1

Calculate the pH of a mixture containing 0.100 M $\text{HC}_3\text{H}_5\text{O}_2$ and 0.100 M $\text{NaC}_3\text{H}_5\text{O}_2$. $K_a = 1.3 \times 10^{-5}$



	$\text{HC}_3\text{H}_5\text{O}_2$	H^+	$\text{C}_3\text{H}_5\text{O}_2^{1-}$
Initial	0.100M	0	0
Change	-x	+x	x + 0.100 [The 0.100 comes from the $\text{NaC}_3\text{H}_5\text{O}_2$.]
Equilibrium	0.100M - x	x	x + 0.100

$$K_a = \frac{[x][0.100 + x]}{[0.100M - x]} = 1.3 \times 10^{-5}$$

If you consider x to be negligible, then this simplifies to :

$$K_a = \frac{[0.100x]}{[0.100M]} = 1.3 \times 10^{-5} \text{ and } x = 1.3 \times 10^{-5} \text{M} = [\text{H}^+]$$

$$\text{pH} = -\log[\text{H}^+]$$

$$\text{pH} = -\log(1.3 \times 10^{-5})$$

$$\text{pH} = 4.89, \text{ which is consistent with a weak acid.}$$

Buffers

Combinations of weak acids or weak bases with their salts form buffers. Buffers are solutions that resist changes in pH when hydrogen or hydroxide ions are added. When working with buffers, be sure to look at the stoichiometry before setting up the equilibrium.

Example 2

What is the difference in pH of a solution containing 2.00 mol of ammonia and 3.00 mol of ammonium chloride in 1.00 L of solution versus the pH of the ammonia alone? $K_b = 1.81 \times 10^{-5}$

2.00 mol NH_3 only	2.00 mole NH_3 + 3.00 mol NH_4Cl
$\text{NH}_3 + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$	$\text{NH}_3 + \text{H}_2\text{O}(\text{aq}) \leftrightarrow \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$

	NH_3	NH_4^{1+}	OH^{1-}	NH_3	NH_4^{1+}	OH^{1-}
Initial	2.00 M	0	0	2.00 M	0	0
Change	-x	+x	+x	-x	3.00 + x	x
Equilibrium	2.00M - x	x	x	2.00M - x	x	x

$K_a = \frac{[x][x]}{[2.00M - x]} = 1.81 \times 10^{-5}$	$K_a = \frac{[3.00M + x][x]}{[2.00M - x]} = 1.81 \times 10^{-5}$
--	--

Considering x to be negligible:	Considering x to be negligible:
$x^2 = 2.00 \text{ M} \times (1.81 \times 10^{-5})$	$3x = 2.00 \text{ M} \times 1.81 \times 10^{-5}$
$x = 6.01 \times 10^{-3} \text{ M} = [\text{OH}^-]$	$x = 1.21 \times 10^{-5} \text{ M} = [\text{OH}^-]$
$\text{pOH} = -\log[\text{OH}^-]$	$\text{pOH} = -\log[\text{OH}^-]$
$\text{pOH} = 2.221$	$\text{pOH} = 4.917$
$\text{pH} + \text{pOH} = 14$	$\text{pH} + \text{pOH} = 14$
$\text{pH} + 2.221 = 14$	$\text{pH} + 4.917 = 14$
$\text{pH} = 11.779$	$\text{pH} = 9.083$

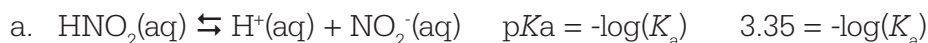
The Henderson-Hasselbalch equation can also be used to solve for pH.

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]} \right) \qquad \text{pOH} = \text{p}K_b + \log \left(\frac{[\text{X}^-]}{[\text{WB}]} \right)$$

Titration is a laboratory procedure used to determine the concentration of acids or bases. Along the way, the pH of the mixture can be calculated. Problems like this have appeared in the past on the AP Exam.

A 50.0 mL sample of 0.300 M HNO_2 ($\text{p}K_a = 3.35$) was titrated with 0.450 M NaOH. Determine the pH after the following quantities of base have been added to the acid solution and draw the resulting titration curve:

- 0.00 mL
- 16.5 mL
- 32.0 mL
- 33.3 mL
- 35.0 mL
- 50.0 mL



$$K_a = 4.5 \times 10^{-4}$$

$$K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = 4.5 \times 10^{-4}$$

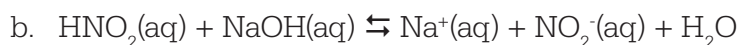
	[HNO₂]	[H¹⁺]	[NO₂¹⁻]
Initial	0.300 M	0	0
Change	-x	+x	+x
Equilibrium	0.300 M - x	x	x

$$K_a = \frac{[x][x]}{[0.300M - x]} = 4.5 \times 10^{-4}$$

$$x = 1.2 \times 10^{-2}M = [H^+]$$

$$pH = -\log[H^+]$$

$$pH = 1.92$$

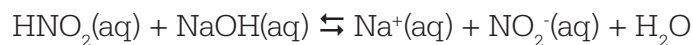


$$50.0 \text{ mL } HNO_2 \times 1L/1000mL \times 0.300 \text{ M} = 0.0150 \text{ mol } HNO_2$$

$$16.5 \text{ mL } NaOH \times 1L/1000mL \times 0.450 \text{ M} = 0.00743 \text{ mol } NaOH$$

$$0.0150 \text{ mol} - 0.007425 \text{ mol} = 0.007575 \text{ mol } HNO_2 \text{ left after reaction}$$

$$50.0mL + 16.5mL = 66.5 \text{ mL or } 0.0665 \text{ L}$$

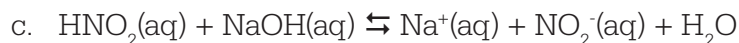


	[HNO₂]	[NaOH]	[Na¹⁺]	[NO₂¹⁻]
Initial	0.0150 mol	0.0743 mol	0	0
Change	-0.0743mol	-0.0743 mol	+ 0.0743 mol	+ 0.0743mol
Equilibrium	0.0757 mol	0	0.0743 mol	0.0743 mol

$$pH = pK_a + \log ([A^-]/[HA])$$

$$pH = 3.35 + \log(0.0743 \text{ mol}/0.0665 \text{ L} \div 0.0757 \text{ mol}/0.0665 \text{ L})$$

$$pH = 3.34$$

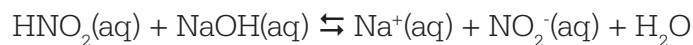


$$50.0 \text{ mL } HNO_2 \times 1L/1000mL \times 0.300 \text{ M} = 0.0150 \text{ mol } HNO_2$$

$$32.0 \text{ mL } NaOH \times 1L/1000mL \times 0.450 \text{ M} = 0.0144 \text{ mol } NaOH$$

$$0.015 \text{ mol} - 0.014 \text{ mol} = 0.001 \text{ mol } HNO_2 \text{ left after reaction}$$

$$50.0mL + 32.0mL = 82.0 \text{ mL or } 0.0820 \text{ L}$$

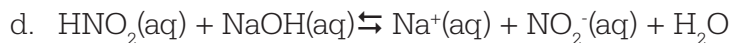


	[HNO₂]	[NaOH]	[Na¹⁺]	[NO₂¹⁻]
Initial	0.0150 mol	0.0144 mol	0	0
Change	-0.0144 mol	-0.0144 mol	+ 0.0144 mol	+ 0.0144 mol
Equilibrium	0.0006 mol	0	0.0144 mol	0.0144 mol

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

$$\text{pH} = 3.35 + \log(0.0144 \text{ mol}/0.0820 \text{ L} \div 0.0006 \text{ mol}/0.0820 \text{ L})$$

$$\text{pH} = 4.73$$

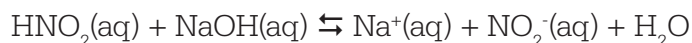


$$50.0 \text{ mL HNO}_2 \times 1\text{L}/1000\text{mL} \times 0.300 \text{ M} = 0.0150 \text{ mol HNO}_2$$

$$33.3 \text{ mL NaOH} \times 1\text{L}/1000\text{mL} \times 0.450 \text{ M} = 0.0150 \text{ mol NaOH}$$

$$0.0150 \text{ mol} - 0.0150 \text{ mol} = 0.00 \text{ mol HNO}_2 \text{ left after reaction}$$

$$50.0\text{mL} + 33.3\text{mL} = 83.3 \text{ mL or } 0.0833 \text{ L}$$



	[HNO₂]	[NaOH]	[Na⁺]	[NO₂¹⁻]
Initial	0.0150 mol	0.0150 mol	0	0
Change	0.0150 mol	0.0150 mol	+ 0.0150 mol	+ 0.0150 mol
Equilibrium	0	0	0.0150 mol	0.0150 mol

$$\frac{0.0150 \text{ mol NO}_2^{1-}}{0.0833 \text{ L}} = 0.180 \text{ M}$$

NO₂⁻ is the conjugate base of a weak acid so

$$\text{p}K_a + \text{p}K_b = 14.0 \quad \text{p}K_b = 14.0 - 3.35 = 10.65$$



	[NO ₂ ⁻]	[H ₂ O]	[OH ⁻]	[HNO ₂]
Initial	0.180M		0	0
Change	-x		+x	+x
Equilibrium	0.180M-x		x	x

$$\text{p}K_b = -\log(K_b)$$

$$K_b = 2.24 \times 10^{-11}$$

$$K_b = \frac{[\text{OH}^-][\text{HNO}_2]}{[\text{NO}_2^-]} = 2.24 \times 10^{-11}$$

$$x^2 = (0.180\text{M}) \times 2.24 \times 10^{-11}$$

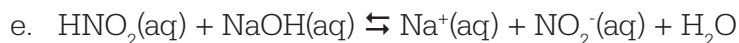
$$x = 2.01 \times 10^{-6} = [\text{OH}^-]$$

$$\text{pOH} = -\log[\text{OH}^-]$$

$$\text{pOH} = 5.697$$

$$14 - \text{pOH} = \text{pH}$$

$$\text{pH} = 8.303$$

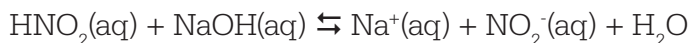


$$50.0 \text{ mL HNO}_2 \times 1\text{L}/1000\text{mL} \times 0.300 \text{ M} = 0.0150 \text{ mol HNO}_2$$

$$35.0 \text{ mL NaOH} \times 1\text{L}/1000\text{mL} \times 0.450 \text{ M} = 0.0158 \text{ mol NaOH}$$

0.0158 mol – 0.0150 mol = 0.0008 mol NaOH left after reaction

50.0 mL + 35.0 mL = 85.0 mL or 0.0850 L

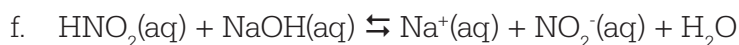


	[HNO ₂]	[NaOH]	[Na ⁺]	[NO ₂ ⁻]
Initial	0.0150 mol	0.0158 mol	0	0
Change	0.0150 mol	0.0150 mol	+ 0.0150 mol	+ 0.0150 mol
Equilibrium	0	0.0008 mol	0.0150 mol	0.0150 mol

Here the concentration of NaOH controls the pH since it is a strong base.

$$pOH = -\log[OH^-] \qquad pOH = -\log(0.0008 \text{ M}) \qquad pOH = 3$$

$$pH + pOH = 14 \qquad pH = 14 - pOH \qquad pH = 11$$

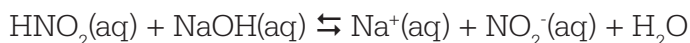


50.0 mL HNO₂ × 1L/1000mL × 0.300 M = 0.0150 mol HNO₂

50.0 mL NaOH × 1L/1000mL × 0.450 M = 0.0225 mol NaOH

0.0225 mol – 0.0150 mol = 0.0075 mol NaOH left after reaction

50.0mL + 50.0mL = 100.0 mL or 0.1000 L



	[HNO ₂]	[NaOH]	[Na ⁺]	[NO ₂ ⁻]
Initial	0.0150 mol	0.0225 mol	0	0
Change	0.0150 mol	0.0150 mol	+ 0.0150 mol	+ 0.0150 mol
Equilibrium	0	0.0075 mol	0.0150 mol	0.0150 mol

Here the concentration of NaOH controls the pH since it is a strong base.

$$pOH = -\log[OH^-] \qquad pOH = -\log(0.0075\text{M}) \qquad pOH = 2.125$$

$$pH + pOH = 14 \qquad pH = 14 - pOH \qquad pH = 11.875$$

Indicators and Titrations

Common indicators used in acid base titrations are:

- phenolphthalein (clear to pink pH = 8-10)
- bromothymol blue (yellow to blue pH = 6-8)
- universal indicator (red to purple pH = 1-13)

To prepare a buffer with a specific pH (part of pre-lab discussion)

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$6.0 = \text{p}K_a + \log \frac{[A^-]}{[HA]}$$

Acids to choose from:		Their K_a values	
H_2SO_3	1.5×10^{-2}	1.0×10^{-7}	
HOAc	1.8×10^{-5}		
H_3PO_4	7.3×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
HSO_4^{1-}	1.2×10^{-2}		
H_2SO_4	Large	1.2×10^{-2}	

So if I am not mistaken, for a buffer with a pH of 6, you would choose HOAc and NaOAc since the $\text{p}K_a$ of HOAc is closest to 6.

$$6.0 = \text{p}(1.8 \times 10^{-5}) + \log \frac{[A^-]}{[HA]}$$

$$6.0 = 4.74 + \log \frac{[A^-]}{[HA]}$$

$$1.26 = \log \frac{[A^-]}{[HA]}$$

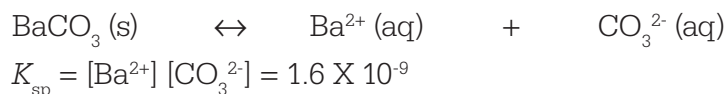
$$10^{-1.26} = \frac{[A^-]}{[HA]}$$

$$0.055 = \frac{[A^-]}{[HA]}$$

If $[HA] = 0.1 \text{ M}$, then $[A^-] = 0.0055 \text{ M}$.

Solubility Equilibria

When solids dissolve to form aqueous solutions, the equilibrium involved is the solubility equilibria. When a salt is added to water at first, none is dissolved, then as the water molecules collide with the salt and the intermolecular forces interact with the water, the formula units of the salt begin to dissolve. Eventually, the maximum amount of solid that can dissolve at that particular temperature does dissolve and equilibrium is reached.



Why is the BaCO_3 not included in the K_{sp} expression?

Barium carbonate is a solid and solids are not found in equilibrium expressions.

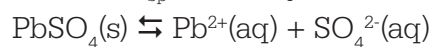
Notice that the K value is very small. We would expect this since barium carbonate is not considered soluble in water, based on what we have learned from solubility rules. Do realize, however, that solubility and the solubility product are not the same. Solubility is a position that changes with temperature and the concentration of common ions present in the solution. The solubility product is a constant value for a particular temperature (usually room temperature when you look it up on a chart).

K_{sp} problems are much like K_a and K_b problems.

Calculating K_{sp} from solubility

$PbSO_4$ has a measured solubility of 1.14×10^{-4} mol/L

What is the K_{sp} of $PbSO_4$?



$$K_{sp} = [Pb^{2+}][SO_4^{2-}]$$

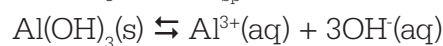
$$K_{sp} = (x)(x)$$

$$K_{sp} = (1.14 \times 10^{-4})^2$$

$$K_{sp} = 1.30 \times 10^{-8}$$

Calculating solubility from K_{sp}

$Al(OH)_3$ has a K_{sp} of 2×10^{-32} at $25^\circ C$



$$K_{sp} = [Al^{3+}][OH^-]^3$$

$$2 \times 10^{-32} = (x)(3x)^3$$

$$x = 5 \times 10^{-9} M$$

Relative Solubilities

If salts produce the same number of ions when they dissolve, then their K_{sp} values can be used to determine their solubilities relative to each other. The smaller the K_{sp} , the less soluble it is.

If the salts produce different numbers of ions when they dissolve, then you have to calculate the solubilities from the K_{sp} values, as in the previous example.

The Common Ion Effect on Solubility

A common ion affects the solubility of a solid, generally reducing the amount that dissolves by providing an initial concentration of one of the ions. RICE diagrams are very useful in demonstrating this effect.

Example 3

The K_{sp} of silver sulfate is 1.2×10^{-5} . Calculate the solubility of silver sulfate in a 0.20 M solution of potassium sulfate.



$K_{\text{sp}} = [\text{Ag}^+]^2[\text{SO}_4^{2-}]$ The K_2SO_4 solution contributes 0.20 M of SO_4^{2-}

	[Ag¹⁺]	[SO₄²⁻]
Initial	0	0.20
Change	+2x	+ x
Equilibrium	2x	0.20 + x

$$1.2 \times 10^{-5} = (2x)^2(0.20 + x)$$

$$x = 3.9 \times 10^{-3} \text{ M}$$

$$[\text{Ag}^+] = 2x = 7.7 \times 10^{-3} \text{ M}$$

The rest of Chapter 15 discusses qualitative analysis, selective precipitation, and complex ion equilibria—topics that generally receive very little attention on the AP Exam. Read about it if you have time, otherwise, we will come back to it after all the other AP material has been covered or after the AP Exam.

Appendix H

Study Guides and Worksheets

Chapter 14

Answer the following questions, in order, on notebook paper.

Due date: _____

1. Make a chart comparing the definitions of an acid and a base according to the Arrhenius concept, the Bronsted-Lowry model, and the Lewis acid–base model.
2. What is a hydronium ion?
3. What is a conjugate acid–base pair? Give an example.
4. What is K_a ?
5. What is the difference between a strong and weak acid?
6. What is a diprotic acid? Give an example.
7. Organic acids are generally strong or weak? Why?
8. Water is amphoteric. What does that mean?
9. What is K_w ? What is its value at 25 °C?
10. When calculating pH from $[H^+]$, how do you determine the number of significant digits in your answer?
11. How does calculating the pH of a strong acid differ from calculating the pH of a weak acid?
12. How do you calculate percent dissociation?
13. How do you calculate the pH of a strong base?
14. Give examples of salts that produce acidic solutions, basic solutions, and neutral solutions.
15. Hydrofluoric acid is the only weak acid consisting of a halogen. Why?

Read through the In-Class Discussion Questions. They may be used for warm-ups.

Complete the following problems, in order, from pages 712–717. (19, 21–23, 27, 29, 31–32, 37–38, 43–46, 49–54, 61, 63, 81, 89, 95–96, 103–04, 109–10, 115–118, 123, 129, 138, 142–143, and 153)

Chapter 15

Answer the following questions, in order, on notebook paper.

Due date: _____

1. What is a common ion?
2. How do common ions affect equilibrium?
3. What is a buffered solution? What does it do? What substance in our body is considered a buffered solution?
4. When dealing with a strong acid or strong base being added to a buffer, what do you do before setting up the ICE chart?
5. What is the Henderson-Hasselbalch equation? When can you use it?
6. What is buffer capacity and how is it calculated?
7. Draw the pH curves for a strong acid/strong base titration, a weak acid–strong base titration, and a weak base–strong acid titration.
8. What is the solubility product?
9. What is the common ion effect?
10. How are pH and solubility related?
11. What is the ion product? How is it related to K_{sp} and precipitation?
12. What is selective precipitation and what is it used for?
13. What is qualitative analysis?
14. What is a complex ion?
15. What is a ligand?

Read through the In-Class Discussion Questions. They may be used for warm-ups.

Complete the following problems, in order, from pages 781–789. (13–14, 18–19, 23–24, 33–36, 40, 51–53, 55, 57–60, 61, 64, 69, 71–72, 79–82, 84–85, 88, 92, 97–99, 106, 119–121, and 123)

Acid–Bases, Reactions, and Titration Calculation Review Worksheet

1. Complete the following table. Show all work on a separate sheet of paper.

$[\text{H}_3\text{O}^+]$	$[\text{OH}^-]$	pH	pOH
$7.23 \times 10^{-2} \text{ M}$			
	$8.89 \times 10^{-7} \text{ M}$		
		10.3	
			9.39
	$3.99 \times 10^{-5} \text{ M}$		
$1.19 \times 10^{-10} \text{ M}$			

2. The approximate pH of oranges is 3.5. What are the pOH, the $[\text{OH}^-]$, and the $[\text{H}_3\text{O}^+]$?
3. The approximate pOH of tomatoes is 9.8. What are the pH, the $[\text{H}_3\text{O}^+]$, and the $[\text{OH}^-]$?
4. Write and balance the chemical equation for the reaction between:
 - a. barium hydroxide and sulfuric acid
 - b. aluminum hydroxide and nitric acid
 - c. phosphoric acid and potassium hydroxide
5. How many mL of 1.50M magnesium hydroxide are necessary to titrate 25.0 mL of 2.50 M phosphoric acid?
6. What is the molarity of a lithium hydroxide solution if 15.0 mL is neutralized by 7.5 mL of a 0.020 M acetic acid solution?
7. A student reacted a 25.00 mL sample of vinegar (acetic acid solution) with 38.25 mL of 0.500 M sodium hydroxide.
 - a. Write and balance the chemical equation for the reaction.
 - b. Calculate the molarity of the vinegar solution.
 - c. How many grams of acetic acid would be in 1.00 L of the vinegar?
 - d. What is the percent by mass of acetic acid in the vinegar solution (assume a density of 1.00 g/mL)?

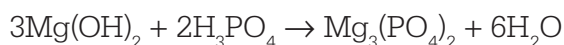
Acid–Bases, Reactions, and Titration Calculation Review Worksheet— Teacher’s Edition

1. Complete the following table. Show all work on a separate sheet of paper.

[H ⁺]	[OH ⁻]	pH	pOH
$7.23 \times 10^{-2} \text{ M}$	$1.38 \times 10^{-13} \text{ M}$	1.141	12.859
$1.12 \times 10^{-8} \text{ M}$	$8.89 \times 10^{-7} \text{ M}$	7.949	6.051
$1.38 \times 10^{-13} \text{ M}$	$1.38 \times 10^{-13} \text{ M}$	10.3	3.7
$1.38 \times 10^{-13} \text{ M}$	$1.38 \times 10^{-13} \text{ M}$	4.61	9.39
$2.51 \times 10^{-10} \text{ M}$	$3.99 \times 10^{-5} \text{ M}$	9.601	4.399
$1.19 \times 10^{-10} \text{ M}$	$8.40 \times 10^{-5} \text{ M}$	9.924	4.076

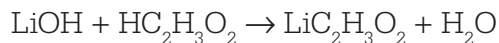
2. The approximate pH of oranges is 3.5. What are the pOH, the [OH⁻], and the [H⁺]?
 a. pOH = 10.5
 b. [OH⁻] = $3 \times 10^{-11} \text{ M}$
 c. [H⁺] = $3 \times 10^{-4} \text{ M}$
3. The approximate pOH of tomatoes is 9.8. What are the pH, the [H⁺], and the [OH⁻]?
 a. pH = 4.2
 b. [H⁺] = $6 \times 10^{-5} \text{ M}$
 c. [OH⁻] = $2 \times 10^{-10} \text{ M}$
4. Write and balance the chemical equation for the complete reaction between:
 a. barium hydroxide and sulfuric acid $\text{Ba}(\text{OH})_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + 2\text{H}_2\text{O}$
 b. aluminum hydroxide and nitric acid $\text{Al}(\text{OH})_3 + 3\text{HNO}_3 \rightarrow \text{Al}(\text{NO}_3)_3 + 3\text{H}_2\text{O}$
 c. phosphoric acid and potassium hydroxide $\text{H}_3\text{PO}_4 + 3\text{KOH} \rightarrow \text{K}_3\text{PO}_4 + 3\text{H}_2\text{O}$

5. How many mL of 1.50M magnesium hydroxide are necessary to completely titrate 25.0 mL of 2.50 M phosphoric acid?



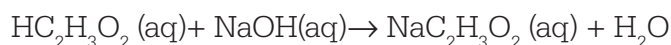
$$\frac{25.0 \text{ mL H}_3\text{PO}_4 \times \frac{1 \text{ L H}_3\text{PO}_4}{1100 \text{ mL H}_3\text{PO}_4} \times \frac{2.50 \text{ mol H}_3\text{PO}_4}{1 \text{ L H}_3\text{PO}_4} \times \frac{3 \text{ mol Mg}(\text{OH})_2}{2 \text{ mol H}_3\text{PO}_4} \times \frac{1 \text{ L Mg}(\text{OH})_2}{1.50 \text{ mol Mg}(\text{OH})_2} \times \frac{1000 \text{ mL Mg}(\text{OH})_2}{1 \text{ L Mg}(\text{OH})_2} = 62.5 \text{ mL Mg}(\text{OH})_2$$

6. What is the molarity of a lithium hydroxide solution if 15.0 mL is completely titrated by 7.5 mL of a 0.020 M acetic acid solution?



$$\frac{7.5 \text{ mL HC}_2\text{H}_3\text{O}_2}{1} \times \frac{0.020 \text{ mmol HC}_2\text{H}_3\text{O}_2}{1 \text{ mL HC}_2\text{H}_3\text{O}_2} \times \frac{1 \text{ mmol LiOH}}{1 \text{ mmol HC}_2\text{H}_3\text{O}_2} \times \frac{1}{15.0 \text{ mL LiOH}} = 0.010 \text{ M LiOH}$$

7. A student reacted a 25.00 mL sample of vinegar (acetic acid solution) with 38.25 mL of 0.500 M sodium hydroxide.
- a. Write and balance the chemical equation for the reaction.



- b. Calculate the molarity of the vinegar solution.

$$\frac{38.25 \text{ mL NaOH}}{1 \text{ mL NaOH}} \times \frac{0.500 \text{ mmol NaOH}}{1 \text{ mmol NaOH}} \times \frac{1 \text{ mmol HC}_2\text{H}_3\text{O}_2}{25.00 \text{ mL HC}_2\text{H}_3\text{O}_2} \times \frac{1}{1} = 0.765 \text{ M HC}_2\text{H}_3\text{O}_2$$

- c. How many grams of acetic acid would be in 1.00 L of the vinegar?

$$\frac{1.00 \text{ L HC}_2\text{H}_3\text{O}_2}{1} \times \frac{0.765 \text{ M HC}_2\text{H}_3\text{O}_2}{1 \text{ L HC}_2\text{H}_3\text{O}_2} \times \frac{60.05 \text{ g HC}_2\text{H}_3\text{O}_2}{1 \text{ mol HC}_2\text{H}_3\text{O}_2} = 45.9 \text{ g HC}_2\text{H}_3\text{O}_2$$

- d. What is the percent by mass of acetic acid in the vinegar solution (assume a density of 1.00 g/mL)?

$$\frac{45.9 \text{ g HC}_2\text{H}_3\text{O}_2}{1 \text{ L HC}_2\text{H}_3\text{O}_2} \times \frac{1 \text{ L HC}_2\text{H}_3\text{O}_2}{1000 \text{ mL HC}_2\text{H}_3\text{O}_2} \times \frac{1 \text{ mL HC}_2\text{H}_3\text{O}_2}{1.00 \text{ g HC}_2\text{H}_3\text{O}_2} \times 100 = 4.59\% \text{ HC}_2\text{H}_3\text{O}_2$$

Appendix I

Dissociation and pH Practice

Weak Acid or Weak Base Systems

The ionization constant (or equilibrium constant) is very important here. Only ions contribute. Water, which is usually the solvent, does not participate in any major way here.

The general form for a reaction containing an acid is: $HA + 2H_2O \leftrightarrow H_3O^+ + A^-$ so:

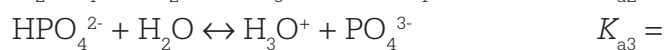
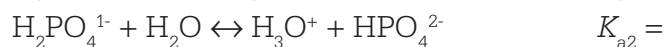
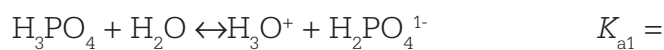
$$K_a =$$

HA is an acid because it begins with hydrogen or because it donates a proton to form H_3O^+ . The A^- is the element or polyatomic ion portion of the acid with a negative charge. Write the K_a for the dissociation of chlorous acid, $HClO_2$, and formic acid, $HCOOH$.

$$K_a =$$

$$K_a =$$

Weak polyprotic acids dissociate (break apart) stepwise. Each step is written as a different reaction. Generally there is a different value for K_a each time an acid loses a hydrogen ion.



Examples:

Write the dissociation reactions for sulfuric acid and carbonic acid.



This also holds true for weak bases like ammonia.

Write the K_b for $NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$

$$K_b =$$

Steps for calculating the pH of a weak acid or base:

- 1) Write and balance the equation if it is not already done for you.
- 2) Determine the equilibrium expression, K_a or K_b .
- 3) Develop the ICE table.
- 4) Substitute the final values into the equilibrium expression.
- 5) Solve for the concentrations.
- 6) Solve for pH or pOH based on the $[H^+]$ or $[OH^-]$.

Calculate the pH of a 1.00M acetic acid solution with a $K_a = 1.8 \times 10^{-5}$

- 1) $HC_2H_3O_2 (aq) + H_2O (l) \leftrightarrow H_3O^{1+} (aq) + C_2H_3O_2^{1-} (aq)$
- 2) $K_a =$
- 3)

	$HC_2H_3O_2$	H_3O^{1+}	$C_2H_3O_2^{1-}$
Initial			
Change			
Equilibrium			

- 4) $K_a =$
- 5) $pH = -\log[H_3O^{1+}]$

Try this one: Calculate the pH of a 0.500M ammonia solution with a $K_b = 1.75 \times 10^{-5}$

- 1) $NH_3 (aq) + H_2O (l) \leftrightarrow NH_4^{1+} (aq) + OH^{1-} (aq)$
- 2) $K_b =$
- 3)

	NH_3	NH_4^{1+}	OH^{1-}
Initial			
Change			
Equilibrium			

- 4) $K_b =$
- 5) $pOH = -\log[OH^{1-}]$ $pH + pOH = 14$

Appendix J

Dissociation and pH Practice—Teacher's Edition

Weak Acid or Weak Base Systems

The ionization constant (or equilibrium constant) is very important here. Only ions contribute. Water, which is usually the solvent, does not participate in any major way here.

The general form for a reaction containing an acid is: $HA + 2H_2O \leftrightarrow H_3O^+ + A^-$ so:

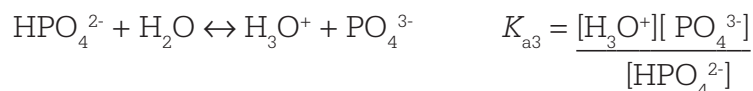
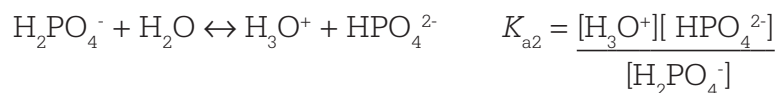
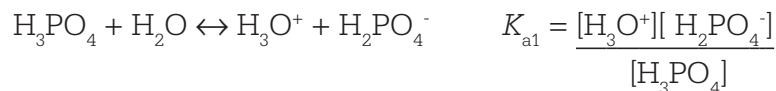
$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

HA is an acid because it begins with hydrogen or because it donates a proton to form H_3O^+ . The A^- is the element or polyatomic ion portion of the acid with a negative charge. Write the K_a for the dissociation of chlorous acid, $HClO_2$, and formic acid, $HCOOH$.

$$K_a = \frac{[H^+][ClO_2^-]}{[HClO_2]}$$

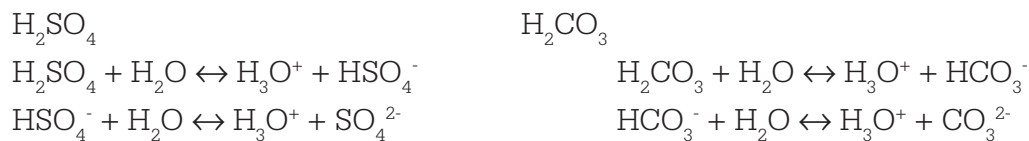
$$K_a = \frac{[H^+][COOH^-]}{[HCOOH]}$$

Polyprotic acids dissociate (break apart) stepwise. Each step is written as a different reaction. Generally there is a different value for K_a each time an acid loses a hydrogen ion.



Practice

Write the dissociation reactions for sulfuric acid and carbonic acid.



Equilibrium expressions also can be written for weak bases like ammonia.

Write the K_b for $\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^-$

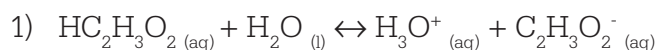
$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

Steps for calculating the pH of a weak acid or base:

- 1) Write and balance the equation if it is not already done for you.
- 2) Determine the equilibrium expression, K_a or K_b .
- 3) Develop the ICE table.
- 4) Substitute the final values into the equilibrium expression.
- 5) Solve for the concentrations.
- 6) Solve for pH or pOH based on the $[\text{H}^+]$ or $[\text{OH}^-]$.

Examples:

Calculate the pH of a 1.00M acetic acid solution with a $K_a = 1.8 \times 10^{-5}$



$$2) K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

3)

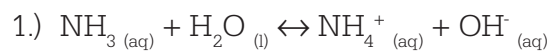
	$[\text{HC}_2\text{H}_3\text{O}_2]$	$[\text{H}^+]$	$[\text{C}_2\text{H}_3\text{O}_2^-]$
Initial	1.00 M	0	0
Change	-x	+x	+x
Equilibrium	1.00 M - x	x	x

$$4) K_a = \frac{[x][x]}{[1.00-x]} = 1.8 \times 10^{-5}$$

$$5) x = 4.2 \times 10^{-3} \text{M} = [\text{H}^+]$$

$$6) \text{pH} = -\log[\text{H}^+] = 2.87$$

Calculate the pH of a 0.500M ammonia solution with a $K_b = 1.75 \times 10^{-5}$



$$2) K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

3.)

	[NH₃]	[NH₄⁺]	[OH⁻]
Initial	0.500 M	0	0
Change	-x	+x	+x
Equilibrium	0.500-x	x	x

$$4) K_b = \frac{[x][x]}{[0.500-x]} = 1.75 \times 10^{-5}$$

$$5) x = 2.96 \times 10^{-3} \text{M} = [\text{OH}^-]$$

$$6) \begin{array}{ll} \text{pOH} = -\log[\text{OH}^-] & \text{pH} + \text{pOH} = 14 \\ \text{pOH} = 2.529 & \text{pH} = 14 - \text{pOH} \\ & \text{pH} = 11.471 \end{array}$$

Appendix K

Lab: Determining the pH of a Substance

Introduction

Many classification systems for compounds exist. One way to classify substances is based on the relative amount of acid present. An acid produces hydrogen ions in an aqueous solution according to the Arrhenius concept. The pH scale was developed to measure the amount of hydrogen ions present in a solution. The use of an indicator, a weak organic acid that changes colors, is another way to measure the hydrogen ion concentration. Different indicators work in different pH ranges.

Use the following table as a reference:

Indicators	Color at a bottom of range	Color at top of range	pH range
Methyl red	Red	Yellow	4.8-6.0
Litmus	Red	Blue	5.2-7.5
Bromothymol blue	Yellow	Blue	6.0-7.6
Phenolphthalein	Clear	Pink	8.0-10.0

Universal indicator: changes colors at different pH values as follows

3.0 red-orange 4.0 orange 5.0 yellow 6.0 green-yellow 7.0 green
8.0 blue-green 9.0 blue-gray 10.0 violet

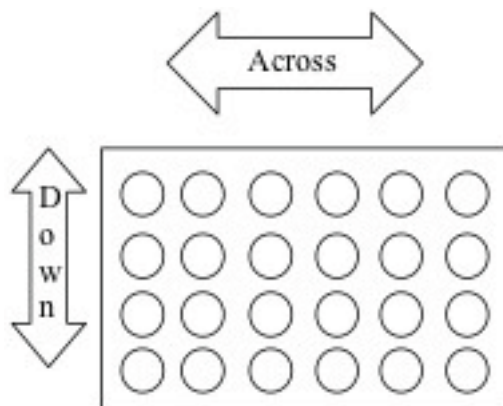
Objectives

1. To observe typical reactions of several indicators when treated with acids and bases.
2. To estimate the pH of some common household products using these reactions.

Procedure

Part 1:

1. Obtain a set of standard solutions and a set of indicators.
2. Add 1–3 drops of each standard across a row in wells according to data table 1.
3. Add 1 drop of indicator down the wells according to data table 1.
4. Record the colors observed for each reaction in the data table.
5. Estimate the pH of each solution. Record in the data table.
6. Rinse out the spot plate with deionized water.



Part 2:

1. Obtain a set of household products.
2. Add 1–3 drops of each product across a row in wells according to data table 2.
3. Add 1 drop of indicator down the wells according to data table 2.
4. Record the colors observed for each reaction in the data table.
5. Estimate the pH of each solution. Record in the data table.
6. Rinse out the spot plate with deionized water.

Part 3: (To be done after you estimate the pH of each household substance based on the indicator colors.)

1. Go to a station set up for measuring the pH of the products.
2. Follow the directions for calibrating your pH probe.
3. Submerge the probe tip in a small amount of the first solution to be measured.
4. Record the pH value in the data table.
5. Rinse the probe thoroughly with deionized water.
6. Repeat steps 3–5 with each household product to be tested.

Data Table 1:

Standard Solution	Methyl Red	Litmus Indicator	Bromthymol Blue	Phenolphthalein	Universal Indicator	Estimated pH
0.1 M HCl						
0.1 M acetic acid						
distilled water						
0.1 M NH ₃ (ammonia)						
0.1 M NaOH						

Data Table 2:

Product	Methyl Red	Litmus Indicator	Bromthymol Blue	Phenolphthalein	Universal Indicator	Estimated pH
aspirin						
bleach						
detergent						
eggs						
lemon juice						
milk						
milk of magnesia						
clear soft drink						
tea						

Analysis:

1. Based on your observations, how does the estimated pH of the hydrochloric acid compare to the estimated pH of the acetic acid?

2. Based on your observations, how does the estimated pH of ammonia compare to the estimated pH of sodium hydroxide?

3. Using your textbook, find the strengths of the listed acids and bases. How do your estimated pH values compare to the rankings of these substances?

4. Indicators also can come from objects found in nature, your home, or even in an office. Locate one such indicator through research and explain how you could tell the difference between an acid and a base using this indicator.

Conclusions

Describe your results. Where they as you expected?

Does one indicator work better than another? If so, which one and in what cases?

Was it difficult to determine the color of the indicator in any particular substance? If so, which one(s)? Why do you think this might have been the case?

If you start with 15.0 mL of hydrochloric acid in a beaker, add a couple drops of methyl red and a couple drops of phenolphthalein, what would you expect to happen as you add 10.0 mL of sodium hydroxide? 15.0 mL of NaOH? 20.0 mL of NaOH?

About the Editor

Marian DeWane teaches AP Chemistry at Centennial High School in Boise, Idaho. She has a long list of accomplishments including Teacher of the Year, National Board Certification in Chemistry, and Presidential Scholar Teacher. She is currently a Question Leader for the AP Chemistry Examination and has also served as a Reader and Table Leader. She also serves on the ACS Exams Institute Advanced High School Committee and National Chemistry Olympiad Task Force, and is a National Leader for the College Board.

About the Authors

Lew Acampora currently teaches AP Chemistry at the St. Francis School in Louisville, Kentucky. For the last 16 years he has taught AP Chemistry at independent schools across the country. Since 1995, he has served as a Reader, Table Leader, and Question Leader at the AP Chemistry Exam Reading. He is a consultant for the College Board and serves on the ACS Exams Institute Advanced High School Committee.

Valerie Ferguson teaches AP Chemistry at Moore High School in Moore, Oklahoma. She has served as a Reader and Table Leader for the AP Chemistry Examination. She also works as a consultant for the College Board and teaches Summer Institutes for AP Chemistry teachers. She has served as chair of the Oklahoma ACS, president of the Oklahoma Science Teachers Organization, and was co-organizer of the Teaching AP Chemistry symposium at the 14th Biennial Conference on Chemistry Education.

Adele Mouakad is an award-winning teacher at St. John's School in San Juan, Puerto Rico. She has been teaching AP Chemistry since 1983. She has won the Presidential Award for Excellence in Science Teaching, and has been a member of the Woodrow Wilson Foundation Teacher Outreach Program and a Dreyfus Master Teacher. She has also been a Reader for the AP Chemistry Examination and a member of the National Chemistry Olympiad Task Force.

Cheri Smith is an award-winning teacher of AP Chemistry at Yale Secondary School in Abbotsford, British Columbia in Canada. She has been a Reader and Table Leader for the AP Chemistry Examination. She has also served as a consultant for the College Board, conducting AP workshops worldwide. Smith has contributed to numerous

publications and served as a reviewer for the *AP Vertical Teams® Guide for Science* and the Pre-AP®: Topics for Vertical Teams in Science workshop.

Arden Zipp is a distinguished faculty member at State University of New York College at Cortland in Cortland, New York. He has served in every capacity for the College Board in the development and scoring of the AP Examination: He has been a Reader, Table Leader, Questions Leader, Chief Reader, and Development Committee member and chair. He is also involved in the development and scoring of the IB Chemistry Program, and is chair of the National Chemistry Olympiad Examination Task Force.

Heather Hattori teaches AP Chemistry, AP Environmental Science, pre-AP chemistry, and pre-AP physics at John H. Guyer High School in Denton, Texas. Hattori received her bachelor's degree in chemistry and English from Stephen F. Austin State University in 1991 and is currently attending the University of North Texas in pursuit of a Ph.D. in chemistry. She has been teaching AP Chemistry and/or AP Environmental Science since 2000 and has been an AP Chemistry Reader since 2005. Hattori was a College Board consultant in the mid-90s, but has been taking a break to raise Arabian horses and most recently attend graduate school in her spare time.

George E. Miller is a senior lecturer emeritus in the Chemistry department at the University of California Irvine, where he is also principal scientist and supervisor of the nuclear reactor facility and responsible for K-12 science teacher professional development. He has been on the chemistry faculty at UCI since 1965, and has taught freshman chemistry, analytical chemistry, radiochemistry, and instrumental analysis. He was member and chair of the AP Chemistry Development Committee and a member of the College Board Subject Test in Chemistry Committee. He has been a Reader, Table Leader, and Question Leader for AP Chemistry over a period of 20 years, and has presented both day- and weeklong workshops for AP and general chemistry teachers. He has more than 60 publications in analytical chemistry and in science education.



F08CMSF131