

base. Both tables of pK_b and of pK_a values are published for weak bases. Note that these two quantities are simply related. Given one, the other can be calculated. By multiplying Equations 1.15 and 1.16 together, we obtain

$$(K_a)(K_b) = [H^+][OH^-] = K_w$$

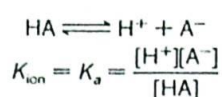
or

$$pK_a + pK_b = -\log K_w = 14$$

(1.17)

1.11 THE HENDERSON-HASSELBALCH EQUATION

Henderson and Hasselbalch have rearranged the mass law equation, as it applies to the ionization of weak acids, into a useful expression known as the Henderson-Hasselbalch equation. Consider the ionization of a generalized weak acid HA.



Rearranging terms, we have

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

Taking logarithms, we find

$$\log [H^+] = \log K_a + \log \frac{[HA]}{[A^-]}$$

and multiplying by -1 ,

$$-\log [H^+] = -\log K_a - \log \frac{[HA]}{[A^-]}$$

If $-\log K_a$ is defined as pK_a and $\log [A^-]/[HA]$ is substituted for $-\log [HA]/[A^-]$, we obtain

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \quad (1.18)$$

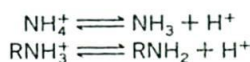
Note that when $[A^-] = [HA]$, $pH = pK_a$ because the logarithm of 1 is zero.

This form of the Henderson-Hasselbalch equation can be written in a more general expression, in which we replace $[A^-]$ with the term "conjugate base" and $[HA]$ with "conjugate acid."

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{conjugate acid}]} \quad (1.19)$$

This expression may then be applied not only to weak acids such as acetic acid, but also to the ionization of ammonium ions and those substituted amino groups found in amino acids. In this case, NH_4^+ ions or the protonated amino

groups RNH_3^+ are the conjugate acids that dissociate to form protons and the conjugate bases NH_3 and RNH_2 , respectively.



Applying Equation 1.19 to the protonated amine, we have

$$\text{pH} = \text{p}K_a + \log \frac{[\text{RNH}_2]}{[\text{RNH}_3^+]} \quad (1.20)$$

Biochemistry handbooks often list the K_a (or $\text{p}K_a$) for the conjugate acids of substances we normally consider as bases (e.g., NH_4OH , amino acids, organic amines). If they do not, the K_b (or $\text{p}K_b$; see Equation 1.17) for the ionization of the weak base will certainly be listed, and the K_a or ($\text{p}K_a$) must first be calculated before employing the generalized Henderson-Hasselbalch equation. Although more care must be taken to identify correctly the conjugate acid–base pairs in that expression, its use leads directly to the pH of mixtures of weak bases and their salts.

1.12 TITRATION CURVES AND BUFFERING ACTION

The titration curve obtained when 100 ml of 0.1N CH_3COOH is titrated with 0.1N NaOH is shown in Figure 1.1. This curve can be obtained experimentally in the laboratory by measuring the pH of 0.1N CH_3COOH before and after the addition of different aliquots of 0.1N NaOH . The curve may also be calculated by the Henderson–Hasselbalch equation for all the points except the first, for which no NaOH has been added, and the last, for which a stoichiometric amount (100 ml) of 0.1N NaOH has been added. Clearly, the Henderson–Hasselbalch equation cannot be used to determine the pH at the limits of the titration, when the ratio of salt to acid is either zero or infinite.

The pH of the acetic acid solution, before any NaOH has been added, may be calculated from Equation 1.11. Equal concentrations of acetate ion and protons are generated by the dissociation of pure acetic acid in water. If we set the concentration of acetate ion and protons equal to x and the concentration of undissociated acetic acid equal to $(C - x)$, Equation 1.11 becomes

$$K_a = x^2/(C - x)$$

or

$$x^2 = K_a(C - x) \quad (1.21)$$

which is a quadratic equation. This can be solved for x by the standard methods for quadratic equations. Alternatively, we can simplify the equation for a limited extent of dissociation by recognizing that $(C - x)$ is approximately equal to C . Then,

$$x = \sqrt{K_a C} \quad (1.22)$$

Since the K_a for acetic acid is 1.8×10^{-5} and the concentration of acetic acid in our example is 0.1M, $x = 1.3 \times 10^{-3}$. Since x is small compared to C (0.1M), our assumption in making the above approximation is justified, and the same

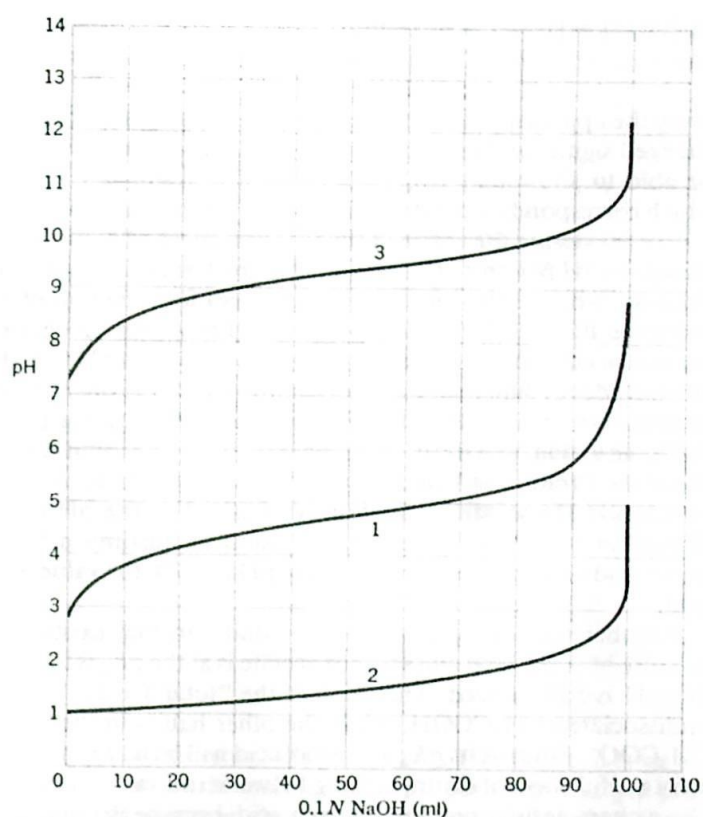


FIGURE 1.1 Titration curve of 100 ml of 0.1N CH_3COOH (1), 100 ml 0.1N HCl (2), and 100 ml of 0.1N NH_4Cl (3) with 0.1N NaOH .

answer would, in fact, be obtained by solution of the quadratic equation. For $x = [\text{H}^+] = 0.0013M$, $\text{pH} = 2.88$, in agreement with curve 1 of Figure 1.1.

At the end of the titration of acetic acid (curve 1, Figure 1.1), we will have a 200 ml solution of 0.05M sodium acetate. The reaction that describes the equilibrium at this point in the titration, the titration end point, is



We write an equilibrium constant as

$$K = \frac{[\text{HAc}][\text{OH}^-]}{[\text{Ac}^-][\text{H}_2\text{O}]}$$

From this, we derive

$$K_{\text{Hydr}} = K[\text{H}_2\text{O}] = \frac{[\text{HAc}][\text{OH}^-]}{[\text{Ac}^-]}$$

because the concentration of water remains approximately constant. The subscript "Hydr" recognizes that the acetate anion is undergoing a hydrolysis reaction. By analogy with the equation developed in the previous paragraph, we

set $[\text{OH}^-] = [\text{HAc}] = x$. Then,

$$x = \sqrt{CK_{\text{Hydr}}}$$

using the approximation that the concentration of acetate anion, C , will not be changed significantly from $0.05M$ by the hydrolysis reaction. The student will be able to show that $K_{\text{Hydr}} = K_w/K_a$. The result is $[\text{OH}^-] = 5.3 \times 10^{-6}M$, which corresponds to a pH of 8.7, again in agreement with curve 1 of Figure 1.1.

In considering the shape of the titration curve of acetic acid, we see that the change in pH per unit of alkali added is greatest at the beginning and end of the titration, whereas the smallest change in pH for each unit of alkali is obtained when the titration is half-complete. In other words, an equimolar mixture of sodium acetate and acetic acid shows less change in pH initially, when acid or alkali is added, than a solution consisting mainly of either acetic acid or sodium acetate. We refer to the ability of a solution to resist a change in pH as its **buffering action**, and it can be shown that a buffer exhibits its *maximum* action when the titration is half-complete. This corresponds to $[\text{HA}] = [\text{A}^-]$ in the Henderson-Hasselbalch equation, that is, when the pH is equal to the $\text{p}K_a$ (Equation 1.18). In Figure 1.1, the point of maximum buffering action for acetic acid and acetate anions is at the pH of 4.74, the value of the $\text{p}K_a$ of acetic acid.

Another way of representing the condition that exists when the pH of a mixture of acetic acid and sodium acetate is at the $\text{p}K_a$ is to state that the acid at this pH is half-ionized. That is, half the "total acetate" species is present as undissociated CH_3COOH , while the other half is in the form of acetate ion, CH_3COO^- . Since at its $\text{p}K_a$ any weak acid will be half-ionized, this is one of the most useful ways of distinguishing between individual weak acids. The $\text{p}K_a$ is also a characteristic property of each acid, because the ionization constant is a function of the inherent properties of the weak acid.

The titration curve of $0.1N$ HCl is also represented in Figure 1.1. The Henderson-Hasselbalch equation is of no use in calculating the curve for HCl, since it applies only for weak electrolytes. However, the pH at any point on the HCl curve can be calculated by determining the milliequivalents of HCl remaining and correcting for the volume. Thus, when 30 ml of $0.1N$ NaOH has been added, 7.0 meq of HCl will remain in a volume of 130 ml. The concentration of H^+ will therefore be $7.0/130$ or $0.054M$. If the activity coefficient is neglected, the pH may be calculated from Equation 1.7 as 1.27.

Curve 3 in Figure 1.1 is the titration curve obtained when 100 ml of $0.1N$ NH_4Cl is titrated with $0.1N$ NaOH. In this titration, the protons contributed by NH_4^+ are neutralized by the OH^- ions provided by the NaOH.



Again, the Henderson-Hasselbalch equation is of no value when calculating the pH of the solution of NH_4Cl before any NaOH has been added. Instead, we can use an equation of the form of Equation 1.21 or 1.22, with NH_4^+ as the acid and NH_3 as the conjugate base. However, the Henderson-Hasselbalch equation can be employed to determine any of the other points on the curve, so long as the NH_4Cl has not been completely titrated.

Up to this point, we have considered only monobasic acids, such as acetic acid. Polybasic or polyprotic acids, which commonly are encountered in biochemistry, are acids capable of ionizing to yield more than one proton per