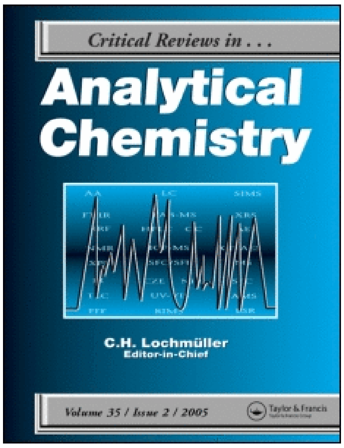

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The pH in grapH

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The pH in grapH

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ABSTRACT: We describe stick diagrams, which are simple graphs designed to provide quick insight into complicated ionic equilibria. Despite their inherent crudeness, they can be used to obtain numerical solutions to quantitative equilibrium problems. Moreover, they show when those quantitative answers are likely to be too approximate. Finally, we discuss how to make activity corrections, and conclude that activity corrections are often as large or larger than the errors involved in using stick diagrams. Therefore, in the absence of activity corrections, stick diagrams are usually quite adequate.

KEY WORDS: pH calculations, stick diagrams, activity corrections.

I. INTRODUCTION

The use of graphs for displaying equilibria, and for solving corresponding quantitative problems, is certainly not new: graphs were already used by Niels Bjerrum[1] in connection with acid-base titration curves and more recently were advocated strongly by Sillén,[2] and then popularized by Freiser and Fernando[3] and by Butler.[4] Such graphs can serve several purposes: (1) they can provide a convenient overview of multicomponent equilibria, (2) they can take the guesswork out of approximations by showing which assumptions are appropriate, (3) they can be used to get quantitative estimates of equilibrium properties, and (4) they allow for subsequent refinement to the level of the precision of equilibrium constants. Consequently, they largely obviate the more complicated (and typically less transparent) computer calculations, which tend to draw attention toward mathematical manipulation rather than toward the chemistry involved. However, despite these obvious advantages of graphs, their use in equilibrium calculations has hardly penetrated the teaching of undergraduate chemistry. As a result, equilibrium problems are often considered difficult, regardless of the time and effort spent on them by teachers of general chemistry and quantitative analysis, and speciation is often simplified to suit the calculation rather than the other way around. (For an example, see de Levie.[5]) As demonstrated below, this is not necessary: the use of simple, hand-drawn graphs can illuminate equilibrium problems and can greatly facilitate solving them.

The form of the mass action law of Guldberg and Waage[6] dictates the type of graph that is most useful for all kinds of chemical equilibria. According to that law, chemical equilibrium is described by an equilibrium constant defined as the quotient of two terms: the (mathematical) product of the concentrations of the reagents, each raised to an appropriate stoichiometric factor, and that of the concentrations of the (chemical) products. Such a law is most readily represented in terms of logarithms, because products and quotients then reduce to sums and differences, while powers reduce to products. In terms of graphs, the most useful representation is therefore a double-logarithmic

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plot, in which the logarithms of the various species are plotted vs. the logarithm of some reference concentration. Logarithmic plots strongly condense the available information and they thereby provide an overview covering a wide range of experimentally accessible conditions. The pH is, of course, a logarithmic measure of proton concentration precisely for this reason: how else could one represent [H$^+$] as it varies over more than ten orders of magnitude in a typical titration of a concentrated strong acid with a concentrated strong base?

In aqueous acid-base problems, the obvious reference species is H$^+$, and the independent variable in such a plot will usually be the (negative) logarithm of [H$^+$], that is, the pH. This is the **logarithmic concentration diagram**. We have recently introduced a minor simplification, the **stick diagram**, which is easier to draw but is only approximately correct. Below we start with the logarithmic concentration diagram.

II. THE LOGARITHMIC CONCENTRATION DIAGRAM

Figure 1 shows a simple example of a logarithmic concentration diagram, for the aqueous solution of a single weak monoprotic acid HA (such as acetic acid, pK_a (≈4.76), at a total analytical concentration

$$C = [\mathrm{HA}] + [\mathrm{A}^-] \qquad (1)$$

of, say, 0.01 *M*. The diagram shows the concentrations of the various species involved, namely, H$^+$, HA, A$^-$, and OH$^-$. More precisely, because we use a double-logarithmic graph, it shows the logarithms of these concentrations, plotted against pH = – log[H$^+$].

Figure 1 contains four species: the logarithms of the concentrations of H$^+$ and OH$^-$ are represented by straight lines, and those of HA and A$^-$ by curves with straight-line asymptotes. The four asymptotes (shown as thin lines) all extrapolate to the **system point** S, which has the coordinates pH = pK_a (4.76 in our example) and log c = log C (here: –2.00).

For [H$^+$] we plot log[H$^+$] vs. pH = –log[H$^+$], and therefore obtain a line with slope –1. For [OH$^-$] = K_w/[H$^+$] or log[OH$^-$] = log K_w – log[H$^+$] = log K_w + pH we find a slope of +1 when plotted vs. pH; K_w is the ion product of water, of the order of 10^{-14} M^2.

The shapes of the curves for log[HA] and log[A$^-$] vs. pH are best understood in

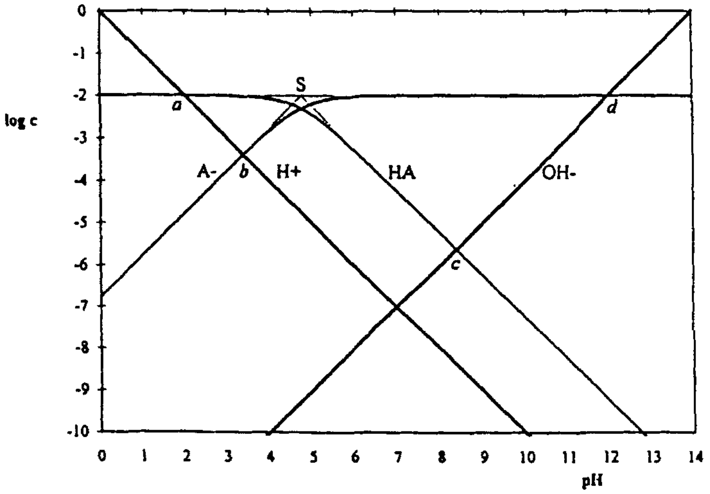

FIGURE 1. The logarithmic concentration diagram for an aqueous solution of a weak acid HA, pK_a = 4.76, at a total analytical concentration C = 0.01 *M*. (See the text for an explanation of the symbols used.)

terms of the total analytical concentration $C = [\mathrm{HA}] + [\mathrm{A}]$ and the equilibrium expression for the acid dissociation constant,

$$K_a = [\mathrm{H}^+][\mathrm{A}]/[\mathrm{HA}] \qquad (2)$$

We have

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

$$= \frac{[\mathrm{H}^+]C}{[\mathrm{H}^+]+K_a} \qquad (3)$$

and

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

$$= \frac{K_aC}{[\mathrm{H}^+]+K_a} \qquad (4)$$

Consequently, for pH << pK_a (i.e., for $[\mathrm{H}^+] >> \mathrm{K}_a$), the denominator in Equation 3 reduces to $[\mathrm{H}^+] \approx C$, which yields a horizontal straight line in the diagram, whereas Equation (4) reduces to $[\mathrm{A}^-] \approx (K_aC/[\mathrm{H}^+]$ or $\log[\mathrm{A}^-] \approx (\log K_a + \log C - \log \mathrm{H}^+]$ $\log K_a + \log C + \mathrm{pH}$ which, when plotted versus pH, yields a straight line of slope +1.

Likewise, for pH >> pK_a (i.e., for $[\mathrm{H}^+] << K_a$), the denominator in Equation 3 reduces to K_a , so that $[\mathrm{HA}] \approx ([\mathrm{H}^+]C/K_a$ or $\log[\mathrm{HA}] \approx (\log \mathrm{H}^+] + \log C - \log K_a = -\mathrm{pH} + \log C - \log K_a$. When plotted vs. pH, this yields a straight line of slope –1. Under the same conditions, Equation 4 reduces to $[\mathrm{A}^-] \approx$, which yields a horizontal straight line.

Finally, for $[\mathrm{H}^+] = K_a$ (i.e., for pH = pK_a), we have $[\mathrm{HA}] = [\mathrm{A}^-]$, which combines with $C = [\mathrm{HA}] + [\mathrm{A}^-]$ to $[\mathrm{HA}]\ [\mathrm{A}^-] = C/2$ or $\log[\mathrm{HA}] = \log[\mathrm{A}^-] = \log C - \log 2 \approx \log C - 0.30$. Therefore, the curves for $\log[\mathrm{HA}]$ and $\log[\mathrm{A}^-]$ intersect at a point 0.30 below the system point S.

III. THE PROTON BALANCE

While the logarithmic concentration diagram of Figure 1 is useful to get an idea of the concentrations of the various species as a function of pH, it is in and of itself insufficient to calculate a pH. In order to do that, we need the **proton balance**, an accounting of which species have gained and lost a proton, in this case starting from the neutral species H_2O and HA. In general, the proton balance either is equal to the charge balance, or can be obtained from it in combination with the applicable mass balance expression(s). In practice, the proton balance can often be written down *by inspection*, merely by counting species that gain or lose protons with respect to the starting materials. In the present example, the starting materials are H_2O and HA, and the proton balance reads

$$[\mathrm{H}^+] = [\mathrm{A}^-] + [\mathrm{OH}^-] \qquad (5)$$

where H^+ denotes a hydrated proton. $[\mathrm{H}^+]$ and $[\mathrm{OH}^-]$ represent the gain and loss, respectively, of a proton by H_2O. $[\mathrm{A}^-]$ represents the loss of a proton by HA; there is no corresponding proton gain. Note that Equation 5 also happens to be the charge balance for this solution.

In the diagram we therefore look for the intersection of the line for $\log[\mathrm{H}^+]$ with the line for $\log\ \{[\mathrm{A}^-] + [\mathrm{OH}^-]\}$, because that intersection corresponds to the pH at which Equation (5) is satisfied. We start at the top left corner of the diagram, with the line for $\log[\mathrm{H}^+]$, and follow it down until it encounters the line for either $\log[\mathrm{A}^-]$ or $\log[\mathrm{OH}^-]$. In the example shown in Figure 1, we first meet the line for $\log[\mathrm{A}^-]$, at the point marked *b* in Figure 1. Furthermore, we note that *at that intersection* $[\mathrm{A}^-]$ is larger than $[\mathrm{OH}^-]$ by many orders of magnitude (because $\log[\mathrm{A}^-]$

lies many units above log[OH$^-$]) so that we can approximate log {[A$^-$] + [OH$^-$]} by log[A$^-$]. Consequently, the intersection of log [H$^+$] and log[A$^-$] is the sought one.

Figure 1a illustrates this in another way, as it shows explicitly the curves representing log [H$^+$] and log {[A$^-$] + [OH$^-$]} of which we seek the intersection. Clearly, that intersection coincides for all practical purposes with the intersection of log [H$^+$] and log [A$^-$]. Note that log(a + b) is emphatically *not* equal to log(a) + log(b); instead, the latter is equal to log(ab).

Next comes the question of *reading* the diagram. If we had graph paper and were to use great care in constructing the plot, we might read off the pH at the intersection of the lines for log[H$^+$] and log[A$^-$]. Usually, we have neither graph paper at hand nor the patience to construct a precise drawing. Fortunately, neither of these is needed; instead, *a crude sketch will do*. This is so because the lines have simple slopes: that of log[H$^+$] vs. pH = –log[H$^+$] has slope –1, that of log[A$^-$] vs. pH has slope +1 in the region near their intersection. Therefore, the triangle *abS* has angles of 45°, 90°, and 45°, respectively, so that the pH of point B lies exactly halfway between the pH values of points *a* and S. Consequently, we have pH = (pC + pK_a)/2 ≈ (2.00 + 4.76)/2 = 3.38. This is, of course, equivalent to the well-known result [H$^+$] = $\sqrt{(CK_a)}$.

Why go through all this trouble to find a simple, well-worn result? Because the diagram not only yields this particular result but also shows us the correct answer when the solution $\sqrt{(CK_a)}$ does *not* apply. For example, when we consider 10^{-6} *M* acetic acid instead, we still have [H$^+$] = [A$^-$] + [OH$^-$] ≈ [A$^-$], but the intersection of the lines for log [H$^+$] and log [A$^-$] now lies near pH = pC, corresponding to the equation [H$^+$] = C or, numerically, pH ≈ 6.0, see Figure 2a. For 10^{-8} *M* acetic acid, the diagram shows that [H$^+$] = [A$^-$] + [OH$^-$] ≈ [OH$^-$] instead, so that the pH is 7.0, and is now given by pH = $\sqrt{K_w}$, as shown in Figure 2b.

Likewise, when we use 0.01 *M* trichloroacetic acid, with a pK_a of about 0.66, we still have [H$^+$] = [A$^-$] + [OH$^-$] ≈ [A$^-$], but the intersection of the lines for log[H$^+$] and log[A$^-$] now lies near pH = pC, again corresponding to the equation [H$^+$] = C, as illus-

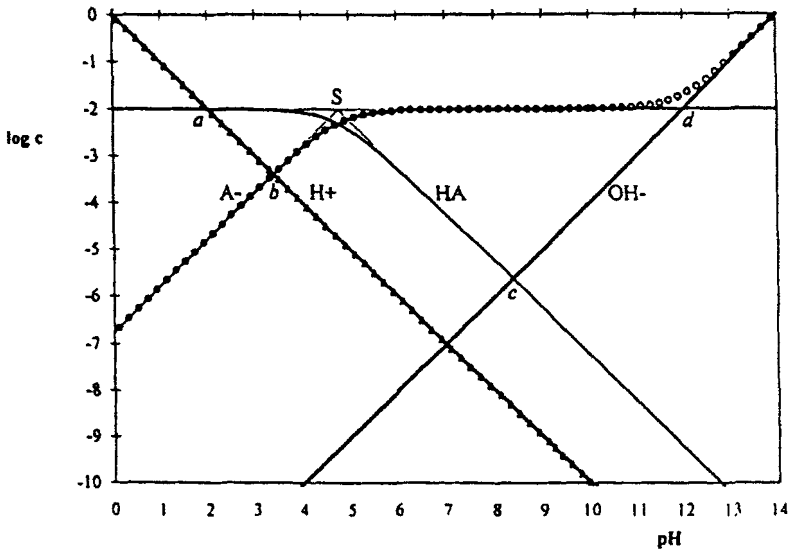

FIGURE 1a. The logarithmic concentration diagram for an aqueous solution of a weak acid HA, pK_a = 4.76, at a total analytical concentration C = 0.01 *M*, explicitly showing the curves for log[H$^+$] (open triangles) and log{[A$^-$] + [OH$^-$]} (open circles).

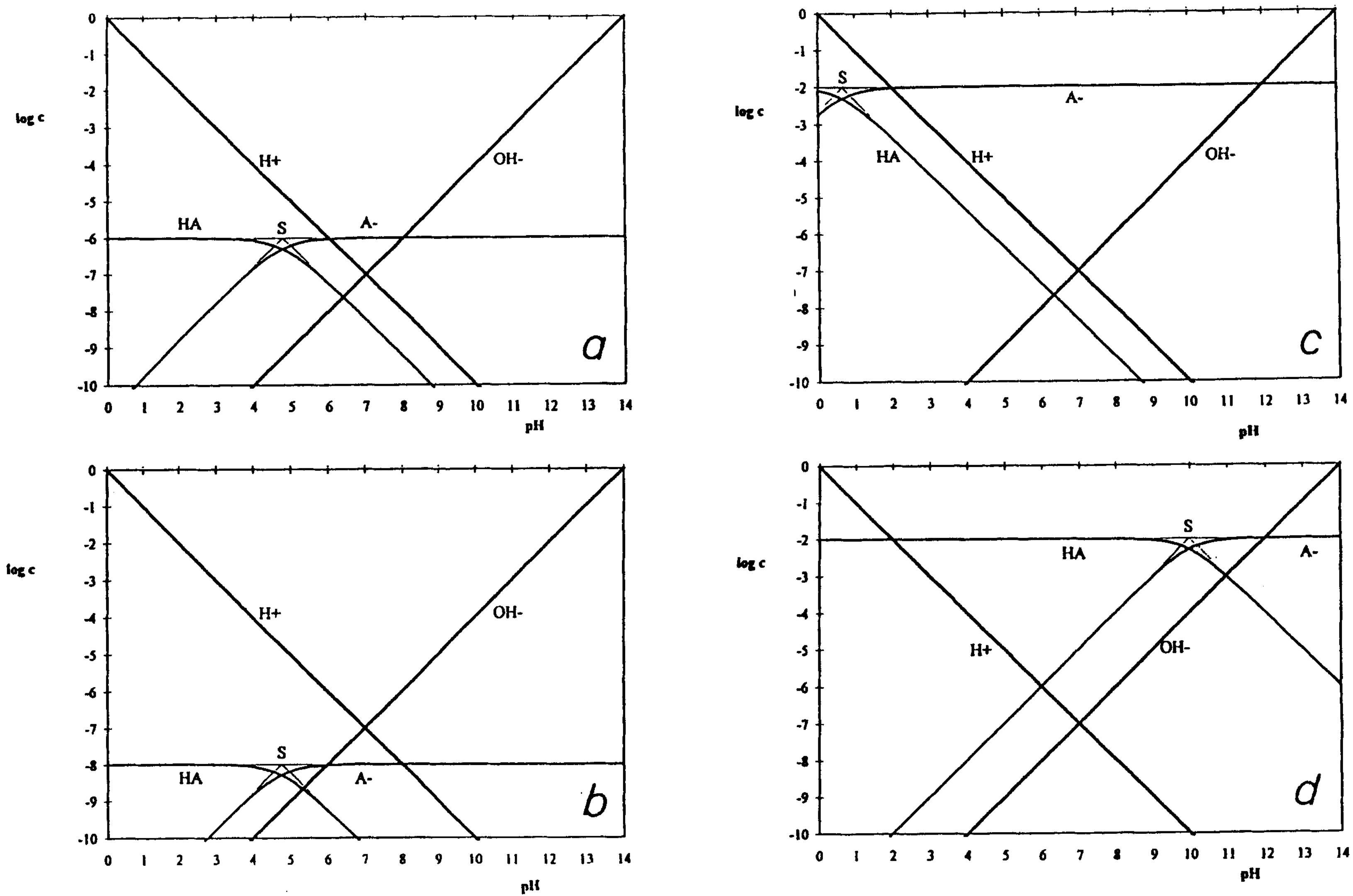

FIGURE 2. The logarithmic concentration diagram for an aqueous solution of a weak acid HA with (a) $pK_a = 4.76$, $pC = 6$; (b) $pK_a = 4.76$, $pC = 8$; (c) $pK_a = 0.66$, $pC = 2$; (d) $pK_a = 9.98$, $pC = 2$.

trated in Figure 2c. In other words, at this concentration, trichloroacetic acid is almost completely ionized and therefore acts as a strong acid. (It would not do so at, say, a 1 *M* concentration.)

And when we use 10^{-2} *M* phenol, $pK_a = 9.98$, we find again that $[H^+] = [A^-] + [OH^-] \approx [A^-]$, so that $pH \approx (2.00 + 9.98)/2 = 5.99$, compare Figure 2d. The logarithmic concentration diagram always shows all concentrations involved. Its logarithmic scale makes it easy to identify those concentrations in the proton balance that are negligible with respect to others (in a particular pH region), because each logarithmic unit corresponds to a factor of ten. In other words, the diagram *shows* us what approximations can be made and then yields the numerical value of the pH as well. *The diagram takes the guesswork (and much of the math) out of traditional pH calculations.*

The pH of the corresponding salts with strong bases can also be read directly from these graphs. In this case the proton balance, starting from H_2O and NaA (which, for the sake of finding the proton condition, is taken as a salt, i.e., as Na^+ and A^-) reads

$$[H^+] = [HA] + [OH^-] \qquad (6)$$

that is, H_2O can either gain a proton to form H_3O^+ (which we here denote as H^+) or lose a proton to yield OH^-, A^- can gain a proton to form HA but cannot lose a proton, and Na^+ can do neither (as NaOH is traditionally considered to be a strong base).

Figure 1 shows that, at the intersection of log[HA] with log$[OH^-]$, log$[H^+]$ is much smaller than log[HA], so that $[H^+] \ll [HA]$, hence Equation 6 can be simplified to $[HA] \approx [OH^-]$. Therefore we find $pH \approx (4.76 + 12)/2 = 8.38$ for aqueous 0.01 *M* sodium acetate at the intersection of log[HA] and log$[OH^-]$, see point *c*, halfway between points S and *d* on the pH scale.

We note that the diagram shows the concentrations of the acid HA, and its conjugate base A^-. For a base (such as ammonia) the same diagram can be used, again with the system point at the coordinates $pH = pK_a$ and $pc = pC$, in which case the corresponding species would be labeled NH_4^+ and NH_3 or, in general, HB^+ and B, respectively. Figure 3 shows the logarithmic concentration diagram for 0.1 *M* ammonia ($pK_a \approx 9.26 =$

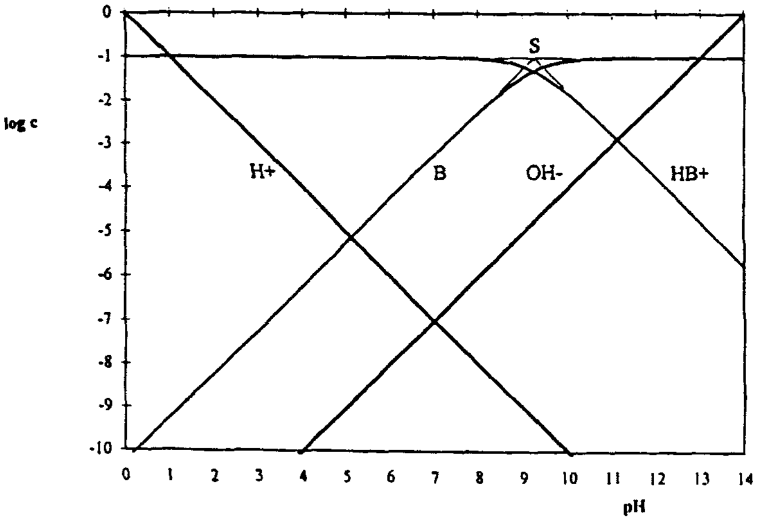

FIGURE 3. The logarithmic concentration diagram for an aqueous solution of ammonium, $pK_a = 9.24$, at a total analytical concentration $C = 0.1$ *M*.

$14 - pK_b$). In this case we find the pH of the base from the proton balance (starting from the neutral species H_2O and B)

$$[H^+]+[HB^+]=[OH^-] \qquad (7)$$

while the pH for the salt of the weak base with a strong acid (such as NH_4Cl) follows from the proton balance (based on the neutral species H_2O plus the ionic components $HB^+ + Cl^-$ of the salt)

$$[H^+]=[B]+[OH^-] \qquad (8)$$

IV. THE STICK DIAGRAM

For the examples shown so far, the traditional calculations are rather straightforward; consequently, the gain associated with the use of diagrams is rather limited. For more complicated equilibria, however, the diagrams remain fairly simple, while the corresponding mathematical expressions can become forbiddingly complicated. As illustrated below, the use of graphical solutions has its greatest advantages with the more complicated equilibria. However, before we venture into that territory, we first simplify the logarithmic concentration diagrams to make them even more suitable for such use.

Logarithmic concentration diagrams exhibit asymptotes with integer slopes. Because the curvature of the lines near the system point is often of little consequence, we here will reduce the diagram to one that is really simple to sketch, by merely deleting all such curvature. We do this by extending all asymptotes all the way to their system points. The resulting plots contain only straight-line sections, and therefore are called **stick diagrams**; they can be imagined as being made of match sticks.

Figure 4 shows the stick diagram for 0.01 *M* acetic acid, with the corresponding logarithmic concentration diagram for comparison in thin lines. As can be seen, a stick diagram is clearly an approximation at pH values close to pK_a, a fact we take into account whenever necessary. Furthermore, in using stick diagrams, we will make the following *additional approximation:* when one and/or the other side of the proton balance contains more than one concentration, we only consider the largest of these on each

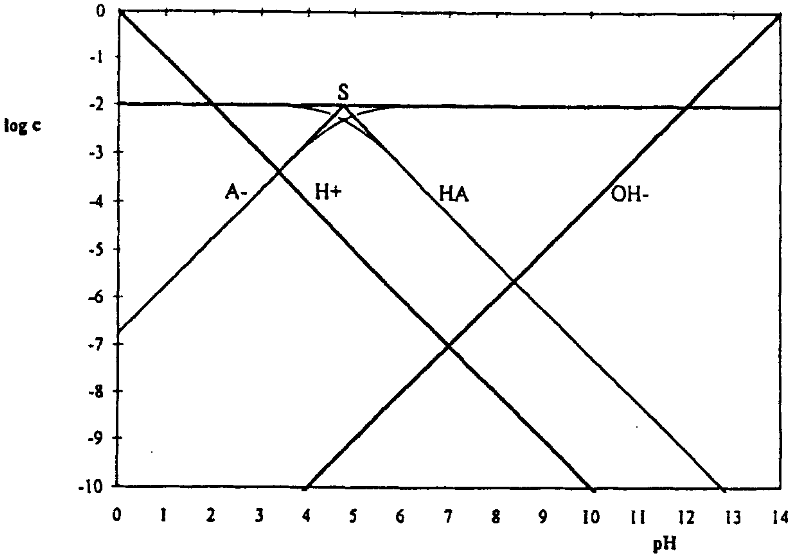

FIGURE 4. The stick diagram for a 0.01 *M* aqueous solution of acetic acid, $pK_a = 4.76$.

side. Again, we will make amends for this approximation whenever needed, but most often it will be unnecessary to do so.

In summary, then, the logarithmic concentration diagram is exact and yields exact solutions to pH problems when used with exact balance relations such as the proton balance. It is most useful for, say, spreadsheet calculations, where no approximations need be made, and where a numerical solution can readily be found using, say, a Newton–Raphson or Levenberg-Marquardt algorithm. On the other hand, the stick diagram (which can be made on the proverbial "back of the envelope") is approximate, and is used here together with approximate balance equations. Below we use stick diagrams; *with a minimum of effort they typically yield estimates correct to within 0.3 pH units*. For many problems that is perfectly adequate, and it is better than the precision of most indicator papers. Subsequently, we show that it is usually possible to obtain more precise answers, to ±0.01 pH units, by making some simple corrections, "simple" being defined here as not exceeding taking logs and antilogs, or solving more than a quadratic equation. Because the precision of few tabulated p*K* values is better than ±0.01, such numerical precision is all that is usually meaningful; higher "precision" in the pH is usually illusory. Incidentally, the stick diagram will indicate whether it may be necessary to make such a refinement in cases where the extra effort is deemed to be justified.

V. THE CENTRAL TRIANGLE

Before we embark on a demonstration of the use of these diagrams for numerical calculations, we first use a feature of the stick diagram that lets us characterize the behavior of acids (and bases) from the stick diagram. For example, for a monoprotic acid we distinguish the following simple cases.

1. When the system point falls well within the **central triangle** bounded by the top of the diagram and the straight lines for $\log[H^+]$ and $\log[OH^-]$, then the acid acts like a typical weak acid, and the base like a typical weak base.
2. When the system point lies well to the left of the central triangle, the acid is fully dissociated, while its conjugate base will be so weak that it need not be considered as a proton acceptor in pH problems.
3. Likewise, when the system point lies well to the right of the central triangle, the acid is so weak that its dissociation can be ignored in pH problems, whereas the conjugate base will be a strong one.
4. When the system point lies well below the central triangle, the concentration of both the acid and its conjugate base are too small to affect the pH.

Figure 5 summarizes these four simple cases. Note that we have used the term *well* in rules (1) through (4), because borderline cases yield borderline behavior and therefore must be considered in somewhat greater detail, as we do below. (Such borderline cases invariably require refinement when answers to within ±0.01 pH units are needed. For a precision of ±0.01 pH units the definition of the term *well* is at least two logarithmic units away from the relevant boundary.)

VI. SIMPLE, APPROXIMATE pH CALCULATIONS

What is the pH of the aqueous solution of a single monoprotic acid, $pK_a = 5$, at a concentration of C *M*? Here we answer the question approximately, for $C = 1$ *M*, 10 m*M*, 1 μ*M*, etc., indicated here with the mathematical shorthand notation $pC = 0\ (2)\ 8$ by specifying the first and last p*C* value and, within brackets, its increment. In Section VII we then reconsider these answers, refine them, and compare them with exact results.

Using the proton balance (5), and considering only the higher of the concentrations

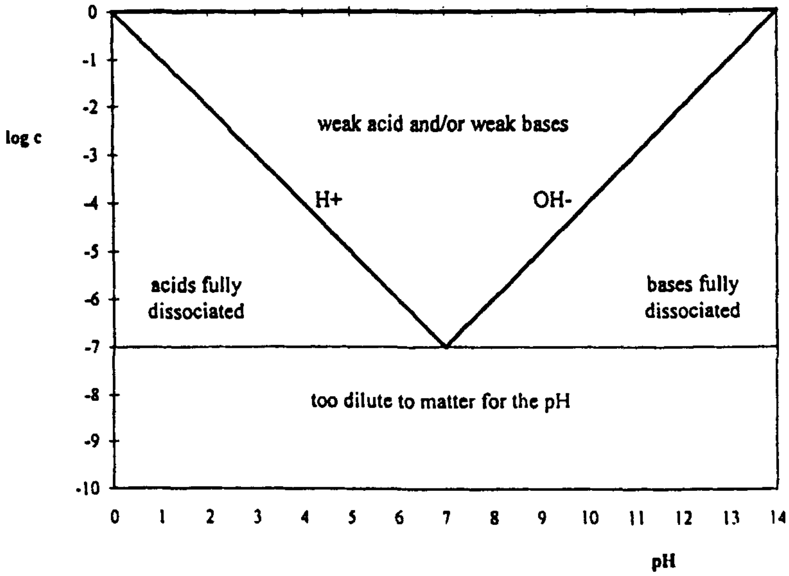

FIGURE 5. The central triangle. The location of a system point (with the coordinates pH = pK_a and pc = pC) immediately indicates how an acid or base will behave in pH problems. The "top" of the central triangle is here drawn arbitrarily at pc = 0 but is, in fact, determined by solubility.

[A$^-$] and [OH$^-$], we find the approximate answers indicated in Figure 6 by the letters *a* through *e*, and shown in the second column of Table 1. We see that, for p$C \le 7$, the proton balance (5) can be simplified to [H$^+$] ≈ [A$^-$] so that pH ≈ (pC + pK_w)/2. For p$C \ge 7$, (5) reduces to [H$^+$] ≈ [OH$^-$] and, consequently, pH ≈ pK_w/2 = 7.0.

What is the pH of the aqueous solution of a 0.01 *M* aqueous solution of a single monoprotic acid of any given pK_a? Again we first answer the question approximately, for various values of pK_a. The proton balance is again (5). Considering only the higher of the concentrations [A$^-$] and [OH$^-$], we find the approximate answers shown in the second

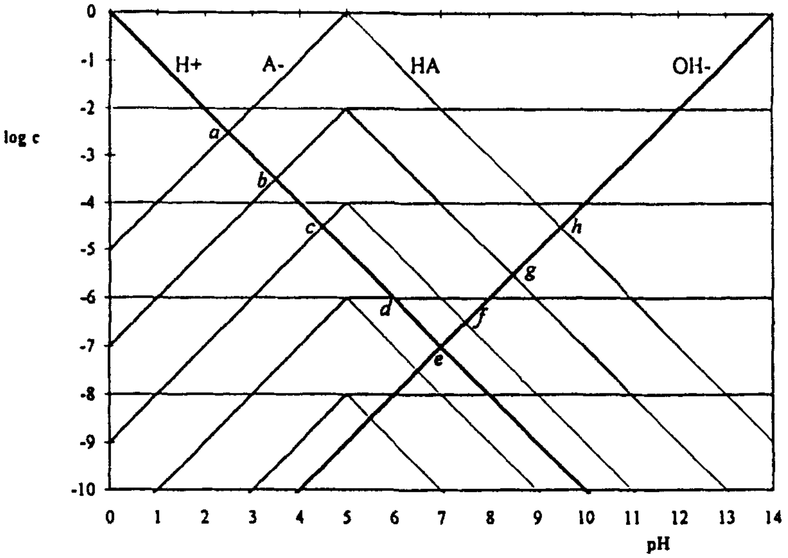

FIGURE 6. Stick diagrams for a single monoprotic acid, pK_a = 5, pC = 0 (2) 8.

TABLE 1
The pH of an aqueous solution of a monoprotic acid, $pK_a = 5$, $C = 0$ (1) 10 estimated from a stick diagram such as Figure 6 (2nd column), as refined (3rd column) using the equation listed, and as calculated exactly (4th column)

p*C*	pH from the stick diagram	pH after refinement	pH as computed exactly
0	2.5_0 *a*		2.50
1	3.0_0	3.00 (10)	3.00
2	3.5_0 *b*	3.51 (10)	3.51
3	4.0_0	4.02 (10)	4.02
4	4.5_0 *c*	4.57 (10)	4.57
5	5.0_0	5.21 (10)	5.21
6	6.0_0 *d*	6.04 (10)	6.03
7	7.0_0	6.79 (11)	6.79
8	7.0_0 *e*	6.98 (11)	6.98
9	7.0_0	7.00 (11)	7.00
10	7.0_0		7.00

column of Table 2, while Figure 7 illustrates some of the corresponding stick diagrams. Similar questions asked for a base can be answered in similar fashion, keeping in mind that in this case the acid is HB^+, the protonated conjugate of the base B.

What is the pH of a 0.01 *M* aqueous solution of the sodium salt of a single monoprotic acid of given pK_a? Making the usual assumption that sodium hydroxide is a strong base, and simplifying the proton balance (6) by considering only the larger of $[H^+]$ and [HA], we obtain the approximate answers listed in column 2 of Table 3, and illustrated in Figure 7 as points *g* through *m*. Similarly, when we vary p*C* while keeping the pK_a constant, we find stick diagrams and numerical estimates like those labeled *e* through *h* in Figure 6, with the numerical values listed in column 2 of Table 4.

For the salt of a weak monoprotic acid and a weak monoprotic base, such as NH_4F, the proton balance is

$$[H^+]+[HA]=[B]+[OH^-] \qquad (9)$$

and the pH can again be read off the stick diagrams, see Figure 8 and Table 5.

VII. REFINEMENTS

We now take a second look at the results we have obtained so far. Specifically, we make corrections whenever required because,

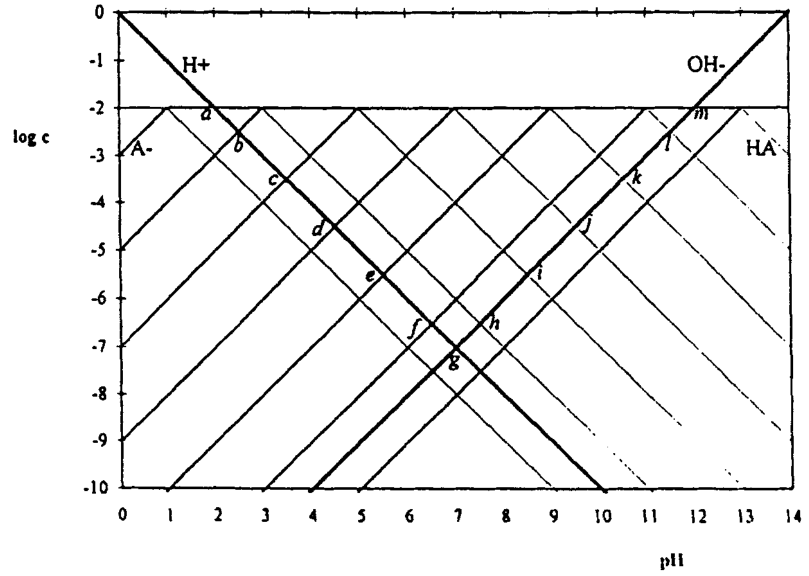

FIGURE 7. Stick diagrams for a single monoprotic acid, $pK_a = 1$ (2) 13, p*C* = 2. The letters *a* through *g* denote the pH of the acid, and *g* through *m* those of their salts with a strong base.

TABLE 2
The pH of an aqueous solution of a monoprotic acid, pK_a = 0 (1) 14, pC = 2 estimated from a stick diagram such as Figure 7 (2nd column), as refined (3rd column) using the equation listed or an auxiliary line (AL), and as calculated exactly (4th column)

pC	pH from the stick diagram	pH after refinement	pH as computed exactly
0	2.0_0	2.00 (10)	2.00
1	2.0_0 *a*	2.04 (10)	2.04
2	2.0_0	2.21 (10)	2.21
3	2.5_0 *b*	2.57 (10)	2.57
4	3.0_0	3.02 (10)	3.02
5	3.5_0 *c*	3.50 (10)	3.51
6	4.0_0	4.00 (10)	4.00
7	4.5_0 *d*		4.50
8	5.0_0		5.00
9	5.5_0 *e*		5.50
10	6.0_0	6.00 AL	6.00
11	6.5_0 *f*	6.48 AL	6.48
12	7.0_0	6.85 AL	6.85
13	7.0_0 *g*	6.98 AL	6.98
14	7.0	7.00 AL	7.00

TABLE 3
The pH of an aqueous solution of the salt of a monoprotic acid and a strong base, pK_a = 0 (1) 14, pC = 2, as estimat- from a stick diagram such as Figure 7 (2nd column), as subsequently refined (3rd column) using the equation listed, and as calculated exactly (4th column)

pC	pH from the stick diagram	pH after refinement	pH as computed exactly
0	7.0_0	7.00 AL	7.00
1	7.0_0 *g*	7.02 AL	7.02
2	7.0_0	7.15 AL	7.15
3	7.5_0 *h*	7.52 AL	7.52
4	8.0_0	8.00 AL	8.00
5	8.5_0 *i*		8.50
6	9.0_0		9.00
7	9.5_0 *j*		9.50
8	10.0_0		10.00
9	10.5_0 *k*	10.50 (12)	10.50
10	11.0_0	10.98 (12)	10.98
11	11.5_0 *l*	11.43 (12)	11.43
12	12.0_0	11.79 (12)	11.79
13	12.0_0 *m*	11.96 (12)	11.96
14	12.0_0	12.00 (12)	12.00

TABLE 4
The pH of an aqueous solution of the salt of a monoprotic acid, pK_a = 5, pC = 0 (1) 10 and a strong base, as estimated from a stick diagram such as Figure 6 (2nd column), as refined (3rd column), and as calculated exactly (4th column)

pC	pH from the stick diagram	pH after refinement	pH as computed exactly
0	9.5_0 *h*		9.50
1	9.0_0		9.00
2	8.5_0 *g*		8.50
3	8.0_0	8.00 AL	8.00
4	7.5_0 *f*	7.52 AL	7.52
5	7.0_0	7.15 AL	7.15
6	7.0_0 *e*	7.02 AL	7.02
7	7.0_0	7.00 AL	7.00
8	7.0_0		7.00
9	7.0_0		7.00
10	7.0_0		7.00

in using stick diagrams, we have made several simplifying assumptions: (1) we neglected the curvature near the system points, and (2) we only considered the largest concentrations on either side of a proton balance. Because such approximations were involved, it is wise to specify the resulting pH values to only one decimal place or at least (as we have done here) indicate that the value in the second decimal place is uncertain. This is so because our first estimates were just that and may well be off by a few tenths of a pH unit. Below we compute the pH to ±0.01 pH units, i.e., to a precision comparable to or better than that of most pK_a values in the literature.

We first revisit the data in column 2 of Table 1, which were obtained from Figure 6. As we can see from the stick diagrams, at high values of C the neglect of the term $[OH^-]$ in the proton balance is clearly inconsequential. However, the curvature of $[A^-]$ near the system point is likely to have affected the data for pC = 3, 4, and 5, and perhaps even those for pC = 2 and pC = 6. Here, then, we describe how to make a simple correction for that curvature. In order to do so we return to the complete expression for $[A^-]$ as given in (4),

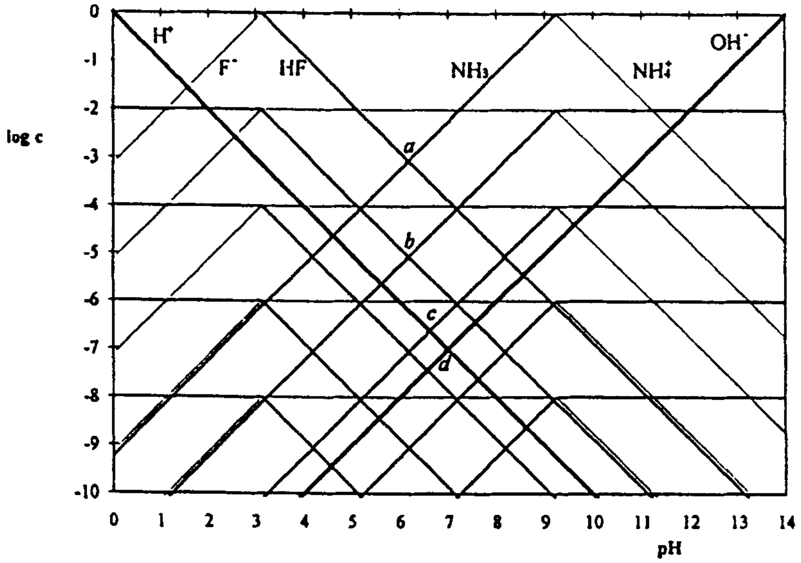

FIGURE 8. Stick diagrams for ammonium fluoride at various total analytical concentrations C. HF: pK_a = 3.13, NH_4^+: pK_a = 9.24.

that is, $[A^-] = K_aC/([H^+] + K_a)$. Because it is still justified to neglect $[OH^-]$ with respect to $[A^-]$ in the proton balance, we now write (5) as $[H^+] = [A^-] + [OH^-] \approx [A^-] = K_aC/([H^+] + K_a)$, which leads to a quadratic expression in $[H^+]$, namely, $[H^+]^2 + K_a[H^+] - K_aC = 0$. This yields the solution

$$[H^+] = -\tfrac{1}{2}K_a + \tfrac{1}{2}\sqrt{(K_a^2 + 4K_aC)} \quad (10)$$

from which the pH can be calculated. Column 3 in Table 1 shows the numerical results of such computations. We note that the differences between the earlier estimates and the present calculations are relatively small, except when the system point lies on or very near the line for $[H^+]$. Even then, the errors in Table 1 are always less than 0.3 pH units.

TABLE 5
The pH of aqueous solutions of NH_4F as estimated from a stick diagram such as Figure 8 (2nd column), as refined (3rd column), and as calculated exactly (4th column)

pC	pH from the stick diagram	pH after refinement	pH as computed exactly
0	6.1_8 *a*		6.19
1	6.1_8		6.19
2	6.1_8 *b*	6.19 AL	6.20
3	6.1_8	6.28 AL	6.30
4	6.6_2 *c*	6.63 AL	6.61
5	7.0_0	6.90 AL	6.90
6	7.0_0 *d*	6.99 AL	6.99
7	7.0_0		7.00
8	7.0_0		7.00
9	7.0_0		7.00
10	7.0_0		7.00

At lower concentrations, Figure 6 suggests that another approximation made earlier may require attention, namely, the neglect of either $[A^-]$ or $[OH^-]$ when these concentrations are of a similar order of magnitude. The stick diagram shows that, in our example, we may then assume that $[A^-] \approx C$, in which case the proton balance simplifies to $[H^+] = [A^-] + [OH^-] \approx C + K_w/[H^+]$. This, again, yields a quadratic equation in $[H^+]$, viz. $[H^+]^2 - C\,[H^+] - K_w = 0$, with the solution

$$[H^+] = \tfrac{1}{2}C + \tfrac{1}{2}\sqrt{(C^2 + 4K_w)} \quad (11)$$

The numerical results computed with (11) are listed in column 3 of Table 1. Again, we see that the differences between our earlier estimates and the refined answers are relatively small. We can almost always estimate the pH to within 0.3 units (and will usually do much better) simply from a sketched stick diagram. Subsequently, we can refine the answer to ±0.01 pH units by solving a quadratic equation. Moreover, the stick diagram shows us where such refinements are needed and what needs to be done. In the present example, refinements are only necessary around pC = 4 (where the system point lies on the edge of the central triangle) and pC = 7.

Shown in Table 1 column 4 are the results obtained on a spreadsheet, based on the exact expressions, $[H^+] - [A^-] - [OH^-] = [H^+] - K_aC/([H^+] + K_a) - K_w/[H^+]$ 0, and finding the pH from this cubic equation by using a Newton–Raphson or Lavenberg-Marquardt algorithm. (Modern spreadsheets have such algorithms already built in.) We see that the refinements indeed yield pH values to within ±0.01.

Now consider the data in Table 2, which are based on Figure 7. Here the stick diagram indicates that there are two regions where refinement might be needed, namely, for pK_a ≈ 2 and pK_a ≈ 12, as in both of these cases the system point lies on the very boundary of the central triangle. For pK_a ≈ 2 we use Equation (10), but for pK_a ≈ 12 another approach is needed. In this latter case, $[A^-]$ and $[OH^-]$ in the region of interest around pH 7 are represented in the diagrams as parallel lines, that is, as differing only by a given, constant factor. In fact, for pK_a = 12 and pC = 2, $[A^-]$ and $[OH^-]$ are of the same magnitude at pH ≈ 7. We take this into account by sketching an *auxiliary line* to represent $\log\{[A^-] + [OH^-]\}$. When $[A^-] = [OH^-]$, $\log\{[A^-] + [OH^-]\} = \log\{2[OH^-]\} = \log(2) + \log[OH^-] \approx \log[OH^-] + 0.30$ because log 2 ≈ 0.30103. Consequently, the auxiliary line representing $\log\{[A^-] + [OH^-]\}$ will run with slope +1, parallel to $\log[OH^-]$ but 0.30 above it. Its intersection with the line for $\log[H^+]$, of slope −1, will then occur at a pH that is 0.30/2 = 0.15 lower than the earlier pH estimate, as one will realize by simple geometric consideration of the region near that intersection. Here, then, we find pH = 7.00 − 0.15 = 6.85.

For pK_a = 11 and pC = 2, $[A^-] = 0[OH^-]$ in the region of the sought intersection, so that $\log\{[A^-] + [OH^-]\} = \log\{1.1[A^-]\}$ =

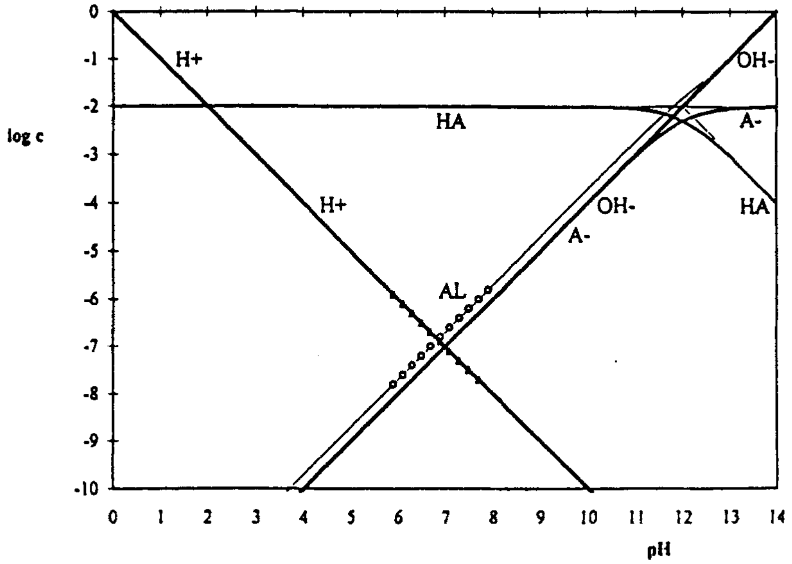

FIGURE 1b. The logarithmic concentration diagram for pK_a = 12, pC = 2, together with the auxiliary line representing $\log\{[A^-] + [OH^-]\}$ (open circles) and the entire curve for $\log\{[A^-] + [OH^-]\}$ (thin line).

log(1.1) + log[A–] (log[A–] + 0.04, and the resulting pH is that of the earlier, crude estimate minus ½ × 0.04 =–0.02 or 6.48. Likewise, the pH for pK_a = 13 and pC = 2 is 0.02 less than the value obtained from the stick diagram, because here $[A^-]$ = 0.1 $[OH^-]$ so that $\log\{[A^-]+[OH^-]\} = \log\{1.1[OH^-]\} = \log(1.1) + \log[OH^-] \approx \log[OH^-] + 0.04$. For p$K_a$ = 14 and pC = 2, the corresponding correction can be neglected because $\log\{[A^-] + [OH^-]\} = \log\{1.01[OH^-]\} = \log(1.01) + \log[OH^-] \approx \log[OH^-] + 0.004 \approx \log[OH^-]$, and the same applies to pK_a = 10 and pC = 2 where $\log\{[A^-] + [OH^-]\} = \log\{1.01[A^-]\} = \log(1.01) + \log[A^-] \approx \log[A^-] + 0.004 \approx \log[A^-]$.

For the data in Table 3, around pK_a = 2 and pC = 2, we draw an auxiliary line to represent $\log\{[H^+] + [HA]\}$. Around pK_a = 12 and pC = 2 we simplify the proton condition $[H^+] + [HA] = [OH^-]$ to $[HA] \approx [OH^-]$, which we rewrite as $[H^+]C/([H^+] + K_a) = K_w/[H^+]$ or

$$[H^+] = \{K_w + \sqrt{(K_w^2 + 4CK_aK_w)}\}/(2C) \tag{12}$$

Again, as shown in the fourth column of Table 3, the results so obtained agree to within ±0.01 pH units with the exact results calculated by using the complete proton condition. A similar conclusion is drawn from the data in Table 4.

The situation in Table 5 is more complicated and may require that we draw two auxiliary lines. For pC = 2 the line for HF runs 1.31 logarithmic units above that for $[H^+]$, so that $\{[HF] + [H^+]\} = (1 + 10^{-1.31})[HF]\;\; 1.04_9\,[HF]$ or $\log\{[HF] + [H^+]\} = \log[HF] + 0.02$, from which we obtain a shift of pH of = 0.02/2 =+0.01.

For pC = 3 the line for [HF] runs only 0.31 logarithmic units above that for $[H^+]$, so that $\log\{[HF] + [H^+]\} = \log\{(1+10^{-0.31})[HF]\} = \log[HF] + \log(1+10^{-0.31}) = \log[HF] + 0.17_3$ hence the required correction on the pH value from the stick diagram is $+0.17_3/2 = +0.09$.

For pC = 4 the line for $\log[H^+]$ runs 0.69 pH units above that for [HF], so that $\log\{[HF] + [H^+]\} = \log\{(1 + 10^{-0.69})[H^+]\} = \log[H^+] + \log(1.204) = \log[H^+] + 0.08$, with a resulting shift of the pH by +0.04. For pC = 5 the correction is less than 0.005, and is therefore negligible.

So far, we have conveniently ignored the right–hand side of the proton condition. However, here we may also have to use an auxiliary line, because we have a similar situation in that, at the pH of interest, the lines for $\log[NH_3]$ and $\log[OH^-]$ are parallel and close to each other. For pC = 3 their distance is 1.76 units, and the effect is negligible: $\log(1 + 10^{-1.76}) = \log(1.017)\;\; 0.007$, so that half of that results in a pH shift of less than 0.005, just enough to affect the round–off of the pH. However, for pC = 4 we have $\log(1+10^{-0.76}) = \log(1.174) = 0.0696$, which results in a pH shift of -0.03_5, mostly neutralizing the earlier–calKelated shift of +0.04.

At pC = 5 the system point for NH_4^+ has also dropped out of the central triangle, and we calculate the correction for $\log[OH^-]$ as $\log(1 + 10^{-0.24}) = \log(1.575) = 0.197$, leading to a pH shift of –0.10. For pC = 6 we find likewise $\log(1 + 10^{-1.24}) = \log(1.058) = 0.024$ and a resulting pH shift of –0.01.

While the above may seem to be a lot of work, we have only needed two auxiliary lines in *one* case, pC = 4, and even that beats having to solve a quartic expression (unless, of course, we have a computer nearby).

The above discussion shows that quick–and –dirty estimates based on stick diagrams often yield pH estimates that are quite close. Moreover, the diagrams indicate when the approximations made are questionable, either because curvature near a system point is neglected or because a concentration ignored in the proton balance is not quite negligible. Both cases correspond with a system point near the edge of the central triangle and therefore are spotted easily. Even so, the resulting errors are almost always less than 0.3 pH units. Moreover, they can readily be corrected, either by solving a quadratic equation or by taking logs and antilogs. In that case, a precision of ±0.01 pH units is usually achieved, a perfectly sufficient level given the typical experimental uncertainties in equilibrium data.

Finally, we need to face the obvious question: when would refinement be justified? There are two answers. (1) When only approximate equilibrium constants are available and/or only an approximate answer is required (as, e.g., in deciding whether a titration is feasible), refinement is usually overkill, and need not be considered. (2) When a precise answer is required, and the available equilibrium data justify the extra effort, look at the stick diagram. In many cases the stick diagram already yields a sufficiently precise answer, that is, to within ±0.01 pH units. However, extra work may be required when a system point involved in the calculation lies close to the edge of the central triangle. In that case there are two reasons why refinement may then be needed: (a) the neglect of curvature near that system point may be consequential and (b) we may have neglected one or more concentrations in the proton balance that are not much smaller than the dominant term we have used. Typically, when the dominant term *in the pH region around the value estimated from the stick diagram* is at least a factor of ten larger than the others on that side of the proton balance (so that its representation in the stick diagram lies at least one logarithmic unit above the others), refinement yields only minor improvement (log 1.1 = 0.04); when the dominant term lies two orders above the others, the error resulting from the neglect of the smaller terms is always less than 0.01 (log 1.01 = 0.004) and is therefore completely negligible. Consequently, *we can see from the stick diagram and the proton balance whether refinement is needed* in case it might be justified.

VIII. APPLICATIONS TO POLYPROTIC ACIDS, BASES, AND SALTS

A simple example is that of orthophosphoric acid, H_3PO_4. There are now three pK_a values, and therefore also three system points, with the coordinates pH = pK_{a1}, pc = pC; pH = pK_{a2}, pc = pC; and pH = K_{a3}, pc = pC. The corresponding stick diagram now has lines of slopes ±3, ±2, ±1, and 0, reflecting the number of protons by which the species shown differs from that of the dominant phosphate-containing species, see Figure 9.

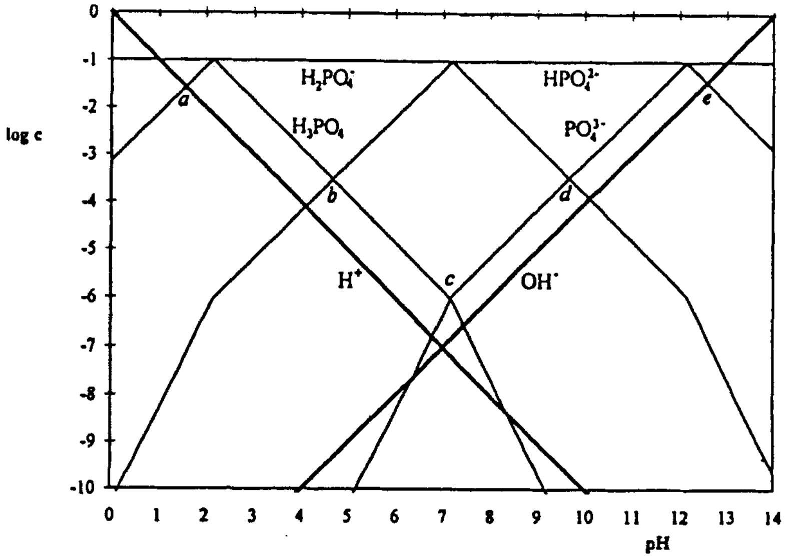

FIGURE 9. The stick diagram for orthophosphoric acid (pK_{a1} = 2.15, pK_{a2} = 7.20, pK_{a3} = 12.15) and its sodium salts at a total analytical concentration of 0.1 *M*.

The slopes change every time a line crosses a pH value equal to a pK_a In the corresponding logarithmic concentration diagram there would of course be more gentle curves instead of the sharp knees of the stick diagram.

In order to find the pH of the acid and its salts, we again consider the proton balance. For H_3PO_4 we have

$$[H^+] = [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}] + [OH^-] \tag{13}$$

where the multipliers reflect the numbers of protons lost by H_3PO_4. For the salt NaH_2PO_4 we have instead

$$[H^+] + [H_3PO_4] = [HPO_4^{2-}] + 2[PO_4^{3-}] + [OH^-] \tag{14}$$

while the proton balances for Na_2HPO_4 and Na_3PO_4 are

$$[H^+] + 2[H_3PO_4] + [H_2PO_4^-] = [PO_4^{3-}] + [OH^-] \tag{15}$$

and

$$[H^+] + 3[H_3PO_4] + 2[H_2PO_4^-] + [HPO_4^{2-}] = [OH^-] \tag{16}$$

respectively.

Using these proton balances, and typical pK_a values as compiled by Martell and Smith[7], viz. pK_{a1} = 2.15, pK_{a2} = 7.20, and pK_{a3} = 12.15, we estimate the corresponding pH–values for, say, C = 0.1 M, as (1.00 + 2.15)/2 = 1.5_8, (2.15 + 7.20)/2 = 4.6_8, (7.20 + 12.15)/2 = 9.6_8, and (12.15 + 13.00)/2 = 12.5_8, see Figure 9. The stick diagram suggests that all but the second value may need refinement.

For the pH of 0.1 M H_3PO_4 the stick diagram shows that we can indeed simplify (13) to $[H^+] \approx [H_2PO_4^-]$ but that the curvature in the line for $\log[H_2PO_4^-]$ must be taken into account. We therefore write

$$[H^+] = [H_2PO_4^-] = K_{a1}C/([H^+] + K_{a1}) \tag{17}$$

which leads to the quadratic expression $[H^+]^2 + K_{a1}[H^+] - K_{a1}C = 0$ with the solution $[H^+] - \frac{1}{2}\sqrt{(K_{a1}^2 + 4K_{a1}C)}$, compare Equation (10). Substitution of $C = 0.1$ and $K_{a1} = 2.15$ then yields $[H^+] = 0.0233$ M and pH = 1.63, only 0.05 higher than our earlier, rough estimate.

For 0.1 M Na_2HPO_4 the refinement involves approximating (15) to $[H_2PO_4^-] = [PO_4^{3-}] + [OH^-]$ by including the term for $[OH^-]$ in the proton balance. We have $[OH^-] = 10^{0.8}[PO_4^{3-}] = 0.14[PO_4^{3-}]$ so that $\{[PO_4^{3-}] + [OH^-]\}$ $14[PO_4^{3-}]$ and $\log\{[PO_4^{3-}] + [OH^-]\} = 0.06 + \log[PO_4^{3-}]$. Consequently, pH = 9.68 – 0.03 = 9.65.

For the pH of 0.1 M Na_3PO_4 the stick diagram indicates that (16) can be simplified to $[H_2PO_4^-] = [OH^-]$ but that, again, we need to take into account curvature, in this case of the line for $\log[H_2PO_4^-]$. We have

$$[HPO_4^{2-}] = [H^+]C/([H^+] + K_{a3}) = [OH^-] = K_w/[H^+] \tag{18}$$

which leads to $[H^+]^2C - K_w[H^+] - K_{a3}K_w = 0$, so that $[H^+] = \{K_w + \sqrt{(K_w^2 + 4CK_{a3}K_w)}\}/(2C)$ hence $[H^+]$ 3.21×10^{-13} and pH = 12.49 for C = 0.1, $K_{a3} = 10^{-12.15}$, $K_w = 10^{-14.00}$. In this case, the refinement corrects the answer by –0.09 pH units. Table 6 summarizes these results.

The example of phosphoric acid is a relatively simple one, because its pK_a values are quite widely spaced. To use a more challenging example, we now consider citric acid, a triprotic acid with pK_{a1} = 3.13, pK_{a2} = 4.76, and pK_{a3} = 6.40. Figure 10 shows the corresponding stick diagram for C = 0.05 M (i.e., pC = 1.30), as well as the pH values for the acid and its salts with a strong base at that concentration. The proton balances are the

TABLE 6
The pH of 0.1 *M* aqueous solutions of H_3PO_4 and its sodium salts, as estimated from the stick diagram (2nd column), as refined (3rd column), and as calculated exactly (4th column)

Species	pH from the stick diagram	pH after after refinement	pH as computed exactly
H_3PO_4	1.5_8	1.63	1.63
NaH_2PO_4	4.6_8		4.69
Na_2HPO_4	9.6_8	9.65	9.65
Na_3PO_4	12.5_8	12.49	12.49

equivalents of (13) through (16), and we simply read off the stick diagram to find for our first estimates pH = (1.30 + 3.13)/2 = 2.22, (3.13 + 4.76)/2 = 3.94, (4.76 + 6.40)/2 = 5.58, and (6.40 + 12.30)/2 = 9.55.

In this case, refinement is more complicated, because the proximity of the various pK_a values requires that we use more complete expressions. Even so, the rough estimates are quite close: exact solution of the pH on a spreadsheet (where no such approximations need be made) yield pH = 2.24, 3.95, 5.58, and 9.55, respectively. Although one can select concentrations where the rough estimates do not yield such good agreement with the results of exact computations, one usually finds that the stick diagram generates quite good estimates in cases where further refinement would be much more complicated.

Matters become still more complicated for salts of a weak acid and a weak base. Here we consider the ammonium salts of phosphoric acid. For $NH_4H_2PO_4$ the proton balance is

$$[H^+]+[H_3PO_4]=[NH_3]+[HPO_4^{2-}]$$
$$+2[PO_4^{3-}]+[OH^-] \qquad (19)$$

which is similar to (14) except for the term $[NH_3]$; the latter reflects the possible loss of protons by the ammonium ions. Figure 11 shows the corresponding stick diagram, from which we conclude that (19) can be simplified to $[H_w\%_oO_4] \approx [HPO_4^{2-}]$. Consequently, the pH is not noticeably affected in this case by the presence of ammonium ions, and the pH is 4.68.

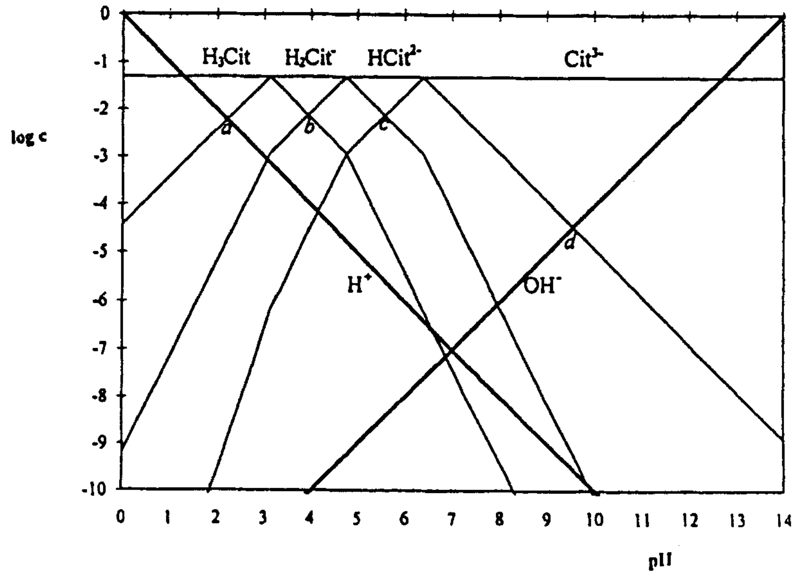

FIGURE 10. The stick diagram for citric acid (pK_{a1} = 3.13, pK_{a2} = 4.76, pK_{a3} = 6.40) and its sodium salts, at a total analytical concentration of 0.05 *M*.

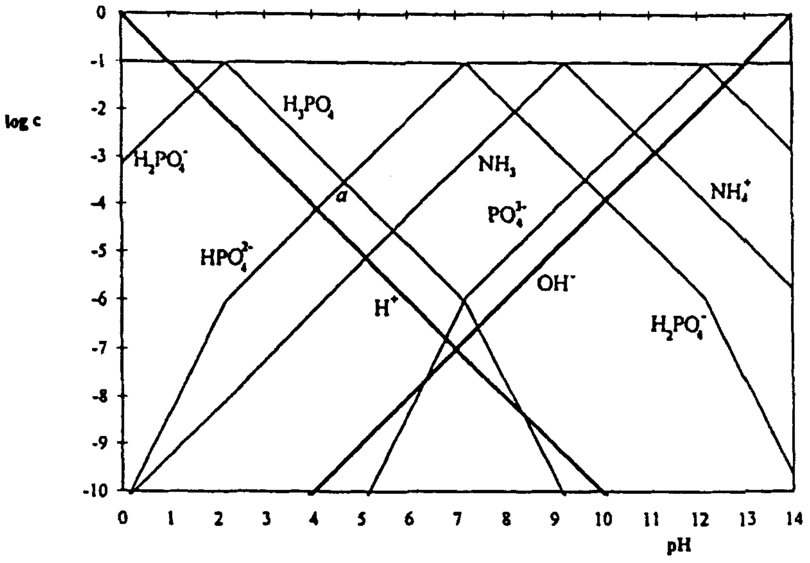

FIGURE 11. The stick diagram for aqueous 0.1 *M* $NH_4H_2PO_4$. Orthophosphoric acid: pK_{a1} = 2.15, pK_{a2} = 7.20, pK_{a3} = 12.15; ammonium: pK_a = 9.24.

For $(NH_4)_2HPO_4$ the proton balance is

$$[H^+]+2[H_3PO_4]+[H_2PO_4]=[NH_3] \\ +[PO_4^{3-}]+[OH^-] \qquad (20)$$

which differs from (15) by the term $[NH_3]$. Note that $\{[NH_3]+[NH_4^+]\} = 2C$ because $(NH_4)_2HPO_4$ contributes two ammonium ions per molecule. The corresponding stick diagram, Figure 12, shows that (19) can now be simplified to $[H_2PO_4^-] \approx [NH_3]$, and it also provides an estimate of the pH as (7.20 + 9.24 – 0.30)/2 = 8.07 where the pK_a of NH_4^+ is 9.24. The factor 0.30 comes about because the system point for NH_4^+ lies 0.30 above that for $H_2PO_4^-$ as a consequence of the 2:1

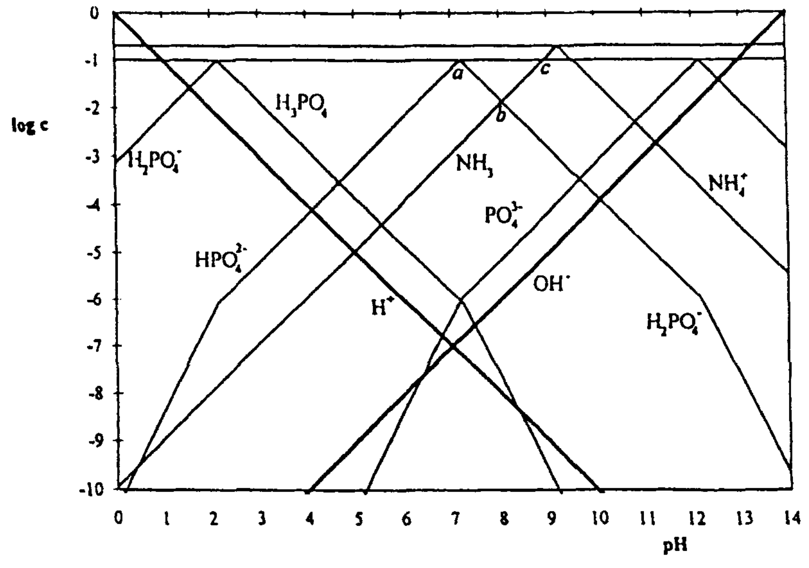

FIGURE 12. The stick diagram for aqueous 0.1 *M* $(NH_4)_2HPO_4$.

stoichiometric ammonia–phosphate ratio, so that the pH value of point *b* in Figure 12 is midway between those of points *a* and *c*, where the latter lies 0.30 to the left of (and below) the system point of NH_4^+.

Finally, the proton balance for $(NH_4)_3PO_4$ is

$$[H^+]+3[H_3PO_4]+2[H_2PO_4^-]+[HPO_4^{2-}] = [NH_3]+[OH^-] \tag{21}$$

which again is similar to (16) except that it contains the additional term $[NH_3]$. The stick diagram is shown in Figure 13; note that the system point for NH_4^+ now lies log 3 = 0.48 above those for the phosphates. For the salt concentration shown, the proton balance can now be reduced to $[HPO_4^{2-}] \approx [NH_3]$ so that pH = 9.24 – 0.48 = 8.76.

IX. APPLICATIONS TO MIXTURES

In order to estimate the pH of a mixture containing, say, C_1 *M* HCl and C_2 *M* HA (a monoprotic weak acid), the first step is again the formulation of the proton balance. For mixtures the result is often difficult to write down by inspection, in which case it is best to go back to the charge and mass balance relations in order to derive the proton balance. For the present example we have the charge balance

$$[H^+]=[Cl^-]+[A^-]+[OH^-] \tag{22}$$

and the mass balances

$$[Cl^-]=C_1 \tag{23}$$

$$[HA]+[A^-]=C_2 \tag{24}$$

Substitution of (23) into (22) does not alter the latter substantially, but substitution of (24) leads to another form (indicating that the proton balance is not always unique)

$$[H^+]+[HA]=C_1+C_2+[OH^-] \tag{25}$$

Equations (22) and (25) are mathematically equivalent, but they are not necessarily equivalent for use in a stick diagram, as illustrated in Figure 14 for $C_1 = 10^{-2}$ *M*, $C_2 = 10^{-4}$ *M*, and $K_a = 10^{-4}$ *M*. In this case, pH ≈ 3.0, in the range where $[HA] \approx C_2$, so that the proton balance (25) does not yield an unambiguous answer, while (22) does.

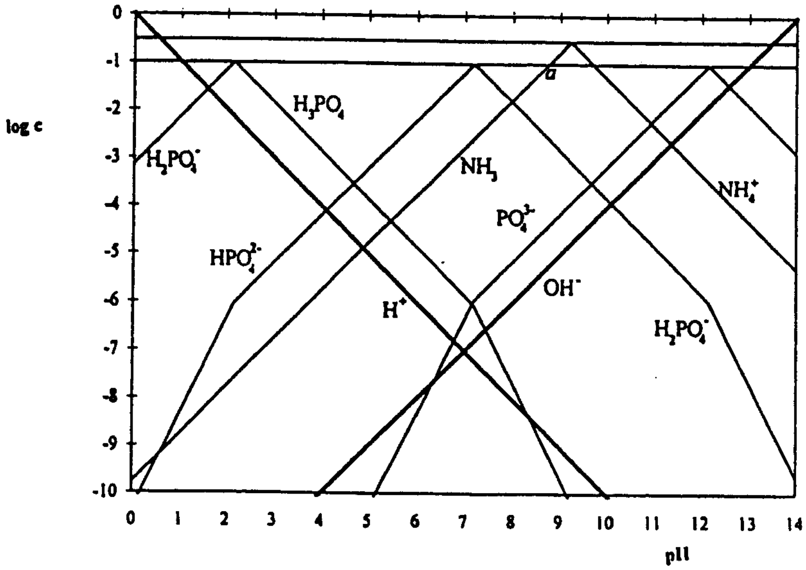

FIGURE 13. The stick diagram for aqueous 0.01 *M* $(NH_4)_3PO_4$.

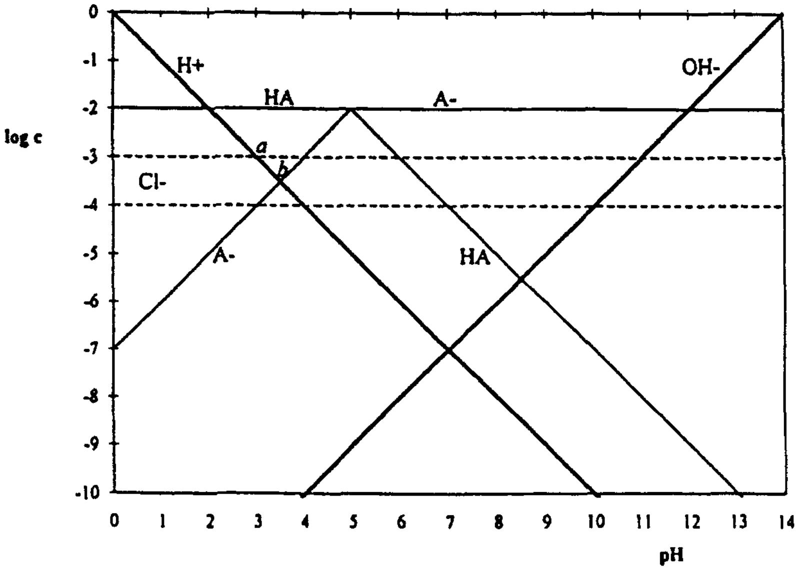

FIGURE 14. The stick diagram for an aqueous mixture containing 0.01 *M* HCl and 0.1 m*M* HA, pKa = 4.

Buffer mixtures, that is, mixtures of an acid and its conjugate base, are probably the most important category of mixtures for which the pH must be calculated. When the corresponding system point lies well within the central triangle, we can use the Henderson approximation

$$[\mathrm{H}^+] = K_a C_a / C_b \quad \text{or} \quad \mathrm{pH} = \mathrm{p}K_a + \log(C_b/C_a) \qquad (26)$$

where C_a and C_b are the initial concentrations of the acidic and basic forms of the buffer mixture. However, when the system point lies outside the central triangle, the Henderson approximation cannot be used. The stick diagram does not suffer from such a restriction, but instead shows us in each case what are the appropriate approximation. Here we illustrate this for a buffer mixture listed by Bates:[8] the aqueous mixture of 50 ml 0.05 *M* $\mathrm{Na_2HPO_4}$ + x ml 0.1 *M* NaOH, diluted to 100 ml; the corresponding stick diagram is shown in Figure 15 for x = 10. In this case we have the mass and charge balance equations (deleting all minor components, as identified by the stick diagram)

$$[\mathrm{Na}^+] = (0.050 + 0.001x)M \qquad (27)$$

$$[\mathrm{HPO_4^{2-}}] + [\mathrm{PO_4^{3-}}] \approx 0.0025M \qquad (28)$$

$$[\mathrm{Na}^+] \approx 2[\mathrm{HPO_4^{2}}] + 3[\mathrm{PO_4^{3-}}] + [\mathrm{OH}^-] \qquad (29)$$

so that

$$0.001x \approx [\mathrm{PO_4^{3-}}] + [\mathrm{OH}^-] \qquad (30)$$

which can be solved directly because

$$x = 1000\left(\frac{0.025K_{a3}}{[\mathrm{H}^+] + K_{a3}} + \frac{K_w}{[\mathrm{H}^+]}\right) \qquad (31)$$

from which we can calculate a table of values of x as a function of $[\mathrm{H}^+]$, and hence of pH.

X. APPLICATIONS TO TITRATIONS

Stick diagrams are very convenient tools to estimate whether a titration is feasible. Here we merely illustrate this with the examples of Figures 9 and 10. The measure we

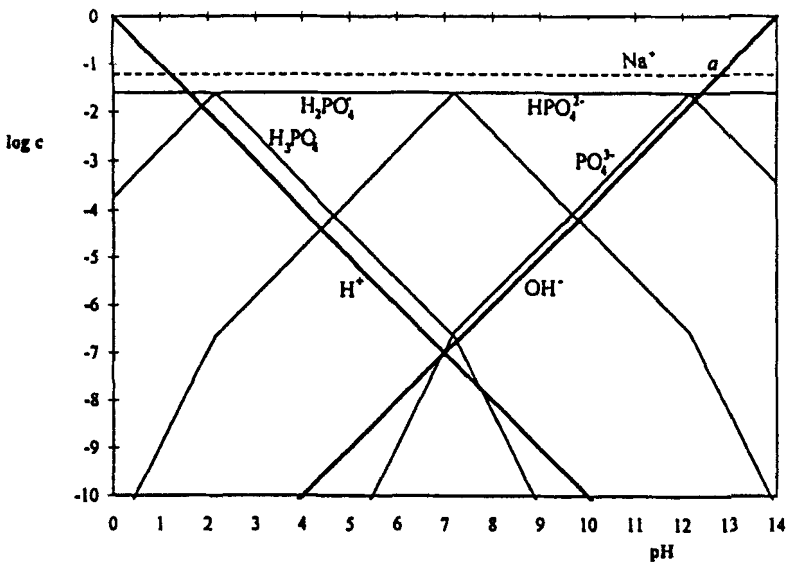

FIGURE 15. The stick diagram for an aqueous mixture made by mixing 50 ml 0.05 *M* Na_2HPO_4 and 10 ml NaOH, and adding H_2O to make a total volume of 100 ml.

use is the distance between the intersection in the stick diagram associated with the relevant equivalence point, and the horizontal line at pc = pC. When this distance is at least two logarithmic units, the titration is sufficiently steep at its equivalence point, so that a color indicator can be used. When the distance is more than about one logarithmic unit, a potentiometric titration can be performed, albeit with limited precision, but a colorimetric titration is inadvisable. When the distance is less than about one logarithmic unit, the titration has little analytical usefulness. Note that these criteria are based solely on the sample and do not take into account the nature and concentration of the titrant. They are therefore valid as guidelines as long as the titrant is not much less concentrated than the sample.

The stick diagram of phosphoric acid, Figure 9, shows that the vertical distances between points b, c, and d and the line at log C are about 2½, 2½, and ½ logarithmic units. Indeed, the first two equivalence points are analytically useful, while the third is not. The stick diagram for citric acid shows a case where only the third equivalence point is useful. Both conclusions are in full agreement with the corresponding titration curves.

XI. ACTIVITY EFFECTS

An often-raised question is the role of activity coefficients in pH calculations. In order to address this we consider two separate problems: (1) what do these diagrams represent and (2) what does the pH measure.

(a) The diagrams reflect concentrations, not activities. There is a simple reason for this: the charge and mass balance equations and the resulting proton balance are all accounting rules dealing directly with concentrations. On the other hand, the pK_a values reflect activities. Insofar as activity coefficients can be estimated, corrected pK_a values should therefore be used in these diagrams when precise results are needed. Unfortunately, ionic activity coefficients depend strongly on the ionic strength I, which often varies across the diagram. Consequently, the simplest solution for the computation of individual pH values is to proceed as follows: first determine the pH neglecting activity effects (i.e., as if all activity coefficients were equal to 1), then use the diagram to estimate the ionic strength I, use this to correct the relevant pK_a values, and, finally, use these corrected pK_a values to refine the pH. In principle, this process should be repeated iteratively until the pH values so obtained become constant; in practice, a single cycle through this procedure usually suffices.

(b) The second aspect is the pH measurement itself. When the pH is measured potentiometrically (but *not* when it is measured photometrically, e.g., using color indicators or NMR shifts) such measurements yield values that are believed to be a close approximation to the negative logarithm of the activity (the product of concentration c and activity coefficient f). In that case, a second activity correction is required. Note that this second correction is specific for potentiometric pH measurements, that is, when using a pH meter.

The entire procedure is illustrated below for the potentiometric determination of the pH of phosphoric acid and its sodium salts. We use the Davies[9] equation as our model for activity corrections and write it in the form

$$\log f_i = z_i^2 \log f \qquad (32)$$

with

$$\log f = -\frac{1}{2}\left[\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right] \qquad (33)$$

where the ionic strength I is defined in terms of ionic valencies z_i and concentrations c_i as

$$I = \frac{1}{2}\sum_i z_i^2 c_i \qquad (34)$$

In Section VIII we computed the pH of 0.1 M H_3PO_4 as 1.63 and the corresponding value of $[H^+]$ as 0.0233 M. At that point we have $[H^+] = [H_2PO_4^-]$. The stick diagram, Figure 9, shows that H^+ and $H_2PO_4^-$ are the dominant ionic species at that pH, and therefore we find the ionic strength as $I = ½ \times (0.0233 + 0.0233) = 0.0233\,M$. For this ionic strength we calculate f from (33) as

$$\log f = -0.5\left\{\sqrt{I}/\left(1+\sqrt{I}\right) - 0.3I\right\} = -0.0627$$

or

$$f = 10^{-0.5\{\sqrt{I}/(1+\sqrt{I})-0.3I\}} = 0.866$$

The effect on K_a is most readily seen when we denote the "true" (i.e., activity–corrected) K_a value by K_a^t and realize that most tables of equilibrium constants list pK_a values obtained by extrapolation of experimental data to infinite dilution, thereby approximating pK_a^t. We therefore calculate the concentration–based K_{a1} as

$$K_{a1}^t = \frac{[H^+]f_+[H_2A^-]f_-}{[H_3A]f_0} = K_{a1}f^2 \qquad (35)$$

or

$$pK_{a1} = pK_{a1}^t + 2\log f = 2.15 - 0.12_5 = 2.02_5$$

Note that the Davies equation, through its factor z_i^2, only considers the effects of charged species, that is, $f_+ = f_- = f$ and $f_0 = 0$.

For part (b) we assume that the pH is measured potentiometrically and then is given by $-\log\ \{[H^+]f_+$. This is, of course, an approximation: if it were exact, one would be able to use pH measurements to determine single ion potentials, a thermodynamic impossibility. Nonetheless, the measured pH is believed to approximate $-\log\ \{[H^+]f_+$ rather closely, and we will make this assumption here. Consequently, we have $pH_m = pH_c - \log f = pH_c + 0.06_3$, where pH_m denotes the *measured* pH, and pH_c the earlier–calculated, concentration–based value computed with the aid of activity–corrected equilibrium constants. This term $-\log f$ counteracts the activity correction under (a) so that, in total, inclusion of an activity correction in this case does not lead to an appreciable pH shift: the final result is a pH of $1.57_7 + 0.06_3 = 1.64$. The insignificance of an activity correction in this case is largely the result of the low ionic strength I of the solution.

For 0.1 M NaH_2PO_4, we found earlier a pH of 4.67_5 by simply taking the average of pK_{a1} and pK_{a2}. We again start by estimating the ionic strength I. A quick glance at the stick diagram will convince us that, at that pH, the dominant anion is $[H_2PO_4^-]$, while the dominant cation is clearly Na^+, both at a concentration of 0.1 M. The ionic strength is, therefore, also 0.1 M, so that $\log f = -0.105$. We saw that the activity correction shifts pK_{a1} by $+2 \log f$; the corresponding correction for pK_{a2} is $+4 \log f$, as can be seen from

$$K^{t}_{a2} = \frac{[H^+]f_+[HA^{2-}]f_{2-}}{[H_2A^-]f_-} = K_{a2}f^4 \qquad (36)$$

or

$$pK_{a2} = pK^{t}_{a2} + 4\log f = 7.20 - 0.42 = 6.78$$

where $\log f_{2-} = (-2)^2 \log f = 4 \log f$ follows from (32). The value of pH_c calculated from the stick diagram is therefore $(pK_{a1} + pK_{a2})/2 = (pK^{t}_{a1} + pK^{t}_{a2} + 6 \log f)/2 = (2.15 + 7.20 - 0.63)/2 = 4.36$. (Because the ionic strength is different, we cannot use the earlier-computed value for pK_{a1} but must combine the formula $pK_{a1} = pK^{t}_{a1} + 2 \log f$ with the new value for $\log f$.) Finally, $pH_m = pH_c - \log f = 4.36 + 0.10_5 = 4.46$. In this case, there is a difference of 0.25 with the value of 4.69 listed in Table 6.

For 0.1 M Na_2HPO_4 the stick diagram yielded a first estimate of $(7.20 + 12.15)/2 = 9.67_5$, while subsequent refinement added a correction of -0.03 to a pH of 9.65. At that pH, the dominant species are Na^+ (at 0.2 M) and HPO_4^{2-} (at 0.1 M), so that the ionic strength is $\frac{1}{2} \times (1^2 \times 0.2 + 2^2 \times 0.1) = 0.3$ M. Consequently, (33) yields $\log f = -0.13_2$, hence

$$K^{t}_{a3} = \frac{[H^+]f_+[A^{3-}]f_{3-}}{[HA^{2-}]f_{2-}} = K_{a3}f^6 \qquad (37)$$

or

$$\begin{aligned} pK_{a3} &= pK^{t}_{a3} + 6\log f \\ &= 12.15 - 0.79 = 11.35_8 \end{aligned}$$

so that the initial result from the stick diagram\$Ñ>ould be modified to $(pK_{a2} + pK_{a3})/2 = (pK^{t}_{a2} + pK^{t}_{a3} + 10 \log f)/2 = (7.20 + 12.15 - 1.32)/2 = 9.01_5$.

Refinement now must take into account that K_w is also affected by the activity correction, i.e.,

$$K^{t}_w = [H^+]f_+[OH^-]f_- = K_w f^2 \qquad (38)$$

or

$$\begin{aligned} pK_w &= pK^{t}_w + 2\log f \\ &= 14.00 - 0.26_4 = 13.73_6 \end{aligned}$$

so that the line for $[OH^-]$ now lies 1.37_8 logarithmic units below that for PO_4^{3-}. Refinement then yields a pH of 9.01_2.

Finally, we have $pH_m = pH_c - \log f = 9.01_2 + 0.13_2 = 9.14$ for a total activity–related pH shift of $9.14 - 9.65 = -0.51$. Note that, in this case, the activity correction is considerably greater than any errors involved in disregarding refinements in the stick diagrams.

The pH of 0.1 M Na_3PO_4 was earlier estimated from the stick diagram as 12.58 and, after refinement, as 12.49. At this pH the dominant ionic species are Na^+ (at 0.3 M) and PO_4^{3-} (at 0.1 M) so that the ionic strength is approximately $\frac{1}{2} \times (1^2 \times 0.3 + 3^2 \times 0.1) = 0.6$ M, from which we calculate $\log f = -0.12_8$. The consequent activity corrections of the equilibrium constants are $pK_{a3} = pK^{t}_{a3} + 6 \log f = 12.15 - 0.76_8 = 11.38_2$ and $pK_w = pK^{t}_w + 2 \log f = 14.00 - 0.25_6 = 13.74_4$, so that a stick diagram yields $pH \approx (11.38_2 + 12.74_4)/2 = 12.06_3$. Af-

TABLE 7

The pH of 0.1 *M* aqueous solutions of H_3PO_4 and its sodium salts, as estimated from the stick diagram (2nd column), as refined (3rd column), and after activity correction based on the Davies equation (4th column)

Species	pH from the stick diagram	pH after after refinement	pH after activity correction
H_3PO_4	1.58	1.63	1.64
NaH_2PO_4	4.68	4.69	4.69
Na_2HPO_4	9.68	9.65	9.14
Na_3PO_4	12.58	12.49	12.15

ter refinement for the curvature of the line for $\log[HPO_4^{2-}]$, see Equation (12), we obtain $pH_c = 12.01_8$. The pH measurement contributes an additional shift of $pH_m - pH_c = -\log f = +0.13_2$ to bring the pH to 12.15. Table 7 lists these results and facilitates their comparison with those without activity corrections.

XII. SUMMARY

Stick diagrams are easily sketched plots consisting of straight line segments with integer slopes. They closely resemble logarithmic concentration diagrams, except that the curvature near the system points is neglected. In using them we typically make a further simplifying approximation: we only consider the leading terms on each side of the proton balance. The result is a very quick and easy method for estimating the pH, a method that almost always yields results that are precise to within ±0.3 pH units, and typically much closer, as long as we disregard activity corrections. A significant advantage of the stick diagram is that it remains simple even when many different species are involved.

Double-logarithmic graphs such as the logarithmic concentration diagram and the stick diagram provide a continuous overview of the speciation, something that is easily lost when a chemical problem is converted into one of solving simultaneous mathematical equations. Use of stick diagrams takes the emphasis away from mathematical manipulations and instead focuses on the chemistry involved, while the math is reduced to formulating the proper balance equation, such as the proton balance in pH problems. In sketching these graphs, the students learn to recognize the relative magnitudes of the various system components. Stick diagrams are also very convenient tools for use with titrations, because they show at a glance which equivalence points can yield sharp pH changes and which cannot.

A stick diagram is a piecemeal approximation of a logarithmic concentration diagram, just as the traditional treatment of titration curves is a piecemeal approximation of the corresponding master equation. Interestingly, the two approximations use different pH values to cut the continuous curves into separate pieces: the stick diagram generates abrupt bends (though no discontinuities) at pH = pK_a, whereas the traditional treatment of titration curves introduces discontinuities at the pH of each equivalence point.

When more precise numerical values are required, the stick diagram (1) shows whether refinement is needed and (2) which terms to consider in that case. We have given a number of examples of such refinements. Usually, refinements can be made using a pocket calculator in order to find a few logs and antilogs or to solve a quadratic equation. Sometimes refinements are more complicated than that, as when several pK_a values lie close together. In that case the pK_a values may not be known to sufficient precision to justify refinement anyway; otherwise, a spreadsheet may be needed.

The approximate nature of stick diagrams illustrates the limited precision with which concentrations can be computed from equilibrium constants. Because few pK_a values are known to better than ±0.01, concentrations are usually known only to a factor of

$10^{\pm 0.01}$ or ±2.3% at best, and calculations of concentrations to a much higher precision are usually exercises in make-believe. This does not even take into account the inherent uncertainties of activity corrections.

Finally, in Section XI, we have considered activity effects, the skunk at any pH party. We have illustrated activity corrections with an example involving polyvalent ions (such as PO_4^{3-}) in a range of ionic strengths near where the activity coefficient f in the Davies equation goes through a minimum. The calculations show explicitly how such activity corrections should be made. Activity calculations require that one make a clear distinction between the parameters that are true concentrations (those that appear in charge, mass, and proton balance equations, as well as spectrometrically determined concentrations) and those that need activity corrections (equilibrium constants, and potentiometric pH measurements), because proper activity corrections are *not* made by simply multiplying all concentrations by activity coefficients.

If there is any take-home lesson from the section on activity effects, it is that activity corrections can easily be larger than any differences between crude pH estimates based on stick diagrams and their subsequent refinements (see Table 7). To put it differently, if one does not want to go through the tedium of computing activity corrections (which are laborious and therefore are often neglected) then there is no good reason to reject the first estimates of stick diagrams as too crude. Moreover, activity corrections are inherently approximate themselves. This is not because we have here used approximate relations such as the Davies equation (a deficiency that then might be remedied by using another, "better" formula) but precisely because it is not known how to calculate activity coefficients exactly, that is, there *is* no precise formula for ionic strengths above about 0.01 *M*.

Here we have used the Davies relation merely to demonstrate the protocol to be followed. Moreover, it appears to be the best available approximation that is still relatively simple to apply, because it does not involve any ion-specific parameters. If one wants to go beyond this level, the reader might want to consult the elaborate work of Pitzer et al.[10] on this subject. Some of the most popular textbooks of quantitative chemical analysis still advocate use of the Debye-Hückel equation with specific ionic radii, such as those estimated by Kielland,[11] even though this procedure, while much more complicated than use of the Davies equation, does not appear to be more realistic for practical solutions with concentrations in the range of 0.01 *M* to 1 *M*. At any rate, the protocol is similar regardless of the specific model used for activity corrections, and the availability of choice merely illustrates that we really do not have good predictors for single ion activity coefficients. Unfortunately, single ion activity coefficients (rather than the experimentally accessible mean activity coefficients) are the ones needed to relate potentiometric pH measurements to proton concentrations. Single-ion activity coefficients are the Achilles heel of pH calculations.

Stick diagrams and logarithmic concentration diagrams are not restricted to acid–base problems and can be used to similar advantage for complex formation, precipitation, and redox equilibria. In such cases the independent variable is the negative logarithm of the relevant concentration (that of the complexing or precipitating agent); in the case of redox equilibria, the independent variable is the potential in units of (RT/F) $\ln(10)$, about 0.059 V at room temperature. Likewise, the proton balance must be replaced by its appropriate analog. For redox reactions, that analog is the electron balance.

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