



Chemical Equilibrium

IV. Weak Acids and Bases

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In this article in the series¹ on chemical equilibrium we examine weak acids and bases and the various assumptions that are implied by the simplified equations given in most introductory texts.

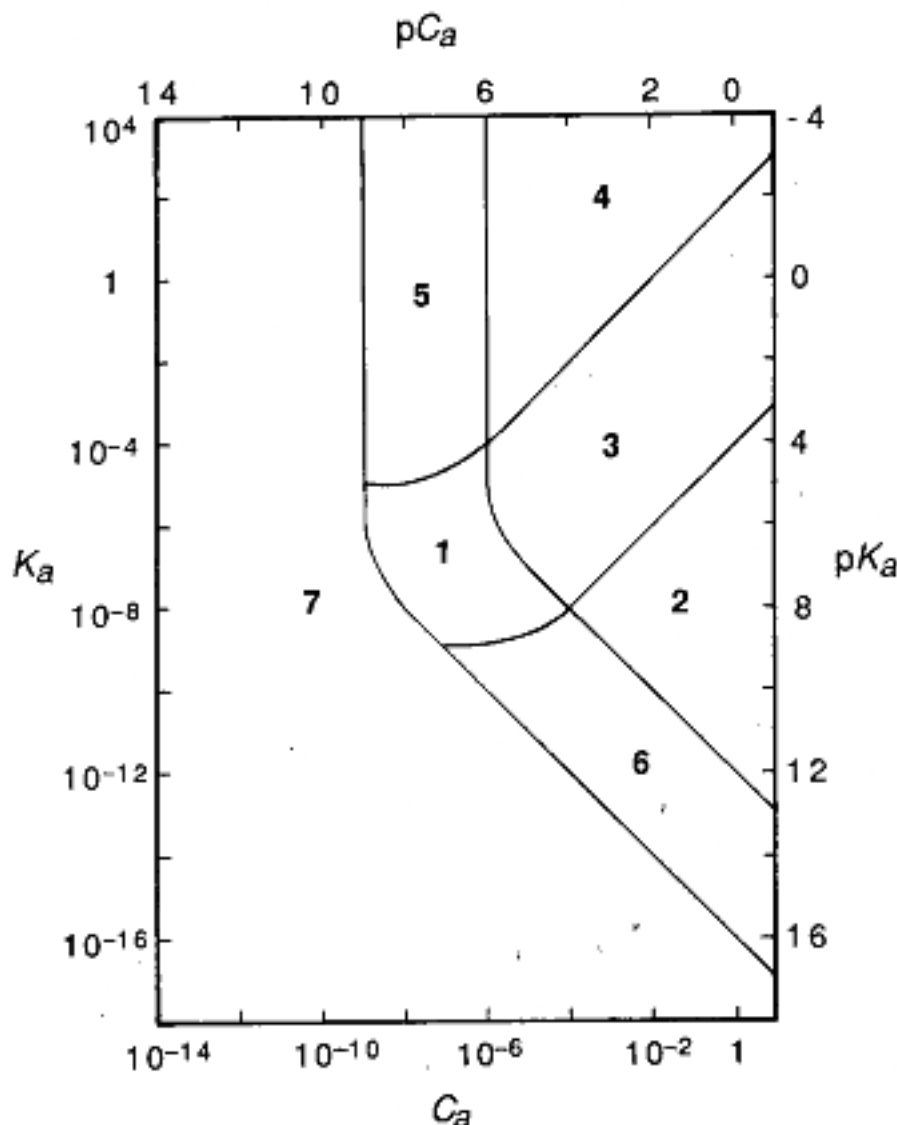
In article II of this series¹ we derived a completely general expression for a mixture of a weak triprotic acid, H_3X , with a weak base, ROH. The expression reduced to a cubic equation in $[H^+]$ for a single solution of a monoprotic acid, HA. The purpose of this article is to discuss the conditions for which various approximations, valid to within 1%, result in even simpler equations.

We use a method of inequalities² similar to that used in article III¹ to define the pH ranges over which the water equilibrium can be neglected. Here, we define regions on a plot of C_a (the concentration of the acid) versus K_a (the acid ionization constant) over which various assumptions are valid to within 1%.

There are only four possible assumptions that can apply to a solution of a C_a M solution of an acid HA. They are:

- The water equilibrium can be neglected³.
- There is at most 1% ionization of HA; this is the weak acid approximation.
- The $[H^+]$ produced by dissociation of HA is less than 10^{-9} M. This results in the approximation⁴ that the $pH = 7.00$; it corresponds to a solution that is either so very, very dilute and/or that involves an acid that is so very, very weak that the H^+ from the acid is negligible compared with the H^+ from the water.
- The acid HA is more than 99% ionized. This is the strong acid approximation.

The equations that result from the introduction of the various assumptions^{5,6} are given in Table 1. The regions⁷ on a plot of $-\log K_a = pK_a$ versus $-\log C_a = pC_a$ over which the various simplifying assumptions and the resulting equations⁶ are valid to within 1% are shown in the figure.



Regions where various simplified equations given in Table 1 are valid for a C_a M solution of an acid HA with K_a .

¹ The previous articles in this series are: Gordus, A. A.; "I. The Thermodynamic Equilibrium Constant", *J. Chem. Educ.* **1991**, *68*, 138-140; "II. Deriving an Exact Equilibrium Equation", *J. Chem. Educ.* **1991**, *68*, 215; "III. A Few Math Tricks", *J. Chem. Educ.* **1991**, *68*, 291.

² The algebra can become rather complicated. A supplement to this and the sixth paper in this series is available from the author. It shows the complete derivations for weak acids as well as for the full titration range.

³ The water equilibrium can be neglected when the pH is less than 6.00 or greater than 8.00 as was shown in article III of the series (see footnote 1).

⁴ For a maximum error of 1% the maximum H^+ that can be added so that the pH remains at 7.00 will equal 1% of 1.00×10^{-7} or 1.00×10^{-9} M. Similarly, the maximum added OH^- that will permit the pH to be 7.00 will also be 1.00×10^{-9} M OH^- . (There is an alternate way of defining the maximum error in terms of the shift in the water equilibrium; in this case the maximum added concentration of H^+ or OH^- is 2×10^{-9} M.)

⁵ The derivations of these equations are given in: Gordus, A. A. *Schaum's Outline of Analytical Chemistry*; McGraw-Hill: New York, 1985; Chapter 5.

⁶ To simplify the notation, we use K_a , K_b , and K_w to signify the equilibrium constants. If the solution is ideal, then these K values are the thermodynamic equilibrium constants. If the solution is nonideal, then these K values are the thermodynamic constants divided by K_f , which is the activity-coefficient "constant" as discussed in article I (see footnote 1).

⁷ This graph is similar, but not identical to that given by Burke, J. D. *J. Chem. Educ.* **1976**, *53*, 79-80 and by King, E. *Chemistry*; Painter-Hopkins: Sausalito, CA, 1979; p 561, except that their graphs are based on a maximum error in the calculated $[H^+]$ rather than in the assumptions. Algebraically, it is much easier to derive the conditions needed to define the areas of the graph if the maximum error is imposed on the assumptions.

Table 1. Simplified Equations for a C_a M Acid with K_a

Assumptions ^a	Equation	Region on figure
None	$[H^+]^3 + K_a[H^+]^2 - (C_a K_a + K_w)[H^+] - K_a K_w = 0$	1
a,b	$[H^+] = \sqrt{C_a K_a}$	2
a	$[H^+]^2 + K_a[H^+] - C_a K_a = 0$	3
a,d	$[H^+] = C_a$	4
d	$[H^+]^2 - C_a[H^+] - K_w = 0$	5
b	$[H^+] = \sqrt{C_a K_a + K_w}$	6
c	$[H^+] = 1.00 \times 10^{-7} \text{ M}$	7

^a Refer to text.

The equation usually given in introductory texts for the hydrogen-ion concentration of a C_a M weak acid with an ionization constant K_a involves the *implied* assumptions a and b. Under these conditions, $[H^+] = [A^-]$ and $[HA] = C_a$. This results in $K_a = [H^+][A^-]/[HA] = [H^+]^2/C_a$ so that $[H^+] = \sqrt{C_a K_a}$, which applies only in region 2 of the figure. Fortunately, a number of $C_a = 0.100$ M acids have K_a values that fall in this region of the graph, and most texts limit their discussion of weak acid calculations to these acids. However, acids can range from the very strong (HCl) to the very, very weak (HCN, $K_a = 6.17 \times 10^{-10}$). Their concentrations can also range from very high to very low values. The use of the figure allows one to determine, for any specified C_a and K_a values, which assumptions are valid and which equation applies.

The figure shows that there must be a smooth transition from strong to weak to very weak acidity. For instance, begin in region 2 where assumptions a and b apply, and consider what happens as the acid being considered is made stronger. This corresponds to larger K_a values and requires moving upward on the graph. Eventually region 3 is reached where the degree of ionization of the acid can no longer be neglected. At this point the degree of ionization is greater than 1%, and a quadratic equation is required to solve for the hydrogen-ion concentration. For even stronger acids (a further upward movement on the graph) the point is reached at which the acid is more than 99% ionized and region 4 is entered. This is the strong-acid region and $[H^+] = C_a$. We still are able to neglect the water equilibrium. However, if we now move to the left in region 4, corresponding to lower concentrations of the strong acid, the strong-acid solution eventually is so dilute and the $[H^+]$ from the acid is so small that we must begin including the water equilibrium; a quadratic equation for $[H^+]$ is now required. As we cross into region 5, where the water equilibrium must be included, we are in a pH range >6.00 . Further dilution (movement to the left) eventually results in a solution that has a pH = 7.00 which is region 7; the strong acid contributes a negligible amount to the pH; the water equilibrium predominates.

Again start in region 2, and ask what happens as the acid is made weaker. This involves moving downward on the graph. The solution becomes less acidic and when in region 6 the pH is >6.00 . At this stage, the water equilibrium can no longer be neglected and $[H^+] = \sqrt{C_a K_a + K_w}$. For even weaker acids (corresponding to a further downward movement) or for more dilute solutions (corresponding to a leftward movement) the acid contributes even less to the $[H^+]$ and eventually the pH = 7.00 (region 7) because the water equilibrium will predominate.

It should also be noted that for any two adjacent regions in the figure the more complicated equation (i.e., less restrictive in terms of assumptions) will also be valid in an adjacent region where the simpler equation is also valid. For example, the equations for regions 6 and 3 are also valid in region 2. Similarly, the equations for regions 3 and 5 are also valid in region 4. The general cubic equation, used in region 1, is of course valid throughout the full graph.

Table 2. Equations for Lines on Graph of Figure for $C_a > 10^{-4}$ M

Regions separated	Equation
4 from 3	$C_a = 10^{-2} K_a$
3 from 2	$10^{-4} C_a = K_a$
2 from 6	$C_a K_a = 10^{-12}$
6 from 7	$C_a K_a = 10^{-16}$

Solutions of Bases

Although the figure is labeled in terms of C_a and K_a for use with solutions of acids, an identical graph results for solutions of a C_b M solution of a base with K_b . And, a similar set of equations also applies. The only differences will be in the notation, where a is replaced by b in the subscripts for the equations in Tables 1 and 2 and in the labels of the figure and $[H^+]$ is replaced by $[OH^-]$ in the equations. The equation for region 2, for example, becomes: $[OH^-] = \sqrt{C_b K_b}$. This is the expression that is derived in most texts for use at the equivalence point in the titration of an acid HA. In this case, at the equivalence point, there exists a C_b M solution of the conjugate base, A^- , which undergoes hydrolysis: $A^- + H_2O \rightarrow HA + OH^-$. The equilibrium constant for this reaction of the conjugate base, A^- , is K_b where $K_b = K_w/K_a$. If we assume that less than 1% of A^- hydrolyzes and that the water equilibrium can be neglected (which is usually what is assumed in most texts and here corresponds to pH >8.00) then $[HA] = [OH^-]$ and $[A^-] = C_b$ so that $K_b = [HA][OH^-]/[A^-] = [OH^-]^2/C_b$. This leads to $[OH^-] = \sqrt{C_b K_b}$.

Equations for Lines on Graph

As an example of the method of inequalities used to define the lines that separate regions in the figure, we can examine region 2 where the applicable equation is $[H^+] = \sqrt{C_a K_a}$. The first assumption is that the water equilibrium can be neglected, i.e., $[H^+] > 10^{-6}$. Therefore, $\sqrt{C_a K_a} > 10^{-6}$ or, squaring both side, $C_a K_a > 10^{-12}$. This is the same as $pC_a + pK_a < 12.0$ and is the equation for the line separating regions 2 and 6. The line that separates regions 2 and 3 results from the requirement that the degree of dissociation be $<1\%$ so that $[H^+] < 0.01 C_a$. Thus, $\sqrt{C_a K_a} < 10^{-2} C_a$ or, squaring both sides, cancelling C_a , and taking $-\log$ s: $pK_a > pC_a + 4.0$. These two inequalities define the boundaries for region 2. Thus, for the region 2 equation to be valid, the acid must have $C_a K_a > 10^{-12}$ and $K_a < 10^{-4} C_a$. For instance, if $C_a = 0.1$ M, then K_a must be between 10^{-5} and 10^{-11} . The conditions for the equivalent weak base, where the equation is $[OH^-] = \sqrt{C_b K_b}$, are similar: $C_b K_b > 10^{-12}$ and $K_b < 10^{-4} C_b$.

The equations for the straight lines of the figure that apply to $C_a > 10^{-4}$ M are given in Table 2. These expressions can be used to determine if a particular simplified equation is valid for values of C_a and K_a and, thus, could be useful when creating homework or exam problems to ensure that the selected simplified equation can be used. For instance, if we want to consider an acid with $K_a = 2.6 \times 10^{-11}$ (which can fall in either region 2 or 6), the equation separating these two

regions is $C_a K_a = 10^{-12}$ so that $C_a = 0.0385$ M. If we choose a value of C_a slightly greater than 0.0385 M, then the equation for region 2 will apply, but, if we choose a value of C_a slightly less than 0.0385 M, then the equation for region 6 will apply.

The curve in the figure that separates regions 4-3-2 from regions 5-1-6 corresponds to $\text{pH} = 6.00$ because the water equilibrium must be included in the region to the left of regions 4-3-2. The equation⁸ for the curve is:

$$C_a K_a = 10^{-12} + 10^{-6} K_a \quad (1)$$

Similarly, the curve that separates 5-1-6 from region 7 corresponds to $\text{pH} = 7.00$ because an acid at these low concentrations and/or with these very small K_a values has negligible effect on the pH to the left of regions 5-1-6. The equation⁹ for this curve is:

$$C_a K_a = 10^{-9} (K_a + 10^{-7}) \quad (2)$$

pH at Start and End of Titration of an Acid

The Henderson-Hasselbalch equation is often used in texts to calculate the pH in the buffer region of the titration of a weak acid with a strong base, as will be discussed in article VI. Students sometimes ask if there is an equivalent equation that can be used at the start or at the end of the titration. The answer is yes. The start of the titration is simply a C_a M solution of a weak acid, and the equation that most texts use for calculation of the hydrogen-ion concentration of a solution of a weak acid is the expression for region 2: $[\text{H}^+] = \sqrt{C_a K_a}$, which implies assumptions a and b. Taking the negative log of this equation results in:

$$\text{pH} = \frac{1}{2} (\text{p}C_a + \text{p}K_a) \quad (3)$$

for the pH at the start of the titration.

The equivalence point in the titration of a weak acid HA with a strong base is a C_b M solution of the conjugate base A^-

with a $K_b = K_w/K_a$. As discussed above, if it is assumed that there is less than 1% hydrolysis of A^- , and, if the water equilibrium can be neglected, which is what most texts assume, then $[\text{OH}^-] = \sqrt{C_b K_b}$. Taking the negative log of this equation results in:

$$\text{pOH} = \frac{1}{2} (\text{p}C_b + \text{p}K_b) \quad (4)$$

for the pOH at the equivalence point.

Because $\text{pOH} = \text{p}K_w - \text{pH}$ and because $\text{p}K_b = \text{p}K_w - \text{p}K_a$, eq 4 can be converted to:

$$\text{pH} = \frac{1}{2} (\text{p}K_w + \text{p}K_a - \text{p}C_b) \quad (5)$$

for the pH at the equivalence point.

As was done in the figure, eqs 3-5 can be converted for use in the titration of a base by substituting b for a, a for b, pH for pOH, and pOH for pH.

If a C_a M H_nX polyprotic weak acid is titrated with NaOH, eq 3 will apply¹⁰ to the start of the titration with K_{1a} substituted for K_a . For the same titration of H_nX , eqs 4 and 5 will apply¹⁰ to the last equivalence point (which is a solution of C_b M Na_nX) with K_{nb} substituted for K_a and $K_{nb} = K_w/K_{na}$ substituted for K_b .

⁸ The equation is derived as follows: A C_a M solution of HA ionizes to the extent of a moles/liter producing a moles/liter of H^+ and the same amount of A^- . When $\text{pH} = 6.000$, we can neglect the water equilibrium so that $[\text{H}^+] = 1.00 \times 10^{-6} \text{ M} = a = [\text{A}^-]$. Thus, $K_a = (10^{-6})(10^{-6})/(C_a - 10^{-6})$. Rearrangement leads to eq 1.

⁹ The equation can be derived in a manner similar to that described in footnote 8. In this case, $a = [\text{A}^-] = 1.00 \times 10^{-9} \text{ M}$, but, because the H^+ from the acid can be neglected, $[\text{H}^+] = 1.00 \times 10^{-7} \text{ M}$ so that $K_a = (10^{-7})(10^{-9})/(C_a - 10^{-9})$. Rearrangement leads to eq 2.

¹⁰ In addition to the assumptions of less than 1% reaction and neglect of the water equilibrium, there is another assumption, i.e., that K_1/K_2 is greater than about 10^4 for the start of the titration and that K_{n-1}/K_n is greater than about 10^4 for the last equivalence point.

Pedagogical Symposium on Graph Theory in Chemistry

A special pedagogical symposium on graph theory in chemistry will be held August 27, 1991, at the 202nd National ACS Meeting in New York City. The symposium will have a unique tutorial format so teachers may want to plan to attend the entire day's sessions. The morning session will be conducted by M. Randic and N. Trinajstić and will cover the Graph Theoretical Approach to Structure/Property/Activity Relationships. It will start with a review of fundamentals followed by an hour in which participants are given four representative problems to solve. The last hour will be a discussion of the solutions to those problems. The afternoon session will cover the Graph Theoretical Approach to Conjugated Molecular Systems and will be conducted by J. R. Dias and D. J. Klein. The format will parallel the morning session. Participants will receive handouts at both sessions.