

Advances in Acid-Base Gran Plot Methodology

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A number of articles¹ have appeared in *this Journal* describing the use of Gran plots for finding the equivalence point of potentiometric titration experiments. A recent paper by Bolani² surveys this literature, describes the advantages of Gran plots compared to alternative methods, derives the relevant equations for pH potentiometric titrations of strong and weak acid analytes by strong-base titrant, and demonstrates the applicability of these methods to the analysis of a solution containing a mixture of a strong and weak acid. We wish to show here that by suitable modifications in the data analysis, Gran plot methodology can be extended to acidic or basic analyte solutions that would be difficult to treat by the conventional equations. In particular we will show how to analyze (1) weak acids or bases that are stronger than can be treated by the conventional equations, (2) extremely weak acids or bases, (3) diprotic acids or bases for which the successive pK values are quite close, and (4) a mixed strong and weak acid (or base) in circumstances that would be difficult to treat by the method used by Bolani². By the phrase "difficult to treat" we mean that if pH vs. volume data are plotted in the form dictated by the conventional Gran plot equations, the line would have such severe curvature that the analyst would not see a sufficiently straight segment to be able to draw the requisite straight line to the horizontal axis. The methods that we show here effectively straighten out curvature due to certain predictable effects. However, curvature that results from extraneous factors will interfere with these methods. For example, Gran plot theory (or, indeed, any other titration method) assumes that

- the analyte and titrant solutions are free of extraneous reactive acids or bases,
- the titrant solution has a fixed concentration, that is, is well mixed,
- the total moles of dissolved analyte is invariant during the course of the titration,
- equilibrium is reached in each titration solution,
- solution equilibria are represented by equilibrium constants that are invariant during the course of the titration,
- activity coefficients and electrode junction potentials are invariant during the titration, and
- the pH meter response is Nernstian.

These assumptions will be invalid in a titration in which

- the analyte or titrant has carbonate contamination,
- the analyte precipitates or evaporates during the titration,
- pH measurements are recorded before the solution and electrodes have equilibrated both thermally and chemically,
- the temperature drifts during the course of the titration,
- the ionic strength of the titration solution changes significantly during the course of the titration, and
- the slope of the pH meter response curve is improperly calibrated.

We will assume that experimental conditions are properly established and maintained to avoid extraneous curvature from these types of problems. In addition we can avoid the inclusion of activity coefficients in the equations by writing conditional equilibrium expressions in terms of molar con-

centrations of solutes dissolved in a specific electrolyte medium chosen to maintain constant ionic strength. This requires that $[H^+]$ also be measured under the same conditions so that the pH meter should be calibrated to read pH as $-\log [H^+]$ rather than $-\log a_{H^+}$. This is done most conveniently by calibrating the meter using solutions with known $[H^+]$ prepared in the electrolyte medium. Standardized HCl or NaOH reagent, for example, rather than commercial buffer solutions should be used for this purpose.

In the following development we take the analyte to be acidic and the titrant to be a strong base. However, with simple modifications the same results apply to the opposite situation, that is, where the analyte is basic and the titrant is a strong acid. These modifications are summarized in a final section. The notation is as follows: F_t is the known molar concentration of titrant M^+OH^- , v is the variable milliliter volume of titrant delivered to the analyte solution, v^* is the unknown milliliter volume of titrant required to reach the first equivalence point, V_0 is the known initial milliliter volume of analyte solution (before addition of any titrant) and $V = V_0 + v$ is the variable milliliter volume of titrant solution. Consequently, the unknown millimolar quantity of analyte is v^*F_t and the analyte solution has a variable formal (molar) concentration v^*F_t/V . $K_w = [H^+][OH^-]$ is the conditional autoprotolysis constant, measured if necessary in the same electrolyte medium used to maintain constant ionic strength during the acid-base titration.

Case 1: Moderately Weak Acid Analyte Titrated with Strong Base

Curve A of Figure 1 shows the Gran plot of a computer-simulated titration of a moderately weak monoprotic acid HA having $pK_a = 2.00$. Computer simulation is useful to avoid interfering curvature effects from any of the other experimental sources listed above. The simulation uses 0.0100 M M^+OH^- to titrate 50.0 mL of 0.250 mol of this acid and the resulting pH vs. v data are plotted as $v10^{-pH}$ vs. v as is appropriate for a conventional Gran plot of a weak acid. We see, however, that curve A has no apparent straight

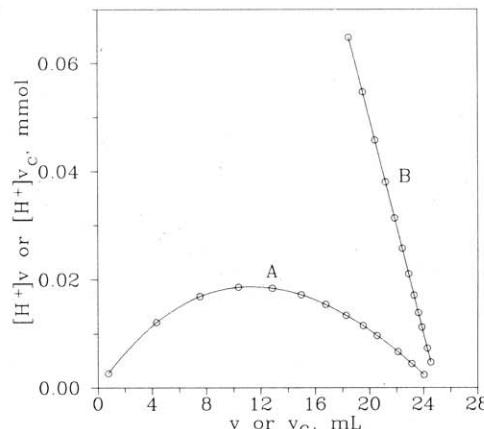


Figure 1. Curve A is a conventional Gran plot of a moderately weak acid ($pK_a = 2.00$) titration. Line B is a modified Gran plot according to eqs 4 and 5.

¹ Gran, G. *Analyst* 1952, 77, 661.

² Bolani, J. A. *J. Chem. Educ.* 1986, 63, 724.

³ Schwartz, L. M.; Gelb, R. I. *Anal. Chem.* 1978, 50, 1571.

segment. Because the simulation does not include random error in either the pH or volume readings, it seems feasible, nevertheless, to estimate v^* by extrapolating curve A to its intersection with the v axis. However, in a real experimental situation the data points will be scattered away from a smooth curve making this intersection difficult to estimate. The curvature in this Gran plot results because there is an assumption in the conventional Gran plot theory for weak acids that $[H^+]$ is a negligible quantity. This assumption is invalid during most of the titration in this case. We will see now that because this assumption is not a necessary one, the Gran plot theory can be modified to avoid curvature from this source. The electroneutrality condition applied to the titration solution is

$$[H^+] + [M^+] = [A^-] + [OH^-] \quad (1)$$

Conventional Gran plot theory omits both $[H^+]$ and $[OH^-]$ from this equation. But when titrating a moderately weak acid, we often find that $[H^+]$ is a substantial quantity and so in these circumstances only $[OH^-]$ may be neglected. The derivation continues by writing the conservation equation for the analyte

$$v^*F_t/V = [HA] + [A^-] \quad (2)$$

and the conditional equilibrium expression for the acid HA

$$K_a = [H^+][A^-]/[HA] \quad (3)$$

After substituting F_tV/V for $[M^+]$, $[A^-]$ in eq 1 becomes $F_tV/V + [H^+]$ and after substituting this result into eq 2, $[HA]$ becomes $(v^* - v)F_t/V - [H^+]$. Using both these results in eq 3 leads to

$$[H^+](v + V[H^+]/F_t) = K_a[v^* - (v + V[H^+]/F_t)] \quad (4)$$

Equation 4 is the modified Gran plot equation we are seeking. This equation implies that if the conventional weak acid Gran plot of $v[H^+]$ vs. v is modified by plotting instead a corrected $v_c[H^+]$ vs. v_c , where

$$v_c = v + V[H^+]/F_t \quad (5)$$

any curvature due to significant $[H^+]$ in eq 1 will be straightened out. Curve B in Figure 1 is such a plot.

Case 2: Very Weak Acid Analyte Titrated with Strong Base

Figure 2 Curve A is a conventional Gran plot of a simulated titration of 50.0 mL of 0.0250 mol of weak acid HA having conditional $pK_a = 9.00$ using 1.00 mM M^+OH^- . The simulation uses a conditional $pK_w = 13.80$ in its equations. In this case the curvature, which makes the equivalence point impossible to estimate, is due to significant OH^- concentration

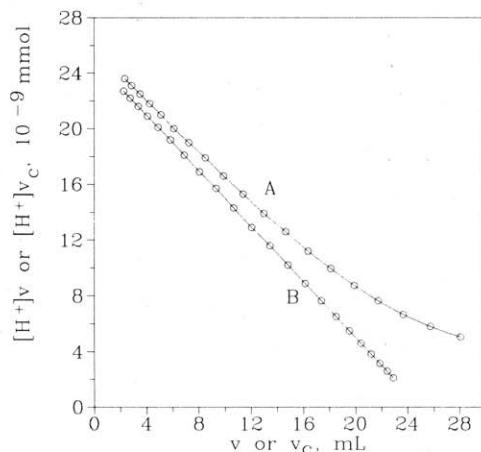


Figure 2. Curve A is a conventional Gran plot of very weak acid ($pK_a = 9.00$) titration. Line B is a modified Gran plot according to eqs 6 and 7.

that was not accounted for in the Gran plot theory. In order to deal with titrations of this nature, we retain the $[OH^-]$ term but not the $[H^+]$ term in eq 1 and proceed as before solving for $[A^-] = vF_t/V - [OH^-]$ and $[HA] = (v^* - v)F_t/V + [OH^-]$. Substituting these concentrations into eq 3 leads to

$$[H^+](v - V[OH^-]/F_t) = K_a[v^* - (v - V[OH^-]/F_t)] \quad (6)$$

Thus if we here define the corrected volume v_c by

$$v_c = v - V[OH^-]/F_t = v - VK_w/([H^+]F_t) \quad (7)$$

and plot $[H^+]v_c$ vs. v_c we straighten out the Gran plot curvature due to free $[OH^-]$ in the titration solution. Curve B in Figure 2 is such a plot calculated with the known $pK_w = 13.80$. In cases where the value of K_w in a particular electrolyte medium is not known, it may be estimated using the titration data or by an independent experiment. Both methods are explained in a later section.

Case 3: Diprotic Acid Analyte Having Closely Spaced K_a Values Titrated with Strong Base

Curve A of Figure 3 is a conventional monoprotic Gran plot calculated from the simulated titration data of 50.0 mL of 0.250 mol of a diprotic acid having $pK_{a1} = 4.00$ and $pK_{a2} = 5.00$ with 0.0100 M M^+OH^- . The observed curvature here results from two inadequacies in the conventional Gran plot theory, the failure of the theory to account for free H^+ ions and the reaction of titrant with both HA^- and H_2A in the same region. The following derivation leads to a modified theory that accounts for a second protonation. The electroneutrality condition corresponding to eq 1 now includes a term for the dianion

$$[H^+] + vF_t/V = [HA^-] + 2[A^{2-}] + [OH^-] \quad (8)$$

Because in any particular titration region $[H^+]$ or $[OH^-]$ may be significant, we retain both terms. The conservation equation for the analyte also has a term for the dianion

$$v^*F_t/V = [H_2A] + [HA^-] + [A^{2-}] \quad (9)$$

where v^* is understood to be the first equivalence point volume so that v^*F_t represents millimoles of analyte. The two acid dissociation equilibria in terms of condition constants are

$$K_1 = [H^+][HA^-]/[H_2A] \quad (10)$$

and

$$K_2 = [H^+][A^{2-}]/[HA^-] \quad (11)$$

The algebraic combination of these equations can be done several ways. One of these is to solve eq 8 for $[HA^-]$: subtract

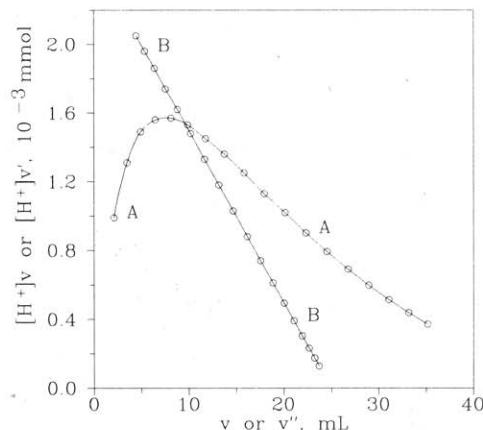


Figure 3. Curve A is a conventional Gran plot of a dibasic acid ($pK_{a1} = 4.00$, $pK_{a2} = 5.00$) titration. Line B is a modified Gran plot according to eqs 15, 16, and 17.

$[\text{OH}^-]$, substitute $[\text{A}^{2-}]$ from eq 11, and factor $[\text{HA}^-]$ from the right-hand side. Also solve eq 9 for $[\text{HA}^-]$: substitute $[\text{H}_2\text{A}]$ from eq 10, substitute $[\text{A}^{2-}]$ from eq 11, and factor $[\text{HA}^-]$ from the right-hand side. Equating these two expressions for $[\text{HA}^-]$ and rearranging will yield the intermediate result

$$(v + h)\{[\text{H}^+] + K_1(1 + r)\} = K_1v^*(1 + 2r) \quad (12)$$

where, in order to condense the notation, we have defined

$$h = \{[\text{H}^+] - K_w/[\text{H}^+]\}V/F \quad (13)$$

and

$$r = K_2/[\text{H}^+] \quad (14)$$

The derivation continues by expanding the left-hand side of eq 12, dividing by $(1 + 2r)$ and collecting all terms which are multiplied by K_1 on the right-hand side. The result is

$$[\text{H}^+](v + h)/(1 + 2r) = K_1\{v^* - (v + h)(1 + r)/(1 + 2r)\} \quad (15)$$

which is the modified Gran plot equation we seek. As in Cases 1 and 2 above, we define a corrected volume to replace v in the conventional Gran plot formulation, except in this case there are different corrections for the two axes. The modified Gran plot is of the form $[\text{H}^+]v_{c'} \text{ vs. } v_{c'}$, where for the ordinate axis the corrected volume is

$$v_{c'} = (v + h)/(1 + 2r) \quad (16)$$

and for the abscissa axis the corrected volume is

$$v_{c''} = (v + h)(1 + r)/(1 + 2r) \quad (17)$$

Curve B of Figure 3 is such a plot. We have used the known constant $pK_2 = 5.00$ in calculating r of eq 14. Also, since the pH measurements in this example did not exceed 5.00, $[\text{OH}^-]$ was never a significant quantity and could be omitted from the calculation by setting K_w to zero in h of eq 13. If K_2 is not known, it can be estimated as described in the next section.

Estimating an Extra Parameter

When we fit a straight line to plotted data, we are essentially finding values for two parameters. In a weak acid (or weak base) Gran plot, the two parameters are the slope of the line, which estimates the dissociation constant, and the intersection of the line with the horizontal axis, which estimates the equivalence point volume. As long as experimental conditions conform to the assumptions of conventional Gran plot theory, these are the only two unknown parameters. However, we have seen in Cases 2 and 3 above that generalization of Gran plot theory to include analytes that are very weakly dissociating or diprotic requires the incorporation of a third parameter. For very weakly dissociating acids the third parameter is the autoprotolysis constant K_w , and for diprotic acids the third parameter is the secondary dissociation constant K_2 , assuming that K_w is known or is irrelevant. If these additional parameters are known quantities, as was assumed in constructing the modified Gran plots in Figures 2 and 3, only two unknown parameters remain in each case and so straight-line analyses serve to estimate them. When the additional parameters are unknown, the analyst must resort to more sophisticated data analysis procedures because the unknown parameters enter into the Gran plot equations in a nonlinear way. One such data analysis procedure is by nonlinear regression, which has been described extensively in the literature of analytical chemistry³, for example. However, nonlinear regression is computer-intensive in such a way that it is easy to feed experimental data values into a packaged software program and to receive output values of the unknown parameters without understanding how the program operates, whether the experiment corresponds properly to the programmed model equations,

and whether the output values are at all reasonable. Many find this type of computer analysis inappropriate for undergraduate instruction and prefer the more visual Gran plotting where graphs are typically constructed point by point and examined by eye for an appropriate straight segment. While it is possible to program a computer to use regression procedures to fit a Gran plot line complicated by nonlinear parameters, we shall describe an approach here that is closer in nature to traditional Gran plot methodology.

The modified Gran plots described above are such that, if a set of titration data plots as a curve in a conventional Gran plot, then the modified plot will straighten out the curve provided that the analyst properly identifies the source of the curvature and properly calculates the corrected coordinate values. If the analyst correctly identifies the source of curvature but incorrectly calculates the coordinates, the modified plot will remain curved, more or less corresponding to the errors in the coordinates. A simplistic but effective way of estimating a value for a third parameter is to construct a series of Gran plots using different values for this parameter and seek by trial and error to find a value that completely eliminates the curvature. Clearly, this would be rather tedious for a single student working with a hand calculator and a stack of graph paper, but a resourceful instructor should be able to devise any number of ways of reducing the tedium, especially if some kind of programmable calculator or computer is available for the students to use. One suggestion is to use "spreadsheet" software which runs on most personal computers. The student should create one column of cells with the fixed titration quantities such as V_0 , F_t , and pK_w , a second column of cells with v data, a third column with pH data, a fourth column with formulas to calculate the modified Gran plot abscissa values, and a fifth column to calculate the modified ordinate values. If the spreadsheet can draw graphs on the screen, an "XY" graph can be set up using the fourth column values as "X" vs. the fifth column values as "Y". If, say, pK_w is the third unknown parameter, the student simply changes the value of pK_w on the spreadsheet and the program automatically recalculates the modified Gran plot. By observing the changes in curvature on the screen, the student can zero in on the proper pK_w value in a few minutes. Figure 4 shows how the curvature of the modified Gran plot for case 2 varies with pK_w in eq 7 ranging from 13.70 to 13.90 and apparently disappears when the correct $pK_w = 13.80$ is tried.

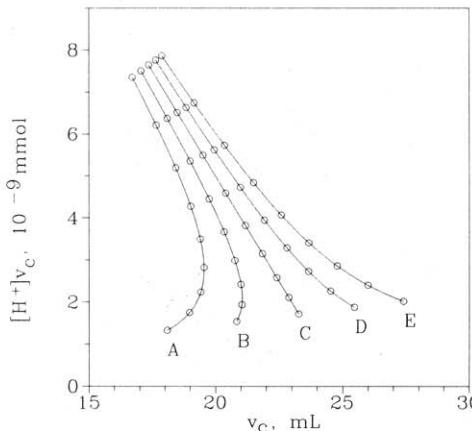


Figure 4. A series of modified Gran plots of a very weak acid ($pK_a = 9.00$) titration using different pK_w values in eq 7. Curves A-E use trial pK_w values of 13.70, 13.75, 13.80, 13.85, 13.90, respectively. $pK_w = 13.80$ is the correct value.

Case 4: Mixed Strong Acid and Monoprotic Weak Acid Titrated with Strong Base

Bolani² shows how this type of mixture is analyzed using two Gran plots, one at the start of the titration to determine the amount of strong acid in the mixture and another later in the titration when the titrant reacts exclusively with the weak acid. This procedure is useful only if there is no overlap region in which an aliquot of titrant reacts partially with each constituent acid. This overlap will occur when the mole ratio of strong to weak acid is low or when the weak acid has a small pK_a value such that its degree of dissociation is significant even in the presence of H^+ from unreacted strong acid. In this section we see that this type of mixture can be analyzed using a modified Gran plot procedure similar to those described above. If v_{X^*} and v_{A^*} are the equivalence point milliliter volumes of base required to neutralize the strong acid H^+X^- and weak acid HA, respectively, and K_a is the weak acid conditional dissociation constant, a modified Gran plot equation can be derived in the form

$$[H^+]v_{cm} = K_a(v_{A^*} - v_{cm}) \quad (18)$$

where v_{cm} is a corrected volume given by

$$v_{cm} = v - v_{X^*} + h \quad (19)$$

Here h of eq 13 accounts for free H^+ from dissociated HA or OH^- from dissociation of H_2O in case HA is very weak and v_{X^*} accounts for any residual unreacted H^+ from the strong acid. If h is negligible and if v_{X^*} can be found independently, eq 18 reduces to Bolani's eq 7 as modified for use in his Figure 2. Here we assume that v_{X^*} cannot be found independently and this quantity represents a third unknown parameter in addition to the unknown parameters v_{A^*} and K_a . In order to estimate all three parameters we proceed, as described above, to construct a series of modified Gran plots with different estimates for v_{X^*} seeking that value for v_{X^*} which straightens out the curvature near the start of the titration. Figure 5 shows the results of such a search. The titration data is taken from a simulated titration of 50.0 mL of a mixture containing 0.250 mol of weak acid ($pK_a = 4.74$) and 0.0200 mol of HCl using 0.0100 M M^+OH^- . The five plots shown in Figure 5 use v_{X^*} values in eqs 18 and 19 ranging from 1.00 mL to 3.00 mL. We see that curve C which uses the correct value of $v_{X^*} = 2.00$ mL has no apparent curvature.

If the weak acid in the mixture had a very large pK_a such that free OH^- is a significant component in the titration solution before v_{A^*} is reached and if K_w were unknown, the modified Gran plot eqs 18 and 19 would involve four unknown parameters, K_a , v_{X^*} , v_{A^*} , and K_w . One way to proceed in this case would be to search for v_{X^*} by observing the effect of trial values on curvature near the beginning of the titration as shown in Figure 5 and then to search for K_w by observing the effect of trial values on curvature later in the titration as shown in Figure 4. A different approach would be to perform an independent experiment to measure K_w . For example, one could titrate a sample of electrolyte medium containing no analyte with strong base and record pH vs. v values. Knowing the initial sample volume V_0 and the concentration of base, one can calculate $[OH^-]$ and then pOH values. The sum pH + pOH is thus an estimate of pK_w in each titration solution. If the solutions are carbonate-free and if the pH meter performs reliably at high pH, these pK_w values should vary only due to random error, and so a mean

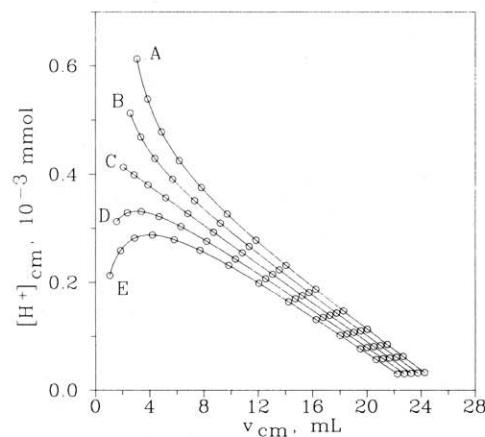


Figure 5. A series of modified Gran plots of a mixed strong and weak acid titration using different v_{X^*} values in eqs 18 and 19. Curves A-E use trial v_{X^*} values of 1.00, 1.50, 2.00, 2.50, and 3.00 mL, respectively. $v_{X^*} = 2.00$ mL is the correct value.

would be an appropriate estimate of pK_w . This type of independent estimation of pK_w is the most convenient approach when the analyte is a very weak diprotic acid. In such a case, curvature in the modified Gran plot due to free OH^- and to reaction of base with HA^- both occur late in the titration so that a trial-and-error graphical approach would be difficult.

Summary of Equations for Basic Analytes Titrated with Strong Acid

For moderately weak or very weak monoprotic basic analytes having conditional basic dissociation constant K_b , the modified Gran plot equation is

$$(v + h_b)/[H^+] = (K_b/K_w)(v^* - v - h_b) \quad (20)$$

where

$$h_b = \{(K_w/[H^+]) - [H^+]\}V/F_t \quad (20)$$

For diprotic basic analytes having conditional basic dissociation constants K_{b1} and K_{b2} , the modified Gran plot equation is

$$[H^+]^{-1}(v + h_b)(1 + 2r_b) = (K_{b1}/K_w)\{v^* - (v + h_b)(1 + r_b)/(1 + 2r_b)\}$$

where

$$r_b = K_{b2}[H^+]/K_w$$

For a mixture of strong base M^+OH^- and weak base BOH having conditional dissociation constant K_b , the modified Gran plot equation is

$$v_{cm}/[H^+] = (K_b/K_w)(v_B^* - v_{cm})$$

where

$$v_{cm} = v - v_M^* + h_b$$

Here v_B^* and v_M^* are the equivalence point volumes for the weak and strong base analytes, respectively. The term $K_w/[H^+]$ in eq 20 corrects for the presence of free OH^- when the weak base is only moderately weak and the term $-[H^+]$ corrects for free H^+ when the base is very weak. Only one of these terms is needed in any particular case.