

Potentiometric Titrations

Using Gran Plots

A textbook omission

A number of recent textbooks (1-10) of analytical chemistry discuss potentiometric acid-base titrations, but none of these mentions Gran's graphical method (11) of end point determination. Gran's method seems to us to be the best yet suggested, and has been successfully used for many years in Stockholm and elsewhere for the precise analysis of acids and bases.

The method is very simple. A volume V of acid of initial concentration H is titrated with a volume v of strong base of concentration B in the galvanic cell (I)



The potential of cell (I) is given by

$$E = E_0' - \frac{RT}{F} \ln [H^+] \gamma_H + E_j \quad (1)$$

where E_0' includes the potential of the reference half-cell and the standard potential of the probe half-cell, and E_j is the liquid junction potential. A cell of type (I) is also used in commercial pH meters, which, when suitably calibrated, give direct readings of pH.

Titration of Strong Acid with Strong Base

For any value of v before the equivalence point v_e ,

$$[H^+] = \frac{VH - vB}{V + v} = \frac{VH(v_e - v)}{v_e(V + v)} = \frac{B(v_e - v)}{V + v} \quad (2)$$

If pH is measured directly, we may make use of a function defined as

$$\phi = (V + v)[H^+] \gamma_H = (V + v)10^{-pH} \quad (3)$$

From equations (2) and (3)

$$\phi = (v_e - v)B\gamma_H \quad (4)$$

If, instead of pH, the potential E is determined, we may

use a similar function defined by

$$\psi = (V + v)10^{-EF/2.303RT} \quad (5)$$

From equations (1), (2), and (5)

$$\psi = 10^{-(E_0' + E_j)F/2.303RT}(v_e - v)B\gamma_H \quad (6)$$

After the equivalence point,

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{K_w(V + v)}{B(v - v_e)} \quad (7)$$

where K_w is the stoichiometric ionic product of water. For use in the alkaline range, functions analogous to ϕ and ψ may be defined in terms of the experimental quantities pH and E respectively, viz.

$$\phi' = (V + v)/[H^+] \gamma_H = (V + v)10^{pH} \quad (8)$$

and

$$\psi' = (V + v)10^{EF/2.303RT} \quad (9)$$

From equations (7) and (8)

$$\phi' = (v - v_e)B/K_w\gamma_H \quad (10)$$

and from equations (1), (7), and (9)

$$\psi' = (v - v_e)B 10^{(E_0' + E_j)F/2.303RT}/K_w\gamma_H \quad (11)$$

If γ_H , E_j , and K_w remain constant throughout the titration, then from equations (4) and (10) the quantities ϕ and ϕ' are linear functions of v , such that $\phi(v)$, $\phi'(v)$ and the abscissa all intersect at the point 0, v_e . Similarly, equations (6) and (11) show that, for constant γ_H , E_j , and K_w , the functions $\psi(v)$ and $\psi'(v)$ are also linear, and both functions again cut the abscissa at the point 0, v_e . Thus the value of v_e may be obtained by plotting any one of the quantities ϕ , ϕ' , ψ , or ψ' against v , and extrapolating the line obtained to cut the abscissa at the point $v = v_e$.

The method may be illustrated by the following

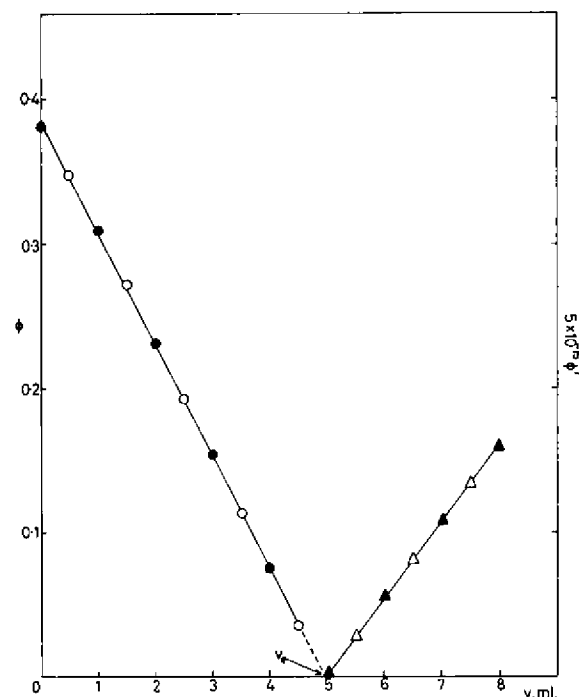


Figure 1. Gran plots $\phi(v)$ and $\phi'(v)$ for the titration of a strong acid with a strong base. Data for the filled points are given in the table.

example which is suitable for inclusion in an undergraduate course on pH. A mixture of 5 ml 0.1 M HCl and 50 ml water was titrated with ~ 0.1 M NaOH, using a cell containing glass, and saturated calomel, electrodes. The calculations¹ are shown in the table, and the resulting points plotted as full circles in Figure 1.

Titration of a Mixture of 5.00 ml 0.1000 M HCl + 50.0 ml H₂O with ~ 0.1 M NaOH Using a Commercial pH Meter

v	$V + v$	'pH'	- 'pH'	$10^{-\text{'pH'}}$	ϕ
0	55.0	2.160	3.840	6.918×10^{-3}	0.831
1.00	56.0	2.257	3.743	5.534×10^{-3}	0.310
2.00	57.0	2.393	3.607	4.050×10^{-3}	0.231
3.00	58.0	2.575	3.425	2.661×10^{-3}	0.154
4.00	59.0	2.897	3.103	1.268×10^{-3}	0.075
5.00	60.0	9.828	...	6.73×10^2	0.002
6.00	61.0	11.268	...	185.2×10^2	0.056
7.00	62.0	11.549	...	354.0×10^2	0.109

From Figure 1, $v_e = 4.97$ ml, whence $B = 0.1006$ M.

Deviations from linearity may be due to one or more of the following factors: (1) Curvature of any of the Gran plots at values of v remote from v_e suggests that the quantity $E_j' = E_j - RTF^{-1} \ln \gamma_H$ is not negligible at the extreme values of $[H^+]$ or $[OH^-]$ used. If the plots are linear nearer the equivalence point, the value of v_e must be obtained from this region alone (Fig. 2). For the junction H₂O/Sat:KCl, linear functions are

¹ From equations (4), (6), (10), and (11), the point of intersection 0, v_e of the plots for acid solution either with those for alkaline solution or with the abscissa, is unaffected by changes in the slopes of the lines. The various quantities ψ , ϕ , ψ' and ϕ' may therefore be multiplied by any constants which make plotting more convenient. The terms $10^{-EF/2.303RT}$ and 10^{-pH} may, if required, be replaced by $10^{(C-E)F/2.303RT}$ and $10^{(C-pH)}$ where C is any constant. A value of 'pH' = pH - C may be obtained merely by using an unstandardized commercial pH meter.

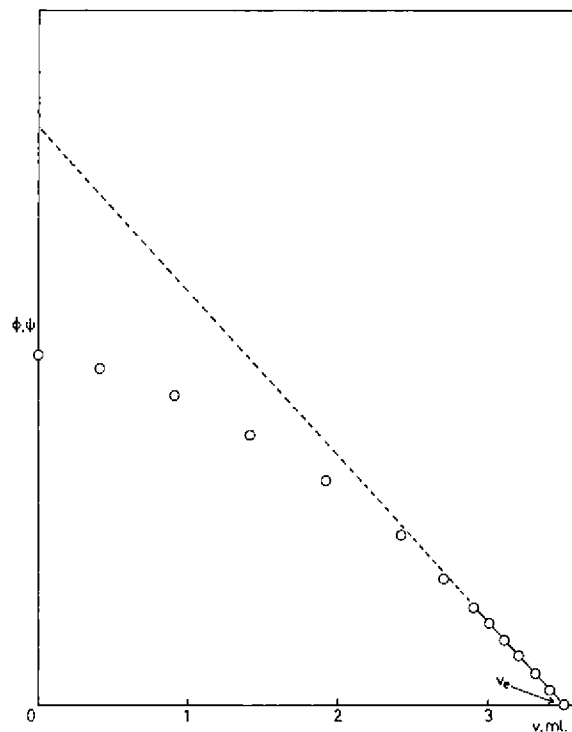


Figure 2. Gran plot $\phi(v)$ or $\psi(v)$ for a system in which $E_j' = (E_j - RTF^{-1} \ln \gamma_H)$ varies with $[H^+]$. 35.0 ml of 0.210 M HNO₃ was titrated with ~ 2 M LiOH in 50% v/v aqueous dioxane containing 0.5 M (Li⁺, H⁺) NO₃⁻.

obtained for $[H^+] \leq 8 \times 10^{-3}$ M. A method for calculating E_j' from Gran plots has been described elsewhere (12) together with a similar method for obtaining γ_{\pm} for HCl from data obtained during titration of HCl in a Harned type cell without liquid junction. (2) If the acid solution contains a metal ion which starts to

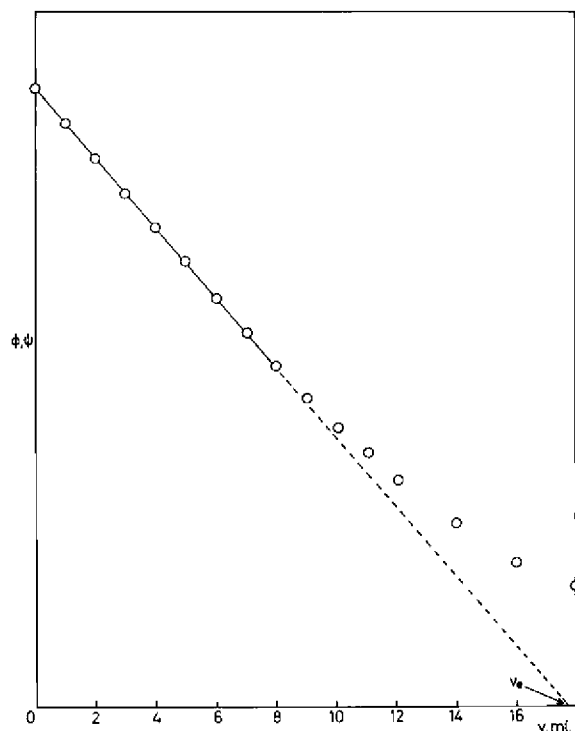


Figure 3. Gran plot $\phi(v)$ or $\psi(v)$ for the standardization of a strong acid containing hydrolyzable metal ions. 40.0 ml of ~ 0.01 M HClO₄ containing ~ 50 mM VO(ClO₄)₂ was titrated with 0.02118 M NaHCO₃ in a 3 M (Na-ClO₄) medium.

hydrolyze at a hydrogen ion concentration in the region $H > [H^+] > 10^{-4} M$ the functions $\psi(v)$ and $\phi(v)$ may become curved as the acidity is decreased. If the plots are linear at the highest acidities used, the equivalence point of the strong acid may again be determined by extrapolation to $\psi = 0$ or $\phi = 0$ (Fig. 3). (3) If the strong base is contaminated with carbonate, the functions $\phi'(v)$ and $\psi'(v)$ are curved in the region of v_e .

The value of $v_e = VH/B$ (where $B = ([OH^-] + 2[CO_3^{2-}])$ is the total concentration of base) may be found using only measurements in the acid region $v < v_e$ (Fig. 4). If the functions $\phi'(v)$ and $\psi'(v)$ are linear over an appreciable range of v , they may be extrapolated to cut the abscissa at the point $v_e' = VH/B'$ (where B' is the total concentration of hydroxyl ions in the solution of base). An estimate of the carbonate ion concentration may therefore be obtained.

Titration of Weak Acid with Strong Base

If an acid HA is not fully dissociated in solution, the free hydrogen ion concentration is no longer given by equation (2) but by the relationship

$$[H^+] = K_a[HA]/[A^-] \quad (12)$$

where K_a is the stoichiometric acid dissociation constant of HA. If the titrant is the monacidic base MOH, then

$$[A^-] = [M^+] + [H^+] - [OH^-] = \frac{vB}{V+v} + [H^+] - [OH^-] \quad (13)$$

and

$$[HA] = C_A - [A^-] = \frac{VH - vB}{V+v} - [H^+] + [OH^-] \quad (14)$$

where C_A is the total concentration of HA in the solution. If

$$\frac{vB}{V+v} \gg [H^+] - [OH^-] \quad (15)$$

and

$$\frac{VH - vB}{V+v} \gg [H^+] - [OH^-] \quad (16)$$

then from equations (12), (13), and (14)

$$[H^+] = \frac{K_a(VH - vB)}{vB} = \frac{K_a(v_e - v)}{v} \quad (17)$$

By analogy with equations (3), (4), (5), and (6) we may define the functions²

$$\tau = v[H^+]\gamma_H = v10^{-pH} = K_a(v_e - v)\gamma_H \quad (18)$$

and

$$\theta = v10^{-EP/2.303RT} = K_a(v_e - v)\gamma_H 10^{-(E_0' + E_j)F/2.303RT} \quad (19)$$

After the end point, $v > v_e$ and equations (7) to (11) are again valid.

Since, for a weak acid, $[H^+]$ is low even at the beginning of a titration, E_j will probably be negligible. If, moreover, the initial solution of HA is not too concentrated, the ionic strength will not vary grossly throughout the titration, and the terms K_a , K_w , and γ_H will remain approximately constant. Then τ and θ

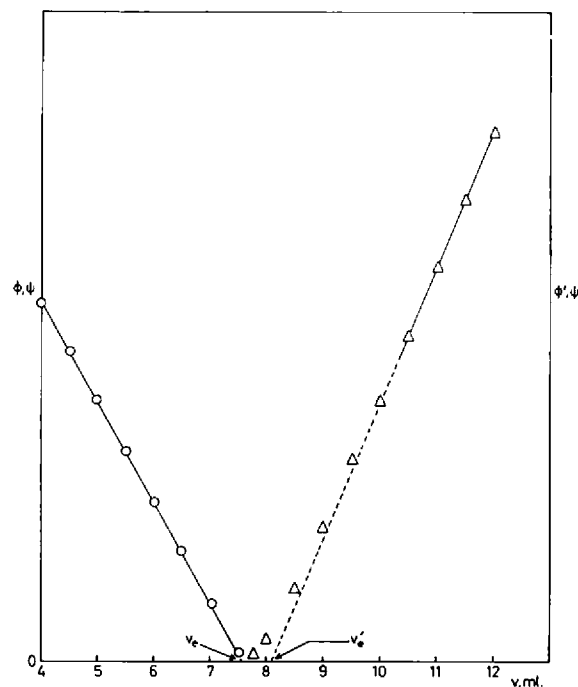


Figure 4. Portions of Gran plots $\phi(v)$ or $\psi(v)$ and $\phi'(v)$ or $\psi'(v)$ for the titration of a strong acid with a solution containing both carbonate and hydroxide.

are linear functions of v , such that $\tau(v)$ intersects $\phi'(v)$ and $\theta(v)$ intersects $\psi'(v)$ at the point 0, v_e (Fig. 5).

Deviations from linearity may be due to one or more of the following factors: (1) At the beginning of the titration, condition (15) may not be fulfilled, especially if the acid is only moderately weak. The value of v_e must then be found using only that part of the function $\tau(v)$ or $\theta(v)$ which is found to be linear (Fig. 5). (2) As v approaches v_e , condition (16) may not be fulfilled if the

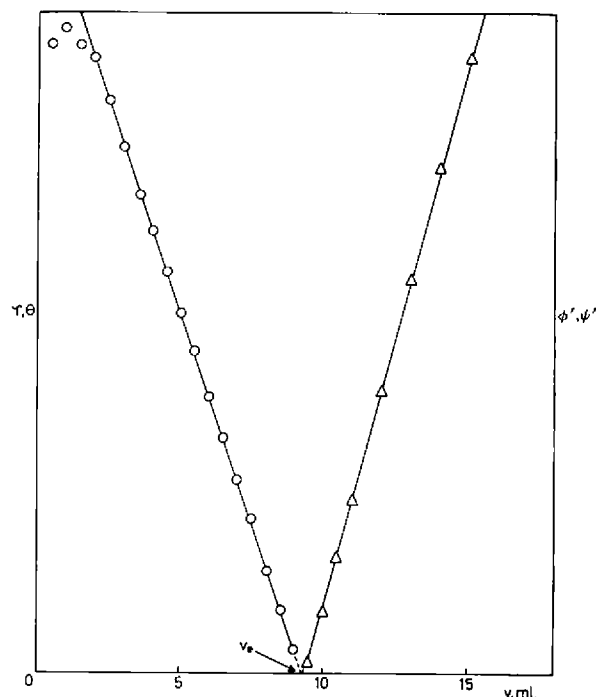


Figure 5. Gran plots $\tau(v)$ or $\theta(v)$ and $\phi'(v)$ or $\psi'(v)$ for the standardization of a weak acid with a strong base. 20.0 ml of $\sim 0.05 M$ acetic acid was titrated with $0.106 M NaOH$.

² The remarks in footnote 1 apply to the quantity τ , and also to Φ , Φ' , and T below.

acid is very weak. The equivalence point may then be found by extrapolation of the linear region of $\tau(v)$ or $\theta(v)$ to $\tau = 0$ or $\theta = 0$. (3) If the acid is contaminated with a metal ion which forms complexes with A^- , equations (13) and (14) will no longer be valid. Deviation of $\tau(v)$ and $\theta(v)$ from linearity will increase as v approaches v_e . (4) Curvature in the alkaline region will again be observed if the base contains carbonate (see p. 377).

Titration of Strong Base with Strong Acid

For the titration of a volume Y of strong base with a volume y of strong acid, the functions analogous to ϕ and ϕ' [equations (4) and (10)] are

$$\Phi = (Y + y)[H^+]_{\gamma_H} = (Y + y)10^{-pH} = (y - y_e)H\gamma_H \quad (20)$$

$$\Phi' = (Y + y)/[H^+]_{\gamma_H} = (Y + y)10^{pH} = (y_e - y)H/K_w\gamma_H \quad (21)$$

in the acidic and alkaline regions respectively.² Here y_e is the equivalence point. Similar functions, Ψ and Ψ' , analogous to (6) and (11) may be obtained from measurements of E .

Titration of Weak Base with Strong Acid

If the base MOH is incompletely dissociated, equation (7) must be replaced by

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{K_w[M^+]}{K_b[MOH]} \quad (22)$$

where $K_b = [M^+][OH^-]/[MOH]$. Now

$$[M^+] = \frac{yH}{Y + y} + [OH^-] - [H^+] \quad (23)$$

and

$$[MOH] = C_M - [M^+] = \frac{YB - yH}{Y + y} - [OH^-] + [H^+] \quad (24)$$

where C_M is the total concentration of base in the solution. If

$$yH/(Y + y) \gg [OH^-] - [H^+] \quad (25)$$

and

$$(YB - yH)/(Y + y) \gg [OH^-] - [H^+] \quad (26)$$

then from equations (22), (23), and (24)

$$[H^+] = \frac{K_w yH}{K_b(YB - yH)} = \frac{K_w y}{K_b(y_e - y)} \quad (27)$$

Thus, in the alkaline range, a function²

$$T = y/[H^+]_{\gamma_H} = y10^{pH} = K_b(y_e - y)/K_w\gamma_H \quad (28)$$

can be plotted against y to give a straight line such that $T = 0$ when $y = y_e$. A similar function can be defined for use with measurements of E . In the acid range, equation (20) is again valid, and y_e can be located using plots of Φ' or Ψ' against y . Even when the plot in the alkaline region is nonlinear owing to the presence of carbonate in the base, or to the fact that conditions (25) and (26) are not fulfilled, a precise value of y_e may be obtained using only the measurements obtained after the end point.

Advantages of Gran's Method

Simplicity of Measurement. Potentiometric readings can be taken after regular increments in v throughout the whole titration; unlike differential plots of dE/dv or

dpH/dv against v , Gran plots do not require large numbers of readings, corresponding to very small changes in v , in the region of the equivalence point.

Simplicity of Calculation. The calculations are quick and easy. One point may be computed and plotted in the one or two minutes which elapse between the addition of base and the taking of a steady potentiometric reading (see the table).

Versatility. The method may be used when only part of the pH range is accessible to measurement, e.g., when the acid contains metal ions which hydrolyze in the region $pH \sim 2.5$ (see Fig. 3). It would be very difficult to determine the concentration of strong acid in a solution of this type by conventional methods. Gran's method has the further advantage that the presence of carbonate in the alkali can readily be detected.

The application of the method to other types of potentiometric data (e.g., those obtained in titrations of polybasic acids and in redox, complex formation, and precipitation reactions) is discussed in Gran's original paper (11).

Precision. The end points obtained by a linear Gran extrapolation are much more precise than those obtained by the differential method, especially if the titration curve is not symmetrical.

The value of v_e obtained from a Gran plot may, if required, be refined to give an even more precise value. If the plot of $\psi(v)$ or $\phi(v)$ is linear, then $E_f' = 0$ and $\gamma_H = 1$, whence from equations (1) and (2)

$$E_0' = E + \frac{2.303RT}{F} \log \frac{B(v_e - v)}{(V + v)} = E + \frac{2.303RT}{F} \log \frac{VH(v_e - v)}{v_e(V + v)} \quad (29)$$

If either H or B is accurately known, values of E_0' may be calculated from (29) using several different values of v_e within the small range permitted by the Gran extrapolation. The most precise value of v_e is obtained by trial and error as that which gives the most nearly constant value of E_0' . A value of y_e may be refined similarly.

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