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Determination of the End Point in Potentiometric Titrations: Gran and Schwartz Methods

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Abstract A titration can be done with different purposes in mind. It may be performed to determine the concentration of one or several components in a sample. Obtaining a correct value for the equivalence volume is the key question in this case. A titration may also be carried out to determine a physicochemical parameter. On this respect, potentiometric titration is, in numerous situations, the method of choice for measuring acidity constants in chemistry and biochemistry. By using the reverse function of pH=pH(V) titration curves for strong acid with a strong base at varying concentrations, as well as titration curves for monoprotic acids titrated with strong base, at the same concentration, but varying pK_a from 1 to 13, may be simulated. On the basis of these curves, a study of the Gran II method is carried out in this work to outline its advantages and limitations. Gran II linearization method is one of the most cited scientific papers (over 2500 cites) and has been applied in a variety of fields. By suitable modification in the data analysis Gran plot methodology may be extended as suggested by Schwartz. The linearization method devised by Schwartz is a powerful tool to determine titrations end point and (simultaneously) acidity constants. Gran and (mainly) Schwartz methods are superior to the differential methods, which fail to give a good sharp point with very weak acids (pK_a 9-10.2). In this paper some applications are outlined such as the evaluation of the autoprotolysis constant of water, and the simultaneous determination of equivalence point and acidity constant in potentiometric titrations. Several bibliographic and experimental systems (hydrochloric acid, perchloric acid, β-alanine, acetic acid, ammonium nitrate and boric acid, titrated with an alkaline solution) are studied to acquire a prior knowledge of how experimental data should be treated to fit the purpose intended.

Keywords Potentiometric titration, Gran method, Schwartz method

1. Introduction

Titrimetry is one of the oldest analytical methods, and as a matter of fact it plays an important role [1-5] in various analytical fields as well as in routine analysis. Titrimetry is often applied in analytical chemistry given its superior speed and simplicity precision [6], with little sacrifice in accuracy. Titrimetry also offers the possibility of simultaneous measurement at low cost. Methods and applications based on pH titrations are used [7] in a variety of fields. On this respect the potentiometric method with a glass electrode is preferably used in analytical laboratories for the quantitative determination of substances [8] with acid-base properties. Potentiometric titration is in numerous situations the method of choice [9] for measuring acidity and stability constants (e.g. proton binding constants) in chemistry and biochemistry.

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The equivalence point in a potentiometric titration is usually determined by finding, in some way or other, the point of maximum slope (inflexion point) of the titration curve [10]. In many instances there are very sharp breaks in titration curves, and then, there is no difficulty in finding the equivalence point. Nevertheless, when very weak acids are titrated with strong bases, the curves are more difficult to evaluate. It is then usual to plot the differential curves, $\Delta pH/\Delta V$ or $\Delta E/\Delta V$ against volume of titrant added. The peak on these curves corresponds to the point of maximum slope of the normal titration curve. Such differential methods need values of potential corresponding to very small change in volume of titrant added near the end point for good result. Note that the derivative, y', is the limit of the ratio increment in y by increment in x, when this later tends to zero.

However, in the immediate vicinity of the end point the concentration of the original reactant becomes very small, and it usually becomes impossible for the ions to control the indicator electrode potential. The e.m.f. cell becomes unstable and indefinite because the indicator electrode is no longer bathed with sufficient quantities of each electroactive species. Therefore the differential methods may not give satisfactory results. Results obtained by this

method or other similar methods based on the determination of the point of maximum slope may also be in error if the titration curve is not symmetrical about the equivalence point.

Gunnar Gran was a scientist in a Swedish forest product laboratory [11], whose day to day job in the early 1950's involved endless potentiometric titrations. Having plotted numerous sigmoidal shaped and derivative curves, he developed two methods [12, 13] for determining equivalence points that were based on the extrapolation of straight line plots. Gran published throughout his life only ten scientific papers, five in the 1950-1956 period, and another four about three decades later, in the 1980-1983 period, when he came back again to the research tasks, in order to complete his PhD Thesis [14]. The tenth was a review [15] on equivalence point determination methods.

One of the most cited articles in *The Analyst* is the second of his methods of determination of the equivalence point in potentiometric titrations [13]. This paper, together with the reviews paper on Biomimetic Chemistry [16], the original full paper on the use of Wilkinson catalyst [17], and a landmark paper pioneering work on organic conducting polymers [18] are mentioned in RSC Journal highlights [19]. Concerning these articles we may read [20] in The Guardian: "*The article contained within the archive span the year 1841 to 1996, and include many landmark papers such as Ronald Breslow's 1972 paper Biomimetic chemistry; Gunnar Gran's famous paper on acid-base reactions in the Analyst; and the original 1966 paper on the use of Wilkinson catalyst*". Wilkinson and Schirakawa were awarded with the Nobel Prize in Chemistry in 1973 and 2000, respectively, whereas Breslow has won notable awards in chemistry. The mentioned papers of Gran, Schirakawa, Wilkinson and Breslow have 2594, 1842, 1739, and 239 cites, respectively, in the ISI Web of Knowledge, at March, 22, 2016. The first Gran [12] method, have in addition 634 cites, and its review on equivalence volumes [15] is 156 times cited.

Gran's first method involves [12, 21] the plotting of either $\Delta V/\Delta pH$ or $\Delta V/\Delta E$ as a function of V, the volume of added titrant, after values of E or pH have been experimentally determined for several values of V. Gran showed that the characteristics hyperbolic shapes of the first derivative curves could be made linear by simply plotting the reciprocal of the derivative. It is of great importance that this approach allows us to make use of the points that are somewhat distant from the equivalence point. In the ideal case the resulting plot consists of two straight lines, which intersect each other and the V-axis at the equivalence point. One of the drawbacks of this method [22, 23] is that the accuracy of the plot is influenced by the accuracy of the experimental data, and another that the lines for titrations of weak electrolytes are more or less curved and do not yield reliable results, because the change in pH or E at the equivalence point is too small.

The second method of Gran [13], was founded upon an idea of Sorensen, and it represent one of the first attempts to linearize titration curves, thereby making possible to calculate the equivalence volume by using several points on the titration curve (far away from the equivalence point) instead of only the inflexion point. If the functions are plotted against V, straight lines are obtained that intersects the V-axis at V_{eq}, the equivalence volume. Gran introduced a correction for the volume change during the course of the titration, what Sorensen had not done, extending also the method to other kinds of titrations. The introduction of selective electrodes in the 70s significantly increases interest in the Gran method.

As it is not necessary to determine absolute [H] values, the electrode system needn't be calibrated, which is a great advantage. Two additional advantages favor the use of Gran plots. On the one hand, fewer titration points need to be taken than with conventional methods. On the other hand, measurements need not be made close to the equivalence point; this point may be easily obtained by extrapolation. Thus, some problems, e.g., those associated with incompleteness of reaction or instability of measurements close to the end point are avoided on this way. Simplicity of measurement, simplicity of pH calculation, versatility and precision have been ascribed [24] to the Gran II method. However, the use of the traditional curves is restricted to a limited range of acid strengths, as we will show later.

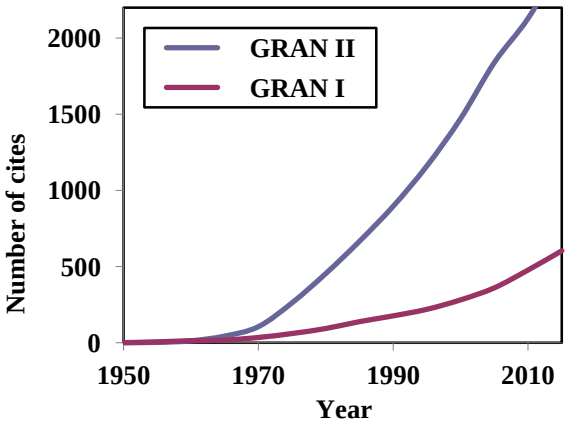

Figure 1. Cumulative diagram of number of citations of Gran I and II papers along years

Gran presented his paper in the International Congress of Analytical Chemistry held at Oxford from September 4th to 9th 1952. The paper was published in the November issue of *The Analyst* together with other four papers corresponding to Section 3 of the Congress (electrochemical methods), authored by Bates (pH standards), Bishop (indicator electrodes in non-aqueous potentiometry), Barker (square wave polarography) and Furness and Davies (polarography of the tetrathionate ion). The paper included at the end a discussion with the participation of eminent chemists such as Lindsey (Chairman), Sillen, Bishop, and Johansson. A survey of seven pages containing the summaries of the papers

presented to the Congress was also published in *Analytical Chemistry* [25]. All these circumstances linked to the fact that Gran had painstakingly worked all details of the method included in the manuscript. Both simple and complex examples have undoubtedly influenced the success and widespread applicability of the method. Figure 1 shows the results of the distribution of number of citations of Gran I and II papers in a continuous cumulative diagram where the increasing tendency is clearly seen.

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. Weak acid or bases that are stronger than pK_a or pK_b=5 can be treated by the conventional equations or extremely weak acids or bases may thus be analyzed. Ingman and Still [21] derived an expression for the titration of a weak acid with a strong base which, when plotted again the titrant volume V, yield a straight line that intersects the V-axis at the equivalence point. However, the acidity constant of the acid involved must be previously known. The same applies to a subsequent paper by Midley and McCallum [26]. Two decades later, Schwartz [27] showed how the equation could be cast in such a form that K_a need not be known in advance, thereby making it much more useful for numerical analysis. In spite of this little attention has been paid to the Schwartz method being not frequently mentioned in the literature, and with regard to textbooks only appears in de Levie [28, 29], though explained with great detail.

In a titration a properly chosen titrant (T) is added in consecutive portions into V_0 mL of the solution titrated (analyte, D). Let V (mL) be the volume of titrant added; then V_0+V mL of D+T mixture is thus obtained at a particular moment of the titration stage. When ionic strength (I) and dielectric constant (ε) of the mixture do not vary distinctly during the titration, the entire equilibrium constant involved may be assumed constant. In a common acid-base titration, the points [V_i, pH_i] registered after consecutive portions of T added, form a continuous plot named the pH titration curve, pH=pH(V). By using the function V=V(pH), the reverse function of pH=pH(V) [7, 30], we may simulate the titration curve with the aid of an Excel spreadsheet. Note that the relationship V=V(pH) may be formulated in a simple and uniform functional manner, even for complicated acid-base systems—contrary to the relationships pH=pH(V) that assume more complex form even for simple acid-base systems or do not exist at all. Note that a commercial potentiometer, called the 'Orion 960', has been available from Orion Research, Boston, USA (now part of ThermoFisher Scientific) since 1984, which does automatic Gran analysis [31-33].

Thus, in the paper we have simulated titration curves for a strong acid with a strong base at varying initial concentrations of acid, and titration curves for monoprotic acids titrated with strong base, at the same concentration, but with varying pK_a values ranging from 1 to 13. A study of the Gran's second method drawing attention to their advantages and limitations, as well as a variant introduced some 40 years later by Schwarz [27, 34] was carried out. Some applications are outlined such as the evaluation of the autoprotolysis constant of water, and the simultaneous determination of equivalence point and acidity constant in potentiometric titrations. Experimental systems such as hydrochloric acid, perchloric acid, acetic acid, ammonium nitrate, and boric acid have been considered in the study.

2. Theory

2.1. Titration of a Strong Acid with a Strong Base. Methods of Schwartz and Gran

Let HX be a strong acid (i.e. completely dissociated), to be titrated with a strong base BOH (which is also a strong electrolyte), $H^+ + OH^- = H_2O$. The electroneutrality rule for the solution is

$$\left[B^+\right]+\left[H^+\right]=\left[X^-\right]+\left[OH^-\right] \tag{1}$$

It may be noted that in Eqn. (1), the concentration $[H^+]$ and $[OH^-]$ occurs, whose values should be calculated from the activities when the hydrogen ion activity is determined potentiometrically. The relationship between activities and concentrations are defined according to the equations

$$\left(H^+\right)=\left[H^+\right]\gamma_{H^+} \tag{2}$$

$$\left(OH^-\right)=\left[OH^-\right]\gamma_{OH^-} \tag{3}$$

where γ_H and γ_{OH} are the respective activities coefficients at a certain ionic strength. It is thus practical to adjust the ionic strength of the solution at a fixed value. Note that the ionic product of water, K_w^c in term of molarities (concentration constant) is given by

$$K_w^c=\left[H^+\right]\left[OH^-\right]=\frac{\left(H^+\right)\left(OH^-\right)}{\gamma_{H^+}\gamma_{OH^-}}=\frac{K_w^T}{\gamma_{H^+}\gamma_{OH^-}} \tag{4}$$

At an ionic strength of 0.1, log γ_H= -0.08 and log γ_{OH} = -0.12 [21]. Equation (1) should also include concentration of ions originating from the neutral salt added to adjust ionic strength. The salts used for this purpose are completely dissociated, so the concentration of the anion and cation are the same and cancel each other out in the equation.

The concentration of the B^+ and X^- ions can be expressed for the following equations

$$\left[B^+\right]=\frac{C_BV}{V_0+V} \tag{5}$$

$$\left[X^-\right]=\frac{C_AV_0}{V_0+V} \tag{6}$$

where V_0 is the initial volume, V the titrant volume of base added and C_A and C_B the molarities of acid and titrant base, respectively. Then, by substituting Eqns. (5) and (6) into Eqn.

(1) we get

$$\frac{C_B V}{V_0+V}+\left[H^+\right]=\frac{C_A V_0}{V_0+V}+\left[OH^-\right] \tag{7}$$

which on rearrangement gives

$$\Delta=\left[H^+\right]-\left[OH^-\right]=\frac{C_A V_0-C_B V}{V_0+V} \tag{8}$$

From Eqn. (8) after a simple mathematical manipulation we obtain

$$V=V_0\frac{C_A-\Delta}{C_B+\Delta} \tag{9}$$

The choice of pH as the independent variable gives a linear equation in the unknown V (whereas a choice of V as the independent variable lead to an equation of third degree in $[H^+]$), which easily allow with the aid of an Excel spreadsheet to calculate the complete titration curve without any approximation. Note that

$$\Delta=\left[H^+\right]-\left[OH^-\right]=10^{-p[H]}-10^{\left(p[H]-pK_w^c\right)} \tag{10}$$

where p[H] is the minus logarithm of the concentration of hydrogen ions and pK_w^c is the ionic product of water in terms of molarities as indicated above. Figure 4 (top) illustrates a family of hydrochloric acid/ sodium hydroxide titration curves at the same (and varying) concentration in each case, obtained from Eqn. (9). The titration fraction, T, may be expressed, taking into account Eqn. (9) as

$$T=\frac{C_B V}{C_A V_0}=\frac{C_B}{C_A}\left[\frac{C_A-\Delta}{C_B+\Delta}\right]=\frac{1-\frac{\Delta}{C_A}}{1+\frac{\Delta}{C_B}} \tag{11}$$

On the other hand the following equation should be valid at the equivalence point,

$$C_A V_0=C_B V_{eq} \tag{12}$$

where V_{eq} is the equivalence volume. By substituting Eqn. (12) into (8) on rearrangement we have

$$\left(V_0+V\right)\Delta=C_A V_0-C_B V=C_B\left(V_{eq}-V\right) \tag{13}$$

A graph of the left hand side of Eqn. (13) against V gives a straight line with slope C_B that intersects the V axis at the point Veq.

Before the equivalence point, $C_B V < C_A V_0$, i.e. in acid medium, we can often use the approximation $\Delta\approx[H^+]$ in which case Eqn. (13) simplifies to

$$\left(V_0+V\right)\left[H^+\right]\approx C_A V_0-C_B V=C_B\left(V_{eq}-V\right) \tag{14}$$

Beyond the equivalence point $C_B V > C_A V_0$, we can similarly approximate $\Delta\approx -[OH^-]$, and as $[H^+] = Kw/[OH^-]$ we get

$$\frac{V_0+V}{\left[H^+\right]}\approx\frac{C_B V-C_A V_0}{K_w^c}=\frac{C_B}{K_w^c}\left(V-V_{eq}\right) \tag{15}$$

These approximations to Eqn. (13) were first given by Gran [13] and the corresponding plots are therefore called Gran plots. Equations (14) and (15) are usually appropriate approximations, as illustrated in Figure 2 (middle and bottom).

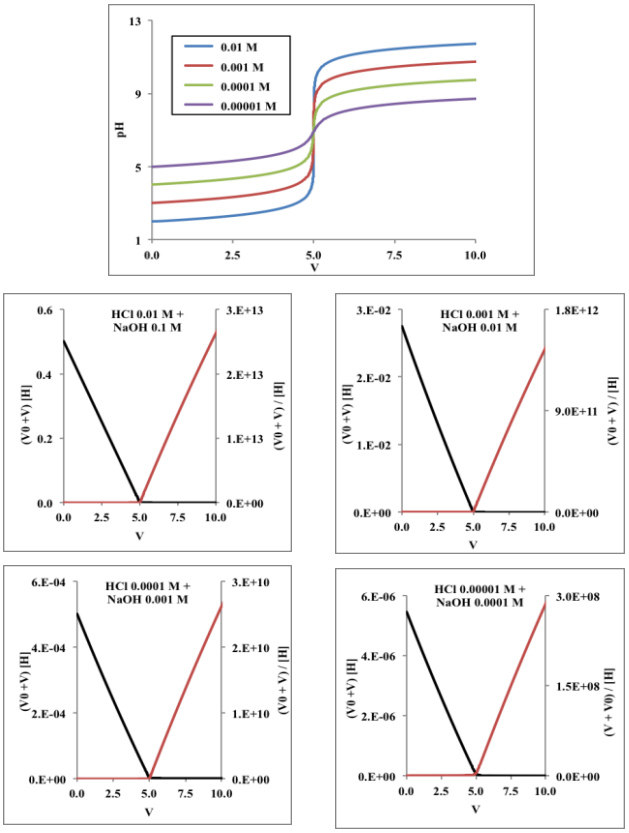

Figure 2. Top: Family of hydrochloric acid/sodium hydroxide titration curves at the same (and varying) concentration. Middle and botton: Gran methods before (black lines) and beyond the equivalence point (red lines) corresponding to the curves drawn in top

2.2. Titration of a Moderate, Weak or very Weak Strength Acid with a Strong Base. Methods of Schwartz and Gran

Let HA be an acid (of moderate, weak, or very weak strong) of mixed or Bronsted acidity constants K_a^B to be titrated with a strong base BOH. Let C_A and V_0 denote the initial concentration and volume of the acid, respectively. Let C_B and V denote the concentration of base and volume of base added, respectively. The following reaction occurs

$$HA+OH^- \rightleftharpoons A^- + H_2O \tag{16}$$

The law of mass action states

$$K_a^B=\frac{\left(H^+\right)\left[A^-\right]}{\left[HA\right]}=K_a^c\gamma_{H^+} \tag{17}$$

where K_a^c is the concentration constant,

$$K_a^c = \frac{\left[H^+\right]\left[A^-\right]}{\left[HA\right]} \tag{18}$$

and γ_H, as before, the activity coefficient of the hydrogen ion.

The expression for the total concentration of the acids HA is

$$C_A \frac{V_0}{V_0 + V} = \left[HA\right] + \left[A^-\right] \tag{19}$$

The solution must be electrically neutral, meaning that

$$\left[B^+\right] + \left[H^+\right] = \left[A^-\right] + \left[OH^-\right] \tag{20}$$

At any point during the titration the concentration of B^+ is given by Eqn. (5) which substituted into Eqn. (20) gives

$$\frac{C_B V}{V_0 + V} + \left[H^+\right] = \left[A^-\right] + \left[OH^-\right] \tag{21}$$

The molar fraction of the A^- species is given by

$$\begin{aligned} f_0 &= \frac{\left[A^-\right]}{C_A \frac{V_0}{V_0 + V}} = \frac{\left[A^-\right]}{\left[HA\right] + \left[A^-\right]} = \frac{1}{1 + \frac{\left[HA\right]}{\left[A^-\right]}} \\ &= \frac{1}{1 + \frac{\left[H^+\right]}{K_a^c}} = \frac{K_a^c}{K_a^c + \left[H^+\right]} \end{aligned} \tag{22}$$

Equations (22) and (21) led to

$$\frac{C_B V}{V_0 + V} + \left[H^+\right] = \frac{f_0 C_A V_0}{V_0 + V} + \left[OH^-\right] \tag{23}$$

and then

$$\Delta = \left[H^+\right] - \left[OH^-\right] = \frac{f_0 C_A V_0 - C_B V}{V_0 + V} \tag{24}$$

From Eqn. (21), we get

$$\left(V_0 + V\right)\Delta = f_0 C_A V_0 - C_B V \tag{25}$$

and by dividing through C_B

$$\frac{\left(V_0 + V\right)\Delta}{C_B} = f_0 \frac{C_A V_0}{C_B} - V \tag{26}$$

which on rearrangement led to

$$\frac{\left(V_0 + V\right)\Delta}{C_B} + V = f_0 \frac{C_A V_0}{C_B} \tag{27}$$

For the sake of simplicity let denote the left hand of Eqn. (26) or (27) by V'

$$\frac{\left(V_0 + V\right)\Delta}{C_B} + V = V' \tag{28}$$

Substitution of Eqns (12), (22) and (28) into Eqn. (27) yields

$$V' = f_0 V_{eq} = \frac{K_a^c V_{eq}}{K_a^c + \left[H^+\right]} \tag{29}$$

Equation (29) on rearrangement gives

$$V'\left[H^+\right] = K_a^c \left(V_{eq} - V'\right) \tag{30}$$

A plot of $V'[H^+]$ against V' gives a straight line [27] (Schwartz, 1987) with slope K_a^c which intersects the V' axis at the point Veq.

On the other hand, from Eqn. (24) on appropriate rearrangement we may derive

$$V = V_0 \frac{f_0 C_A - \Delta}{C_B + \Delta} \tag{31}$$

This means that the choice of pH as the independent variable will give a linear equation in the unknown V. From Eqn. (31) we may derive the fraction titrated as

$$T = \frac{C_B V}{C_A V_0} = \frac{C_B}{C_A}\left[\frac{f_0 C_A - \Delta}{C_B + \Delta}\right] = \frac{f_0 - \frac{\Delta}{C_A}}{1 + \frac{\Delta}{C_B}} \tag{32}$$

Figure 3 illustrates a family of curves corresponding to monoprotic acids with pK_a varying from 1 to 13, at a concentration 0.005 M titrated with NaOH 0.01 M.

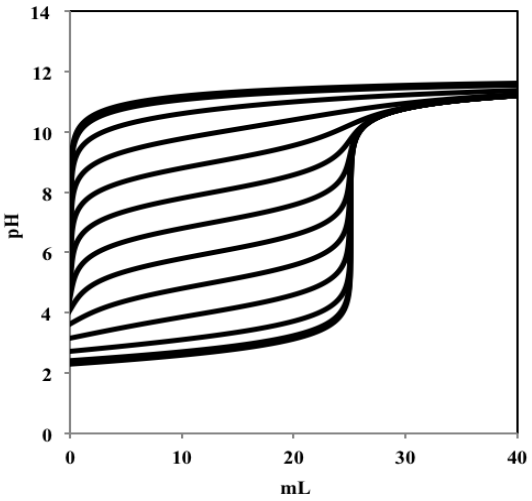

Figure 3. Titration curves corresponding to 50 mL of a monoprotic acid 0.005 M with varying pK_a from 1 to 13, titrated with a strong monoprotic base 0.01 M

An approximate treatment may be obtained by dividing the titration curve into two parts, one before and one after reaching the equivalence point. From Eqn. (21) we get

$$\left[A^-\right] = \frac{C_B V}{V_0 + V} + \left[H^+\right] - \left[OH^-\right] = \frac{C_B V}{V_0 + V} + \Delta \tag{33}$$

and then by combining with Eqn. (19) we have

$$[HA]=\frac{C_A V_0}{V_0+V}-[A^-]=\frac{C_A V_0-C_B V}{V_0+V}-\Delta \qquad (34)$$

Combining Eqns. (33) and (34) with Eqn. (18)

$$[H^+]=K_a^c\frac{\frac{C_A V_0-C_B V}{V_0+V}-\Delta}{\frac{C_B V}{V_0+V}+\Delta} \qquad (35)$$

Before the equivalence point we may drop Δ in both numerator and denominator of Eqn. (35), obtaining an approximate expression

$$[H^+]\approx K_a^c\frac{C_A V_0-C_B V}{C_B V} \qquad (36)$$

which combined with Eqn. (12), on rearrangement finally gives

$$[H^+]V\approx K_a^c\left(V_{eq}-V\right) \qquad (37)$$

so that a plot of $[H^+]$ V versus V should be linear, with slope K_a^c, intersection the horizontal axis at $V=V_{eq}$ (see Figure 4).

Beyond the equivalence point, from Eqn. (21), the concentration of hydroxyl ion is given by

$$[OH^-]=\frac{C_B V}{V_0+V}-[A^-]+[H^+]\approx\frac{C_B V-C_A V_0}{V_0+V} \qquad (38)$$

so that we finally obtain the same expression corresponding to the titration of a strong acid with a strong base beyond the equivalence point, as expected

$$\frac{V_0+V}{[H^+]}\approx\frac{C_B}{K_w^c}\left(V-V_{eq}\right) \qquad (39)$$

These approximations were first given by Gran [13] and the corresponding plots are therefore called Gran plots. Equation (37) yields a straight line intersecting the axis at $V=V_{eq}$ (see Figure 5); Gran plots can be extrapolated to the equivalence point, but do not actually go through that point.

The somewhat complicated form of the Schwartz Eqn. (30) reflects the added complication of the autodissociation of water. Such autodissociation is neglected to different degrees in the Gran plot. Before the Schwartz plot was available, it was customary to use the above approximations to derive (equally approximate) linear relations as aids in determining the equivalence point. Unfortunately, because of the approximations introduced in the derivation of Eqn. (37), especially when the pK_a-pC_A is smaller than about 2 or larger than about 12, some judgement must therefore exercise about which data to use in drawing the best Gran plot line. The Gran plot involves somewhat less calculational effort, but that is seldom a sufficient reason to prefer Eqns. (38) and (39) over the Schwartz plot under any circumstances. We show in the Figures 4 and 5 under what conditions the above approximate relations are appropriate.

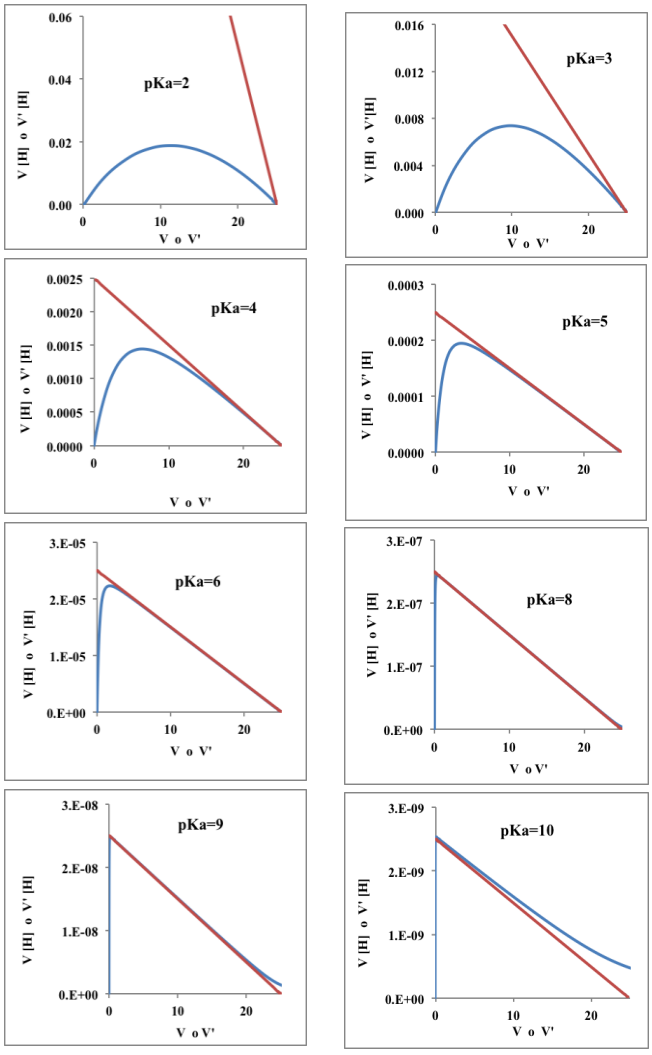

Figure 4. Gran (blue lines) and Schwartz (red line) method applied to curves of Figure 3

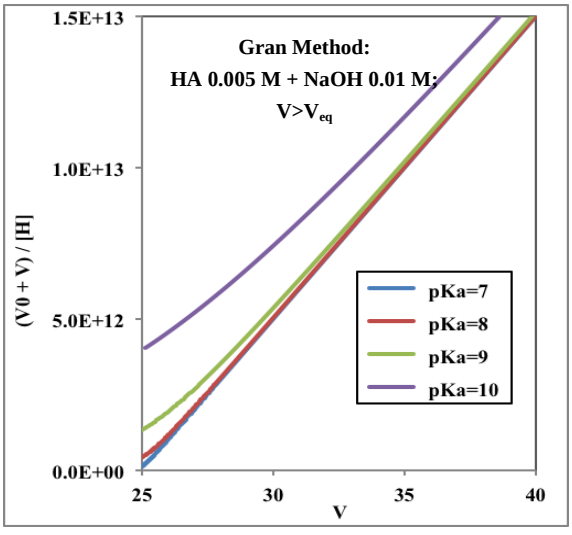

Figure 5. Gran plot beyond the equivalence point applied to curves of Figure 3 (weak acids with varying pK_a from 7 to 10)

Over twenty years before the Swartz [27] paper, Ingman and Still [21] derived the equation that follows

$$V_{eq} - V = \frac{V\left(H^+\right)}{K_a^B} + \frac{\left(V_0 + V\right)\Delta}{C_B}\left(1 + \frac{\left(H^+\right)}{K_a^B}\right) \tag{40}$$

which is equivalent to Eqn. (30). However the mixed or Bronsted constant K_a^B must be known in advance (its value was taken from the literature). The same applies to a paper published by Midley and Mc Callum [26] later. Schwartz derived its equation in such a form that K_a^B need not be known previously, thereby making it much more useful for numerical analysis.

2.3. Calibration of the Glass Electrode. Determination of the Ionic Product of Water

Though the glass electrode responds in principle to activity of hydrogen ions, it may be calibrated in term of hydrogen ion concentrations by using ionic media of constant ionic strength [35]. Thus activity factors are kept constant. By using this approach, the composition of the calibration and the test solution can be as close to each other as possible thus reducing discrepancies in the liquid junction potential.

The potential of the glass electrode system, at a fixed ionic strength, assuming that it exhibits a Nernstian response, is given by

$$E = E_0' + 59.16\log\left[H^+\right] \tag{41}$$

(E_0' includes the standard glass electrode potential, the reference glass cell potential, activity coefficients, and liquid junction potentials). We may calibrate the glass electrode by addition of a strong base to a strong acid, both of known concentration. The ionic strength adjusted using an excess of background salt electrolyte is the same for both strong acid and base solutions, which results in the ionic strength remaining constant thorough the titration. Once the data for the average potential versus volume of added base, E, is obtained, the concentration of the hydrogen ions in solution was calculated before the equivalence point

$$\left[H^+\right] = \frac{C_A V_0 - C_B V}{V_0 + V} \tag{42}$$

and after the equivalence point

$$\left[OH^-\right] = \frac{C_B V - C_A V_0}{V_0 + V} \tag{43}$$

$$\left[H^+\right] = \frac{K_w^c}{\left[OH^-\right]} = \frac{K_w^c\left(V_0 + V\right)}{C_B V - C_A V_0} \tag{44}$$

The theoretical p[H] of the solution was calculated and the calibration graph of potential versus p[H] of the solution was calculated and the calibration graph of potential versus pH was ten plotted

$$E = E_{0a}' - 59.16p\left[H\right] \tag{45}$$

A straight line of unity slope should be obtained from which intercept the value of E_{0a}' may be known. Note that Eqn. (45) is most accurate in the pH 1.5 to 11.5 interval, since at the extremes of pH, junction potential effects impart nonlinearity on the equation.

On the other hand, as

$$p\left[H\right] + p\left[OH\right] = pK_w^c \tag{46}$$

By combining Eqns. (45) and (46) we have

$$\begin{aligned} E &= E_{0a}' - 59.16\left(pK_w^c - p\left[OH\right]\right) \\ &= E_{0a}' - 59.16pK_w^c + 59.16p\left[OH\right] \end{aligned} \tag{47}$$

That is

$$E = E_{0b}' + 59.16p\left[OH\right] \tag{48}$$

and then by equaling Eqns. (45) and (49)

$$E_{0a}' - 59.16p\left[H\right] = E_{0b}' + 59.16p\left[OH\right] \tag{49}$$

which on rearrangement gives the ionic product of water (in term of molarities)

$$pK_w^c = p\left[H\right] + p\left[OH\right] = \frac{E_{0a}' - E_{0b}'}{59.16} \tag{50}$$

3. Gran and Schwartz Methods: Application to Systems Described in the Literature

3.1. Potentiometric Titration of Hydrochloric Acid with Sodium Hydroxide

Table 1. Potentiometric Titrations of 100 mL of 0.01 M HCl with 0.09956 M NaOH [36]. Results obtained by applying the Excel LINEST function

C_{HCl} **0.01 M** **V0 = 100 mL**

C_{NaOH} **.09956 M**

V	pH	$(V_0 + V)(H)$	$(V_0+V)/(H)$
0.00	2.07	0.851	
1.00	2.11	0.784	
2.00	2.18	0.674	
3.00	2.23	0.607	
4.00	2.30	0.521	
5.00	2.39	0.428	
6.00	2.50	0.335	
7.00	2.61	0.263	
8.00	2.80	0.171	
9.00	3.18	0.072	
11.00	10.95		9.893E+12
12.00	11.30		2.235E+13
13.00	11.46		3.259E+13
14.00	11.59		4.435E+13
15.00	11.65		5.137E+13
16.00	11.71		5.949E+13
17.00	11.80		7.382E+13

a_1=	**-8.6459E-02**	**8.5960E-01**	=a_0
s(a_1)=	**9.9126E-04**	**5.2910E-03**	=s(a_0)
r^2=	**0.99895**	**9.0035E-03**	=s(y/x)

V_{end}= 9.943 mL

a_1=	**1.0173E+13**	**-1.0045E+14**	=a_0
s(a_1)=	**3.7416E+11**	**5.2914E+12**	=s(a_0)
r^2=	**0.99328**	**1.9799E+12**	=s(y/x)

V_{end}= 9.874 mL

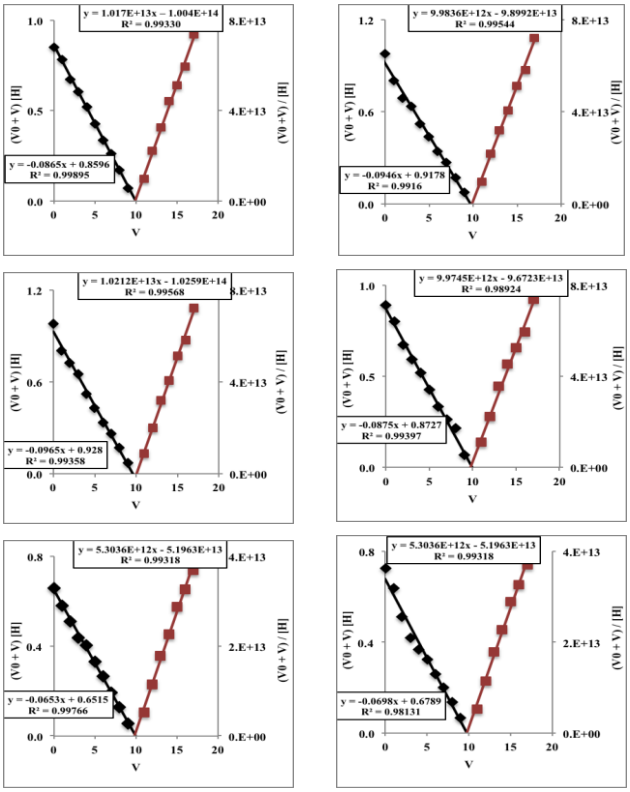

Figure 6. Gran method applied to the titrations of 100 mL of 0.01 M HCl with 0.09956 M NaOH. The first series is shown in Table 1

Figure 6 shows the Gran method applied to six titrations of hydrochloric acid with sodium hydroxide published by Burden and Euler [36]. Refer to the numerical values of [V, pH] in Burden and Euler, Anal. Chem. 1987, 47 (6), 793-797, p. 794 (see Table 1 for the 1st titration) [36].

The high ratio of sample to titrant volume minimizes errors due to variations in ionic strength. The number of points chosen, their distance, the precision of the experimental data and deviations in the Nernstian behavior of the glass electrode influence the results. Volume end point values of 9.88 ± 0.10 mL and 9.86 ± 0.12 mL were obtained, with the data before and after the equivalence point, respectively.

3.2. Potentiometric Titration of Perchloric Acid with Sodium Hydroxide: Determination of the Ionic Product of Water

In Table 2 the potentiometric titration data of perchloric acid with sodium hydroxide published by Meloun et al. [37] along with the necessary calculations are collected. Values of estimated parameters in the following, e.g. pK_w or pK_a, are reported with three digits in all cases, even if they are not significant.

The experimental data of the titration are more accurate than those of the previous section. Figure 7 shows the representation of E versus the values of p[H] and p[OH] for acidic and alkaline solutions, respectively. The values of 373.64 ± 0.63 and -457.73 ± 2.45 mV (Eqns. (45) and (48), respectively) are obtained for E_{0a} and E_{0b} (absence of ionic strength), and applying Eqn. (50) the pK_w and its standard deviation values are obtained (pK_w = 14.04 with the ESBA program using nonlinear regression (RNL)):

$$pK_W = \frac{E_{0a} - E_{0b}}{59{,}16} = \frac{373.64 - (-457.73)}{59.16} = 14.053 \quad (51)$$

$$s_{pK_w} = \frac{1}{59.16}\sqrt{s_{E_{0a}}^2 + s_{E_{0b}}^2} = \frac{1}{59.16}\sqrt{0.63^2 + 2.45^2} = 0.043 \quad (52)$$

Table 2. Potentiometric titration of 20 mL of 0.0987 M $HClO_4$ with 1.0767 M NaOH, T=25°C [37]

Point nº	mL	E, mV	F1	[H]	p[H]	59.16 p[H]
1.00	1.40	280.5	2.18E+06	2.12E-02	1.675	99.075
2.00	1.42	279.3	2.08E+06	2.01E-02	1.696	100.345
3.00	1.44	277.6	1.94E+06	1.91E-02	1.719	101.678
4.00	1.46	276.2	1.83E+06	1.81E-02	1.742	103.081
5.00	1.48	274.7	1.73E+06	1.71E-02	1.767	104.563
6.00	1.50	273.2	1.62E+06	1.61E-02	1.794	106.132
7.00	1.52	271.5	1.52E+06	1.51E-02	1.822	107.801
8.00	1.54	269.8	1.41E+06	1.41E-02	1.852	109.582
9.00	1.56	267.9	1.31E+06	1.30E-02	1.885	111.491
10.00	1.58	266.0	1.21E+06	1.20E-02	1.919	113.550
11.00	1.60	263.8	1.11E+06	1.10E-02	1.957	115.785
12.00	1.62	261.4	1.01E+06	1.00E-02	1.998	118.227
13.00	1.64	258.9	9.08E+05	9.04E-03	2.044	120.922
14.00	1.66	255.9	8.03E+05	8.04E-03	2.095	123.926
15.00	1.68	252.7	7.46E+05	7.04E-03	2.152	127.322
16.00	1.70	249.1	6.08E+05	6.05E-03	2.218	131.228
17.00	1.72	244.8	5.10E+05	5.06E-03	2.296	135.828
18.00	1.74	239.7	4.14E+05	4.07E-03	2.391	141.423
19.00	1.76	233.1	3.16E+05	3.08E-03	2.511	148.570
20.00	1.78	224.6	2.23E+05	2.10E-03	2.679	158.484

Point nº	mL	E, mV	F2	[OH]	p[OH]	59.16 p[OH]
24.00	1.86	-256.8	6.39E+03	1.83E-03	2.737	161.917
25.00	1.88	-271.6	1.03E+04	2.81E-03	2.551	150.936
26.00	1.90	-281.7	1.43E+04	3.79E-03	2.422	143.279
27.00	1.92	-288.2	1.77E+04	4.76E-03	2.322	137.398
28.00	1.94	-294.2	2.16E+04	5.73E-03	2.242	132.623
29.00	1.96	-298.6	2.51E+04	6.70E-03	2.174	128.605
30.00	1.98	-303.0	2.91E+04	7.67E-03	2.115	125.137
31.00	2.00	-306.3	3.26E+04	8.64E-03	2.064	122.087

Points nº 21, 22 and 23; [V; E]: [1.80; 211.5] [1.82; 183.2] [1.84; -219.1]

$$F_1 = (V_0 + V)10^{\frac{E}{g}} \qquad F_2 = (V_0 + V)10^{-\frac{E}{g}} \qquad g = P\frac{\ln 10 RT}{nF}$$

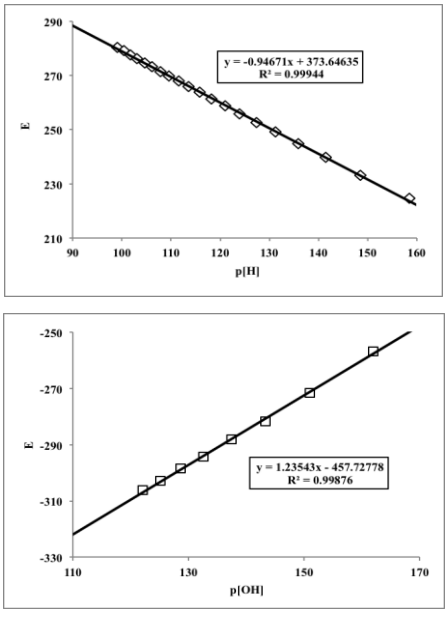

Figure 7. Potentiometric titration of 20 mL perchloric acid 0.0987 M with sodium hydroxide 1.0767 M. Top and bottom: Potentiometric evaluation of the autoprotolysis constant of water; acid and basic media, respectively

3.3. Potentiometric Titration of β-Alanine and Ammonium Nitrate

The data [V, pH] for the titrations of β-alanine and ammonium nitrate published by Ingman and Still [21] are depicted in Figure 8, along with Gran and Schwartz methods. It is observed how the Schwartz method allows the evaluation, without difficulty, of very weak acids ($pK_a \approx 10.1$), being superior to that of Ingman and Still, since this last one requires the previous knowledge of the values of pK_a. The pK_a values obtained for β-alanine and ammonium nitrate, 10.107 and 9.279, respectively, closely match [21] with those published in the literature; 10.12 and 9.28. The obtained V_{end} 5.222 mL and 7.819 mL were, as well, compared to those obtained by Ingman and Still [21] 5.28 and 7.78 mL.

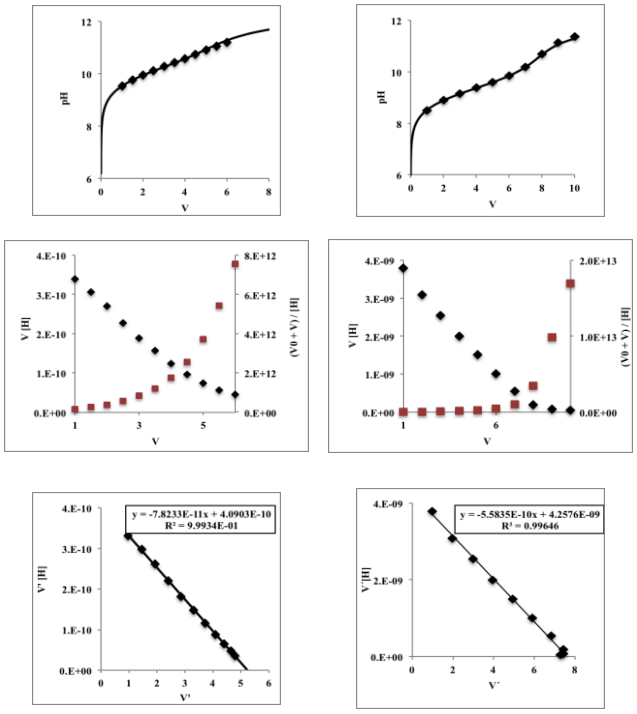

Figure 8. Left: Titration of 0.0107 M β-alanine ($pK_a^B = 10.2$) with 0.100 M sodium hydroxide; I = 0.1 M ($NaClO_4$). Right: Titration of 77 mL ammonium nitrate 0.0102 M ($pK_a^B = 9.36$) with 0.100 M sodium hydroxide; I = 0.1 ($NaClO_4$). Top: Titration curve; Middle: Gran method; Bottom: Schwartz method

3.4. Potentiometric Titration of Boric Acid

The boric acid titration data published by Ivaska and Wänninen [38] are represented in Figure 9, along with Gran and Schwartz methods. In accordance with the theoretical part of this work, the Gran method is not applicable. The V_{end} obtained were 7.66 and 12.44 mL, in concordance with the 7.65 and 12.41 mL published by Ivaska and Wänninen [38] by applying a computerized calculation program. There is also a close coincidence in the pK_a values obtained: 9.031 and 9.022 (this work), 9.035 and 9.029 (Ivaska and Wänninen), and 9.036 published in the bibliography (https://es.wikipedia.org/wiki/ Boric acid), already corrected at I = 0.1 M.

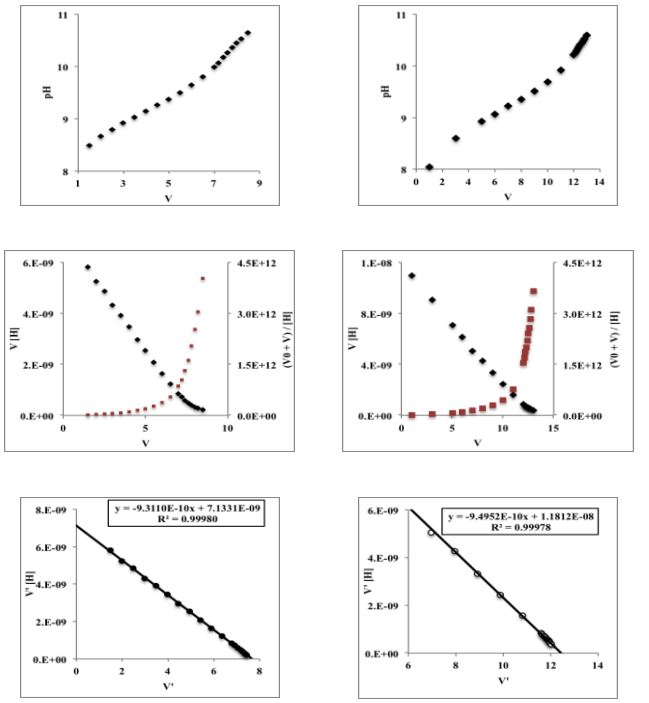

Figure 9. Left: First titration of 100 mL of boric acid with 0.05984 M sodium hydroxide at 25 ℃; I = 0.1 (KNO_3). Right: Second titration of 100 mL of boric acid with 0.05984 M sodium hydroxide at 25℃; I = 0.1 (KNO_3). Top: Titration curve; Middle: Gran method; Bottom: Schwartz method

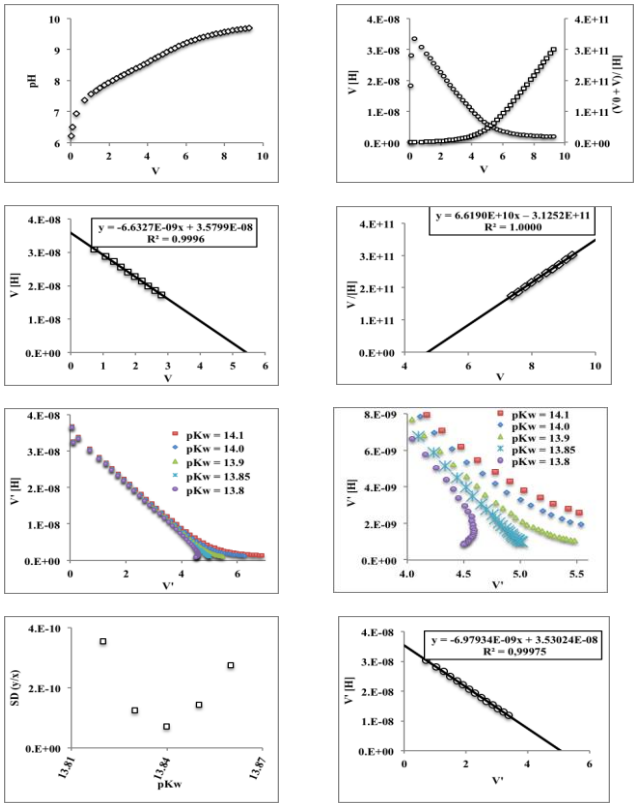

Figure 10. Top: HA titration curve with 0.001 M NaOH (left) and Gran method (right). Top Middle: Gran method in acid (left) and basic (right) medium. Lower Middle: Schwartz method with variable values of pK_w (left and right). Bottom: Standard deviation of the regression line as a function of pK_w tested (left) and better representation of Schwartz (right)

3.5. Potentiometric Evaluation of a Weak Acid of $pK_a \approx 8$. Indirect Determination of the Ionic Product of Water

Figure 10 shows the corresponding simulated data [34] for the evaluation of a weak acid of $pK_a \approx 8$, together with the application of the Gran method, which does not allow the exact location of the final point, and the Schwartz method, assuming various values of pK_w for water. It is observed that in the vicinity of the final point the straight lines obtained are curved, except when the real value (optimum) is assumed, which leads to a V_{end} = 5.058 mL (distant from the 5.40 and 4.72 mL obtained by the Gran method).

4. Gran and Schwartz Methods: Application to Experimental Systems

Reagents

Acetic acid ($C_2H_4O_2$) M=60 g/mol (Merck> 99.5%, 1.049 g/mL); Ammonium nitrate (NH_4NO_3) M=80.043 g/mol (Merck, analytical grade); Boric acid (H_3BO_3) M=61.83 g/mol (Merck> 99.5%); Potassium chloride (KCl) M=74.55 g/mol (Merck, analytical grade); 1M hydrochloric acid (HCl) (Merck, analytical grade); Potassium hydroxide (KOH) 1M (Merck, analytical grade); Sodium carbonate (Na_2CO_3) M=105.99 g/mol (Merck, analytical grade; Potassium hydrogen phthalate ($C_8H_5KO_4$) M=204.22 g/mol (Merck, analytical grade); Water for ACS analysis (Panreac).

Instruments

Analytical balance (Metler AE200) (4 decimals), Granatario (Metler PJ 400) (2 decimals), pH-meter Crison GLP 21 (3 decimals), with a combined Ag/AgCl glass electrode. The pH-meter is calibrated using pH buffers 3, 4.01, 5 and 7, using a two-point calibration method. Burette of 5 mL (Brand) (± 0.01 at 20ºC).

4.1. Potentiometric Titration of Acetic Acid with Potassium Hydroxide

Twenty five mL of acetic acid solution (0.01 M) is pipetted into a 100 mL flask containing 25 mL of a KCl solution (0.2 M). Then the acetic acid solution was titrated potentiometrically with a mixture of KOH and KCl solution (0.1 M) (previously standardized with potassium hydrogen phthalate) using the glass pH electrode.

The titration curve and the graphical representation of the Gran method before and after the equivalence point, with the whole dataset, is shown in the top of Figure 11. It is observed how the points corresponding to the beginning of the titration are deviated from the Gran straight line prior to the equivalence point. So, selected points are used for the application of Gran method in the region of 0.9 to 2.6 mL (V <Veq) and from 2.8 to 5.0 mL (V> Veq). The equations of the straight lines, the coefficient of determination, the number of points, and the calculated final volume are shown in the legend of the graphs (Figure 11, middle part).

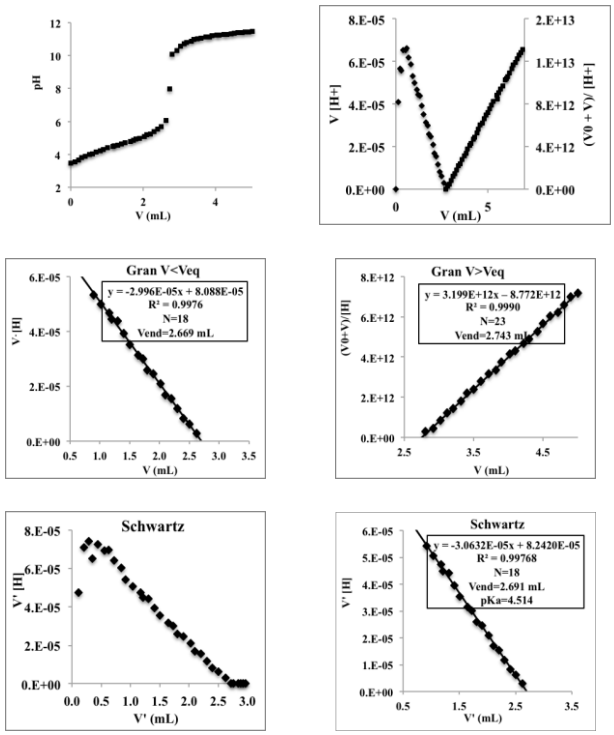

Figure 11. Top: Titration curve of 25 mL of 0.01 M acetic acid with 0.10 M potassium hydroxide, and Gran method applied to all of the data (Right). Middle. Gran method applied to the acetic acid data for V <Veq and V> V_{eq}. Bottom: Schwartz method applied to all data (V <Veq) (Left), and to a restricted range (Right). I = 0.1 (KCl)

There is a difference of 0.044 mL in the volume corresponding to the final point calculated with the data before and after the equivalence point.

At the bottom of Figure 11 the graphical representation corresponding to the Schwartz method is shown for all points prior to equivalence and for a selected range between 0.9 to 2.6 mL. A dispersion corresponding to the addition of the initial volumes is observed, which could be associated to the measurements in an unbuffered zone, although this problem is not observed in the vicinity of the equivalence point. A final volume of 2.691 mL and a pK_a value of 4.514 are obtained. The acidity mixed or Bronsted constant of acetic acid, at ionic strength 0.1, is 4.65 [39], whereby its stoichiometric value is 4.57 ($pK_a^c = pK_a^B + \log \gamma_H$). The difference obtained in the final volume by applying Gran and Schwartz methods is less than 0.01 mL in this case.

4.2. Potentiometric Titration of Ammonium Nitrate with Potassium Hydroxide

Twenty five mL of ammonium nitrate solution (0.01 M) is pipetted into a 100 mL flask containing 25 mL of a KCl solution (0.2 M). Then the ammonium solution was titrated potentiometrically with a mixture of KOH and KCl solution (0.1 M) (previously standardized with potassium hydrogen phthalate) using the glass pH electrode.

The first derivative curve does not allow the location of the final point in the case of very weak acids, hence the advantage of the Schwartz method. Figure 12 (top) shows the

titration curve, and a graphical representations of the Gran (middle) and Schwartz (bottom) methods, for data corresponding to volumes of 0.82 to 2.5 mL. A volume of 2.670 mL is obtained for the end point and a pK_a^c of 9.187. The value of the mixed or Bronsted acidity constant of the ammonium ion is 9.36 [21], whereby the pK_a^c is 9.28, so it can be said that the pK_a values are close. The difference in this case is less than 0.1 units of pK_a.

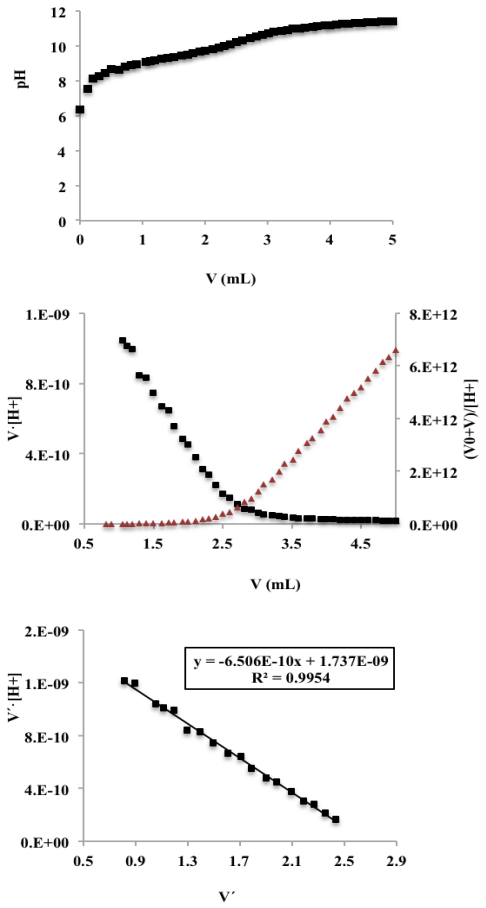

Figure 12. Top: Titration curve of 25 mL of 0.01 M ammonium nitrate with 0.10 M potassium hydroxide; I = 0.1 M (KCl). Middle: Gran method. Bottom: Schwartz method

4.3. Potentiometric Titration of Boric Acid with Potassium Hydroxide

Ten mL of boric acid solution (0.009 M) is pipetted into a 50 mL flask containing 10 mL of a KCl solution (0.2 M). Then the ammonium solution was titrated potentiometrically with a mixture of KOH and KCl solution (0.1 M) (previously standardized with potassium hydrogen phthalate) using the glass pH electrode.

The data corresponding to the boric acid titration are represented in Figure 13, similar to those for the ammonium nitrate. A V_{end} of 2.836 mL and a pK_a of 9.030 were obtained, close to the 9.035 and 9.029 described in the literature under similar conditions by Ivaska and Wänninen [38] (9.031 and 9.022 taking into account the calculations proposed in this work for those data).

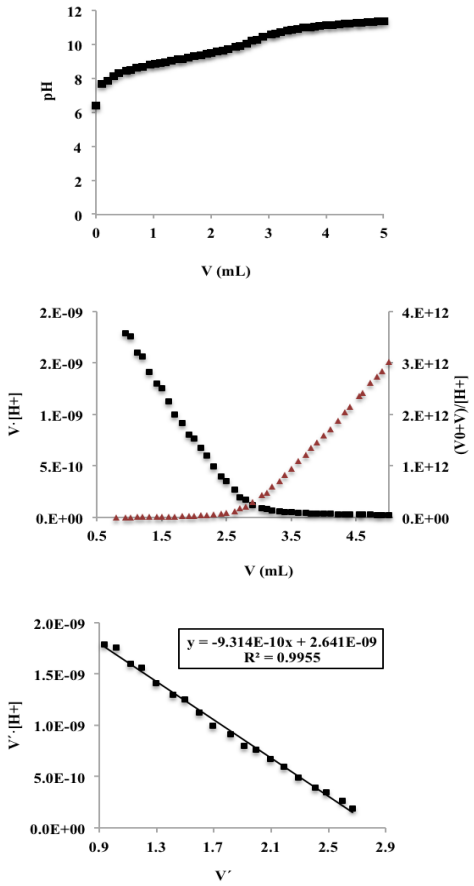

Figure 13. Top: Titration curve of 10 mL of 0.009 M boric acid with 0.10 M potassium hydroxide; I = 0.1 M (KCl). Middle. Gran method. Bottom: Schwartz method

4.4. Potentiometric Titration of Hydrochloric Acid with Potassium Hydroxide: Determination of the Ionic Product of Water

Twenty five mL of hydrochloric acid solution (0.00968 M) (previously standardized with sodium carbonate) is pipetted into a 100 mL flask containing 25 mL of a KCl solution (0.2 M). Then the hydrochloric acid solution was titrated potentiometrically with a mixture of KOH and KCl (0.1 M) (previously standardized with potassium hydrogen phthalate) using the glass pH electrode. The experience was carried out in triplicate.

The potential E (mV) is measured in each case and the corresponding theoretical values of the proton and hydroxyl ion concentrations are calculated from the added titrant mL, before (Eqn. 42) and after (Eqn. 43) the equivalence point, respectively, given the molarities of the solutions involved. Then the potential values, E (mV), are plotted against the values of p[H] ($V < V_{eq}$), and p[OH] ($V > V_{eq}$) (Figure 14). The values of the apparent (conditional) normal potentials, E_{0a}' and E_{0b}', are calculated as the intercept of the straight lines indicated for $V < V_{eq}$ and $V > V_{eq}$, respectively (Eqns 45 and 48). The value of pK_w^c is calculated by means of Eqn. (50), and its standard deviation $s(pK_w^c)$ by applying the law of propagation of errors. The analysis of residuals shows in

(almost) all cases a random pattern, indicating that the applied model fits the data well. The use of more complex models (multiple linear regression) has been unsuccessful. The electrode response, however, moves away from Nernstiana, as happened in the example of Meloun [37] (Figure 7). From the data obtained for the corresponding straight lines, obtained by applying the Excel LINEST function, we have

$$pK_{w,1} = \frac{388.64-(-427.30)}{59.16} = 13.792 \qquad s_{pK_{w,1}} = \frac{\sqrt{1.4047^2+2,3008^2}}{59.16} = 0.046$$

$$pK_{w,2} = \frac{381.18-(-436.29)}{59.16} = 13.818 \qquad s_{pK_{w,2}} = \frac{\sqrt{1.1473^2+2.3610^2}}{59.16} = 0.044$$

$$pK_{w,3} = \frac{379.18-(-434.76)}{59.16} = 13.758 \qquad s_{pK_{w,3}} = \frac{\sqrt{1.0904^2+1.4128^2}}{59.16} = 0.030 \qquad (53)$$

The pK_w values obtained show close agreement with those found in the literature; Egneus [40] reported a value of 13.81 at I = 0.1 ($NaClO_4$), and Hawkes [41] indicated the value of 13.81 at I = 0.1, conditions in which carried out our experience.

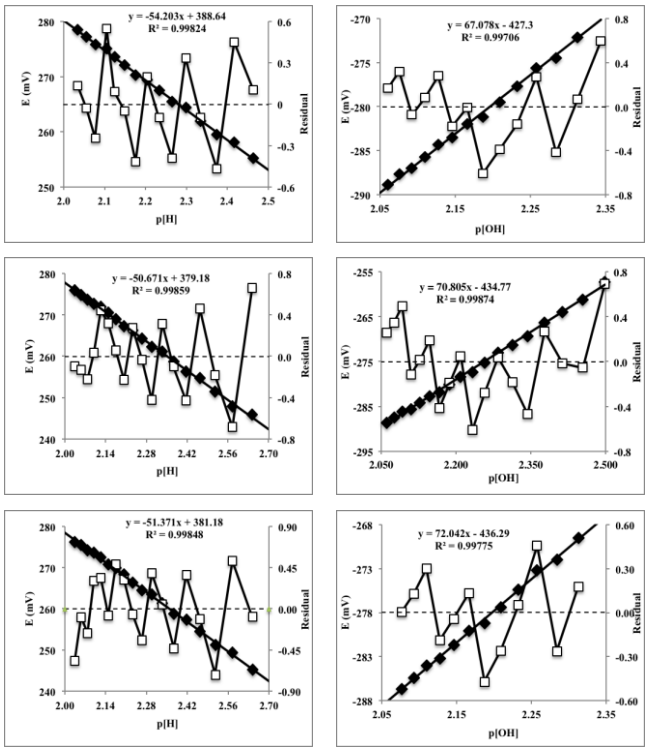

Figure 14. Representations of the potential versus p[H] (acid medium) and p[OH] (alkaline medium), left and right, respectively

5. Conclusions

Potentiometric methods in the analytical work depend upon the interpretation of e.m.f. data obtained from electrochemical cell consisting of a glass (and reference) electrode (pair). Two kind of problems may be solved by a potentiometric titration, either to locate the correct value for the equivalence point in order to determine the concentration of one component in a sample, or to determine a physicochemical parameter, being on this respect a method of choice applied in a great number of cases.

To check a priori the worth of a given acid-base potentiometric method, it is advisable to acquire a previous knowledge based on a mathematical approach with equations for the titration curves involved. A thoroughly theoretical study of the linearization Gran II method (Gran, 1988, 1952) shows its limitation for very weak acids (pKa 9-10,1) whereas the Schwartz [27] method gives good results. The Schwartz method unlike the Gran II one is non- approximate and does not require the previous knowledge of the acidity constants as the method of Ingman and Still [21]. When using a spreadsheet or other computer aid, there seems to be no good reason to favor a Gran plot over a Schwartz plot under any circumstance. However, the titrant concentration must be accurately known, an unnecessary requirement in Gran II method.

Schwartz's method has proved to be very accurate in the location of equivalence point and simultaneously determination of acidity constant, when applied to experimental data described in the literature for a series of chemical system, e.g. ammonium nitrate, β-alanine or boric acid. In addition, titration data has been obtained in our laboratory, e.g. for the acetic acid (pKa = 4.514), ammonium nitrate (pKa = 9.187) and boric acid (pKa = 9.030), being the Schwartz method applied with good results; the acidity constants of such systems closely agree with the values found in the literature.

The classical potentiometric method based on the addition of a titrant (e.g. strong base) to the solution of titrand (e.g. strong acid) has been applied to the determination of ionic product of water, first to Meloun [37] perchloric acid with sodium hydroxide titration data, and then to laboratory data obtained in this work for the titration of hydrochloric acid with potassium hydroxide. Values of ionic product of water, pKw, equals to 13.792 ± 0.046, 13.818 ± 0.044 and 13.758 ± 0.030 were obtained in closely agreement with literature data. Egneus [40] and Hawkes [41] give 13.81 and 13.78, at I=0.1, adjusted with sodium perchlorate, and potassium chloride (as in this work), respectively.

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