

## A Novel Approach to the Calculations Concerning the Titration Curves of Weak Monoprotic Acids or Bases

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### Introduction

Here we present a mathematical method to calculate the pH values along the titration curve of a weak monoprotic acid (WMA) with a strong monoprotic base (SMB), or vice-versa. The ionization constant and initial concentration of the weak electrolyte, as well as the concentration of the titrant, are supposed to be known.

To the same purpose, the traditional method, usually employed in general chemistry courses (and textbooks) at not-advanced levels, makes use of four different formulae, each of them relying upon a different simplifying assumption, and relating to a different point, or segment, of the curve. This fragmented approach may induce the student to consider these various formulae as pertaining to loosely interrelated subjects, instead of regarding at them as describing different aspects of a system that is basically the same.

On the contrary, our method employs an approach that is quite unitary, and turns out to be more accurate and, in our opinion, more firmly sound than the traditional method, yet remaining as intuitive as the latter.

Here are the guidelines along which our method proceeds. First, we derive the exact equation, describing a titration curve of the type under examination in its whole extension. This result is accomplished through straightforward stoichiometric arguments, already employed for similar cases [1,2], with no reference to such "sophisticated" concepts as mass or charge balance. Then, from this exact equation, which turns out to be cubic in the variable  $[H^+]$ , two quadratic equations are generated on the basis of reasonable simplifying assumptions. The first will de-

scribe the curve segment from the initial point to just before the neutrality point, the second, from just beyond this point to the equivalence point and farther.

It will be shown that the curve obtained in this way is coincident, at any practical purpose, with the exact one, for any titration that may be actually carried out as an analytical operation.

The method will be illustrated with reference to a titration of a WMA, denoted as HX, with NaOH as SMB. The symmetrical case of a WMB being titrated with a SMA will be left to the reader, after giving him some simple rules about the way to operate. Therefore, henceforth, the term "titration curve" will be employed to mean a titration curve of a WMA with a SMB. Throughout the whole treatment, it will be assumed that the effects of the internal ionic strength of a solution on its pH value are negligible.

### Theory

By dissolving in water HX and NaOH, a solution is obtained where the five species HX,  $X^-$ ,  $Na^+$ ,  $H_3O^+$ , and  $OH^-$  are contemporarily present at their equilibrium concentrations (henceforth, briefly, concentrations)  $[HX]$ ,  $[X^-]$ , etc. The symbol  $[H^+]$  will be used instead of  $[H_3O^+]$ , for conciseness' sake.

The above species have originated from, or disappeared through :

i) the partial ionization of HX :



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ii) the complete dissociative dissolution of NaOH to give Na<sup>+</sup> and OH<sup>-</sup> ions

iii) the partial reassociation of H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> ions to produce water :



Let us now designate as  $c_a$  and  $c_b$  the analytical concentrations of the acid HX and the base NaOH, respectively, and as  $\Delta'$  [ ] and  $\Delta''$  [ ] the concentration variations that a given species undergoes as a result of reactions R' and R'', respectively. The following equalities will apply :

$$[\text{HX}] = c_a - \Delta'[\text{HX}] \quad (1)$$

$$[\text{X}^-] = c_b + \Delta'[\text{X}^-] = \Delta'[\text{X}^-] \quad (2)$$

$$[\text{H}^+] = K_w^{1/2} + \Delta'[\text{H}^+] - \Delta''[\text{H}^+] \quad (3)$$

$$[\text{OH}^-] = c_b + K_w^{1/2} - \Delta''[\text{OH}^-] \quad (4)$$

where  $K_w$  is the auto-ionization constant of water. Obviously,  $[\text{Na}^+] = c_b$ .

From simple stoichiometric considerations about R' and R'', it comes out that :

$$\Delta'[\text{HX}] = \Delta'[\text{X}^-] = \Delta'[\text{H}^+] \quad (5)$$

and

$$\Delta''[\text{H}^+] = \Delta''[\text{OH}^-] \quad (6)$$

Through (5), equalities (1) and (2) can be rewritten as :

$$[\text{HX}] = c_a - \Delta'[\text{H}^+] \quad (7)$$

and

$$[\text{X}^-] = \Delta'[\text{H}^+] \quad (8)$$

while, through (6), equalities (3) and (4), explicitated with respect to  $\Delta''[\text{H}^+]$  and  $\Delta''[\text{OH}^-]$ , respectively, can yield :

$$\Delta'[\text{H}^+] = c_b + \{[\text{H}^+] - [\text{OH}^-]\} \quad (9)$$

Upon insertion of (9) into (7) and (8), it follows that :

$$[\text{HX}] = (c_a - c_b) - \{[\text{H}^+] - [\text{OH}^-]\} \quad (10)$$

and

$$[\text{X}^-] = c_b + \{[\text{H}^+] - [\text{OH}^-]\} \quad (11)$$

which are the exact expressions of the concentrations of HX and X<sup>-</sup> as functions of [H<sup>+</sup>] and [OH<sup>-</sup>] (cf. \*).

$$\text{Since } [\text{OH}^-] = K_w/[\text{H}^+] \quad (12)$$

equalities (10) and (11) can be turned into :

$$[\text{HX}] = (c_a - c_b) - \{[\text{H}^+] - (K_w/[\text{H}^+])\} \quad (13)$$

and

$$[\text{X}^-] = c_b + \{[\text{H}^+] - (K_w/[\text{H}^+])\} \quad (14)$$

respectively. Upon insertion of (13) and (14) into the equilibrium law of reaction R', i.e. :

$$K_a = [\text{H}^+][\text{X}^-]/[\text{HX}] \quad \text{or} \quad [\text{H}^+] = K_a[\text{HX}]/[\text{X}^-] \quad (15)$$

one obtains :

$$[\text{H}^+] = K_a \frac{(c_a - c_b) - \{[\text{H}^+] - K_w/[\text{H}^+]\}}{c_b + \{[\text{H}^+] - K_w/[\text{H}^+]\}} \quad (16)$$

which is the third-degree equation in the unknown [H<sup>+</sup>] to be used for an exact calculation of the H<sub>3</sub>O<sup>+</sup> ion concentration in an aqueous solution containing both a WMA and a SMB.

When a titration is actually being performed, a solution of NaOH, at analytical concentration  $c_b^0$ , is gradually added to a volume  $V_a^0$  of the solution of HX, whose analytical concentration let us now suppose to be known, and equal to  $c_a^0$ . Let  $V_b$  be the volume of titrant which has been added from the beginning of the titration up to a given point. The analytical concentrations of the acid and the base in the resulting solution will depend on  $V_b$  according to the expressions :

$$c_a = c_a^0 V_a^0 / (V_a^0 + V_b) \quad \text{and} \quad c_b = c_b^0 V_b / (V_a^0 + V_b) \quad (17)$$

which are strictly exact only if the volumes of the solutions being mixed are strictly additive.

Correspondingly, upon insertion of (17) into (16), an expression relating [H<sup>+</sup>] to  $V_b$  will be obtained, whence a traditional titration curve, i.e., a "pH vs.  $V_b$  (or  $c_b^0 V_b$ )" curve, can be drawn.

However, in this paper, as "titration curve" we will mean a "pH vs. r" curve, where :

$$r = V_b/V_a^0 \quad (18)$$

which, when inserted into (17), yields :

$$c_a = c_a^0 / (1 + r) \quad \text{and} \quad c_b = c_b^0 r / (1 + r) \quad (19)$$

The ratio r is dimensionless ; so, unlike  $V_b$  or  $c_b^0 V_b$ , it does not depend on the units employed, and its value,  $r_e$ , at the equivalence point is not affected by the "size" of the sample being titrated. Indeed,

$$r_e = c_a^0 / c_b^0 \quad (20)$$

while :

$$(V_b)_e = c_a^0 V_a^0 / c_b^0 \quad \text{and} \quad (c_b^0 V_b)_e = c_a^0 V_a^0 \quad (21)$$

By inserting the values of  $c_a$  and  $c_b$ , as defined according to (19), into eq (16), an expression is obtained which is cubic with respect to [H<sup>+</sup>], but linear with respect to r, and can be rearranged in the form

$$r = \frac{K_w K_a + (K_w + K_a c_a^0) [\text{H}^+] - K_a [\text{H}^+]^2 - [\text{H}^+]^3}{[\text{H}^+]^3 + (K_a + c_b^0) [\text{H}^+]^2 - (K_w - K_a c_b^0) [\text{H}^+] - K_w K_a} \quad (22)$$

\* The sum of eqs (10) and (11) yields  $[\text{HX}] + [\text{X}^-] = c_a$  that represents the mass balance of the solute HX. In addition, since  $c_b = [\text{Na}^+]$ , eq (11) can be rearranged as  $[\text{H}^+] + [\text{Na}^+] = [\text{OH}^-] + [\text{X}^-]$  which expresses the electrical neutrality (or charge balance) of the solution phase.

whence the exact pH values along a titration curve will be obtained by numerical inversion [3].

As obvious, a titration curve begins at acidic pH values, and ends at alkaline ones, passing through a neutrality point where  $[H^+] = K_w^{1/2}$ . Upon insertion of this value into eq (22), the corresponding  $r_n$  value of  $r$  at the neutrality point will be found to be :

$$r_n = (c_a^0/c_b^0) \cdot [K_a/(K_a + K_w^{1/2})] \quad (23)$$

$$= K_a/(K_a + K_w^{1/2}) \quad (\text{if } c_a^0 = c_b^0) \quad (24)$$

Since  $[H^+]$  is a decreasing function of  $r$ , along the titration curve it will be  $[H^+] > [OH^-]$  for  $r < r_n$ , and  $[H^+] < [OH^-]$  for  $r > r_n$ , and as the abscissa of a point of the curve will move farther and farther away from the neutrality point, the absolute value of the difference between the concentrations of these two ions will become larger and larger.

On the basis of this simple observation, a reasonable approximated form, valid for  $0 \leq r < r_n$  (the "acidic portion" of the curve), of the exact eq (16), can be obtained by rewriting it as :

$$[H^+]^2 + c_b[H^+] - K_w \cong K_a \{ (c_a - c_b) - [H^+] + \frac{K_w}{[H^+]} \} \quad (r < r_n) \quad (25)$$

which turns out to be quadratic in the unknown  $[H^+]$  once the term  $K_w/[H^+]$  *i.e.*,  $[OH^-]$ , has been neglected with respect to  $[H^+]$ .

As regards the "basic portion" of the curve, let us first rewrite eq (16) in terms of  $[OH^-]$  :

$$[OH^-] = K_b^* \cdot \frac{c_b - [OH^-] + K_w/[OH^-]}{(c_a - c_b) - K_w/[OH^-] + [OH^-]} \quad (26)$$

where :

$$K_b^* = K_w/K_a \quad (27)$$

is the ionization constant of  $X^-$ , the conjugated base of  $HX$ , usually designated as the hydrolysis constant of  $X^-$ . Eq (26) can be rearranged as :

$$[OH^-]^2 + (c_a - c_b) \cdot [OH^-] - K_w \cong K_b^* (c_b - [OH^-] + \frac{K_w}{[OH^-]}) \quad (r > r_n) \quad (28)$$

where  $K_w/[OH^-]$  has been neglected with respect to  $[OH^-]$  ; this approximated equation, valid for  $r > r_n$ , is perfectly similar to eq (25), and is quadratic in  $[OH^-]$ .

Therefore, a titration curve may be approximately described :

i) for its acidic portion ( $r < r_n$ ), by the formula :

$$[H^+] \cong - \frac{K_a + c_b}{2} + \sqrt{\left(\frac{K_a + c_b}{2}\right)^2 + K_a \cdot (c_a - c_b) + K_w + \frac{K_a K_w}{[H^+]}} \quad (29)$$

which immediately comes out of (25), and :

ii) for its basic portion ( $r > r_n$ ), through the formula (generated by eq (28)) :

$$[OH^-] \cong - \frac{K_b^* + c_a - c_b}{2} + \sqrt{\left(\frac{K_b^* + c_a - c_b}{2}\right)^2 + K_b^* \cdot c_b + K_w + \frac{K_b^* K_w}{[OH^-]}} \quad (30)$$

by calculating the corresponding  $[H^+] = K_w/[OH^-]$  values.

Of course, in formulae (29) and (30), the terms  $c_a$  and  $c_b$  are given by eqs (19) for each value of  $r$ .

Since the barred terms in (29) and (30) are positive, the approximate values of the radicands are lower than the exact ones ; so, while formula (29) produces  $[H^+]$  values approximate by defect, formula (30), through  $[OH^-]$  values by defect, yields  $[H^+]$  values approximate by excess.

It is to be remarked that, when  $c_b = 0$  and  $K_w$  is much lower than the other addends under the square root of formula (29), it reduces to the familiar expression

$$[H^+] \cong - (K_a/2) + \sqrt{(K_a/2)^2 + K_a c_a} \quad (31)$$

which gives  $[H^+]$  for a solution where a WMA is the only solute ; similarly, when  $c_b = c_a$  (*i.e.*, at the equivalence point), and if  $K_w$  can be neglected with respect to the other terms of radicand of formula (30), it reduces to the well-known formula to calculate  $[OH^-]$  in a solution containing the salt  $NaX$  as the only solute, at an analytical concentration  $c_s = c_a = c_b$  :

$$[OH^-] \cong - (K_b^*/2) + \sqrt{(K_b^*/2)^2 + K_b^* c_s} \quad (32)$$

All the relations and formulae derived in this section for a titration of a WMA with a SMB can be extended to the symmetric case of a WMB being titrated with a SMA, just by interchanging :

- i)  $[H^+]$  with  $[OH^-]$  ;
- ii)  $K_a$  with  $K_b$ , and  $K_b^*$  with  $K_a^*$  ;
- iii)  $c_a$  with  $c_b$ , and  $c_a^0$  with  $c_b^0$  ;
- iv)  $V_a$  with  $V_b$ , and  $V_b$  with  $V_a$ .

## Test of the performance of the method

When a titration is being actually performed, the pH indicator employed to detect the equivalence point has to be chosen such that its  $pK$  is as close as possible to the expected pH at the equivalence point. In addition, to obtain a sufficiently accurate value (say, within 1 % ca.) of the analytical concentration of the WMA being titrated, its ionization constant and analytical concentration have to be such that [4]  $K_a c_a^0 > 10^{-8}$ , when  $c_a^0$  is given as  $\text{mol} \cdot \text{L}^{-1}$ . On the other hand, in practise, titrations are better performed if both the acid and the base have analytical concentrations around  $10^{-1} \text{ mol} \cdot \text{L}^{-1}$ .

Keeping these requirements into account, and considering that the order of magnitude of the ionization constants of most WMA's ranges between  $10^{-1}$  and  $10^{-12}$ , we tested the performance of our method under the following conditions :  $c_a^0 = c_b^0 = 10^{-1} \text{ mol} \cdot \text{L}^{-1}$ , and  $K_a = 10^{-1}, 10^{-2}, \dots, 10^{-7}$ . In other words, we calculated the  $[H^+]$  values along various titration curves by means of (29) plus (30), and compared them with the exact ones, obtained from (22) by employing numerical inversion together with the "interval bisection" method, which allows to calculate  $[H^+]$  (and pH) values in correspondence with pre-selected, evenly spaced, round values of  $r$ .

Under the above-specified conditions, the approximate values of pH coincide with the exact ones at least up to the fourth decimal digit, *i.e.*, beyond the limit of practical significance, along the almost complete extension of the curve. Only in a very tiny interval of  $r$  in the proximity of the neutrality point some minor discrepancies, affecting the fourth decimal digit, can be sometimes observed. This result was not unexpected, since, around the neutrality point, the barred terms in (29) and (30) are no more negligible with respect to the other addends under the square roots.

Upon decreasing  $c_a^0$  and/or  $c_b^0$ , these discrepancies become larger, but the interval of  $r$  values where they can be detected remains quite narrow \*\*.

## Final remarks

In our opinion, the approach here proposed is unitary, simple, and intuitive ; so, it could be a valid tool in teaching acid-base equilibria in aqueous solutions and their quantitative aspects, to

\*\* However, should a pH value be calculated very exactly in the immediate vicinity of the neutrality point, the following two-step method may be used. If  $r \cong r_n$ , then  $[H^+] \cong [OH^-]$  ; so, the barred term in (29) will result larger, about equal, or smaller than the barred term in (30), according to which one of the three conditions  $K_a \cong K_b^*$  will be valid. Correspondingly, formula (29) will turn out to be more inaccurate, about as accurate, or more accurate than (30).

A first-approximation  $[H^+]$  (or  $[OH^-]$ ) value will be calculated by means of the more accurate formula, chosen on the basis of the above criterion, and disregarding the condition  $r \geq r_n$ .

This value will then be reinserted into the right-hand member of the same formula, where the barred term now has no more to be treated as negligible with respect to the other addends.

The second-approximation  $[H^+]$  (or  $[OH^-]$ ) value obtained by this route yields a pH value always coincident with the exact one, at least within the first three decimal digits, i.e., at any practical purpose.

be employed, at least, in parallel with the compartmentalized, sometimes grossly approximate, approach of the traditional method.

In particular, it should help the student to grasp the concept that a titration curve is described, along its whole extension, by only one general equation, and that to build it piecewise is just an artifice to work with equations easier to handle. In comparison with the four, apparently not interconnected, formulae of the traditional method (the initial point, the buffering region, the equivalence point, the excess of titrant), the two quadratic formulae here proposed in place of the exact cubic equation, immediately show their common origin. As for the accuracy of the results they yield, it is quite good along the whole extension of the curve, with the exception, in some cases, of a very narrow interval of  $r$  around the neutrality point. In comparison, the results of the traditional method may be rather poor along not negligible portions of the curve.

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