The Journal of the
American Chemical Society

VOL. 50 JANUARY, 1928 No. 1

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 547]

THEORY OF THE END-POINT IN ELECTROMETRIC TITRATION

BY P. S. ROLLER

RECEIVED JUNE 17, 1927 PUBLISHED JANUARY 5, 1928

In a paper recently published by Eastman[1] on the theory of the electrometric titration of an acid by a base, certain conclusions among others were drawn to the effect that the inflection point in the e.m.f. titration curve would not appear when the ionization constant of the acid of a given concentration is below a certain magnitude, in particular that it would not appear when $K_A \leqq 10^{-12}$ for a 1.0 molar acid, or when $K_A \leqq 10^{-9}$ for a 0.001 molar acid. In attempting to confirm this result, we have been able to generalize the theory of the end-point in electrometric titration, and in a subsequent paper consider by the method of analysis here used the electrometric (and colorimetric) titration of polybasic acids, weak base salts, and their mixtures, by a base or mixture of bases.

We also find here that there is a discrepancy between our result for the appearance of the inflection point and that of Eastman. We may without sensible error consider the exact equation (10a) below as of the third degree and, testing for real roots, we find that the condition of the appearance of an inflection point in the titration of a weak acid by a strong base is that $cK_A > 27K_w$, where K_A is the ionization constant of the acid, K_w the ion product constant of water and c is a concentration defined by the following equation:

$$\frac{1}{c} = \frac{1}{a} + \frac{1}{b} \tag{1}$$

where a is the initial concentration of the acid and b is the initial concentration of the base in the titrating solution. We have checked this condition numerically. We see then that an inflection point should appear when K_A is as low as 3×10^{-13} for a 1 normal acid, neglecting dilution. The discrepancy between this result and that of Eastman appears to be due to an oversight in his numerical calculation of an otherwise correctly derived equation.

---

[1] Eastman, THIS JOURNAL, **47**, 332 (1925).

Determination of the H-Ion Concentration at the End-Point and at the Inflection Point

In a plot of E, the e.m.f. of the H_2 half cell, against n/n_e, the fraction of the number of cc.'s required to reach the end-point, the condition for an inflection point is, from the equation

$$E = 0.059 \log x = -0.059\, px \tag{2}$$

that

$$\frac{d^2n}{dx^2} = -\frac{1}{x}\frac{dn}{dx} \tag{3}$$

where x is the H-ion concentration in the solution, px is the P_H of the solution and n is the number of cc. of titer.

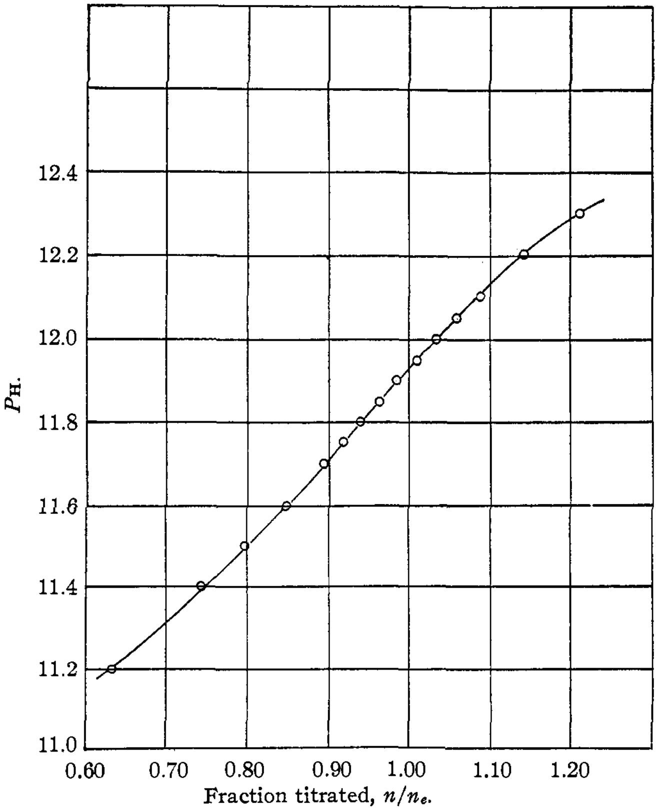

Fig. 1.—P_H *vs.* fraction titrated, n/n_e. $K_A = 10^{-11}$, $a = 0.1$, $b = 0.4$.

We can obtain an exact relation between n and x as follows. Let b represent the concentration of the base in moles per liter, v the initial volume of the solution, x the concentration of the non-ionized part of the acid HA of initial concentration a, and y the OH^- concentration in solution. In an infinitesimal addition of titrating solution the number of moles of

OH-ion added per unit volume is $[b/(V+n)]\mathrm{d}n$. This quantity is divided in the solution between increasing the OH^--ion concentration, and decreasing the H^+ and HA concentrations. The following equation accounts for the distribution within the solution of the added OH^- ion, allowing for dilution of the solution by the added titer

$$\frac{b}{V+n}\,\mathrm{d}n = \mathrm{d}y - \mathrm{d}x - \mathrm{d}z + \frac{(y-x-z)}{V+n}\,\mathrm{d}n \qquad (4)$$

This equation may be simply integrated if we take as the variables b and $(y - x - z)$. The integration constant is determined by the condition that, when $n = 0$, $(a - z) + y = x$, which expresses the electrical neutrality of the solution, so that upon integration of (4) we obtain

$$\frac{bn}{V} = a + \left(1 + \frac{n}{V}\right)(y - x - z) \qquad (5)$$

n in (5) may be obtained as a function of x alone by eliminating y and z by means of the following ionization equations

$$xy = K_w \qquad (6)$$

$$\frac{x\left(a\dfrac{V}{V+n} - z\right)}{z} = K_A \qquad (7)$$

In (7), the ionization equation of the acid, we have assumed that the salt formed is 100% ionized. If it is not, a simple correction must be made to K_A for the degree of dissociation; or an activity coefficient correction may be applied to both K_A and K_w.

At the end-point we have by definition that

$$\frac{bn_e}{V} = a \qquad (8)$$

We have then upon substituting from (6), (7) and (8) in (5) an equation in x_e, the H-ion concentration at the end-point

$$\left(1 + \frac{a}{b}\right)\left(\frac{K_w}{x_e} - x_e\right) - \frac{ax_e}{(K_A + x_e)} = 0 \qquad (9a)$$

This is a third-degree equation in x_e, but from the physical nature of the problem two of these roots must be imaginary. Expanding $1/(K_A + x_e)$ in powers of x_e/K_A, we finally obtain, in the titration of a weak acid, that

$$x_e = \sqrt{\frac{K_w K_A}{c}}\left[1 + \frac{1}{2}\sqrt{\frac{K_w}{cK_A}} - \frac{1}{8}\,\frac{K_w}{cK_A}\cdots\right] \qquad (9)$$

where c is a concentration defined by Equation (1).

This equation for the H-ion concentration at the end-point is practically identical with the usual result obtained in the calculation of the hydrolysis of a normal salt. The effect of dilution by the added titer is contained by virtue of c in the term $1/b$, the reciprocal of the concentration of the base in the titrating solution, which may usually be neglected, against $1/a$, the reciprocal of the initial concentration of the acid in the solution. In that event, we may replace c by a in (9).

We must now determine x_i, the H-ion concentration at the inflection point. Differentiating (4), (6) and (7) with respect to x and substituting in (2) we finally obtain

$$2\left(1+\frac{a}{b}\right)\frac{K_w}{x_i^3}+\frac{2aK_A}{(K_A+x_i)^3}=\left(1+\frac{a}{b}\right)\frac{K_w}{x_i^3}+\frac{aK_A}{x_i(K_A+x_i)^2}+\left(1+\frac{a}{b}\right)\frac{1}{x_i} \tag{10a}$$

This fifth-degree equation has at least one real root. We are interested in the root in the neighborhood of the end-point. Expanding then in a binomial series in powers of x_i/K_A we find for the H-ion concentration at the inflection point

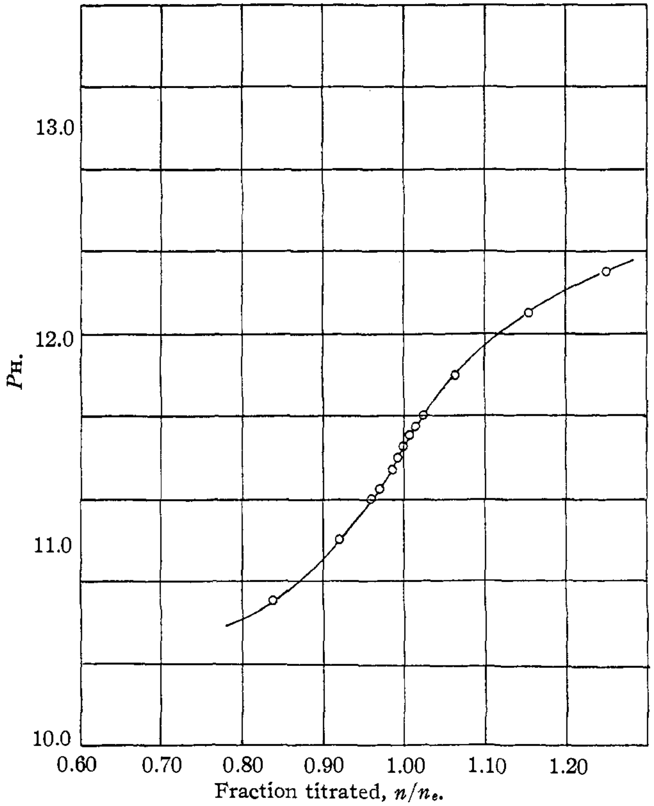

Fig. 2.—PH *vs.* fraction titrated, n/n_e. $K_A = 10^{-10}$, $a = 0.1$, $b = 0.4$.

$$x_i = \sqrt{\frac{K_wK_A}{c}}\left[1+2\sqrt{\frac{K_w}{cK_A}}+\frac{3}{2}\frac{K_w}{cK_A}+\ldots\right] \tag{10}$$

From this approximation equation for a weak acid, which holds very closely for K_w/cK_A as large as 10^{-2}, we see that the H-ion concentration at the inflection point is finite and real, at least for all values such that the series is convergent, that is, for $cK_A > K_w$. However, from the exact equation (10a), the condition is $cK_A > 27K_w$. Since $x_i > x_e$ the inflection point always precedes the end-point, except when the acid is strong ($K_A \longrightarrow \infty$). In that case $x_i = x_e = \sqrt{K_w}$, a result obtained from (9a) and (10a).

We have for the difference in P_H between the end-point and the inflection point from (9) and (10)

$$Px_e - Px_i = 0.65\sqrt{\frac{K_w}{cK_A}} \tag{11}$$

Thus from this equation the difference in P_H between the end-point and the inflection point, which is seen to be very small, depends not only upon K_A but also, and in the same way, upon the acid and base concentration, that is, upon the product cK_A, where $1/c = 1/a + 1/b$ by (1), and increases as cK_A decreases.

This difference in P_H may be obtained in terms of the difference in cc. of titer between the inflection point and end-point by means of the general relation

$$\frac{\Delta n}{n_e} = \left(\frac{dn}{dx}\right)_{x_e < x < x_i} \Delta x \tag{12}$$

$\Delta n/n_e$ represents the deviation of the end-point from the inflection point as a fraction of the total titer required to reach the end-point, Δx being equal to $x_i - x_e$, and Δn to $n_i - n_e$.

We thus obtain for the fractional deviation, $\Delta n/n_e$, upon calculation by means of this equation

$$\frac{\Delta n}{n_e} = -\frac{3K_w}{cK_A} \tag{13}$$

Table I

Results of Calculations

cK_A	$Px_e - Px_i$	Px_e ($c = 1.10$)	$100\,\dfrac{Px_e - Px_i}{Px_e}$	$-100\,\dfrac{\Delta n}{n_e}$
10^{-8}	0.00065	10.0	0.01	0.0003
10^{-10}	.0065	11.0	.06	.03
10^{-11}	.0206	11.50	.18	.30
10^{-12}	.065	12.00	.54	3.0

In Table I above, we have made numerical calculations of the deviation of the end-point from the inflection point for a series of acids. In Col. 1 is given the product cK_A ranging from 10^{-8} to 10^{-12}. In the second column is given corresponding to each product cK_A the difference in P_H between the inflection and end-points calculated from (11) with $Kw = 10^{-14}$, in the third column is the P_H at the end-point for $c = 0.10$ calculated from (9), in the fourth column is the percentage deviation in P_H between the end-point and the inflection point and in the last column is given the percentage titer deviation calculated from (13).

From this table it is seen that when the product of the concentration into the ionization constant is equal to 10^{-11} the titer deviation of the end-point from the inflection point is 0.3%, but only 0.03% when the product is equal to 10^{-10}, decreasing rapidly thereafter. For $cK_A = 10^{-12}$, the deviation is 3.0%. Inasmuch as when the product cK_A is as small as 10^{-12} the error of titration, if it can be performed at all, is of a greater magnitude than the last result would indicate, we must look for a different cause of the increased error. The answer seems to lie in the physical difficulty of locating the inflection point, in a plot of E against n/n_e, when the product of the concentration into the ionization constant becomes so small. This, of course, is a matter apart from the error due to the difference, $px_e - px_i$.

The Error of Locating the Inflection Point

In the neighborhood of the inflection point the curve is symmetric about a horizontal axis passing through it. Consider the points P and P' in the neighborhood of the inflection point symmetrically located with respect to it. If the tangent to all three points is the same, it is clear that it will be impossible to distinguish the inflection point lying between P and P', since then the curve degenerates into a straight line.

This leads us to suspect that it is the difference in slope at P (or P') and at the inflection point that determines the error of locating the latter on the curve. We distinguish the inflection point from other points by the fact that at that point the slope of the curve is a maximum and therefore is the more readily differentiated as its slope is greater than that of other points in its neighborhood. This may perhaps be more readily seen when we consider a plot[2] of $\Delta E/\Delta\left(\frac{n}{n_e}\right)$ against n/n_e, in which case the ordinates are proportional to the slope of the usual titration curve while the inflection point is now a maximum point. This maximum is the more accurately located the steeper the curve.

We have for the slope of the tangent to the curve at any point by differentiating (2)

$$\frac{dE}{d\left(\frac{n}{n_e}\right)} = -\frac{0.059}{2.302}\,\frac{1}{\left[\frac{K_w}{cx} + \frac{x}{a} + \frac{K_A x}{(K_A + x)^2}\right]} \tag{14}$$

At the inflection point, substituting for x_i from (10), we have

$$\left[\frac{dE}{d\left(\frac{n}{n_e}\right)}\right]_{x_i} = \frac{0.059}{4.604}\sqrt{\frac{cK_A}{K_w}} \tag{15}$$

Let us choose our arbitrary reference point P at the 91% neutralization point. We have by (7) for the H-ion concentration at P, $x_P = 0.1K_A$.

Upon substitution in (14) we obtain for the slope at the point of reference, P

---

[2] Cox, This Journal, 47, 2138 (1925).

$$\left[\frac{dE}{d\left(\frac{n}{n_e}\right)}\right]_{xP} = -\frac{0.059}{2.302}\,\frac{1}{\left(\frac{10K_w}{cK_A} + 0.0825\right)} \tag{16}$$

Thus the difference in slope at P and at the inflection point depends by equations (15) and (16) only upon the product, cK_A, with $1/c = 1/a + 1/b$, similarly to previous results.

TABLE II

CALCULATED DIFFERENCES

cK_A	$\frac{1}{0.059}\left[\frac{dE}{d\left(\frac{n}{n_e}\right)}\right]_{xi}$	$\frac{1}{0.059}\left[\frac{dE}{d\left(\frac{n}{n_e}\right)}\right]_{xP}$	Difference
10^{-6}	2160	5.2	2155
10^{-8}	216	5.2	211
10^{-10}	21.6	5.2	16.4
10^{-11}	6.9	4.6	2.3
10^{-12}	2.4	2.4	0.0

In Table II we have calculated the differences in a plot of $E/0.059(=P_{\rm H})$ against n/n_e between the slope at the 91% neutralization point and at the inflection point for cK_A from 10^{-6} to 10^{-12}. The first column gives the magnitude of the product cK_A, the second gives the slope at the inflection point, the third gives its value at the 91% neutralization point, the fourth shows the difference in slope at these two points.

It is seen that the difference falls off rapidly as we go from cK_A equal to 10^{-6} to cK_A equal to 10^{-11}. At cK_A equal to 10^{-12}, the slopes are practically equal, so that the whole curve in the vicinity of the inflection point tends to contract into a straight line. However, in spite of this, the inflection point may still be located even for $cK_A = 10^{-12}$, though here the error may be considerable in the usual plot of E against n/n_e, where, in order to observe that there is any inflection in the curve at all, it must be plotted over a large range in n/n_e, say from 0.65 to 1.25.

Graphical Illustration

In the titration of a weak monobasic acid by a strong base, we have plotted $P_{\rm H}$ against n/n_e from Equation (5) for the two acids $K_A = 10^{-10}$, $K_A = 10^{-11}$, each of initial molar concentration $a = 0.10$, and with b, the strength of the titrating solution, equal to 0.4.

Examination of these curves shows the following.

1. There is an inflection point in both cases. It is visible for $K_A = 10^{-11}$ only upon close scrutiny of the curve as a whole, but it may not be sharply located. The error of locating it will by comparison of the curves obviously be much less for the stronger acid, $K_A = 10^{-10}$.

2. Ascertaining the position of the inflection point as best we may, the difference in $P_{\rm H}$ at the end-point where $n/n_e = 1.0$ and at the in-

flection point appears to be +0.09 ± 0.06 for $K_A = 10^{-11}$ and +0.02 ± 0.02 for $K_A = 10^{-10}$. By Equation (11) we would calculate these P_H differences to be +0.073 and +0.023, respectively.

Corresponding to the above P_H differences, we have again from the curves for the deviations in cc. of titer for $K_A = 10^{-11}$ 4 ± 4%, for $K_A = 10^{-10}$ 0.3 ± 0.3%. By Equation (13) we calculate these titer deviations to be 3.7 and 0.37%, respectively. While the calculated P_H and titer differences agree well with the observed, there is an error in the observed values which is due to the uncertainty of locating the inflection point on the curve. The magnitude of this error is closely equal to the differences themselves.

The graphs here considered represent an ideal case in that there are no errors of reading the e.m.f., buret, etc., and the number of points taken is greater. Consequently in any experimental plot of e.m.f. against n/n_e, the error of locating the inflection point will doubtless be greater than is indicated by the above results.

The writer wishes to record his appreciation of the helpful advice rendered by Professor H. A. Fales of this University.

Summary

1. In the electrometric titration of a monobasic acid by a strong base, an inflection point in the e.m.f. titration curve will appear if $cK_A < 27K_w$.

2. Simple equations are deduced for the difference in P_H and in cc. of titer between the inflection point and the end-point. The former always precedes the latter. The differences which are usually negligible increase with the weakness of the acid and with the dilution.

3. Apart from these calculable differences, there is an error of locating the inflection point. This error arises from the tendency of the curve to compress into a straight line in the neighborhood of the inflection point as the acid is weaker or the dilution greater.

NEW YORK, N. Y.