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A MODIFIED GRAN METHOD FOR DETERMINATION OF EQUIVALENCE POINTS IN POTENTIOMETRIC PRECIPITATION TITRATIONS

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SUMMARY

Gran's method is frequently applied in potentiometric titration to obtain a more precise estimate of the equivalence point, particularly when the analyte concentration is too low to give well defined end-points. With precipitation reactions, however, when the analyte concentration is comparable to the solubility of the precipitate, even the use of Gran's method will not avoid significant errors. A correction term is introduced and a computer program outlined to overcome this problem. Titrations of 10^{-4} M chloride are used for illustration.

Gran [1] utilized algebraic manipulation of the Nernst equation and the stoichiometry to obtain various expressions which describe all cases of potentiometric titrations.

In precipitation titrations of the general type $xA + yB \rightarrow A_xB_y$, the expression is

$$(V_0 + V)\, 10^{16.9\, nA\,(E - K_1)} = K_2\,(V_e - V) \qquad (1)$$

where V_0 is the initial volume, V the volume added, and V_e the volume added at the equivalence point; nA or nB is the number of electrons involved in the electrode reaction of A or B, respectively; K_1 and K_2 are arbitrary constants; $F(2.30\ RT)^{-1} = 16.9\ V^{-1}$ (at 25°C). Equation (1) is applicable for an electrode which is sensitive to ion A before the equivalence point is reached. After the equivalence point, the expression is

$$(V_0 + V)\, 10^{16.9\, nA\,(K_3 - E)}\, x/y = K_4\,(V - V_e) \qquad (2)$$

The analogous expressions when the electrode is sensitive to ion B are

$$(V_0 + V)\, 10^{16.9\, nB\,(K_5 - E)}\, y/x = K_6\,(V_e - V) \qquad (3)$$

$$(V_0 + V)\, 10^{16.9\, nB\,(E - K_7)} = K_8\,(V - V_e) \qquad (4)$$

before and after the equivalence point. In all cases it is assumed that A is the analyte and B the titrant added.

The plots of the left-hand sides of eqns. (1)–(4) vs. V are straight lines. Figure 1 shows the plots obtained for eqns. (3) and (4) applied to chloride titration with silver(I) standard solutions and the Orion model 94-16 Ag_2S indicator electrode. When the initial concentration of chloride is 10^{-3} M (or more), the V_e results are exact, but when this is decreased to 10^{-4} M the values are considerably different from the theoretical values. With 10^{-4} M solutions, the straight lines do not intersect on the abscissa as predicted by the equations. Further, the intersection point does not indicate the true value of V_e, as would be expected if the errors of both lines were compensated.

Various workers have described improvements of the method of calculation to determine V_e. McCallum and Midgley [2] developed a more general expression than Gran's equations. They took into account the solubility of the ionic species precipitated and the activity coefficients. In the present paper, Gran's general development is retained and the solubility effect is considered as a correction term. The calculations are then the same as in Gran's method and the correction term can be included or not, depending on the error expected, which can be estimated in advance. Isbell and Pecsok [3] used a method based on a rigorous non-linear least-squares adjustment to fit experimental variables. They considered theoretically a solubility term but it was neglected during derivation of the equations.

Another method of data handling in the evaluation of low concentrations is the standard addition method. Still [4] compared this method to Gran's

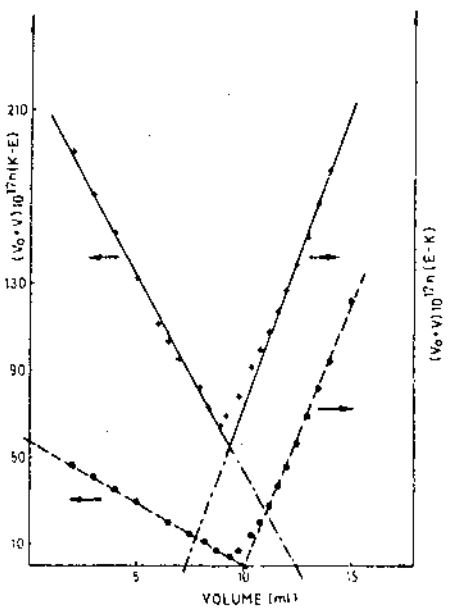


Fig. 1. Gran plots based on eqns. (1–4). (•) Titration of 10 ml of 10^{-3} M chloride with 10^{-2} M silver nitrate in 1 M HNO_3; (+) titration of 100 ml of 10^{-4} M chloride with 10^{-3} M silver nitrate in 1 M HNO_3.

method for complexation reactions. Horvai et al. [5] used a different method of data handling for the standard addition calculation. Although this technique is simpler and faster than others, standard addition still gives less reliable results than titration methods.

THEORY

The same general precipitation reaction as used by Gran and as cited above is considered. In all cases, species A is active at the electrode, exchanging n electrons, while B is electrochemically inert.

First, the case where A is the analyte and B the standard is considered. Before the equivalence point, the concentration of B (C_B) is equal to the concentration (S_B) predicted by the solubility product. $C_{A'}$ becomes the excess with respect to C_B. Thus $C_B = S_B$ and

$$C_A = C_{A'} + S_B\, x/y \tag{5}$$

Two other equations related to the solubility product and the stoichiometry of the reaction are well known:

$$K_{so} = C_A^x C_B^y = S_B^y\ (C_{A'} + S_B x/y)^x \tag{6}$$

$$C_A^0 V_0 = C_B^0 V_e x/y \tag{7}$$

where C_A^0 and C_B^0 are the original concentrations of the reactants. From here, the development of the theory proceeds similarly to Gran, but with some modifications. The value of $C_{A'}$ for V ml of standard added is

$$C_{A'} = (C_A^0 V_0 - C_B^0 V x/y)/(V_0 + V) = C_B^0 (x/y)\ (V_e - V)/(V_0 + V) \tag{8}$$

Substitution of eqn. (8) in eqn. (5) gives

$$C_A = (x/y)\ \{[C_B^0 (V_e - V)/(V_0 - V)] - S_B\} \tag{9}$$

Another expression for C_A can be obtained from the Nernst equation:

$$E = E' + f\, RT(nF)^{-1} \ln C_A \tag{10}$$

where $E' = E_0' + E_j - E_r + f\, RT(\mathrm{nF})^{-1} \ln \gamma$. Here E is the electrode potential, E' is the electrode formal potential, E_0' is a function which depends on electrode construction, E_j is the junction potential, E_r the reference electrode potential, γ is the activity coefficient of A and $f = S_L nF(RT)^{-1}$ is the fraction of the ideal Nernstian response of the electrode (S_L = slope). It is assumed that E' will remain constant during the titration and then E' can be expressed as $E' = f\, RT(nF)^{-1} \ln K_A^0$, where K_A^0 is a constant.

Together with eqn. (10), this expression for E' gives

$$E = f\, RT(nF)^{-1} \ln (C_A^0 K_A^0) \tag{11}$$

Changing to decimal logarithms and replacing $F(2.30\, RT)^{-1}$ by its value 16.9 V^{-1} (at 25°C) gives

$$C_A = (K_A^0)^{-1}\, 10^{16.9nE/f} \tag{12}$$

Comparison of eqn. (12) with the second term of eqn. (9) and rearrangement gives

$$(V_0 + V)\,[10^{16.9nE} - K_A\,(x/y)\,S_B] = K_A^0\,(x/y)\,C_B^0(V_e - V) \tag{13}$$

To express eqn. (13) in a form similar to that of Gran's equation, the following substitutions are made: $K_A^0\ (x/y)\ C_B^0 = K_1\ 10^{16.9nK_2}$, where K_1 and K_2 are arbitrary constants, and $K_A^0 = 10^{16.9nE'/f}$ (from $E' = f\,RT(nF)^{-1}\ln K_A^0$). With these substitutions, and division by $10^{16.9nK_2}$, eqn. (13) becomes

$$(V_0 + V)\,[10^{16.9n(E-K_2)/f} - (x/y)S_B\ 10^{16.9n(E'-K_2)/f}] = K_1\,(V_e - V) \tag{14}$$

which can be compared with eqn. (1) obtained by Gran. The main term on the left-hand side of eqn. (14) is the same as in eqn. (1), but there is a Gran term. On the same side there is a less significant correction term which is a function of solubility. In eqn. (1) $f = 1$ is assumed, i.e. exactly Nernstian response of the electrode; if this is not the case, the correct value can be introduced in eqn. (14). A critical test for eqn. (14) is that it reduces to eqn. (1) when the solubility becomes negligible, i.e., when S_B approaches zero.

In the reverse case, when A is the standard and B the analyte (similar to Gran's eqn. 3), $C_A = S_A$, $C_B = C_{B'} + S_A\ y/x$, $K_{so} = S_A{}^x\,(S_A\ y/x + C_{B'})^y$, $C_B^0\ V_0 = C_A^0 V_e y/x$, and

$$C_{B'} = (C_B^0 V_0 - C_A^0 V y/x)/(V_0 + V) = C_A^0\,(y/x)\,(V_e - V)/(V_0 + V) \tag{15}$$

Substitution of eqn. (15) in the preceding equation for K_{so} followed by substitution in the expression for C_B, gives an expression equivalent to eqn. (9). Thereafter the development continues in the same way as the previous one giving:

$$(V_0 + V)\,[10^{16.9n(x/y)(K_2-E)/f} - (y/x)\,(S_A/K_{so}^{1/y})\,10^{16.9n(x/y)(K_2-E')/f}]$$
$$= K_1\,(V_e - V) \tag{16}$$

This expression cannot be directly compared with the corresponding Gran equation because of differences in its development. However, the similarities are evident and the considerations are the same as those made for eqn. (14).

When the corresponding derivations are applied to the range in which the equivalence point has been overshot (i.e., $V > V_e$), it is found that for A = analyte and B = standard, eqn. (16) is valid if the sign of the right-hand side is changed. And for A = standard and B = analyte, eqn. (14) is valid with the same change of sign. In the first case, direct comparison with eqn. (2) is possible.

CALCULATIONS

To obtain V_e from eqns. (14) or (16), it is necessary to plot the left side of those equations against V. A problem in resolving the equations arises

from the calculation of S_A or S_B (S generally). This is not a constant but, because of the common ion effect, depends on the excess of reagent present in each aggregate, as is obvious from the equations for K_{so}. However, to calculate $C_{B'}$ or $C_{A'}$ from eqns. (15) or (8), V_e must be known, and so an iterative procedure is required. First, V_e is estimated without taking the correction term into account. With this value S is calculated, and a corrected value of V_e is obtained. Iteration is continued until the desired approximation is reached. Convergence is fast: 3—5 cycles were enough to bring V_e with the required titration error.

Calculations were done with a FORTRAN IV program. The main routine uses two subroutines, one of which calculates the linear regression for successive estimates of V_e; the other carries out the Newton—Raphson iteration method to calculate S from the relevant expression for K_{so} and was taken from IBM FORTRAN SUBROUTINES. Figure 2 shows the program flow chart; a program listing can be obtained on request from the authors.

The values of E' and f were calculated by plotting electrode potential E vs. pAg. The K_2 value (arbitrary) was taken around the average of the measured potential range of the titration. The K_{so} value taken from the literature was corrected for ionic strength (1 M HNO_3 medium) by the modified Debye—Hückel equation [6].

RESULTS AND DISCUSSION

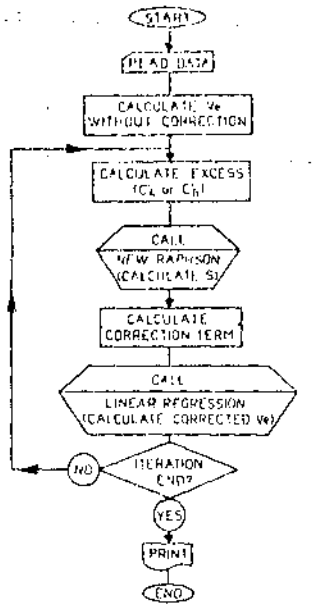
Figure 3 shows the advance of the iteration corresponding to the experimental data of Fig. 1 for 10^{-4} M chloride solution before the equivalence point. The straight lines show the successive corrections of the initial data until the desired approximation is obtained.

The correction was used successfully in the following cases: A = standard and B = analyte before the equivalence point, or A = analyte and B = standard after the equivalence point. In the other two cases, the correction does not approach the correct V_e sufficiently when C_A^0 or C_B^0 are about 10^{-4} M or less. Adsorption of ionic species on the silver chloride precipitate was not taken into account but it can introduce some deviations [7].

Some conclusions can be reached from eqns. (14) and (16) about the concentration range where the correction made is significant. As an example, eqn. (14) is used, and the required error is taken as less than 1%. The relation between the correction term and the main term should then be: $(x/y)S\ 10^{16.9n(E'-K_2)f}/10^{16.9n(E-K_2)f} < 0.01$. By cancelling out $10^{16.9nK_2}$, introducing eqn. (10) and assuming $f = 1$, we then get $(x/y)S\ 10^{16.9n(E-E')} = (x/y)S/C_A < 0.01$.

Rearrangement gives $100(x/y)\ S < C_A$, which implies that the concentration of the electroactive species should be more than 100 times the solubility of the precipitate formed when $x = y$. A general form of this expression for a required error of less than ϵ% would be

$$(100/\epsilon)\ (x/y)S < C_A \qquad (17)$$



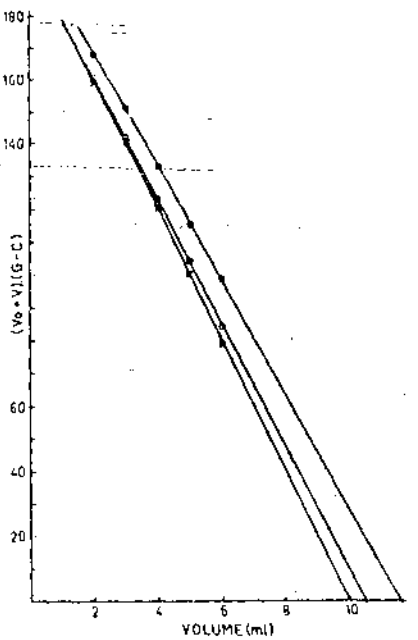


Fig. 2. Flow chart of calculation program.

Fig. 3. Successive approaches in the V_e calculation for the titration of 100 ml of 10^{-4} M chloride with 10^{-3} M silver nitrate in 1 M HNO_3. (•) First iteration (without correction); (○) second iteration; (×) fifth iteration. G is the Gran term ($= 10^{16.9n(x/y)(K_2-E)/f}$), and C is the correction term ($= (y/x)(S_A/K_{so}^{(y)})\ 10^{16.9n(x/y)(K_2-E')/f}$).

Expression (17) is simpler than others given in the literature [2], and is easily evaluated if the calculations must be done with the correction term. Use of eqn. (16) leads to the same conclusion. In the example given, $K_{so}(AgCl) \approx S^2 \approx 10^{-10}$, i.e. $S \approx 10^{-5}$, which explains why there are no appreciable errors for titrations of 10^{-3} M chloride but significant errors in titrations of lower concentrations.

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