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GENERAL DERIVATION OF THE ANGLE COEFFICIENT OF GRAN'S PLOT IN ACID-BASE TITRATIONS (Addendum to B 341A)

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General derivation of the angle coefficient of Gran's plot in acid-base titrations

Acid-base titrations according to Gran (1952) involve the determination of the amount of free hydrogen ion remaining in a solution after successive, known additions of hydroxyl ion. The remaining amount of hydrogen ion is plotted against the added amount of hydroxyl ion in a diagram. The angle coefficient for curves thus obtained is derived in the following.

A solution contains strong acid together with a number of weak acids of different proticity $(H_nA)_1$, $(H_nA)_2$, etc. in total concentrations C_1, C_2 etc. To this solution, without changing its volume, an addition of NaOH is made which corresponds to an addition ΔOH^- expressed in terms of concentration. The state before the addition is indicated by ', after by ". The addition reduces the concentration of hydrogen ion and of all groups containing bound acid hydrogen.

Thus we get the following expression (equation 1):

$$\begin{aligned}\Delta OH = {} & \left[(c_{H^+})' - (c_{H^+})''\right] + \left[(c_{HA})_1' - (c_{HA})_1''\right] + \left[(c_{HA})_2' - (c_{HA})_2''\right] + \ldots \\ & + 2\left[(c_{H_2A})_1' - (c_{H_2A})_1''\right] + 2\left[(c_{H_2A})_2' - (c_{H_2A})_2''\right] + \ldots \\ & \vdots \\ & + n\left[(c_{H_nA})_1' - (c_{H_nA})_1''\right] + n\left[(c_{H_nA})_2' - (c_{H_nA})_2''\right] + \ldots\end{aligned}$$

The quantities in square brackets in equation 1 will no be expressed in terms of total concentration (C) of each weak acid, of the respective dissociation constants (k_1, k_2 .. k_n) and of the hydrogen ion concentration (c_{H^+}) in the solution. This will be facilitated by working in steps. We start by treating a monoprotic acid, followed by a diprotic acid, etc.

1. System containing one monoprotic acid HA with the dissociation constant k_1 and in total concentration C.

According to equation 1

$$\Delta OH^- = \left[(c_{H^+})' - (c_{H^+})''\right] + \left[(c_{HA})' - (c_{HA})''\right]$$

Furthermore,

$$C = c_{HA} + c_{A^-}$$

$$\frac{c_{H^+} \cdot c_{A^-}}{c_{HA}} = k_1$$

$$\therefore c_{HA} = C \cdot \frac{\frac{c_{H^+}}{k_1}}{1 + \frac{c_{H^+}}{k_1}}$$

This gives us

$$\Delta OH^- = \left[(c_{H^+})' - (c_{H^+})''\right] + \left[(c_{H^+})' - (c_{H^+})''\right] \cdot C \cdot \frac{\frac{1}{k_1}}{\left[1 + \frac{(c_{H^+})'}{k_1}\right] \cdot \left[1 + \frac{(c_{H^+})''}{k_1}\right]}$$

Put $\left[(c_{H^+})' - (c_{H^+})''\right] = - \Delta H^+$

$$\therefore \frac{\Delta H^+}{\Delta OH^-} = - \frac{1}{1 + C \cdot \frac{\frac{1}{k_1}}{\left[1 + \frac{(c_{H^+})'}{k_1}\right]\left[1 + \frac{(c_{H^+})''}{k_1}\right]}}$$

For $(c_{H^+})'' \longrightarrow (c_{H^+})'$

we obtain, finally

$$\frac{dH^+}{dOH^-} = - \frac{1}{1 + C \cdot \frac{\frac{1}{k_1}}{\left[1 + \frac{c_{H^+}}{k_1}\right]^2}} \qquad (2)$$

2. System containing one diprotic acid H_2A with the dissociation constants k_1 and k_2 and in total concentration C.

According to equation 1

$$\Delta OH^- = \left[(c_{H^+})' - (c_{H^+})''\right] + \left[(c_{HA^-})' - (c_{HA^-})''\right] + 2\left[(c_{H_2A})' - (c_{H_2A})''\right]$$

Furthermore

$$C = c_{H_2A} + c_{HA^-} + c_{A^{2-}}$$

$$\frac{c_{H^+} \cdot c_{HA^-}}{c_{H_2A}} = k_1 ; \qquad \frac{c_{H^+} \cdot c_{A^-}}{c_{HA^-}} = k_2$$

$$\therefore \quad c_{HA} = C \cdot \frac{c_{H^+}}{k_2} \cdot N^{-1}$$

$$c_{H_2A} = C \cdot \frac{c_{H^+}^{\,2}}{k_1\ k_2} \cdot N^{-1}$$

$$N = 1 + \frac{c_{H^+}}{k_2} + \frac{c_{H^+}^{\,2}}{k_1\ k_2}$$

In the same way as earlier, we get

$$\left[(c_{HA^-})' - (c_{HA^-})''\right] = \left[(c_{H^+})' - (c_{H^+})''\right] \cdot C \cdot \frac{\frac{1}{k_2}\left[1 - \frac{(c_{H^+})' \cdot (c_{H^+})''}{k_1\ \ k_2}\right]}{(N)'\ (N)''}$$

$$\left[(c_{H_2A})' - (c_{H_2A})''\right] = \left[(c_{H^+})' - (c_{H^+})''\right] \cdot C \cdot \frac{\frac{1}{k_1\ k_2}\left[(c_{H^+})' + (c_{H^+})'' + \frac{(c_{H^+})'(c_{H^+})''}{k_2}\right]}{(N)'\ (N)''}$$

which gives, finally

$$\frac{dH^+}{dOH^-} = - \frac{1}{1 + C \cdot \frac{\frac{1}{k_2} + \left[\frac{4c_{H^+}}{k_2\ k_1} + \frac{c_{H^+}^2}{k_2^2\ k_1}\right]}{\left[1 + \frac{c_{H^+}}{k_2} + \frac{c_{H^+}^2}{k_1\ k_2}\right]^2}} \qquad (3)$$

With an identical derivation to that applied above we get the following expression for a triprotic acid H_3A with dissociation constants k_1, k_2 and k_3, and in total concentration C:

$$\frac{dH^+}{dOH^-} = - \frac{1}{1 + C \cdot \frac{\frac{1}{k_3} + \left[\frac{4c_{H^+}}{k_3 k_2} + \frac{c_{H^+}^2}{k_3^2 k_2}\right] + \left[\frac{9c_{H^+}^2}{k_3 k_2 k_1} + \frac{4c_{H^+}^3}{k_3^2 k_2 k_1} + \frac{c_{H^+}^4}{k_3^2 k_2^2 k_1}\right]}{\left[1 + \frac{c_{H^+}}{k_3} + \frac{c_{H^+}^2}{k_3 k_2} + \frac{c_{H^+}^3}{k_3 k_2 k_1}\right]^2}} \qquad (4)$$

Regard the numerators of the fractions standing in the denominators of the expressions (2), (3) and (4). It is

for a monoprotic acid $\frac{1}{k_1}$

for a diprotic acid $\frac{1}{k_2} + \left[\frac{4c_{H^+}}{k_2k_1} + \frac{c_{H^+}^{\,2}}{k_2^{\,2}\,k_1}\right]$

for a triprotic acid $\frac{1}{k_3} + \left[\frac{4c_{H^+}}{k_3k_2} + \frac{c_{H^+}^{\,2}}{k_3^{\,2}\,k_2}\right] + \left[\frac{9c_{H^+}^{\,2}}{k_3k_2k_1} + \frac{4c_{H^+}^{\,3}}{k_3^{\,2}\,k_2k_1} + \frac{c_{H^+}^{\,4}}{k_3^{\,2}\,k_2^{\,2}\,k_1}\right]$

For an n-protic acid the corresponding expression will then for symmetrical reasons be

$$\frac{1}{k_n} + \left[\frac{2^2c_{H^+}}{k_nk_{n-1}} + \frac{c_{H^+}^{\,2}}{k_n^{\,2}\,k_{n-1}}\right] + \ldots + \left[\frac{n^2c_{H^+}^{\,(n-1)}}{k_n\,k_{n-1}\ldots k_1} + \frac{(n-1)^2\cdot c_{H^+}^{\,(n-1)+1}}{k_n^{\,2}\,k_{n-1}\ldots k_1} \ldots + \frac{1^2\,c_{H^+}^{\,(n-1)+n-1}}{k_n^{\,2}\ldots k_2^{\,2}\;k_1}\right]$$

If the entire fraction in the denominator is designated α the following general expression will be obtained:

$$\frac{dH^+}{dOH^-} = - \frac{1}{1 + C_1\alpha_1 + C_2\alpha_2 + \ldots C_n\alpha_n} \qquad (5)$$

where C_i is the total concentration of the i:th n-protic acid and α_i is the corresponding α-function. For α we have

$$\alpha = \frac{\beta_1 + \beta_2 + .. + \beta_n}{\left[1 + \frac{c_{H^+}}{k_n} + \frac{c_{H^+}^2}{k_n\, k_{n-1}} + \ldots + \frac{c_{H^+}^n}{k_n\, k_{n-1} .. k_1}\right]^2} \qquad (6)$$

where

$$\beta_1 = \frac{1}{k_n}$$

$$\beta_2 = \frac{2^2\, c_{H^+}}{k_n\, k_{n-1}} + \frac{1^2\, c_{H^+}^2}{k_n^2\, k_{n-1}}$$

$$\beta_3 = \frac{3^2\, c_{H^+}^2}{k_n\, k_{n-1}\, k_{n-2}} + \frac{2^2\, c_{H^+}^3}{k_n^2\, k_{n-1} .. k_1} + \frac{1^2\, c_{H^+}^4}{k_n^2\, k_{n-1}^2\, k_{n-2}}$$

$$\vdots$$

$$\beta_n = \frac{n^2\, c_{H^+}^{(n-1)}}{k_n\, k_{n-1} .. k_1} + \frac{(n-1)^2\, c_{H^+}^{(n-1)+1}}{k_n^2\, k_{n-1} .. k_1} + .. + \frac{1^2\, c_{H^+}^{(n-1)+n-1}}{k_n^2 .. k_2^2\, k_1}$$

Thus, for a monoprotic acid

$$\alpha = \frac{\beta_1}{1 + \left[\frac{c_{H^+}}{k_1}\right]^2}$$

and for a diprotic acid

$$\alpha = \frac{\beta_1 + \beta_2}{\left[1 + \frac{c_{H^+}}{k_2} + \frac{c_{H^+}^2}{k_2\, k_1}\right]}$$

etc.

It should be pointed out that in practice the protocity of the acids is seldom higher than 3.