# Derivation of relationship used for Gran plot

For a weak acid, HA, in solution,

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

and

$$K_a = \frac{[H_3O^+]\gamma_{H_3O^+}[A^-]\gamma_{A^-}}{[HA]\gamma_{HA}}$$

Consider the titration of this weak acid with a strong base.

$$HA(aq) + OH^-(aq) \rightarrow H_2O(l) + A^-(aq)$$

At any point between the start of the titration and the equivalence point it is a good approximation that each unit of $OH^-$ converts 1 unit of HA into 1 unit of $A^-$. If we have titrated $V_a$ mL of HA solution (with concentration $M_{HA}$) with $V_b$ mL of strong base titrant (with concentration $M_b$), we can write:

$$[A^-] = \frac{\text{moles OH}^- \text{ added}}{\text{total volume}} = \frac{M_b V_b}{V_a + V_b}$$

$$[HA] = \frac{\text{initial moles HA} - \text{moles OH}^- \text{ added}}{\text{total volume}} = \frac{M_a V_a - M_b V_b}{V_a + V_b}$$

Substitution of these values for $[A^-]$ and [HA] into the reaction quotient and cancellation of common terms in the numerator and denominator yields:

$$K_a = \frac{[H_3O^+]\gamma_{H_3O^+} M_b V_b \gamma_{A^-}}{(M_a V_a - M_b V_b)\gamma_{HA}}$$

This can be rearranged to give:

$$[H_3O^+]\gamma_{H_3O^+} V_b = K_a \frac{\gamma_{HA}}{\gamma_{A^-}} \left( \frac{M_a V_a - M_b V_b}{M_b} \right) \tag{1}$$

Since $[H_3O^+]\gamma_{H3O+} = 10^{-pH}$, the term on the left side of the equation 1 is $V_b\ 10^{-pH}$. At the equivalence point volume ($V_e$) the initial moles of acid equal moles of added base ($M_aV_a = M_bV_b$) and $V_b = V_e$. Therefore,

$$V_e = \frac{M_a V_a}{M_b}$$

The term in parentheses on the right side of the equation 1 can be rearranged and this expression for $V_e$ substituted to give:

$$\left( \frac{M_a V_a - M_b V_b}{M_b} \right) = \frac{M_a V_a}{M_b} - V_b = V_e - V_b$$

Substituting these relationships into equation 1 yields the equation used for the Gran plot for pH data as a function of titrant volume:

$$V_b 10^{-pH} = K_a \frac{\gamma_{HA}}{\gamma_{A^-}} (V_e - V_b) \qquad \text{Gran plot equation}$$

A plot of $V_b\ 10^{-pH}$ versus $V_b$ is called a Gran plot. If $\gamma_{HA}/\gamma_{A-}$ is constant, such a plot is a straight line with a slope of $-K_a\ \gamma_{HA}/\gamma_{A-}$. When *y* ($V_b\ 10^{-pH}$) equals zero, $V_b = V_e$ so the *x*-intercept is the equivalence point volume. The value of the Gran plot is that data taken before the equivalence point can be used. These pH measurements tend to be more reliable than values obtained right around the equivalence point where the pH is rapidly changing. If $\gamma_{HA}/\gamma_{A-}$ is known, the $K_a$ of the acid being titrated can be determined from the slope. Note that $V_b\ 10^{-pH}$ does not actually go to zero so the plot must be extrapolated to the *x*-intercept to find $V_e$. We have assumed that each unit of $OH^-$ added produces 1 unit of $A^-$. This is not true as $V_b$ approaches $V_e$ so only the linear portion of the Gran plot, usually data for the last 10% of the titrant volume before $V_e$, is used. In order to ensure that $\gamma_{HA}/\gamma_{A-}$ remains constant, one adds an electrolyte (KCl in our experiment) to the titration solution to establish a high and nearly constant ionic strength.