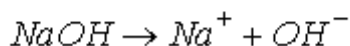
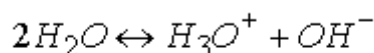
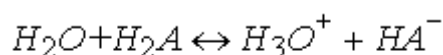


# Titration Equation for Polyprotic Acids

Polyprotic acids have two or more protons that may be removed by reaction with a base. The systematic treatment of chemical equilibrium can be used to find an equation relating proton concentration to the formal concentrations of the acid and the base. Considered herein is the titration of polyprotic acids a strong base, *e.g.*, NaOH.

## Systematic Treatment of the Chemical Equilibria Equations

Consider the generic diprotic acid  $H_2A$ . In aqueous solution, this acid will be distributed in four different species; the acid and the three conjugate bases. In addition, water will disproportionate, and the strong,  $OH^-$  containing, base will dissociate. The chemical equilibrium expressions are



The mathematical equations describing the concentrations of these species in solution are

*Charge Balance:*

$$[H_3O^+] + [Na^+] = [OH^-] + [HA^-] + 2[A^{2-}]$$

*Mass Balance:*

$$F_{NaOH} = [Na^+] \quad F_{HA} = [H_2A] + [HA^-] + [A^{2-}]$$

*Equilibrium Equations:*

$$K_{a1} = \frac{[H_3O^+][HA^-]}{[H_2A]} \quad K_{a2} = \frac{[H_3O^+][A^{2-}]}{[HA^-]} \quad K_w = [H_3O^+][OH^-]$$

The mass balance and equilibrium expressions for the acid result in the  $\alpha$  or relative fraction equations. One follows the usual procedure to obtain the working equation.

1 - Solve for concentration of acids and conjugate bases using the  $\alpha$ ...

$$[H_2A] = F_{H_2A} \alpha_{H_2A} \quad [HA^-] = F_{H_2A} \alpha_{HA^-} \quad [A^{2-}] = F_{H_2A} \alpha_{A^{2-}}$$

where

$$\alpha_{H_2A} = \frac{[H_3O^+]^2}{[H_3O^+]^2 + [H_3O^+]K_{a1} + K_{a1}K_{a2}}$$

$$\alpha_{HA^-} = \frac{[H_3O^+]K_{a1}}{[H_3O^+]^2 + [H_3O^+]K_{a1} + K_{a1}K_{a2}}$$

$$\alpha_{A^{2-}} = \frac{K_{a1}K_{a2}}{[H_3O^+]^2 + [H_3O^+]K_{a1} + K_{a1}K_{a2}}$$

2 - Substitute  $[HA^-]$ ,  $[A^{2-}]$ ,  $[OH^-] = K_w/[H_3O^+]$ , and  $[Na^+] = F_{NaOH}$  into the charge balance equation

$$\begin{aligned} [H_3O^+] + [Na^+] &= [OH^-] + [HA^-] + 2[A^{2-}] \\ [H_3O^+] + F_{NaOH} &= \frac{K_w}{[H_3O^+]} + F_{H_2A} \alpha_{HA^-} + 2F_{H_2A} \alpha_{A^{2-}} \\ &= \frac{K_w}{[H_3O^+]} + F_{H_2A} \frac{[H_3O^+]K_{a1}}{[H_3O^+]^2 + [H_3O^+]K_{a1} + K_{a1}K_{a2}} \\ &\quad + 2F_{H_2A} \frac{K_{a1}K_{a2}}{[H_3O^+]^2 + [H_3O^+]K_{a1} + K_{a1}K_{a2}} \end{aligned}$$

3 - Multiply by denominators...

$$\begin{aligned} [H_3O^+]([H_3O^+] + F_{NaOH})([H_3O^+]^2 + [H_3O^+]K_{a1} + K_{a1}K_{a2}) \\ = K_w([H_3O^+]^2 + [H_3O^+]K_{a1} + K_{a1}K_{a2}) \\ + [H_3O^+]F_{H_2A}([H_3O^+]K_{a1} + 2K_{a1}K_{a2}) \end{aligned}$$

4 - Solve for  $[H_3O^+]$  power series...

$$\begin{aligned} [H_3O^+]^4 + [H_3O^+]^3(F_{NaOH} + K_{a1}) \\ + [H_3O^+]^2(K_{a1}(F_{NaOH} - F_{H_2A}) + K_{a1}K_{a2} - K_w) \\ + [H_3O^+](K_{a1}K_{a2}(F_{NaOH} - 2F_{H_2A}) - K_{a1}K_w) - K_{a1}K_{a2}K_w = 0 \end{aligned}$$

Though difficult, the equation can be used to solve for  $[H_3O^+]$  using iteration methods. Spreadsheet programs often have built-in iteration solving procedures.

To solve the equation, one must know the acid equilibrium constants, and the formal concentrations of acid and base in the solution that is being titrated. The latter are found using the dilutions

$$F_{NaOH} = \frac{V_{tit} F_{NaOH}^o}{V_{tit} + V_{anal}} \quad F_{H_2A} = \frac{V_{anal} F_{H_2A}^o}{V_{tit} + V_{anal}}$$

$V_{tit}$  and  $V_{anal}$  are the titrant and analyte solution volumes, respectively, and the superscript, "o", indicates initial analyte acid and titrant base concentrations.

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## Equations for other acids

Working equations for other polyprotic acids are derived in a similar fashion. For example, a triprotic acid has the intermediate result

$$\begin{aligned} [H_3O^+] & \left( [H_3O^+] + F_{NaOH} \right) \left( [H_3O^+]^3 + [H_3O^+]^2 K_{a1} + [H_3O^+] K_{a1} K_{a2} + K_{a1} K_{a2} K_{a3} \right) \\ & = K_w \left( [H_3O^+]^3 + [H_3O^+]^2 K_{a1} + [H_3O^+] K_{a1} K_{a2} + K_{a1} K_{a2} K_{a3} \right) \\ & + [H_3O^+] F_{H_3A} \left( [H_3O^+]^2 K_{a1} + 2[H_3O^+] K_{a1} K_{a2} + 3K_{a1} K_{a2} K_{a3} \right) \end{aligned}$$

The power series result is

$$\begin{aligned} & [H_3O^+]^5 + [H_3O^+]^4 (F_{NaOH} + K_{a1}) \\ & + [H_3O^+]^3 (K_{a1} (F_{NaOH} - F_{H_3A}) + K_{a1} K_{a2} - K_w) \\ & + [H_3O^+]^2 (K_{a1} K_{a2} (F_{NaOH} - 2F_{H_3A}) + K_{a1} K_{a2} K_{a3} - K_{a1} K_w) \\ & + [H_3O^+] (K_{a1} K_{a2} K_{a3} (F_{NaOH} - 3F_{H_3A}) - K_{a1} K_{a2} K_w) \\ & - K_{a1} K_{a2} K_{a3} K_w = 0 \end{aligned}$$

In general, the governing equation for a  $n$ -proton acid has the intermediate form

$$\begin{aligned} & [H_3O^+] \left( [H_3O^+] + F_{NaOH} \right) D = K_w D \\ & + [H_3O^+] F_{H_nA} \left( [H_3O^+]^{n-1} K_{a1} + 2[H_3O^+] K_{a1} K_{a2} + \dots + n K_{a1} \dots K_{an} \right) \end{aligned}$$

$D$  is the denominator of the  $\alpha$  equation for a  $n$ -proton acid.

$$D = [H_3O^+]^n + [H_3O^+]^{n-1} K_{a1} + [H_3O^+]^{n-2} K_{a1} K_{a2} + \dots K_{a1} K_{a2} \dots K_{an}$$


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[Click here to see more about acid alpha and there relationship to titration curves.](#)

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