Chem M3LC. R. Corn

Diprotic Weak Acid Salt

Constants: K1, K2, Kw, Ctot

Six species: [H2A], [HA-], [A2-], [H+], [OH-], [Na+]

$K1 = [H+][HA-]/[H2A]$ acid dissociation 1

$K2 = [H+][A2-]/[HA-]$ acid dissociation 2

$Kw = [H+][OH-]$ water dissociation

$[Na+] + [H+] = [HA-]+ 2[A2-] + [OH-]$ charge balance

$Ctot = [H2A] + [HA-] + [A2-]$ mass balance 1

$2Ctot = [Na+]$ mass balance 2

Alpha Fractions

$[H2A]/Ctot = (1 + K1/[H+] + K1K2/[H+]^2)^{-1}$

$[HA-]/Ctot = ([H+]/K1 + 1 + K2/[H+])^{-1}$

$[A2-]/Ctot = ([H+]/K2 + [H+]^2/K1K2 + 1)^{-1}$

Iterative Equations for [OH-]

$Kb1 = Kw/K1 = [H2A][OH-]/[HA-]$

$Kb2 = Kw/K2 = [HA-][OH-]/[A2-]$

$[OH-][HA-] = Kb2[A2-]$

$2Ctot + [H+] = [HA-] + 2(Ctot – [HA-] – [H2A]) + [OH-]$

$[HA-] = [OH-] – 2[H2A] – [H+]$

$[OH-]([OH-] – 2[H2A] – [H+]) = Kb2[A2-]$

$[OH-]^2 – 2[OH-][H2A] - Kw = Kb[A2-]$

$[OH^-]^2 = Kb2[A2^-] + 2[OH^-][H2A] + Kw$

$[OH^-]^2 = Kb2[A2^-] + 2Kb1[HA^-] + Kw$

Iterative Equations:

Initial Guess:

$[A2^-] = Ctot$

$[OH^-] = sqrt(Kb2tot + Kw)$

Iterate:

$[A2^-] = Ctot([H^+]/K2 + [H^+]^2/K1K2 + 1)^{-1}$

$[OH^-] = sqrt(Kb2[A2^-] + 2Kb1[HA^-] + Kw)$