Chem 151. R. Corn

Diprotic Weak Acid Ampholyte

Constants: Ka1, Ka2, Kw, C0

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

$Ka1 = [H+][HA-]/[H2A]$ acid dissociation 1

$Ka2 = [H+][A2-]/[HA-]$ acid dissociation 2

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

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

$C0 = [H2A] + [HA-] + [A2-]$ mass balance 1

$C0 = [Na+]$ mass balance 2

Alpha Fractions

$[H2A]/C0 = (1 + Ka1/[H+] + Ka1Ka2/[H+]^2)^{-1}$

$[HA-]/C0 = ([H+]/Ka1 + 1 + Ka2/[H+])^{-1}$

$[A2-]/C0 = ([H+]/Ka2 + [H+]^2/Ka1Ka2 + 1)^{-1}$

Ampholyte Disproportionation:

2HA --> H2A + A2-

$Kd = [H2A][A2-]/[HA-]2 = ([H2A]/[HA-][H+])([H+][A2-]/[HA-]) = Ka2/Ka1 << 1$

$[H2A] = [A2-] = [HA-]sqrt(Kd)$

$[H+] = Ka1[H2A]/ [HA-] = sqrt(Ka1Ka2)$

$pH = (pK1 + pK2)/2$

Full equations for [H+]

$C0 = [H2A] + [HA-] + [A2-]$ mass balance 1

$C0 = [Na+]$ mass balance 2

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

$[H+] = [A2-] - [H2A] + [OH-]$

$[H+] = Ka2[HA-]/[H+] - [H+][HA-]/Ka1 + Kw/[H+]$

$[H+]^2 = (Ka2[HA-] + Kw)/(1 + [HA-]/Ka1)$

$[H+] = sqrt[(Ka2[HA-] + Kw)/(1 + [HA-]/Ka1)]$