

Topic 6F - Autoprotolysis and pH

Very Dilute Solutions of Strong Acids and Bases

If the concentration of a strong acid or base is less than $\sim 10^{-6}$ M, the concentrations of H_3O^+ and OH^- resulting from the autoprotolysis of H_2O must be taken into account. For the reactions



the aqueous species present are A^- , H_3O^+ , and OH^- .
Thus, three equations are needed to determine the three concentrations:

$$\text{Charge Balance: } [\text{A}^-] + [\text{OH}^-] = [\text{H}_3\text{O}^+]$$

$$\text{Material Balance: } [\text{A}^-] = [\text{HA}]_i \Rightarrow [\text{HA}]_i + [\text{OH}^-] = [\text{H}_3\text{O}^+]$$

$$\text{Autoprotolysis: } [\text{H}_3\text{O}^+][\text{OH}^-] = K_w = [\text{H}_3\text{O}^+]([\text{H}_3\text{O}^+] - [\text{HA}]_i)$$

Re-arranging the last equation,

$$[\text{H}_3\text{O}^+]^2 - [\text{HA}]_i [\text{H}_3\text{O}^+] - K_w = 0$$

Thus, as $[\text{HA}]_i$ decreases, $[\text{H}_3\text{O}^+]$ approaches that resulting from autoprotolysis alone.