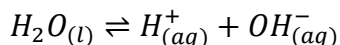


Exercise 12.3

Calculating pH of Weak Acid Solutions

It is important to remember that there is more than one relevant equilibrium when a weak acid or base is added to water. Water itself is both a weak acid and a weak base. As such, even before any additional species are added to water, it already contains three species in equilibrium:

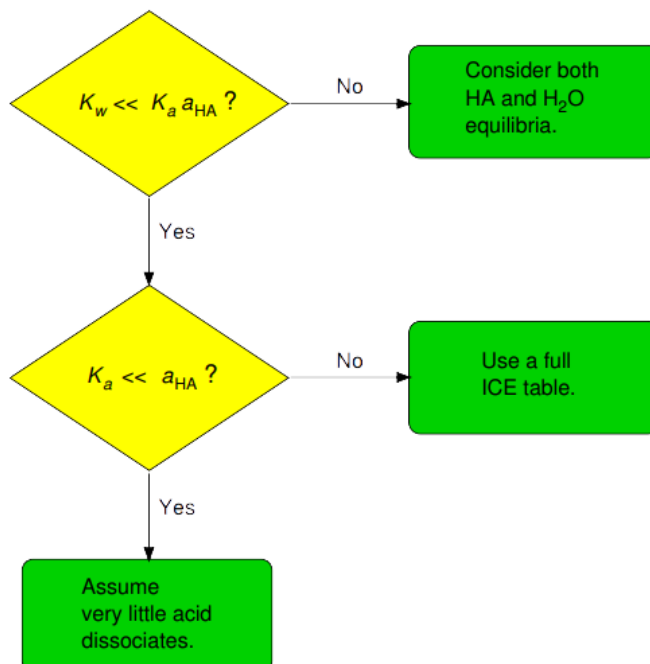


The equilibrium constant for this reaction is referred to as K_w . At 25 °C, $K_w = 10^{-14}$.

In pure water, the concentrations of H^+ and OH^- must be equal. Since $K_w = \frac{a_{H^+} \cdot a_{OH^-}}{a_{H_2O}}$ and the activity of any pure solid or liquid is 1, we can conclude that in pure water, $a_{H^+} = a_{OH^-} = \sqrt{K_w}$ and, at 25 °C, $a_{H^+} = a_{OH^-} = \sqrt{10^{-14}} = 10^{-7}$. As such, it is not entirely accurate to state that the “initial” concentration of H^+ is zero when using an ICE table to calculate equilibrium concentrations when a weak acid is dissolved in water.

This may come as a surprise since most high school chemistry classes teach you to list the “initial” concentration of H^+ as zero when setting up an ICE table. Why do they do that? In cases where dissociation of a weak acid will produce significantly more than $10^{-7} M H^+$, it is reasonable to approximate that the equilibrium concentration of acid will be roughly equal to that produced by dissociation of the acid. This simplifies the math required to solve the problem, and there is no harm in making reasonable approximations – as long as you check their validity after calculating!

Another common approximation is to recognize that if you dissolve a large amount of a weak acid in water, only a small fraction of the acid will dissociate. As such, you can assume that the final concentration of weak acid will be roughly equal to the initial concentration. The flowchart below (courtesy of Prof. Marc Roussel) shows you when you can reasonably make either assumption. “ \ll ” can be loosely translated to “at least 1000 times smaller”. But ALWAYS check any assumptions you make once you have calculated an answer.



1. For each of the following solutions prepared at 25 °C, identify whether it ought to be reasonable to start a pH calculation with either simplifying assumption:
 - i. equilibrium a_{HA} is approximately equal to initial a_{HA} (because a very small fraction of the acid dissociates) and/or
 - ii. that equilibrium a_{H^+} is almost entirely due to dissociation of the acid (so that you don't have to factor in the initial $10^{-7} M H^+$ from the water)
 - (a) A solution is prepared by dissolving 0.015 mol thiophenol ($pK_a = 6.62$) in 1.000 L water.
 - (b) A solution is prepared by dissolving 0.25 mol phenol ($pK_a = 9.95$) in 1.000 L water.
 - (c) A solution is prepared by dissolving 0.025 mol 2,4,6-trinitrophenol ($pK_a = 0.62$) in 1.000 L water.
 - (d) A solution is prepared by dissolving 8×10^{-8} mol benzoic acid ($pK_a = 4.19$) in 1.000 L water.
2. Calculate the approximate pH of each solution described in question 1.
 - (a) A solution is prepared by dissolving 0.015 mol thiophenol ($pK_a = 6.62$) in 1.000 L water.

(b) A solution is prepared by dissolving 0.25 mol phenol ($pK_a = 9.95$) in 1.000 L water.

(c) A solution is prepared by dissolving 0.025 mol 2,4,6-trinitrophenol ($pK_a = 0.62$) in 1.000 L water.

- (d) A solution is prepared by dissolving 8×10^{-8} mol benzoic acid ($pK_a = 4.19$) in 1.000 L water. *Don't worry about sig. fig. for this question.*