15.41 Why do we not usually quote $K_a$ values for strong acids such as HCl and HNO$_3$? Why is it necessary to specify temperature when giving $K_a$ values?

We do not usually quote $K_a$ values for strong acids such as HCl and HNO$_3$ because they ionize virtually 100%, so their $K_a$ values would be nearly infinite. One must specify a temperature when giving $K_a$ values because they vary with temperature (like any $K$ values.)

15.42 Which has the highest pH value: (a) 0.40 M HCOOH, (b) 0.40 M HClO$_4$, or (c) 0.40 M CH$_3$COOH?

Higher pH means weaker acid. HClO$_4$ is a strong acid. Between (a) and (c), CH$_3$COOH, acetic acid, has the lowest $K_a$, so it is the weakest acid and will have the highest pH for the same [HA].

15.44 What are the concentrations of H$^+$, CH$_3$COO$^-$, and CH$_3$COOH at equilibrium in a 50.0 mL solution containing 0.0560 g CH$_3$COOH ($K_a = 1.8 \times 10^{-5}$)? Check that the 5% approximation is valid.

$[\text{CH}_3\text{COOH}] = \frac{0.0560 \text{ g CH}_3\text{COOH}}{0.0500 \text{ L soln}} \times \frac{1 \text{ mol CH}_3\text{COOH}}{60.05 \text{ g CH}_3\text{COOH}} = 0.0187 \text{ M}$

\begin{align*}
\text{CH}_3\text{COOH(aq)} + \text{H}_2\text{O(l)} &\rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{COO}^-(aq) \\
\text{I (M)}: &\quad 0.0187 \quad 0 \quad 0 \\
\text{E (M)}: &\quad 0.0187 - x \quad +x \quad +x
\end{align*}

$K_a = \frac{[H^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(x)(x)}{(0.0187 - x)} \approx \frac{x^2}{0.0187} = 1.8 \times 10^{-5}$

$[H^+] = [\text{CH}_3\text{COO}^-] = x = 5.8 \times 10^{-4} \text{ M; } [\text{CH}_3\text{COOH}] = (0.0187 - 5.8 \times 10^{-4}) \text{ M} = 0.0181 \text{ M}$

Check: $\frac{5.8 \times 10^{-4}}{0.0187} \times 100\% = 3.1\% < 5\%$

15.45 What is the $K_a$ of an acid if a solution with initial concentration 0.010 M has pH = 6.20? At this pH, 1.0$x10^{-7}$ M of [H$^+$] comes from H$_2$O dissociation and must be subtracted from the total [H$^+$] to determine the amount of acid ionized.

$[H^+] = 10^{-6.20} = 6.3 \times 10^{-7} \text{ M; } 1.0 \times 10^{-7} \text{ M comes from the H}_2\text{O, so } 5.3 \times 10^{-7} \text{ M comes from the acid:}$

\begin{align*}
\text{HA(aq)} + \text{H}_2\text{O(l)} &\rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq) \\
\text{Initial (M)}: &\quad 0.010 \quad 1.0 \times 10^{-7} \quad 0 \\
\text{Change (M)}: &\quad -5.3 \times 10^{-7} \quad +5.3 \times 10^{-7} \quad +5.3 \times 10^{-7} \\
\text{Equilibrium (M)}: &\quad \approx 0.010 \quad 6.3 \times 10^{-7} \quad 5.3 \times 10^{-7}
\end{align*}

$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(6.3 \times 10^{-7})(5.3 \times 10^{-7})}{0.010} = 3.3 \times 10^{-11}$

15.49 A 0.040 M solution of a monoprotic acid is 14% ionized. Calculate $K_a$ of the acid.

$\text{HA(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)$

\begin{align*}
\text{I (M)}: &\quad 0.040 \quad 0 \quad 0 \\
\text{C(M)}: &\quad -0.0056 \quad +0.0056 \quad +0.0056 \\
\text{E (M)}: &\quad 0.034 \quad 0.0056 \quad 0.0056
\end{align*}

$[H^+] = [A^-] = 0.14 \times 0.040 \text{ M} = 0.0056 \text{ M}$

$[HA] = (0.040 - 0.0056) \text{ M} = 0.034 \text{ M}$

$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(0.0056)^2}{0.034} = 9.2 \times 10^{-4}$
15.46 What is the original molarity of a solution of formic acid (HCOOH) whose pH is 3.26 at equilibrium? 
\[ K_a = 1.7 \times 10^{-4} \text{. [Hint: set the [HCOOH]}_0 = I \text{ in the ICE table. What must } [H_3O^+]_\text{eq and } [HCOO^-]_\text{eq} \text{ be?] } \]
\[ [H^+] = 10^{-3.26} = 5.5 \times 10^{-4} \text{ M, which is also [HCOO^-] due to stoichiometry.} \]

\[
\begin{array}{c|ccc}
\text{HCOOH}(aq) + H_2O(l) & \rightarrow & H_3O^+(aq) + HCOO^-(aq) \\
\hline
\text{Initial (M):} & I & 0 & 0 \\
\text{Change (M):} & -5.5 \times 10^{-4} & +5.5 \times 10^{-4} & +5.5 \times 10^{-4} \\
\text{Equilibrium (M):} & I - (5.5 \times 10^{-4}) & 5.5 \times 10^{-4} & 5.5 \times 10^{-4} \\
\end{array}
\]

\[ K_a = \frac{[H^+] [HCOO^-]^2}{[HCOOH]} = \frac{(5.5 \times 10^{-4})^2}{I - (5.5 \times 10^{-4})} = 1.7 \times 10^{-4} \text{ so } I = [HCOOH] = 2.3 \times 10^{-3} \text{ M} \]

15.52 Which of the following has a higher pH? (a) 0.20 M NH_3 or (b) 0.20 M NaOH
b) has a higher pH because NaOH is a strong base (NH_3 is a weak base), so it is more basic.

15.54 The pH of a 0.30 M solution of a weak base is 10.66. What is \( K_b \) of the base?
\[ pOH = 14.00 - 10.66 = 3.34; \; [OH^-] = 10^{-3.34} = 4.6 \times 10^{-4} M \]

\[
\begin{array}{c|ccc}
\text{B(aq) + H}_2\text{O(l) } & \rightarrow & \text{BH}^+(aq) + \text{OH}^-(aq) \\
\hline
\text{Initial (M):} & 0.30 & 0 & 0 \\
\text{Change (M):} & -4.6 \times 10^{-4} & +4.6 \times 10^{-4} & +4.6 \times 10^{-4} \\
\text{Equilibrium (M):} & 0.30 - (4.6 \times 10^{-4}) & 4.6 \times 10^{-4} & 4.6 \times 10^{-4} \\
\end{array}
\]

\[ K_b = \frac{[BH^+][OH^-]}{[B]} = \frac{(4.6 \times 10^{-4})^2}{(0.30)} = 7.1 \times 10^{-7} \]

15.56 In a 0.080 M NH_3 solution, what are the pH and the percent ionization of the NH_3 (as NH_4^+)?
The \( K_a \) of NH_4^+ = 5.6 \times 10^{-10}.
\[
\begin{array}{c|ccc}
\text{NH}_3(aq) + H_2O(l) & \rightarrow & \text{NH}_4^+(aq) + \text{OH}^-(aq) \\
\hline
\text{Initial (M):} & 0.080 & 0 & 0 \\
\text{Change (M):} & -x & +x & +x \\
\text{Equilibrium (M):} & 0.080 - x & x & x \\
\end{array}
\]

\[ K_a = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-10}} = 1.8 \times 10^{-4} = \frac{x^2}{(0.080 - x)} \approx \frac{x^2}{0.080}; x = 1.2 \times 10^{-3} \text{ M} \]

\[
\begin{align*}
pOH &= -\log(1.2 \times 10^{-3}) = 2.92; \\
pH &= 14.00 - 2.92 = 11.08; \\
%\text{Ionization} &= \frac{1.2 \times 10^{-3}}{0.080} \times 100\% = 1.5\%
\end{align*}
\]

15.57 Using the NH_3/NH_4^+ system, write the equation relating \( K_a \) for a weak acid and \( K_b \) for its conjugate base and derive the relationship between \( K_a \) and \( K_b \).

\begin{align*}
\text{Eq for NH}_4^+ \text{ in water:} & \quad \text{NH}_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq) \quad K_a = \frac{[H_3O^+][NH_3]}{[NH_4^+]}
\end{align*}

\begin{align*}
\text{Eq for NH}_3 \text{ in water:} & \quad \text{NH}_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \quad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}
\end{align*}

\text{Net Equation:} \quad H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \quad K_c = K_a K_b = [H_3O^+][OH^-] = K_w

\[ K_c K_b = \frac{[H_3O^+][NH_4^+]}{[NH_3]} \times \frac{[NH_4^+][OH^-]}{[NH_3]} = [H_3O^+][OH^-] = K_w; \text{ thus } K_w = K_a K_b \]