TEXTBOOK HOMEWORK

18.15 Lower $[H^+]$ ⇒ higher pH

(a) Ka = 4x10⁻⁵: Lower Ka ⇒ lower $[H^+]$

(b) pKa = 3.5: Higher pKa ⇒ lower Ka ⇒ lower $[H^+]$

(c) 0.01 M: lower concentration ⇒ lower $[H^+]$

(d) Weaker Acid: lower $[H^+]$
(e) 0.01 M Base: Base has lower $[H^+]$
(f) pOH = 6: Has higher pH (8)

18.16 (a) $[OH^-] = 0.0111$ M ⇒ $pOH = -\log(0.0111) = 1.95 \rightarrow pH = 14 - 1.95 \approx 12.05$ Basic

(b) $[H^+] = 1.35\text{x}10^{-3}$ M ⇒ $pH = -\log(1.35 \times 10^{-3}) = 2.87 \rightarrow pOH = 14 - 2.87 \approx 11.13$
Acidic

18.18 (a) pH = 9.85 ⇒ pOH = 14 - 9.85 = 4.15 , $[H^+] = 10^{-pH} = 10^{-9.85} = 1.4\text{x}10^{-10}$ M
$[OH^-] = 10^{-pOH} = 10^{-4.15} = 7.1\text{x}10^{-5}$ M

(b) pOH = 9.43 ⇒ pH = 14 - 9.43 = 4.57 , $[H^+] = 10^{-pH} = 10^{-4.57} = 2.7\text{x}10^{-5}$ M
$[OH^-] = 10^{-pOH} = 10^{-9.43} = 3.7\text{x}10^{-10}$ M

18.20 **Goal:** Calculate initial number of moles of H^+ and final number of moles of H^+. The difference is the number of moles of OH^- which must be added.
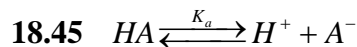$[H^+]_{init} = 10^{-pH_{init}} = 10^{-4.52} = 3.020\text{x}10^{-5}$ M
$n[H^+]_{init} = [H^+]_{init}V = 3.020\text{x}10^{-5}$ M $(5.60\,L) = 1.691\text{x}10^{-4}$ mol

$[H^+]_{fin} = 10^{-pH_{fin}} = 10^{-5.25} = 5.623\text{x}10^{-6}$ M
$n[H^+]_{fin} = [H^+]_{fin}V = 5.623\text{x}10^{-6}$ M $(5.60\,L) = 3.15\text{x}10^{-5}$ mol
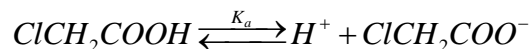
$\Delta n[H^+] = n[H^+]_{fin} - n[H^+]_{init} = 3.149\text{x}10^{-5} - 1.691\text{x}10^{-4} = -1.38\text{x}10^{-4}$ mol
In order to remove 1.38x10⁻⁴ moles of H^+ from the solution, we must **add** 1.38x10⁻⁴ moles of $[OH^-]$.

18.45 $HA \underset{}{\overset{K_a}{\rightleftharpoons}} H^+ + A^-$

$[H^+] = [A^-] = x = 10^{-pH} = 10^{-4.88} = 1.32 \times 10^{-5}$ M , $[HA] = 0.035 - x \approx 0.035$

$K_a = \dfrac{[H^+][A^-]}{[HA]} = \dfrac{(1.32 \times 10^{-5})^2}{0.035} = 4.97 \times 10^{-9} \approx 5.0 \times 10^{-9}$

18.48 $pKa = 2.87 \; \parallel \; K_a = 10^{-pKa} = 10^{-2.87} = 1.35 \times 10^{-3}$

$ClCH_2COOH \underset{}{\overset{K_a}{\rightleftharpoons}} H^+ + ClCH_2COO^-$
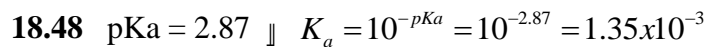
$[ClCH_2COO^-] = [H^+] = x$, $[ClCH_2COOH] = 1.25 - x \approx 1.25$ M**

$K_a = 1.35 \times 10^{-3} = \dfrac{[H^+][ClCH_2COO^-]}{[ClCH_2COOH]} = \dfrac{x^2}{1.25}$

$x^2 = 1.35 \times 10^{-3}(1.25) = 1.69 \times 10^{-3} \rightarrow x = 4.11 \times 10^{-2} \approx 0.041 M$

$[H^+] = [ClCH_2COO^-] = x = 0.041$ M , $[ClCH_2COOH] = 1.25 - x = 1.21$ M ≈ 1.25 M

$pH = -\log(0.041) \approx 1.4$

18.50 $HA \underset{}{\overset{K_a}{\rightleftharpoons}} H^+ + A^-$ $[HA]_o = 0.20$ M , 3% dissociated

(a) **[H⁺] , [OH⁻], pH, pOH**

$[H^+] = [A^-] = \dfrac{3}{100}[HA]_o = \dfrac{3}{100}(0.20 M) = 0.006 M$
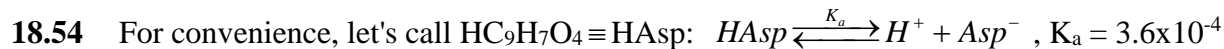
$[HA] = \dfrac{97}{100}[HA]_o = \dfrac{97}{100}(0.20 M) = 0.194 M$

$pH = -\log(0.006) = 2.22$

$pOH = 14 - 2.22 = 11.78$

$[OH^-] = 10^{-11.78} = 1.66 \times 10^{-12} M \approx 1.7 \times 10^{-12} M$

(b) **K$_a$**

$K_a = \dfrac{[H^+][A^-]}{[HA]} = \dfrac{(0.006)(0.006)}{0.194} = 1.86 \times 10^{-4} \approx 1.9 \times 10^{-4}$

18.54 For convenience, let's call $HC_9H_7O_4 \equiv HAsp$: $HAsp \underset{}{\overset{K_a}{\rightleftharpoons}} H^+ + Asp^-$, $K_a = 3.6 \times 10^{-4}$
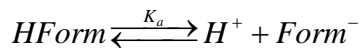
$[H^+] = [Asp^-] = x$, $[HAsp] = 0.018 - x \approx 0.018$

$K_a = 3.6 \times 10^{-4} = \dfrac{[H^+][Asp^-]}{[HAsp]} = \dfrac{x^2}{0.018}$

$x^2 = 3.6 \times 10^{-4}(0.018) = 6.48 \times 10^{-6} \rightarrow x = 2.55 \times 10^{-3} = [H^+]$

$pH = -\log(2.55 \times 10^{-3}) = 2.59 \approx 2.6$

18.55 Formic Acid: HCOOH. For convenience, we'll call this HForm.

$K_a = 1.8 \times 10^{-4}$. This value was looked up in a table. It would be given to you on a test.

$$HForm \underset{}{\overset{K_a}{\rightleftharpoons}} H^+ + Form^-$$

$[H^+] = [Form^-] = x$, $[HForm] = 0.75 - x \approx 0.75$

$$K_a = 1.8 \times 10^{-4} = \frac{[H^+][Form^-]}{[HForm]} = \frac{x^2}{0.75}$$

$$x^2 = 1.8 \times 10^{-4}(0.75) = 1.35 \times 10^{-4} \rightarrow x = 1.16 \times 10^{-2} = [Form^-]$$

The concentration of the dissociated species is [Form⁻]. Therefore, the percent

dissociation is given by: $\% Dissoc = \dfrac{[Form^-]}{[HForm]_o} x100 = \dfrac{1.16 \times 10^{-2}}{0.75} x100 = 1.55\% \approx 1.5\%$

18.65 (a) KCN: The salt dissociates completely to $K^+(aq)$ and $CN^-(aq)$.

KCN ‖ K^+ + CN^-(0.15 M). The K^+ is unimportant because it is the conjugate acid of the infiniely strong base, KOH, and does not react with water.

CN^- is the conjugate base of the weak acid, HCN, $K_a = 6.2 \times 10^{-10}$

(Appendix C of the text). You would be given the value on a test.

Note: Because you have just put the conjugate base of a weak acid in solution, you know that your solution should have pH > 7.

CN^- reacts with water according to: $CN^- + H_2O \underset{}{\overset{K_b}{\rightleftharpoons}} HCN + OH^-$

$[HCN] = [OH^-] = x$, $[CN^-] = 0.15 - x \approx 0.15$ M

We get $K_b(CN^+)$ from:

$$K_a K_b = K_w \rightarrow K_b(CN^-) = \frac{K_w}{K_a(HCN)} = \frac{1 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.61 \times 10^{-5}$$

$$K_b = \frac{[HCN][OH^-]}{[CN^-]} \rightarrow 1.61 \times 10^{-5} = \frac{x \cdot x}{0.15}$$

$$x^2 = (0.15)(1.61 \times 10^{-5}) = 2.42 \times 10^{-6} \rightarrow x = 1.55 \times 10^{-3} = [OH^-]$$

$$pOH = -\log([OH^-] = -\log(1.55 \times 10^{-3}) = 2.81$$

$$pH = 14 - 2.81 = 11.19 \approx 11.2$$

(b) Triethylammonium Chloride, $(CH_3CH_2)_3NHCl$. Let's call this Et_3NHCl for convenience.

Et_3NHCl ⇂ $Et_3NH^+(0.40$ M$) + Cl^-$. The Cl^- is unimportant because it is the conjugate base of the infinitely strong acid, HCl.

Et_3NH^+ is the conjugate acid of the weak base, Et_3N, $K_b = 5.2x10^{-4}$ (Appendix C of the text). You would be given this value on a test.

Note: Because you have just put the conjugate base of a weak acid in solution, you know that your solution should have pH > 7.

Et_3NH^+ dissociates according to: $Et_3NH^+ \overset{K_x}{\rightleftharpoons} H^+ + Et_3N$

$[H^+] = [Et_3N] = x$, $[Et_3NH^+] = 0.40 - x \approx 0.40$

We get $K_a(Et_3NH^+)$ from:

$$K_a K_b = K_w \rightarrow K_a(Et_3NH^+) = \frac{K_w}{K_b(Et_3N)} = \frac{1x10^{-14}}{5.2x10^{-4}} = 1.92x10^{-11}$$

$$K_a = \frac{[H^+][Et_3 N]}{[Et_3NH^+]} \rightarrow 1.92x10^{-11} = \frac{x \cdot x}{0.40}$$

$$x^2 = (0.40)(1.92x10^{-11}) = 7.69x10^{-12} \rightarrow x = 2.77x10^{-6} = [H^+]$$

$$pH = -\log(2.77 \times 10^{-6}) = 5.56 \approx 5.6$$

18.67 $NaClO$ dissociates completely into $Na^+ + ClO^-$. Because Na^+ is the conjugate acid of the infinitely strong base, $NaOH$, it does nothing in solution. On the other hand, ClO^- is the conjugate base of the weak acid, $HClO$. $K_a = 2.9 \times 10^{-8}$ (Appendix C of the text). You would be given this value on a test.

Let's go ahead and get K_b, which we will need in the problem.
$$K_a K_b = K_w \rightarrow K_b(ClO^-) = \frac{K_w}{K_a(HClO)} = \frac{1 \times 10^{-14}}{2.9 \times 10^{-8}} = 3.45 \times 10^{-7}$$

Strategy: (1) We will use the mass percent of $NaClO$ and the density of the solution to calculate the initial concentration, $[ClO^-]$. (2) We will use the base equilibrium equation to determine $[OH^-]$ and pOH/pH.

(1) $[ClO^-]$
Assume $1.0\ L = 1000\ mL$ of solution. Because $d = 1\ g/mL$, we have 1,000 grams.
$M(NaClO) = 74.5\ g/mol$.
$$mass(NaClO) = \frac{6.5}{100}(1{,}000\ g) = 65.0\ g$$

$$n(NaClO) = 65.0\ g \cdot \frac{1\ mol}{74.5\ g} = 0.87\ mol$$

Because $NaClO$ dissociates completely to ClO^- ($+ Na^+$, which is unimportant), $n(ClO^-) = 0.87\ mol$. Therefore, $[ClO^-]_o = 0.87\ mol/1.0\ L = 0.87\ M$.

(2) Determine $[OH^-]$, pOH, pH
ClO^- reacts with water according to: $ClO^- + H_2O \underset{K_b}{\rightleftharpoons} HClO + OH^-$
$[HClO] = [OH^-] = x$, $[ClO^-] = 0.87 - x \approx 0.87\ M$

$$K_b = \frac{[HClO][OH^-]}{[ClO^-]} \rightarrow 3.45 \times 10^{-7} = \frac{x \cdot x}{0.87}$$
$$x^2 = (0.87)(3.45 \times 10^{-7}) = 3.00 \times 10^{-7} \rightarrow x = 5.48 \times 10^{-4} = [OH^-]$$
$$pOH = -\log([OH^-]) = -\log(5.48 \times 10^{-4}) = 3.26$$
$$pH = 14 - 3.26 = 10.74 \approx 10.7$$