CHEM 101B Chapter 14 Acid Equilibria – Mixtures and Polyprotic Acids

Example 1. Acid Mixture

Strong Acid

Calculate the pH of a solution that contains 2.00 *M* HBr and 0.400 *M* HOCl ($K_a = 3.5 \times 10^{-8}$).

$$HBr \xrightarrow{100\%} H^+ + Br^-$$

2.0M   2.0M   2.0M

$$pH = -\log(2.0M) = \boxed{-0.301}$$

$$HOCl \rightleftharpoons H^+ + OCl^-$$

	HOCl	H^+	OCl^-
I	.400	2.00	0
C	−x	+x	+x
E	.400 − x	2.00 + x	x

$$3.5 \times 10^{-8} = \frac{(2.00 + \cancel{x})(x)}{.400 - \cancel{x}}$$

x << .400

x << 2.00

$$x = \frac{(.400)(3.5 \times 10^{-8})}{2.00} \approx 7.0 \times 10^{-9}$$

5% ✓

$$[OCl^-] = 7.0 \times 10^{-9} M$$

$$[H^+] = 2.00 + 7.0 \times 10^{-9} M$$

$$[H^+] = 2.00$$

Example 2. Acid Mixture

Calculate the pH of a solution that contains 1.00 *M* HCN ($K_a = 6.2 \times 10^{-10}$) and 5.00 *M* HNO_2 ($K_a = 4.0 \times 10^{-4}$).

stronger acid

Stronger - 1st

$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]}$

① $HNO_2 \rightleftharpoons H^+ + NO_2^-$

	HNO_2	H^+	NO_2^-
I	1.00	0	0
C	−x	+x	+x
E	1.00 − x	x	x

HNO_2

Weaker - 2nd

② $HCN \rightleftharpoons H^+ + CN^-$

	HCN	H^+	CN^-
I	1.00	0.045	0
C	−x	+x	+x
E	1.00 − x	0.045 + x	x

HCN

$K_a = \frac{[H^+][CN^-]}{}$

① $4.0 \times 10^{-4} = \frac{x^2}{5.00 - \cancel{x}}$

assume $x << 1.00$

$\frac{.045}{1.00} < .05$ ✓

$2.0 \times 10^{-3} = x^2$

$x = 0.045 = [H^+]$

$pH = -\log(.045)$

$pH = 1.35$

② $6.2 \times 10^{-10} = \frac{(.045 + \cancel{x})(x)}{1.00 - \cancel{x}}$

$x << .045$

$1.4 \times 10^{-8} = x$ very small indeed

$[CN^-] = 1.4 \times 10^{-8} M$

$[H^+] = .045 + \cancel{1.4 \times 10^{-8}}$

$= .045 M$ (No Δ)

Example 1. Polyprotic Acid

Calculate the pH of 5.0 *M* H_3PO_4 solution and equilibrium concentrations of all species: H^+, OH^-, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-} ($K_{a1} = 7.5 \times 10^{-3}$, $K_{a2} = 6.2 \times 10^{-8}$, $K_{a3} = 4.8 \times 10^{-3}$)

4.8×10^{-13}

$$H_3PO_4 \underset{}{\overset{Ka_1}{\rightleftharpoons}} H^+ + H_2PO_4^-$$

	H_3PO_4	H^+	$H_2PO_4^-$
I	5.0 M	0	0
C	−x	+x	+x
E	5.0−x	x	x

$X = [H^+] \rightarrow pH$

$K_w = [H^+][OH^-]$

$$H_2PO_4^- \overset{Ka_2}{\rightleftharpoons} H^+ + HPO_4^{2-}$$

0.19 M	0.19 M	0
−x	+x	+x
.19−x	.19+x	x

$$HPO_4^{2-} \overset{Ka_3}{\rightleftharpoons} H^+ + PO_4^{3-}$$

6.2×10^{-8} M	.19M	0
−x	+x	+x
$6.2 \times 10^{-8} - x$	.19 + x	x

$[H^+] = 0.19$ M

$[H_2PO_4^-] = 0.19$ M

$[H_3PO_4] = 4.8$ M

$[OH^-] = \frac{10^{-14}}{.19} = 5.3 \times 10^{-14}$

pH = 0.721

pOH = 13.3

−log

$[HPO_4^{2-}] = 6.2 \times 10^{-8}$ M

$[PO_4^{3-}] = 1.6 \times 10^{-19}$ M

$$Ka_1 = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$$

assume

$x << 5.0$

$$7.5 \times 10^{-3} = \frac{x^2}{5.0 - \cancel{x}}$$

$$x = \sqrt{(5.0)(7.5 \times 10^{-3})} = 0.19$$

$\frac{0.19}{5.0} < .05$

$0.039 < .05$

$$Ka_2 = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}$$

$.19 - \cancel{x}$

$$6.2 \times 10^{-8} = \frac{(\cancel{.19} + \cancel{x})(x)}{\cancel{.19} - \cancel{x}}$$

$[H^+] = .19\,M$

$$x = 6.2 \times 10^{-8}$$

$$Ka_3 = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

$$4.8 \times 10^{-13} = \frac{(.19 + \cancel{x})(x)}{6.2 \times 10^{-8} - \cancel{x}}$$

5% ✓

$$X = \frac{(4.8 \times 10^{-13})(6.2 \times 10^{-8})}{.19} = 1.6 \times 10^{-19}$$

Example 2. Polyprotic Acid

$$H_2SO_4 \xrightarrow{100\%} H^+ + HSO_4^-$$
$$0\,M \qquad 6.0M \qquad 6.0M$$

Calculate the pH of 6.0 M H_2SO_4 solution and equilibrium concentration of SO_4^{2-}.
(K_{a1} = LARGE, $K_{a2} = 1.2 \times 10^{-2}$)

$[H^+] = 6.0M$
$[HSO_4^-] = 6.0M$ } from strong acid 100% diss.

$$HSO_4^- \overset{K_{a2}}{\rightleftharpoons} H^+ \quad SO_4^{2-}$$

	HSO_4^-	H^+	SO_4^{2-}
I	6.0M	6.0M	0
C	$-x$	$+x$	$+x$
E	$6.0-x$	$6.0+x$	x

$$K_{a2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$$

$$1.2 \times 10^{-2} = \frac{(6.0+x)(x)}{6.0-x}$$

maybe $x \ll 6.0$ false
∴ Quadratic

$$0.012(6.0-x) = 6.0x + x^2$$
$$.072 - .012x = 6x + x^2$$
$$0 = x^2 + 6.012x - .072$$
$$a=1 \quad b=6.012 \quad c=-.072$$
$$x = \frac{-6.012 \pm \sqrt{(6.012)^2 - 4(1)(-.072)}}{2(1)}$$
$$= \frac{-6.012 \pm 6.0359}{2}$$

$+ \rightarrow x = 0.012 = [SO_4^{2-}]$

$- \rightarrow x = $ (negative)

$$[H^+] = 6.0 + .012 = 6.0M$$
(no change)