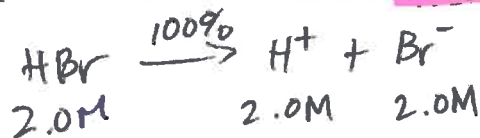


# CHEM 101B Chapter 14 Acid Equilibria – Mixtures and Polyprotic Acids

## Example 1. Acid Mixture

Strong Acid

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



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



I	.400	2.00	0
C	-x	+x	+x
e	.400 - x	2.00 + x	x

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

$x \ll .400$

$x \ll 2.00$

$$x = \frac{(.400)(3.5 \times 10^{-8})}{2.00} = 7.0 \times 10^{-9} \quad 5\% \checkmark$$

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

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

$$\boxed{[\text{H}^+] = 2.00}$$

### 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  $\text{HNO}_2$  ( $K_a = 4.0 \times 10^{-4}$ ).

stronger acid

Stronger - 1st

$$K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$$

$\text{HNO}_2$

	$\text{HNO}_2$	$\rightleftharpoons$	$\text{H}^+$	+	$\text{NO}_2^-$
i	1.00		0		0
c	-x		+x		+x
e	1.00 - x		x		x

Weaker - 2nd

HCN

	HCN	$\rightleftharpoons$	$\text{H}^+$	+	$\text{CN}^-$
i	1.00		0.045		0
c	-x		+x		+x
e	1.00 - x		0.045 + x		x

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

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

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

$$x = 0.045 = [\text{H}^+]$$

$$\text{pH} = -\log(0.045)$$

$$\text{pH} = 1.35$$

assume  $x \ll 1.00$

$$\frac{0.045}{1.00} < 0.05 \checkmark$$

$$6.2 \times 10^{-10} = \frac{(0.045 + x)(x)}{1.00 - x}$$

$x \ll 0.045$

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

very small indeed

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

$$[\text{H}^+] = 0.045 + 1.4 \times 10^{-8} = 0.045 \text{ M (No } \Delta)$$

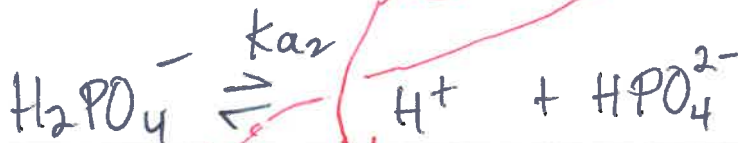
### Example 1. Polyprotic Acid

Calculate the pH of 5.0 M  $\text{H}_3\text{PO}_4$  solution and equilibrium concentrations of all species:

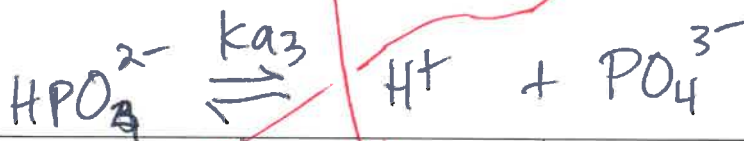
$\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  ( $K_{a1} = 7.5 \times 10^{-3}$ ,  $K_{a2} = 6.2 \times 10^{-8}$ ,  $K_{a3} = 4.8 \times 10^{-13}$ )



I	5.0 M	0	0
C	-x	+x	+x
E	5.0-x	x	x



	0.19 M	0.19 M	0
	-x	+x	+x
	.19-x	.19+x	x



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

$$4.8 \times 10^{-13}$$

$$x = [\text{H}^+] \rightarrow \text{pH}$$

$$K_w = [\text{H}^+][\text{OH}^-]$$

$[\text{H}^+] = 0.19 \text{ M}$   
 $[\text{H}_2\text{PO}_4^-] = 0.19 \text{ M}$   
 $[\text{H}_3\text{PO}_4] = 4.8 \text{ M}$   
 $[\text{OH}^-] = \frac{10^{-14}}{.19} = 5.3 \times 10^{-14}$   
 $\text{pH} = 0.721$   
 $\text{pOH} = 13.3$   
 $[\text{HPO}_4^{2-}] = 6.2 \times 10^{-8} \text{ M}$   
 $[\text{PO}_4^{3-}] = 1.6 \times 10^{-19} \text{ M}$

$$K_{a1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$$

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

assume  
 $x \ll 5.0$

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

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

$$0.039 < .05$$

$$K_{a2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}$$

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

$$.19 - x$$

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

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

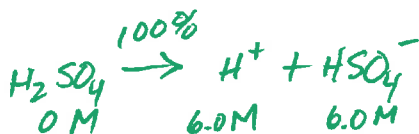
$$K_{a3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

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

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

5% ✓

### Example 2. Polyprotic Acid



Calculate the pH of 6.0 M  $\text{H}_2\text{SO}_4$  solution and equilibrium concentration of  $\text{SO}_4^{2-}$ .  
 ( $K_{a1} = \text{LARGE}$ ,  $K_{a2} = 1.2 \times 10^{-2}$ )

$[\text{H}^+] = 6.0\text{M}$   
 $[\text{HSO}_4^-] = 6.0\text{M}$

} from strong acid 100% diss.

	$\text{HSO}_4^-$	$\text{H}^+$	$\text{SO}_4^{2-}$
i	6.0M	6.0M	0
c	-x	+x	+x
e	6.0 - x	6.0 + x	x

$$K_{a2} = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$$

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

maybe  
 $x \ll 6.0$  false  
 $\therefore$  Quadratic

$$0.012(6.0-x) = 6.0x + x^2$$

$$.072 - .012x = 6x + x^2$$

$$0 = x^2 + 6.012x - .072$$

$$a=1 \quad b=6.012 \quad c=-.072$$

$$x = \frac{-6.012 \pm \sqrt{(6.012)^2 - 4(1)(-.072)}}{2(1)}$$

$$= \frac{-6.012 \pm 6.0359}{2} \rightarrow x = 0.012 = [\text{SO}_4^{2-}]$$

$\rightarrow x = (\text{negative})$

$$[\text{H}^+] = 6.0 + .012 = 6.0\text{M}$$

(no change)