HW # 7 Solutions — EVE 410 Process Chemistry

(1)

HA	$K_a = 10^{1.5}$	strong, $pK_a < 0$
HNO_3	$K_a = 10^{1.3}$	
Trichloracetic acid	$K_a = 10^{0.5}$	
HAc	$K_a = 10^{-4.7}$	
HCN	$K_a = 10^{-9.21}$	
HCO_3^-	$K_a = 10^{-10.3}$	
HPO_4^{2-}	$K_a = 10^{-12.38}$	

A strong acid has a large K_a and tends to completely dissociate (negative pK_a)

(2) Conjugate base of a strong acid is a weak base

strong acid ⇝ large K_a

Example HA → conjugate base is A^-

$$HA \rightleftharpoons H^+ + A^- \quad K_a$$
$$A^- + H_2O \rightleftharpoons HA + OH^- \quad K_b$$
$$\overline{H_2O \rightleftharpoons H^+ + OH^- \quad K_w = K_a K_b}$$

If K_a is large, K_b must be small and therefore A^- must be a weak base. (doesn't pick up alot of H^+ → logical b/c HA is strong acid and tends to dissociate)

3a. 10^{-3} M HCl $pK_a = -3$ $HCl \rightleftharpoons H^+ + Cl^-$ $10^3 = \frac{[H^+][Cl^-]}{[HCl]}$

Alot of acid ($\gg 10^{-7}$), assume acidic $[H^+] \gg [OH^-]$

strong acid ($pK_a < 0$), assume complete dissociation $[Cl^-] \gg [HCl]$

species: H^+, OH^-, Cl^-, HCl

mass Bal. $C_{Cl^-} = [Cl^-] + [HCl] = 10^{-3}$ ([HCl] negl.) $\Rightarrow [Cl^-] = 10^{-3}$ M

Charge bal. $[H^+] = [OH^-] + [Cl^-]$ ($[OH^-]$ negl.) $\Rightarrow [H^+] = [Cl^-] = 10^{-3}$ M

check charge bal $10^{-3} \overset{\checkmark}{=} 10^{-11} + 10^{-3}$ $pH = -\log(10^{-3}) = \underline{\underline{3}}$

check mass bal $10^{-3} \overset{\checkmark}{=} 10^{-3} + 10^{-9}$

(3b) 10^{-7} M HCl

cannot assume acidic or basic because C_T acid $\cong 10^{-7}$

still a strong acid, so $[Cl^-] >> [HCl]$ ~~$[H+] >> [OH-]$~~

charge balance: $[H^+] = [OH^-] + [Cl^-]$

mass balance: $C_{T,Cl^-} = [HCl] + [Cl^-] = 10^{-7}$ ([HCl] negl.)

$[Cl^-] = 10^{-7}$

From charge balance:

$$[H^+] = \frac{K_w}{[H^+]} + 10^{-7}$$

$$[H^+]^2 = K_w + 10^{-7}[H^+]$$

$$[H^+]^2 - 10^{-7}[H^+] - 10^{-14} = 0$$

$$[H^+] = \frac{+10^{-7} \pm \sqrt{10^{-14} + 4(10^{-14})}}{2}$$

$$[H^+] = 1.62 \times 10^{-7}$$

pH = 6.79

Check M.B.

$10^{-7} = 10^{-7} + 1.62 \times 10^{-17}$ ✓

$$K_A = \frac{[Cl^-][H^+]}{[HCl]} = 10^3$$

$$[HCl] = \frac{(10^{-7})(10^{-6.79})}{10^3} = 1.62 \times 10^{-17}$$

(3c) 10^{-3} M NH_4Cl

salt will dissociate $[NH_4Cl] \rightarrow 0$

$C_{T,NH_3} = C_{T,Cl^-}$

$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$

$NH_4^+ \rightleftharpoons NH_3 + H^+$ $\quad K_a = 10^{-9.3} = \frac{[NH_3][H^+]}{[NH_4^+]}$

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

Since adding acid - might try the acidic assumption

$[H^+] >> [OH^-]$

C.B. $[H^+] + [NH_4^+] = [OH^-] + [Cl^-]$ ($[OH^-]$ → neglect)

$[H^+] + [NH_4^+] = [Cl^-]$

M.B. $C_{T,NH_3} = [NH_4^+] + [NH_3] = 10^{-3}$ M

$C_{T,Cl^-} = [Cl^-] + [HCl] = 10^{-3}$ M

($[HCl]$ → neglect as HCL is very strong acid + will completely dissociate)

starting w/ C.B. (want all in terms of H+)

$[H^+] + [NH_4^+] = [Cl^-]$

From m.B. $C_{T,Cl^-} = [Cl^-] = C_{T,NH_3} = [NH_4^+] + [NH_3]$

$[H^+] + \cancel{[NH_4^+]} = \cancel{[NH_4^+]} + [NH_3]$

$[H^+] = [NH_3]$

Want NH_3 in terms of $[H^+]$

Combine M.B. and equilibrium constant

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]} = \frac{[H^+]^2}{C_{T,NH_3} - [NH_3]} = \frac{[H^+]^2}{C_{T,NH_3} - [H^+]}$$

$$K_a \left(C_{T,NH_3} - [H^+] \right) = [H^+]^2$$

$$[H^+]^2 + K_a [H^+] - K_a C_{T,NH_3} = 0$$

$[H^+] = 7.07 \times 10^{-7}$ M

pH = 6.15

check assumptions:

First need other species [ ]

$[OH^-] = K_w / [H^+] = 1.41 \times 10^{-8}$ M

$[NH_3] = 7.07 \times 10^{-7}$ M

$[NH_4^+] = C_{T,NH_3} - [NH_3] = 9.99 \times 10^{-4}$ M

<u>C.B.</u>

$$[H^+] + [NH_4^+] = [OH^-] + [Cl^-]$$

$$7.07 \times 10^{-7} + 9.99 \times 10^{-4} = 1.41 \times 10^{-8} + 10^{-3}$$

$$10^{-3} \overset{\checkmark}{=} 10^{-3}$$

<u>m.B.</u>

$$[NH_4^+] + [NH_3] = 10^{-3}$$

$$9.99 \times 10^{-4} + 7.07 \times 10^{-7} \overset{\checkmark}{=} 10^{-3}$$

O.K.

4. 10^{-3} M NaOCl (sodium hypochlorite) pKa = 7.6 (weak base)

$$NaOCl \rightleftharpoons Na^+ + OCl^-$$ Salt, [NaOCl] ⤳ 0

$$OCl^- + H_2O \rightleftharpoons HOCl + OH^-$$ $C_{T,Na^+} = C_{T,OCl^-} = 10^{-3} M$

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

Adding alot of base → so make basic assumption
$[OH^-] \gg [H^+]$

C.B. $[H^+] + [Na^+] = [OH^-] + [OCl^-]$ (neglect $[H^+]$)

$$[Na^+] = [OH^-] + [OCl^-]$$

m.B. $C_{T,Na^+} = [Na^+] = 10^{-3} M$

$$C_{T,Cl^-} = [OCl^-] + [HOCl] = 10^{-3} M$$

substitute m.B. into C.B.

$$[Na^+] = [OH^-] + [OCl^-]$$

$$\cancel{[OCl^-]} + [HOCl] = [OH^-] + \cancel{[OCl^-]}$$

$$[HOCl] = [OH^-]$$

From equilibrium and mass balance equations:

$$K_a = 10^{-7.6} = \frac{[OCl^-][H^+]}{[HOCl]}$$

$$K_a = \frac{(C_T - [HOCl])[H^+]}{[HOCl]} = \frac{\left(C_T - \frac{K_w}{[H^+]}\right)[H^+]}{\frac{K_w}{[H^+]}}$$

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

$$K_a K_w = C_T [H^+]^2 - K_w [H^+]$$

$$C_T [H^+]^2 - K_w [H^+] - K_a K_w = 0$$

$$10^{-3}[H+]^2 - 10^{-14}[H+] - (10^{-7.6})(10^{-14}) = 0$$

$$[H+] = 5.06 \times 10^{-10}\ M$$

$$pH = 9.30$$

$$[OH-] = 1.97 \times 10^{-5}\ M$$

$$[HOCl] = 1.98 \times 10^{-5}\ M$$

$$[OCl-] = 9.8 \times 10^{-4}\ M$$

C.B. $[H+] + [Na+] = [OH-] + [OCl-]$

$$5.06 \times 10^{-10} + 10^{-3} = 1.97 \times 10^{-5} + 9.8 \times 10^{-4}$$

$$10^{-3} = 10^{-3}$$

✓

m.B. $[OCl-] + [HOCl] = 10^{-3}$

$$9.8 \times 10^{-4} + 1.98 \times 10^{-5}$$

$$10^{-3} \stackrel{\checkmark}{=} 10^{-3}$$

Note: Since you expected the pH to be high (basic) and the pKa is near neutral, you could have tried the assumption that $[OCl-] >> [HOCl]$. You would have gotten pH = 9.25 which is pretty close.

(5) pH > 4

TOC < 250 mg/L as C — NPDES Regulation

HAc = CH_3COOH ? Total amount w/o violating NPDES

Set $C_{T,Ac} = 250$ mg/L as C

$$\left(\frac{250 \text{ mg as C}}{L}\right)\left(\frac{\text{per mol } CH_3COOH}{24 \text{ mg C}}\right) = 1.04 \text{ mM} = 1.04 \times 10^{-3} \text{ M}$$

→ C MW = 12 but 2 per mol of HAc

What will pH be?

m.B.: $C_{T,Ac} = 1.04 \times 10^{-3}$ M $= [HAc] + [Ac]$

Equil: $10^{-4.7} = \frac{[H^+][Ac^-]}{[HAc]}$ $\qquad 10^{-14} = [H^+][OH^-]$

C.B.: $[H^+] = [OH^-] + [Ac^-]$

Alot of acid added $(\sim 10^{-3})$, assume $[H^+] \gg [OH^-]$

$$[H^+] = [Ac^-]$$

$$K_a = \frac{[H^+]^2}{C_T - [Ac^-]} = \frac{[H^+]^2}{C_T - [H^+]}$$

$$K_a C_T - K_a [H^+] = [H^+]^2$$

$$[H^+]^2 + K_a [H^+] - K_a C_{T,Ac} = 0$$

$$[H^+] = 10^{-3.35}$$

pH = 3.35 Violates Regulations!

At pH = 4, how much $C_{T,Ac}$?

$$C_{T,Ac} = [HAc] + [Ac^-] = ??$$

at pH = 4 $[H^+] >> [OH^-]$

so charge balance simplified as follows:

$$[H^+] = [Ac^-]$$

$$K_a = \frac{[H^+][Ac^-]}{[HAc]} = \frac{[H^+][Ac^-]}{C_T - [Ac^-]} = \frac{[H^+][H^+]}{C_T - [H^+]}$$

$$K_a C_T - K_a[H^+] = [H^+]^2$$

$$C_{T,Ac} = \frac{[H^+]^2 + K_a[H^+]}{K_a}$$

$$C_{T,Ac} = \frac{(10^{-4})^2 + (10^{-4.7})(10^{-4})}{10^{-4.7}}$$

$$C_{T,Ac} = 6.01 \times 10^{-4}\ M$$

$$\left(6.01\times10^{-4}\ \frac{\text{Moles}}{L}\right)\left(\frac{24\ g\ C}{\text{mol HAc}}\right)\left(\frac{1000\ mg}{g}\right) = \underline{\underline{14.4\ \frac{mg}{L}\ \text{as C}}}$$