

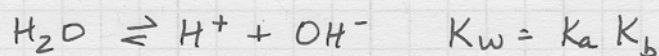
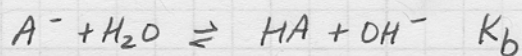
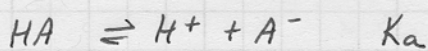
HW # 7 SOLUTIONS

EVE 410 Process Chemistry

- (1)
- | | | |
|--------------------------------|---------------------|---|
| HA | $K_a = 10^{11.5}$ | } strong
$pK_a < 0$ |
| HNO ₃ | $K_a = 10^{1.3}$ | |
| Trichloroacetic acid | $K_a = 10^{0.5}$ | |
| HAC | $K_a = 10^{-4.7}$ | |
| HCN | $K_a = 10^{-9.21}$ | } A strong acid has
a <u>large</u> K_a and tends
to completely dissociate
(negative pK_a) |
| HCO ₃ ⁻ | $K_a = 10^{-10.3}$ | |
| HPO ₄ ²⁻ | $K_a = 10^{-12.38}$ | |

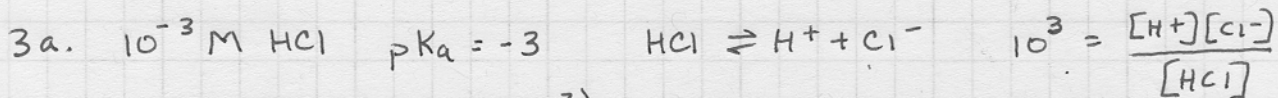
(2) Conjugate base of a strong acid is a weak base
 strong acid \rightsquigarrow large K_a

Example HA \rightarrow conjugate base is A⁻



If K_a is large, K_b must be small
 and therefore A⁻ must be a weak base.

(doesn't pick up a lot of H⁺ \rightarrow logical b/c
 HA is strong acid and tends to dissociate)



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

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

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

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

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

(2)

cannot assume acidic or basic because $C_T \text{ acid} \cong 10^{-7}$
still a strong acid, so $[Cl^-] \gg [HCl]$ $[H^+] \gg [OH^-]$

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

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

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

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.

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

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

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

$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} = \frac{[\text{H}^+]^2}{C_{\text{T,NH}_3} - [\text{NH}_3]} = \frac{[\text{H}^+]^2}{C_{\text{T,NH}_3} - [\text{H}^+]}$$

(4)

$$K_a (C_{\text{T,NH}_3} - [\text{H}^+]) = [\text{H}^+]^2$$

$$[\text{H}^+]^2 + K_a [\text{H}^+] - K_a C_{\text{T,NH}_3} = 0$$

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

$$\text{pH} = 6.15$$

check assumptions:

First need other species []

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

$$[\text{NH}_3] = 7.07 \times 10^{-7} \text{ M}$$

$$[\text{NH}_4^+] = C_{\text{T,NH}_3} - [\text{NH}_3] = 9.99 \times 10^{-4} \text{ M}$$

C.B.

$$[\text{H}^+] + [\text{NH}_4^+] = [\text{OH}^-] + [\text{Cl}^-]$$

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

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

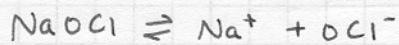
m.B.

$$[\text{NH}_4^+] + [\text{NH}_3] = 10^{-3}$$

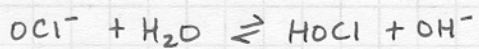
$$9.99 \times 10^{-4} + 7.07 \times 10^{-7} \checkmark = 10^{-3}$$

O.K.

4. 10^{-3} M sodium hypochlorite NaOCl $pK_a = 7.6$ (weak base) (5)



Salt, $[\text{NaOCl}] \rightarrow 0$



$$C_{T, \text{Na}^+} = C_{T, \text{OCl}^-} = 10^{-3} \text{ M}$$



Adding a lot of base \rightarrow so make basic assumption

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

C.B. $\overset{\text{neglect}}{\cancel{[\text{H}^+]}} + [\text{Na}^+] = [\text{OH}^-] + [\text{OCl}^-]$

$$[\text{Na}^+] = [\text{OH}^-] + [\text{OCl}^-]$$

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

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

substitute m.B. into C.B.

$$[\text{Na}^+] = [\text{OH}^-] + [\text{OCl}^-]$$

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

$$[\text{HOCl}] = [\text{OH}^-]$$

From equilibrium and mass balance equations:

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

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

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

$$K_a K_w = C_T [\text{H}^+]^2 - K_w [\text{H}^+]$$

$$C_T [\text{H}^+]^2 - K_w [\text{H}^+] - K_a K_w = 0$$

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

(6)

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

$$\text{pH} = 9.30$$

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

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

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

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

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

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

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

$$10^{-3} \approx 10^{-3}$$

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

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pH > 4

TOC < 250 mg/L as C

NPDES Regulation

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HAc = CH₃COOH ? Total amount w/o violating NPDES

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

$$\left(\frac{250 \text{ mg as C}}{L} \right) \left(\frac{\text{per mol CH}_3\text{COOH}}{24 \text{ mg C}} \right) = 1.04 \text{ mM} = 1.04 \times 10^{-3} \text{ M}$$

→ C MW = 12 but 2 per mol of HAc

What will pH be?

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

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

$$\text{C.B.: } [\text{H}^+] = [\text{OH}^-] + [\text{Ac}^-]$$

A lot of acid added (~10⁻³), assume [H⁺] >> [OH⁻]

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

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

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

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

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

$$\boxed{\text{pH} = 3.35}$$

Violates Regulations!

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

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

$$\text{at } \text{pH} = 4 \quad [H^+] \gg [OH^-]$$

so charge balance simplified as follows:

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

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

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

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

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

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

$$\left(6.01 \times 10^{-4} \frac{\text{Moles}}{\text{L}}\right) \left(\frac{24 \text{ g C}}{\text{mol HAc}}\right) \left(\frac{1000 \text{ mg}}{\text{g}}\right) = \underline{\underline{14.4 \frac{\text{mg}}{\text{L}} \text{ as C}}}$$