Homework #2

1. Acid/Base Equilibria I

Determine the complete solution composition of the following systems (all are added to 1 liter of pure water), based on the governing equations. Make one or more simplifying assumptions, then solve the system of equations based on those assumptions, and check the assumptions.

3 points total

a. 5x10⁻³ moles HOCl

1 point

Approach

- addition of a simple monoprotic acid to water
- try to use simplified solutions developed in class

PBE

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

Assumptions:

1. Acidic Solution: $[H^+] >> [OH^-]$
2. Weak Acid: $[HOCl] >> [OCl^-]$

Solve for $[H^+]$ based on simplifying assumptions

$$[H^+] = \sqrt{k_a C_T}$$

$$pH = 0.5(pk_a + pC_T)$$

$$pH = 0.5(7.6 + 2.3)$$

$$pH = 4.95$$

Solve for all species

$[H^+]$		$= 10^{-4.95}$	or $1.1x10^{-5}$
$[OH^-]$	$= k_w/[H^+]$	$= 10^{-9.05}$	or $8.9x10^{-10}$
$[HOCl]$	$= C_T$	$= 10^{-2.30}$	or $5x10^{-3}$
$[OCl^-]$	$= k_a[HOCl]/[H^+]$	$= 10^{-4.95}$	or $1.1x10^{-5}$

Check Assumptions

1. Acidic Solution: $[H^+] >> [OH^-]$; $10^{-4.95} >> 10^{-9.05}$, OK
2. Weak Acid: $[HOCl] >> [OCl^-]$; $10^{-2.30} >> 10^{-4.95}$, OK

b. $5x10^{-3}$ moles NaCN

1 point

Approach

- addition of a simple monoprotic base to water
- try to use simplified solutions developed in class

Assumptions:

1. Basic Solution: $[OH^-] >> [H^+]$
2. Weak Base: $[CN^-] >> [HCN]$

PBE

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

Solve for $[H^+]$ based on simplifying assumptions

$$[OH^-] = \sqrt{k_b C_T}$$

$$pOH = 0.5(pk_b + pC_T)$$

$$pOH = 0.5(4.8 + 2.3)$$

$$pOH = 3.55$$

$$pH = 14\text{-}pOH = 10.45$$

Solve for all species

$[H^+]$		$= 10^{-10.45}$	or $3.6x10^{-11}$
$[OH^-]$	$= k_w/[H^+]$	$= 10^{-3.55}$	or $2.8x10^{-4}$
$[CN^-]$	$= C_T$	$= 10^{-2.30}$	or $5x10^{-3}$
$[Na^+]$	$= C_T$	$= 10^{-2.30}$	or $5x10^{-3}$
$[HCN]$	$= k_b[CN^-]/[OH^-]$	$= 10^{-3.55}$	or $2.8x10^{-4}$

Check Assumptions

1. Basic Solution: $[OH^-] >> [H^+]$; $10^{-3.55} >> 10^{-10.45}$, OK
2. Weak Base: $[CN^-] >> [HCN]$; $10^{-2.30} >> 10^{-3.55}$, OK

c. $5x10^{-8}$ moles HCl

1 point

Approach

- addition of a simple monoprotic acid to water
- try to use simplified solutions developed in class

Assumptions:

1. Acidic Solution: $[H^+] >> [OH^-]$
2. Strong Acid: $[Cl^-] >> [HCl]$

PBE

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

Solve for $[H^+]$ based on simplifying assumptions

$$[H^+] = C_T$$
$$pH = pC_T$$
$$pH = 7.3$$

Solve for all species

$[H^+]$		$= 10^{-7.3}$	or $5x10^{-8}$
$[OH^-]$	$= k_w/[H^+]$	$= 10^{-6.7}$	or $2x10^{-7}$
$[HCl]$	$= [H^+][Cl^-]/k_a$	$= 10^{-17.6}$	or $2.5x10^{-18}$
$[Cl^-]$	$= C_T$	$= 10^{-7.3}$	or $5x10^{-8}$

Check Assumptions

1. Acidic Solution: $[H^+] >> [OH^-]$; $10^{-7.3} >> 10^{-6.7}$, No!
2. Strong Acid: $[Cl^-] >> [HCl]$; $10^{-7.3} >> 10^{-17.6}$, OK

Try again, but make only a strong acid assumption:

Assumptions:

1. Strong Acid: $[Cl^-] >> [HCl]$

Solve for $[H^+]$ based on simplifying assumptions

$$[H^+] = \frac{C_T + \sqrt{C_T^2 + 4K_w}}{2}$$
$$[H^+] = 10^{-7.3} + (10^{-14.6} + 4x10^{-14})^{0.5}$$
$$[H^+] = 1.28x10^{-7}$$
$$pH = 6.89$$

Solve for all species

$[H^+]$		$= 10^{-6.89}$	or $1.28x10^{-7}$
$[OH^-]$	$= k_w/[H^+]$	$= 10^{-7.11}$	or $7.80x10^{-8}$
$[HCl]$	$= [H^+][Cl^-]/k_a$	$= 10^{-17.2}$	or $6.5x10^{-18}$
$[Cl^-]$	$= C_T$	$= 10^{-7.3}$	or $5x10^{-8}$

Check Assumptions

1. Strong Acid: $[Cl^-] >> [HCl]$; $10^{-7.3} >> 10^{-17.2}$, OK

d. 1x10^{-3} moles HAc + 5x10^{-4} moles NaAc

Note: this one was not graded as we had not covered mixed acids and conjugate bases at the time the homework was assigned.

Approach

- addition of a simple monoprotic acid and its conjugate base to water
- cannot use simplified solutions developed in class
- return to original equations and solve, simplifying wherever possible

Species

H^+, OH^-, HAc, Ac^-, Na^+

Equations

$$K_w = 10^{-14} = [H^+][OH^-]$$
$$K_a = 10^{-4.7} = [Ac^-][H^+]/[HAc]$$
$$C_{T1} = 1.5x10^{-3} = [Ac^-] + [HAc]$$
$$C_{T2} = 5x10^{-4} = [Na^+]$$
$$[H^+] + [Na^+] = [OH^-] + [Ac^-]$$

Assumptions

addition of both an acid and a base keeps the pH from dropping or rising very much, this means that neither the hydrogen ion, nor the hydroxide ion will be significant compared to the added salts (e.g., sodium, acetate).

1. $[Na^+] >> [H^+]$
2. $[Ac^-] >> [OH^-]$

Now Solve using the basic equations

Start with the ENE (cannot use PBE for mixtures of acids and conjugate bases)

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

And combining with the mass balance equations

$$[Na^+] = [Ac^-] = C_{T2} = 5x10^{-4}$$
$$[HAc] = C_{T1} - [Ac^-] = C_{T1} - C_{T2} = 1x10^{-3}$$

Now use the equilibria to get the remaining species

$$K_a = 10^{-4.7} = [Ac^-][H^+]/[HAc]$$
$$[H^+] = 10^{-4.7} [HAc]/[Ac^-]$$
$$[H^+] = 10^{-4.7} 1x10^{-3}/5x10^{-4}$$
$$[H^+] = 4x10^{-5} = 10^{-4.4}$$
$$[OH^-] = k_w/[H^+] = 10^{-9.6}$$