Chemistry 12

Acid-Base Equilibrium VI

IV 19
pg 177-182

Name:
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1. Buffers

Buffers

An acid-base buffer is a solution that resists changes in pH following the addition of relatively small amounts of a strong acid or base.

Example: Consider a solution of 1.0 M acetic acid.

$$CH_3COOH_{(aq)} + H_2O_{(l)} \leftrightharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

- Acetic acid is a weak acid – only a small percent of the weak acid is ionized

	$CH_3COOH_{(aq)}$	+	$H_2O_{(l)}$	$\leftrightharpoons$	$CH_3COO^-_{(aq)}$	+	$H_3O^+_{(aq)}$
I	1.0M		––		0 M		0 M
C	– x		––		+ x		+ x
E	1.0M 1.0M – x		––		4.2×10^{-3}M x		4.2×10^{-3}M x

$K_a = 1.8 \times 10^{-5} = \dfrac{x^2}{1.0 - x}$ assume $1.0 - x \cong 1.0$

$x = \sqrt{(1.0)(1.8 \times 10^{-5})}$

$= 4.2 \times 10^{-3}$ M

[CH₃COOH] > [CH₃COO-]

1.0M $\quad$ 4.2×10^{-3}M

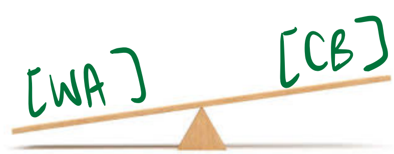
Unbuffered acetic acid solution

If a **strong base** was added to a solution, acetic acid will be there to neutralize the base.

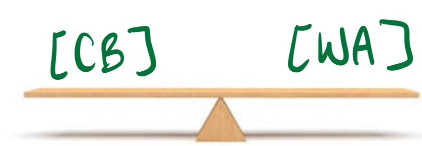
If a **strong acid** was added, there would be no species to neutralize it.

In order for a buffer solution to be effective, EQUIVALENT CONCENTRATIONS of a weak acid and a conjugate base must be in solution.

A **regular** acetic acid solution…



An acetic acid **buffer** solution…



Regular CH_3COOH solution…	Buffer CH_3COOH solution…
$CH_3COOH_{(aq)} + H_2O_{(l)} \leftrightharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$	$CH_3COOH_{(aq)} + H_2O_{(l)} \leftrightharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$
1.0M 0.0042M	1.0M 1.0M
[WA] > [CB]	[WA] ≈ [CB]
- ICE tables	- no ICE table
	- ratio of WA : CB

WA ✓
CB ✓

Consider the following pairs of solutions:

a) Circle the pairs of chemical species below that could be used to prepare a buffer solution.

b) For the pairs that you circled, write the buffer equation.

SA HNO_3 and $NaNO_3$	CB ✓ WA ✓ KF and HF	SA HNO_2 and HNO_3	WA ✓ CB ✓ $HCOOH$ and $LiHCOO$
$NaHSO_4$ and Na_2SO_4 WA ✓ CB ✓	K_2CO_3 and $K_2C_2O_4$ - both bases - not conjugates	HCl and $NaCl$ SA	KH_2PO_4 and K_2HPO_4 WA ✓ CB ✓

$$HSO_4^- + H_2O \rightleftharpoons SO_4^{2-} + H_3O^+$$

$$HF^- + H_2O \rightleftharpoons F^- + H_3O^+$$

$$HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$$

$$H_2PO_4 + H_2O \rightleftharpoons HPO_4^- + H_3O^+$$

General Acid Buffer Equation :

$$WA + H_2O \rightleftharpoons CB + H_3O^+$$

(Acid) Buffer Equation:

$$CH_3COOH_{(aq)} + H_2O_{(l)} \leftrightharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

Because … $K_a = \dfrac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$

Then … $[H_3O^+] = \dfrac{K_a[CH_3COOH]}{[CH_3COO^-]}$

Or in general…

$$\boxed{[H_3O^+] = K_a \underbrace{\left(\frac{[WA]}{[CB]}\right)}_{ratio}}$$

The hydronium ion concentration (and therefore the pH) of a buffer solution depends on:

1. the K_a value.
2. the **ratio** of the concentration of the weak acid to its conjugate base.

Using our acetic acid example…

$$\overset{1.0M}{CH_3COOH_{(aq)}} + H_2O_{(l)} \leftrightharpoons \overset{1.0M}{CH_3COO^-_{(aq)}} + H_3O^+_{(aq)}$$

$[H_3O^+] = K_a \left(\dfrac{[CH_3COOH]}{[CH_3COO^-]}\right)$

$= 1.8\times10^{-5}\left(\dfrac{1.0}{1.0}\right) = 1.8\times10^{-5} M$

pH = $-\log(1.8\times10^{-5})$

$= \boxed{4.74}$ ← Undisturbed buffer solution

Now, let's shift our system! [SA] = $[H_3O^+]$

We now **add 0.10 mol HCl** to 1.0 M buffer solution with no volume change.

- Would we expect the pH to decrease or increase?
- Would the system shift left or right?

$$CH_3COOH_{(aq)} + H_2O_{(l)} \leftrightharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

CH_3COOH	CH_3COO^-
1.0 M	1.0 M
+ 0.10M	− 0.10M
1.1M	0.90M

$[H_3O^+] = Ka\left(\frac{[WA]}{[CB]}\right)$

$= 1.8\times10^{-5}\left(\frac{1.1M}{0.9M}\right) = 2.2\times10^{-5}M$

pH = $-\log(2.2\times10^{-5}) = \boxed{4.66}$ (vs. 4.74)

[SB] = $[OH^-]$

We now **add 0.10 mol NaOH** to 1.0 M buffer solution with no volume change.

- Would we expect the pH to decrease or increase?
- Would the system shift left or right?

$$CH_3COOH_{(aq)} + H_2O_{(l)} \leftrightharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

CH_3COOH	CH_3COO^-
1.0 M	1.0 M
− 0.10M	+ 0.10M
0.9M	1.1M

$[H_3O^+] = Ka\left(\frac{[WA]}{[CB]}\right)$

$= 1.8\times10^{-5}\left(\frac{0.9M}{1.1M}\right) = 1.5\times10^{-5}M$

pH = $-\log(1.5\times10^{-5}) = \boxed{4.82}$ (vs 4.74)

$[H_3O^+] = 0.10M$ $[OH^-] = 0.10M$

$pH = -\log[H_3O^+]$ $= 1$ ← Add 0.10M HCl — **Unbuffered System** pH = 7 — Add 0.10M NaOH → $pOH = -\log[OH^-] = 1$, $pH = 13$

pH = 4.66 ← Add 0.10M HCl — **Buffer System** pH = 4.74 — Add 0.10M NaOH → pH = 4.82

Practice.

WA   equal [ ] of WA & CB

Consider a 1.0 M hydrofluoric acid buffer system.

a. What is the equation?

$$\underset{1.0M}{HF} + H_2O \rightleftharpoons \underset{1.0M}{F^-} + H_3O^+$$

b. Calculate the pH of an undisturbed system.

$$[H_3O^+] = K_a\left(\frac{[HF]}{[F^-]}\right) = 3.5\times10^{-4}\left(\frac{1.0}{1.0}\right) = 3.5\times10^{-4}\,M$$

$$pH = -\log(3.5\times10^{-4}) \quad \boxed{= 3.46}$$

SA = $[H_3O^+]$

c. Calculate the pH when 0.050M hydrobromic acid is added to the original buffer system.

$$HF + H_2O \rightleftharpoons F^- + H_3O^+$$

HF: 1.0M + 0.050M = 1.05M

F^-: 1.0M − 0.050M = 0.95M

$$[H_3O^+] = K_a\left(\frac{[HF]}{[F^-]}\right) = 3.5\times10^{-4}\left(\frac{1.05}{0.95}\right) = 3.9\times10^{-4}\,M$$

$$\boxed{pH = 3.41}$$

d. Calculate the pH when 0.050M Mg**(OH)**$_2$ is added to the original buffer system.

$$\underset{0.050M}{Mg(OH)_2} \rightarrow Mg^{2+} + \underset{0.10M}{2OH^-}$$

x2

$$HF + H_2O \rightleftharpoons F^- + H_3O^+$$

HF: 1.0M − 0.10M = 0.9M

F^-: 1.0M + 0.10M = 1.1M

$$[H_3O^+] = 3.5\times10^{-4}\left(\frac{0.9}{1.1}\right) = 2.9\times10^{-4}\,M \qquad \boxed{pH = 3.54}$$

Hebden Workbook Pg. 181 # 131-133, 136, 137