ACID-BASE EQUILIBRIUM
3: COMMON ION EFFECT AND BUFFERS

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COMMON ION EFFECT

The common–ion effect is the shift in an ionic equilibrium caused by the addition of a solute that takes part in the equilibrium.

For example:

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$

Add 0.05 mol of CH_3COONa

CH_3COONa in H_2O gives $Na^+ + CH_3COO^-$

<u>Net effect</u>: Equilibrium shifts to left because more product is added. pH of the solution will change.

If you have a 0.10 M solution of the acid, the pH of the solution will be 2.87.

(K_a of CH_3COOH is 1.8×10^{-5}).

$$\mathrm{x} = \sqrt{(1.8 \times 10^{-5})(0.1)} = 2.3 \times 10^{-3}\mathrm{M};\, take\ log = 2.87$$

Next slide shows what happens to this pH when sodium acetate is added.

EXAMPLE 1: COMMON ION EFFECT

What is the pH of a 0.100 M acetic acid when 0.0500 ml of CH_3COONa is added. (K_a of CH_3COOH is 1.8×10^{-5}).

Answer: This will add more acetate ion (product) to the equilibrium.

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$

Initial	0.100M		0	0.0500
Change	$-x$		$+x$	$+x$
Eq.	$0.10 - x$		x	$x + 0.05$

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]} = 1.8 \times 1^{-5} = \frac{(x)\,(x + 0.05)}{(0.1 - x)} \qquad \boxed{ignore\ x}$$

$$1.8 \times 1^{-5} = \frac{(x)\,(0.05)}{(0.1)}; x = 3.6 \times 10^{-6}$$

$$pH = -\log\left(3.6 \times 10^{-6}\right) = \boxed{4.44}$$

pH increases from 2.87 to 4.44 by adding a very small amount of basic salt. This validates that the equilibrium has shifted left thus decreasing the$[H^+]$.

EXAMPLE 2: COMMON ION EFFECT

Calculate the pH of a 0.100 *M* HF solution to which sufficient sodium fluoride has been added to make the concentration 0.200 *M* NaF. K_a: HF is 6.8×10^{-4}.

Answer: Conc. of fluoride ion is 0.2 M (from NaF)

$$HF_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)}$$

	$HF_{(aq)}$		$H_3O^+_{(aq)}$	$F^-_{(aq)}$
Initial	0.1 M		0	0.2
Change	$-x$		$+x$	$+x$
Eq.	$0.1 - x$		x	$x + 0.2$

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = 6.8 \times 10^{-4} = \frac{x(0.2 + x)}{(0.1 - x)} \qquad \boxed{\textit{ignore } x}$$

$$[H_3O^+] = x = 6.8 \times 10^{-4}\text{M} \times \frac{0.1}{0.2} = 3.4 \times 10^{-4}$$

$$\text{pH} = -\log[H_3O^+] = -\log(3.4 \times 10^{-4})$$

$$\boxed{\text{pH} = 3.47}$$

BUFFERS

Buffers are solutions containing weak acid and its conjugate base OR weak base and its conjugate acid. This is similar to common ion effect.

- pH of buffers change very little (between 2-3 pH range) on addition of small amounts of acid or base.
- In lab one makes buffers to do reactions in a controlled pH environment.
- pH of buffers can be calculated using the traditional ICE method or by Henderson-Hasselbalch equation, which can be derived from the K_a expression.
  - K_a expression: $$K_a = \frac{[H^+][A^-]}{[HA]}$$
  - Rearrange and take log $$\boxed{pH = pK_a + \log\frac{[A^-]}{[HA]}}$$

$$\boxed{pH = pK_a + \log\frac{[\text{conjugate base}]}{[\text{weak acid}]}}$$

Note:
$pK_a = -\log K_a$

MAKING BUFFERS

A weak acid or base is used since the pH of a buffer cannot be very low or high. Select the weak acid + conjugate base or weak base + conjugate acid.

- The acid or base depends on the pH range needed.
- We look through pK_a data for weak acids and bases and decide from there.
- Once decided; we know the pH we need the buffer to be in; so use the Hendersen-Hasselbalch equation to determine the ratio of the acid to conjugate base.

Example:

If a buffer of 4.5 is needed use benzoic acid (pK_a = 4.19) then the ratio of conjugate base to acid should be 2.04 mol : 1 mol in a 1 L solution.

$$4.5 = 4.19 + \log \frac{[C_6H_5COO^-]}{[C_6H_5COOH]}$$

$$2.04 = \frac{[C_6H_5COO^-]}{[C_6H_5COOH]}$$

EXAMPLE 3: CALCULATION pH BUFFER

What is the pH of a buffer that is 0.250 M in acid and 0.600 M in the corresponding salt if the weak acid $K_a = 5.80 \times 10^{-7}$?

Answer:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

$pK_a = -\log(5.80 \times 10^{-7}) = 6.237$

[base] = 0.600 *M* and [acid] = 0.250 *M*

$$\boxed{pH = pK_a + \log\frac{[base]}{[acid]}}$$

$$pH = 6.237 + \log\frac{[0.600]}{[0.250]}$$

$$pH = 6.237 + \log 2.40$$

$$pH = 6.237 + 0.380 = \boxed{6.62}$$

EXAMPLE 4: BUFFER pH CHANGES

The following three calculations how pH stays about the same on addition of acid or base to an acetic acid buffer. (Acetic acid buffer is made from adding acetic acid and its conjugate base in salt form – sodium acetate). In this example we will take 100 mL of a 0.100 M acetic acid + 0.100 M sodium acetate buffer, and we will add 0.001 mol of HCl and 0.001 mol NaOH and calculate the new pH of the solutions.

1) Calculation of pH: $K_a = 1.8 \times 10^{-5}$ $pK_a = 4.74$

$$\boxed{\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}}$$

$$\mathrm{pH} = 4.74 + \log\frac{[0.100\ M]}{[0.100\ M]}$$

$$\boxed{\mathrm{pH} = 4.74}$$

<u>Note:</u> In the calculations for this problem, mols of acid/base are added, which does not change the volume of solution, which then does not change the molarity/concentration of the solution.

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EXAMPLE 4: ADDITION OF ACID/BASE CONTD…

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- **Adding 0.001 mol HCl, a strong acid.** *(Reacts with conj base)*

$$H^+_{(aq)} \quad + \quad CH_3COO^-_{(aq)} \rightleftharpoons CH_3COOH_{(aq)}$$

Before	0.001 mol	0.01 mol	0.01 mol
After HCl	0 mol	0.01-.001mol = 0.009 mol/0.1L	0.01+ .001mol =0 .011 mol/0.1L

Now with new molarity: $$\text{pH} = 4.74 + \log\frac{[0.09\ M]}{[0.11\ M]}$$ $\boxed{\text{pH} = 4.65}$

- **Adding 0.001 mol NaOH, a strong base**. *(Reacts with acid)*

$$OH^-_{(aq)} \quad + \quad CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H_2O_{(l)}$$

Before	0.001 mol	0.01 mol	0.01 mol
After NaOH	0 mol	0.01-.001mol = 0.009 mol/0.1L	0.01+ .001mol =0 .011 mol/0.1L

Now with new molarity: $$\text{pH} = 4.74 + \log\frac{[0.11\ M]}{[0.09\ M]}$$ $\boxed{\text{pH} = 4.83}$

Original pH = 4.74 ; with little acid 4.65 and little base 4.83, not much pH change!

EXAMPLE 5: ACETIC ACID BUFFER pH CHANGE

Calculate the pH of a 1.00 L buffer:

1) made from 0.500 M acetic acid and 0.500 M sodium acetate.

2) When 0.0200 mol HCl is added and 3) when 0.0200 mol NaOH is added.

Answer:

1) Calculation of pH:

$K_a = 1.8 \times 10^{-5}$ $pK_a = 4.74$

$$\boxed{\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}}$$

$$\mathrm{pH} = 4.74 + \log\frac{[0.500\ M]}{[0.500\ M]}$$

$$\boxed{\mathrm{pH} = 4.74}$$

Note: I will setup the solution for parts 2 and 3 for this problem little different from the one on the previous slide. I am not going to use conc. (molarity), I will just use the new mols in the buffer equation since the volume is the same. It cuts down on one calculation.

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EXAMPLE 5: ADDITION OF ACID/BASE CONTD…

continued from previous slide…

2) Adding 0.020 mol HCl, a strong acid. *(Reacts with conj base)*

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$

	$CH_3COOH_{(aq)}$	$H^+_{(aq)}$	$CH_3COO^-_{(aq)}$
Before	0.5 mol		0.5 mol
HCl reacts with CB	+ 0.02 mol		- 0.02 mol

With new mols: $pH = 4.74 + \log\frac{[0.48\ mol]}{[0.52\ mol]}$ $\boxed{pH = 4.71}$

pH should be lower than original pH since acid has been added.

3) Adding 0.020 mol NaOH, a strong base. *(Reacts with acid)*

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$

	$CH_3COOH_{(aq)}$	$H^+_{(aq)}$	$CH_3COO^-_{(aq)}$
Before	0.5 mol		0.5 mol
NaOH reacts with acid	-0.02 mol		+0.02 mol

With new mols: $pH = 4.74 + \log\frac{[0.52\ mol]}{[0.48\ mol]}$ $\boxed{pH = 4.77}$

pH should be higher than original pH since base has been added.

KEY CONCEPTS

- Be able to identify what acid-base combinations are needed to make buffers.
- Calculate the ratio of acid/base needed to make a buffer of a specific pH.
- Calculate pH of buffers.
- Calculate the change in pH of buffers when acid or base is added.