EXPERIMENT 8
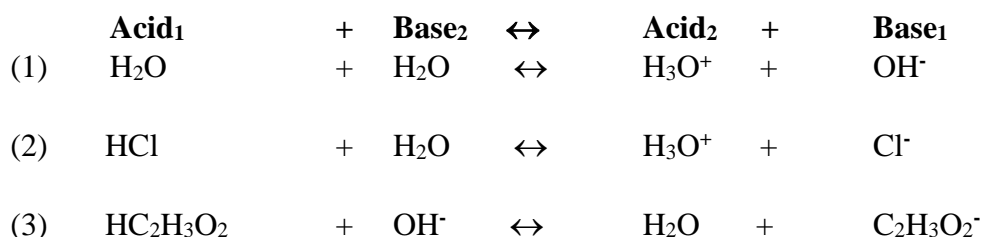
ACID-BASE EQUILIBRIA: BUFFERS

INTRODUCTION:
According the Arrhenius theory of acids and bases, an acid is a substance that dissolves in water yielding aqueous hydrogen ions and a base is a substance that yields hydroxide ions. Relative strengths of acids and bases can be explained in terms of the extent to which acids and bases dissociate. Hydrogen chloride in aqueous solution is a strong acid because it dissociates completely to form an equivalent amount of hydrogen ions. An equivalent amount of acetic acid does not provide an equal number of hydrogen ions, and is therefore a weak acid.

The Bronsted -Lowry theory, or simply the Bronsted theory, of acids and bases emphasizes the role of the solvent in the ionization process and its relation to acid and base character. According to this theory, an acid is any substance (neutral molecule, anion, or cation) which can donate a proton, and a base (likewise a neutral molecule, anion, or cation) as any substance which can accept a proton. Examples of the reactions of Bronsted acids and Bronsted bases are:

	Acid$_1$	+	**Base$_2$**	$\leftrightarrow$	**Acid$_2$**	+	**Base$_1$**
(1)	H_2O	+	H_2O	$\leftrightarrow$	H_3O^+	+	OH^-
(2)	HCl	+	H_2O	$\leftrightarrow$	H_3O^+	+	Cl^-
(3)	$HC_2H_3O_2$	+	OH^-	$\leftrightarrow$	H_2O	+	$C_2H_3O_2^-$

In each case the conjugate base of acid$_1$ is base$_1$ and the conjugate acid of base$_2$ is acid$_2$

The Relative Strengths of Acids and Bases: If a given acid is strong, such as HCl, then its conjugate base, Cl is correspondingly very weak. $HC_2H_3O_2$ is a weaker acid then HCl, so its conjugate base, $C_2H_3O_2$ is a stronger base than is Cl. The Bronsted theory involves a relative competition for a proton by the two bases concerned. It is thus possible to arrange a series of acids (and their conjugate bases) in order of decreasing attraction for protons by the acids (and therefore increasing attraction by bases). This arrangement can be used to predict the possibility and extent of a large number of acid-base reactions. Any table which lists acids in order of decreasing values of K_a is such a table.

Buffer Solutions: Buffer solutions are designed to maintain a relatively fixed pH, even when considerable amount of acid or base is added. This is accomplished by having present in the buffer solution both a weak acid and a weak base. For example, a buffer solution may be prepared which contains acetic acid (a weak acid) and acetate ion (a weak base). If a single species is both a weak acid and a weak base, it may act as a buffer. In buffers the weak acid is capable of reacting with added OH (up to a limit) with very little change in pH and the weak base is capable of reacting with added H+ with very little change in pH.

The equilibrium for the ionization of HA, a weak acid, is
$$HA \quad \leftrightarrow \quad H^+ \quad + \quad A^-$$

The equilibrium constant expression is:

$$K_a = \frac{[H+]\,[A\text{-}]}{[HA]} \quad \text{and} \quad [H+] = K_a \cdot \frac{[HA]}{[A\text{-}]} = K_a \cdot \frac{[\text{weak acid}]}{[\text{weak base}]}$$

The molarity of H^+ (and therefore the pH) is a function of the ionization constant and the ratio of the molarities of the weak acid, HA, and the weak base, A^-. In this experiment you will investigate some of the properties of buffers and will prepare a buffer of a designated pH.

PROCEDURE:

(1) Acetic Acid - Sodium Acetate Solution as a Buffer.

(a) **Preparation of the buffer:** Thoroughly mix 25 mL of 1.0 M $HC_2H_3O_2$ and 25 mL of 1.0 M $NaC_2H_3O_2$. Calculate the theoretical pH of this buffer solution. Pour about 20 mL of the buffer into a 50 mL beaker and measure the actual pH, using a pH meter.

(b) **Preparation of 10^{-4} M HCI.** Make 10^{-2} M HCI by adding 5 mL of 0.1 M HCI to 45 mL of water and mixing thoroughly. Mix 5 mL of 10^{-2} M HCI with 45 mL of water to prepare 10^{-3} M HCI. Add 5 mL of 10^{-3} HCI (Save the rest of the 10^{-3} HCI) and 45 mL of water to prepare 10^{-4} M HCI (save the 10^{-4} M HCI).

(c) **Effect of dilution.** Add 20 mL of 10^{-3} M HCI to a 50-mL beaker then 10^{-4} M HCI (from (b) above) to another 50 mL beaker and measure the pH of each. How did the pH change for the 10-fold dilution of HCI?

Add 5 mL of the buffer prepared in (a) above to 45 mL of water to make a 10-fold dilution of the buffer. Measure the pH of the diluted buffer. How did the pH change after diluting the buffer compared to the pH change upon diluting the non-buffered solution?

(d) **Buffering effect.** Add 10 mL of the buffer solution from (a) to a 50 mL beaker and add 10 mL of the 10^{-4} M HCI from (b) to another 50-mL beaker. To each beaker carefully add 0.2 mL (4 drops) of 1.0 M HCI from a Mohr pipet, mix thoroughly and measure the pH of each. Calculate the pH change that should have occurred in each case and compare with the measured values.

Continue adding 1.0 M HCl drop wise from a pipet to each beaker until the pH reaches 2. Compare the volumes required in each case.

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(1) **Acetic Acid - Sodium Acetate as a Buffer**
  (a) Calculate the theoretical pH of the buffer prepared.

          Measured pH   _____

(b) Show by calculations that the molarity of the solution made by adding 5 mL of 0.1 M HCI to 45 ML of water is 0.01.

(c) **Effect of dilution.**

   Measured pH of 10^{-3} M HCI   _____

   Measured pH of 10^{-4} M HCl   _____

   pH change of HCI upon 10-fold dilution   _____ pH units

   pH of buffer after 10-fold dilution   _____ pH units

   pH change of buffer upon 10-fold dilution   _____ pH units

Summarize the effects of dilution of buffered and non-buffered solutions on the pH:

(d)   Buffering effect.

Measured pH of buffer after addition of 0.2 mL of 1.0 M HCI.   _____

Calculated pH of buffer after addition of 0.2 mL of 1.0 M HCl (show calculations):

_____

Measured pH after addition of 0.2 mL of 1.0 M HCl to 10^{-4} M HCI   _____

Calculated pH after addition of 0.2 mL of 1.0 M HCI to 10^{-4} M HCI (show calculations):

_____

Volume of 1.0 M HCI needed to change pH of 10^{-4} M HCI to pH 2   _____

Volume of mL HCl needed to change pH of buffer to pH 2   _____

Explain, by discussion and net ionic equations, how an acetic acid-sodium acetate solution is able to buffer the solution against pH changes upon addition of either acid or base.

QUESTIONS:

1. Show by 2 net ionic equations how $NaHCO_3$ may act as a buffer.

2. Of the following, check the ones whose aqueous solutions may act a buffer

HNO_3, $NaNO_3$ _____ $NH_4C_2H_3O_2$ _____

NaH_2PO_4 _____ N_2H_4, N_2H_5CI _____

$HCHO_2$, $NaCHO_2$ _____ HNO_2, $LiNO_2$ _____

$.NaHSO_4$ _____ $NaC_2H_3O_2$ _____

3. Calculate the pH of a solution which is 0.50M in HA (a weak acid) and 0.80M in NaA. (K_a for HA = 3.0 x 10^{-8})

4. What is the pH of a solution made by adding 23.5 g of $KC_2H_3O_2$ to 400 mL of 0.80M $HC_2H_3O_2$. (K_a for acetic acid -- 1.8 x 10^{-5})