# Chemical reactions: acid-base buffers 

CHEMICAL REACTIONS: ACID-BASE BUFFERS Short Overview Acids and bases represent two of the most common classes of compounds. Many studies have been done on these compounds, and their reactions are very important. Perhaps the most important reaction is the one in which an acid and base are combined, resulting in the formation of water (in aqueous solution) and a salt; this reaction is called neutralization. A buffer solution is a solution that contains both an acid and a salt containing the conjugate base anion in sufficient concentrations so as to maintain a relatively constant pH when either acid or base is added. In this experiment you will prepare a buffer solution and observe its behavior when mixed both with an acid and a base. You will also compare the behavior with that of solutions containing only the acid. Theory In his theory of ionization in the 1880's, Svante Arrhenius defined acids are substances which form $\mathrm{H}+$ and bases as substances which form OH - in water. He further defined a salt as a substance other than an acid or base which forms ions in aqueous solution. Such substances are thus capable of producing an electric current and are called electrolytes. The amount of electricity produced is directly proportional to the concentration of ions in solution. With regard to electrolytes we have learned previously that strong acids and strong bases ionize completely, and are therefore strong electrolytes because they produce a large electric current. Soluble salts are the other type of strong electrolytes. We also learned that weak acids and weak bases ionize only partially in solution, producing smaller quantities of current; these substances are called weak electrolytes. Materials which do not produce an electric current are called nonelectrolytes. To complete our understanding, we concluded that strong electrolytes exist primarily as ions in solution, while weak electrolytes exist
as both ions and molecules in solution. Nonelectrolytes must exist as polar molecules only in solution. While it is useful, the Arrhenius definition of acids and bases is limited to aqueous solutions. This may seem insignificant to a student in introductory chemistry or general chemistry, but it imposes restrictions for understanding more advanced topics. As such, we now introduce two additional definitions of acids and bases, which expand our understanding. |||Acid || Base ||||||||Arrhenius || forms H+ in water || forms OH - in water || Brã, nsted-Lowry || donates $\mathrm{H}+$ (proton) to base || accepts $\mathrm{H}+($ proton) from acid || Lewis || accepts electron pair from base || donates electron pair to acid | The BrÃ, nsted-Lowry concept of acids and bases was introduced by Johannes BrÃ, nsted and Thomas Lowry in 1923, and led to an understanding of many proton transfer reactions observed to occur in both non-aqueous and aqueous solutions. Gilbert Newton Lewis quickly recognized that a substance which is a proton acceptor must also be one which contains an unshared valence electron pair to accept the positive charge. He therefore proposed his own theory of acids and bases based upon electron transfer rather than proton transfer. The Lewis acid-base concept is the most general and allows us to understand reactions which may not involve proton transfer. However, the BrÃ, nsted-Lowry concept provides the simplest description of acid-base buffer solutions, and it is this one which we will utilize in further discussion. We will use the formula HA for an acid and B: for a base in our discussion. Accordingly, the reaction between an acid and base is described by [1]. $\mathrm{HA}+\mathrm{B}:(: A-+B H+[1]$ In the reaction above, the products which are produced are : $\mathrm{A}-$. and $\mathrm{BH}+$. : A - is called the conjugate base of HA because it has donated a proton $(\mathrm{H}+$ ) to the base B : . Likewise, $\mathrm{BH}+$ is the conjugate acid of B : since it has accepted the proton from HA.

The substances HA and: A- are called a conjugate acid-base pair. Likewise, $\mathrm{BH}+$ and B : are also a conjugate acid-base pair. Some common acid-base pairs are: $\mathrm{H} 3 \mathrm{O} 1+$ / H2O H2O / OH1- HCl / Cl1- HNO3 / NO31- H2SO4 / HSO41-HSO41- / SO42- CH3COOH / CH3COO1- (acetate) NH41+ / NH3 (ammonium) H2CO3 / HCO31- (bicarbonate) H2PO41- / HPO42- (phosphate) The first two pairs show that hydronium ion and hydroxide ion are the conjugate acid and base, respectively, of water. It is the relative concentration of these two ions that determine whether a solution is acidic $([\mathrm{H3O}+]>[\mathrm{OH}-])$, basic $([\mathrm{H} 3 \mathrm{O}+]$ $<[\mathrm{OH}-])$, or neutral $([\mathrm{H} 3 \mathrm{O}+]=[\mathrm{OH}-])$. To accomplish this, we measure the pH of the solution. $\mathrm{A} \mathrm{pH}<7$ is acidic, $\mathrm{pH}>7$ is alkaline (or basic), and $\mathrm{pH}=$ 7 is neutral. pH is defined by the equation $\mathrm{pH}=-\log 10[\mathrm{H} 3 \mathrm{O}+]$. An buffer solution must contain both a weak acid and a salt of its conjugate base. Since $\mathrm{HCl}, \mathrm{HNO} 3$, and H 2 SO 4 are all strong acids, these substances will ionize completely and their concentrations will be too insignificant to maintain constant pH values. On the other hand, a weak acid such as acetic acid, CH 3 COOH , only ionizes to a small extent, so the both the undissociated acid and its anion can exist in sufficient concentration in solution to maintain constant pH . When the acetic acid-sodium acetate buffer is prepared the following equilibrium is established. $\mathrm{CH} 3 \mathrm{COOH}(\mathrm{aq})+\mathrm{H} 2 \mathrm{O}(\mathrm{I})(\mathrm{H} 3 \mathrm{O} 1++$ $\mathrm{CH} 3 \mathrm{COO}-$ - 2 ] The equilibrium constant expression for the reaction is $\mathrm{Ka}=$ [pic] $=1.75 \times 10-5$. Therefore, $\mathrm{pH}=\mathrm{pKa}+\log 10[\mathrm{pic}$. [3] Equation [3] above is called the Henderson-Hasselbach equation. The equation shows that because the acetate/acetic acid ratio does not change significantly during most reactions, thus resulting in a relatively constant pH . When a strong base such as sodium hydroxide is added, the acetic acid in the buffer reacts with the hydroxide ion to produce additional acetate ion ([4]). When a
strong acid such as HCl is added to the buffer, the acetate ion will react with the hydronium ion to produce additional acetic acid ([5]). $\mathrm{CH} 3 \mathrm{COOH}(\mathrm{aq})+$ OH1- ât' CH3COO1- + H2O (I) [4] CH3COO1- + + H3O1+ â†' CH3COOH (aq) +H 2 O (I) [5] The predominant effect of the reactions is that the concentration of $\mathrm{H} 3 \mathrm{O}+$ and $\mathrm{OH}-$ do not increase or decrease significantly during the reactions. However, continued addition of NaOH will eventually consume all of the acetic acid present in the buffer, resulting in a sharp rise in pH . Likewise, addition of a large quantity of HCl will consume all of the acetate ion in the buffer, causing the pH to drop sharply. The amount of strong acid or strong base that can be added to a given volume of a buffer system without a significant change in pH (( 1 unit) is known as the buffering capacity. A buffer system such as $\mathrm{CH} 3 \mathrm{COOH} / \mathrm{CH} 3 \mathrm{COO} 1$ - is representative of an acidic buffer, because the molecular component is a weak acid. On the other hand, a basic buffer solution would contain the acid salt of a weak base in addition to the weak base itself. The NH41+ / NH3 buffer is an example of a basic buffer. Biological systems use buffers to maintain ambient physiological conditions. In this regard the bicarbonate and phosphate buffers listed earlier are the two most significant buffers of body fluids. (See the article " Chemistry and Life: Blood as a Buffered Solution" on page 669 of Chemistry: The Central Science, 9th Ed., Brown, LeMay, \& Bursten. For more background information, you should review chapter 16 " Acid-Base Equilibria" in Chemistry: The Central Science, 9th Ed., . Exercise 1. Examination of the Buffer Properties of a Diprotic Acid Salt, Potassium Hydrogen Phthalate [pic] [pic] potassium hydrogen phthalate phthalate A. Chemicals and Apparatus Chemicals: Water Solids: potassium hydrogen phthalate (KHC8H4O4, KHP, 204. $22 \mathrm{~g} / \mathrm{mole}$ ) Solutions: $0.10 \mathrm{M} \mathrm{HCl}(\mathrm{aq}), 0$.
$10 \mathrm{M} \mathrm{NaOH}(\mathrm{aq})$ (from Acid-Base Titrations experiment), pH 7 buffer solutions Apparatus: Balances, beakers, burets, buret clamps, Erlenmeyer flasks, graduated cylinders, hot plate, pH meters, ring stands, volumetric pipets, pipet pumps, volumetric flasks Safety Equipment: goggles, gloves, hood. Objectives: In this experiment you will learn to: 1. prepare a 0. 10 M KHP solution from a solid and water 2. prepare a solution of the phthalate anion from 0. 10 M KHP and NaOH solutions 3. prepare a buffer solution containing both the hydrogen phthalate and the phthalate ions 4. measure the pH of the buffer solution 5 . measure the pH as HCl is added to the buffer solution 6 . measure the pH as NaOH is added to the buffer solution 7. compare the buffer solution with both a strong acid and a weak acid B. Procedure Part I. Preparation of Solutions CAUTION: Use extreme caution while handling the burets, volumetric pipets, and volumetric flasks. (Student 1) 1. Obtain 250 mL of distilled water in a 400-mL beaker from the DW tap at the sink between the two hoods on the side wall. Add 3 teflon boiling chips to the water, and boil the water for five minutes on a hot plate set on medium high. This will drive off dissolved CO2 from the water which may interfere with the experiment. Allow the water to cool to room temperature. 2. Obtain a pH meter from the instructor. Remove the rubber tip from the electrode and place the electrode in a beaker containing 10 mL of pH 7 buffer. Soak the electrode in the buffer solution for five minutes to condition the electrode. Discard the buffer in the sink. 3. Refer to the instructions for using the pH meter. Standardize the meter to pH 7.00 using a fresh sample of pH 7 buffer. (Student 2) 4. Obtain the following items from the instructor: 1 100mL volumetric flask, with stopper 2 burets, 2 buret clamps, and 2 ring stands 2 10-mL volumetric pipets, and pipet pumps Attach the buret clamp to the
ring stand. 5 . Clean the flask with soap and water, and rinse carefully with two 10-mL portions of distilled water. 6 . Clean the burets with tap water, followed by two rinses with distilled water. Then place each buret in the buret clamp on the ring stand. Label one of the burets " NaOH " and the other one " HCl ". 7. Clean the pipets with tap water, followed by two rinses with distilled water. Label one pipet" A" and the other " B". 8. Pour 125 mL of 0. 10 M NaOH from the hood into a $250-\mathrm{mL}$ beaker. Label the beaker. Record the concentration on line 16 of your lab report. 9. Pour 80 mL of 0.10 M HCl from the hood into a $150-\mathrm{mL}$ beaker. Label the beaker. 10. If it is open, close the stopcock on the " NaOH " buret. Use a funnel to pour approximately 10 mL of 0.10 M NaOH into the buret. Remove the buret from the buret clamp and roll the buret in your hands to allow the NaOH to coat the inside of the buret. Discard the rinse into a 30-mL beaker through the stopcock. 11. Return the buret to the buret clamp and close the stopcock. Now fill the buret with 0.10 M NaOH to one inch above the $0-\mathrm{mL}$ mark. Open the stopcock to drain the buret to 0.0 mL in the $30-\mathrm{mL}$ beaker, thus removing any air bubbles in the buret tip. Discard the rinse into the sink. 12. Repeat steps 10 and 11 for the " HCl " buret, using 0.10 M HCl instead of NaOH . The same $30-\mathrm{mL}$ beaker can be used to collect the drain. (Student 1) Preparation of $0.10 \mathrm{M} \mathrm{KHP}(\mathrm{aq}) .13$. Using the electronic balance, obtain a sample of potassium hydrogen phthalate (KHC8H4O4, " KHP") with a mass between 2. 0 g and 2.1 g . Record the mass of the sample to three decimal places in your notebook. 14. Transfer the KHP sample to the $100-\mathrm{mL}$ volumetric flask, and dissolve in approximately 40 mL of boiled distilled water. Then add boiled distilled water to the flask until the bottom of the meniscus is even with the mark on the neck of the flask. (Use an eyedropper from your desk to
add the last few drops of water.) 15. Stopper the flask, and turn it upside down three or four times to mix the solution totally. Transfer the KHP solution to a clean 250-mL beaker. Label the solution as you have been instructed. 16. Determine the concentration of the KHP solution. Preparation of 0. 025 M KHP / 0. 025 M Phthalate ion Buffer Solution. (Student 1) 17. Use pipet " $A$ " to transfer 25.0 mL of the 0.10 M KHP solution prepared above into a clean 250-mL beaker. Record the volume on the lab report. 18. Use a graduated cylinder to add 25.0 mL of boiled distilled water to the KHP. Mix the solution thoroughly. (Student 2) 19. Use pipet " A" to transfer 25.0 mL of your 0. 10 M KHP solution into a clean 100-mL beaker. Record the volume on the lab report. 20. Read the volume of liquid in the buret to 0.05 mL . You will need to estimate the last digit; remember, buret readings increase from top to bottom. Record the initial buret reading on the lab report. Make certain your eye level is even with the bottom of the meniscus. A piece of white paper behind the buret will assist you in reading the volume. 21. Place the beaker under the tip of the buret and add 25.0 mL of 0.10 M NaOH from the buret to the solution. Stir the solution as the NaOH is added to thoroughly mix the solution. Record the final buret reading to ( 0.05 mL on the lab report. This solution which you just prepared contains 0.050 M phthalate ion. 22. Refill the buret to the 0-mL mark with 0.10 M NaOH .23. Pour the phthalate ion solution which you prepared into the $250-\mathrm{mL}$ beaker containing the KHP solution (Step 18, Student 1). Label the solution as " Buffer". You have now prepared 100 mL of a buffer solution containing 0.025 M potassium hydrogen phthalate (KHP) and 0.025 M potassium sodium phthalate (" phthalate ion"). Part II. Measurement of pH and Determination of Buffer Capacity. (Student 1) 1. Transfer 10. 0 mL of 0.10 M HCl from the
buret to a clean 150-mL beaker. Add 10.0 mL of boiled distilled water to the beaker. Stir the mixture and measure the pH with the pH meter. Record the measurement on the lab report. 2. Place the beaker under the buret containing the 0.10 M NaOH . Record the initial volume of NaOH in the buret to ( 0.05 mL . Add 1.0 mL of NaOH to the HCl solution. Stir the mixture and record the new volume of NaOH in the buret and pH on the lab report. 3. Add another 1.0 mL of NaOH to the beaker. Stir and record the volume and pH on the lab report. Repeat this process until a total of 15 mL of NaOH has been added. 4. Discard the solution in the sink. Thoroughly clean the beaker with soap and water. Rinse the beaker twice with $5-\mathrm{mL}$ portions of distilled water before proceeding to the next step. (Student 2) 5. Repeat steps $1-4$ above using pipet " A" to transfer 10.0 mL of 0.10 M KHP solution to the beaker instead of 10.0 mL of HCl . (Student 1) 6. Use pipet " B" to transfer 20. 0 mL of " Buffer" to a clean 150-mL beaker. Stir the solution and measure the pH with the pH meter. Record the measurement on the lab report. 7. Place the beaker under the buret containing the 0.10 M NaOH . Record the initial volume of NaOH in the buret to ( 0.05 mL . Add 1.0 mL of NaOH to the buffer solution. Stir the mixture and record the new volume of NaOH in the buret and pH on the lab report. 8. Add another 1.0 mL of NaOH to the beaker. Stir and record the volume and pH on the lab report. Repeat this process until a total of 10 mL of NaOH has been added. 9. Discard the solution in the sink. Thoroughly clean the beaker with soap and water. Rinse the beaker twice with $5-\mathrm{mL}$ portions of distilled water before proceeding to the next step. (Student 2) 10. Repeat steps $6-9$ above using pipet " B" to transfer 20. 0 mL of " Buffer" to the beaker. Titrate the buffer with 0.10 M HCl instead of $\mathrm{NaOH} . \mathrm{C}$. Disposal All solutions may be discarded in the sink
with plenty of running water. D. Data Analysis Use the graphing feature of Microsoft Excel or Vernier Graphical Analysis to create graphs of pH vs. mmol added for each of the four titrations.

