

## Hydrogen Phosphate Buffer Systems

### Background

The pH of acid or base solutions is dependent on the concentration of free hydronium ions:

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

This concentration can be altered by adding substances which either react with hydronium ions or supply additional hydronium ions. Some solutions, however, exhibit the ability to resist pH changes--to a point--as additional acid or base is added. Such mixtures are said to be "buffered" and the solutions are known as *buffer solutions*.

A buffer solution consists of an equilibrium system containing a weak acid (or base) and its conjugate. A simple example would be a mixture of acetic acid and sodium acetate. The acetate ion ( $\text{CH}_3\text{COO}^-$ ) is the conjugate base of acetic acid. When only acetic acid is present, the amount of acetate ion in the equilibrium mixture is very small and can be determined from the  $K_a$  value and the Molarity of the acid as the % dissociation.

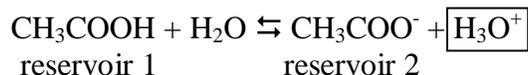


The small value of  $K_a$  tells us that this reaction has very little tendency to occur in the forward direction. Only about 1% of the acetic acid molecules actually donate protons to water at any given time. Thus the equilibrium concentration of acetate ion is very small.

If additional acetate ion is added to acetic acid (in the form of sodium acetate or some other soluble acetate salt) hydronium ions which have been formed by the small amount of dissociation will have a strong tendency to donate protons to the added acetate ions. The result of this "common ion effect" is that the hydronium ion concentration decreases and the pH of the mixture rises a little. We would predict exactly this behavior by LeChâtelier's Principle.

Because the amount of free hydronium ion is small to begin with, adding acetate will most likely result in an excess of acetate ion beyond that consumed by the reverse reaction and exceeding what would normally be present from the forward reaction. This sets up the conditions for "buffering": *reservoirs* of the weak acid (or base) and the conjugate. When these reservoirs are of equal concentration we say that the buffer is "centered". This means it is able to absorb equal moles of acid or base before a significant change in pH occurs. How does this work?

The key to understanding buffer behavior is to keep in mind that the pH of the mixture is related to the amount of free hydronium ion. This is represented in the equilibrium for acetic acid by the boxed species in the reaction below:



If excess acid (e.g., some HCl) is added to this buffer mixture [remember, we are talking about an acetic acid solution with additional acetate ion added] it readily donates protons to the acetate ion in reservoir 2 (the K for this process is  $1/K_a$  or 56,000). *As long as there are enough acetate ions present*, added acid will be "absorbed" by this process and will not affect the boxed concentration of  $H_3O^+$  (or not much). Thus the pH remains close to its original value. Note that this depends on having a large enough reservoir 2 so that some acetate will still remain after the addition of the acid.

The behavior of the mixture when base is added can be viewed from several perspectives. Hydroxide ion is a stronger base than acetate so if sodium hydroxide is added to the buffer, hydronium ions will donate protons to the hydroxide to form water. The loss of "boxed" hydronium ions upsets the equilibrium and acetic acid from reservoir 1 donates protons to water in order to replace some of the lost "boxed" hydronium ions. This nearly restores the original pH *as long as there is a sufficient reservoir of acetic acid*. One could also say that the formation of additional water from the reaction of hydroxide with hydronium ions causes a shift in the equilibrium to the right, although considering the vast quantities of water in the solution this is a less satisfying explanation. Either way, the result is only a small change in the pH.

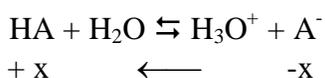
Acid buffer solutions which are "centered" should have pH values which are equal to the  $pK_a$  of the weak acid. Generalizing our example to the weak acid "HA" and its conjugate "A<sup>-</sup>" we can see why this would be so. These two species make up the two reservoirs which will be used to maintain a nearly steady concentration of  $H_3O^+$ . The  $K_a$  expression for this acid would be:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Because the reservoirs appear in both the numerator and denominator, if they are of equal size their concentrations will cancel. This tells us that the hydronium ion concentration in such a mixture is equal to the  $K_a$  for acid, or the  $pH = pK_a$ . In fact, *the pH of a buffer is regulated by some combination of the fixed K value for the weak electrolyte chosen and the ratio of conjugate to acid (or base)*. This is practical information since it is unlikely that a particular weak acid or base will have exactly the right K value to create a buffer of a desired pH. But a close K value will work if the ratio is slightly altered.

The amount of acid or base a buffer can absorb before a significant pH change is called its "capacity". This is governed by the size of the reservoirs (or the concentrations of the weak acid--or base--and the conjugate). While the pH is supposed to remain reasonably constant, it *does* change, even before one of the reservoirs becomes exhausted. The determination of the pH of a buffer solution *after* the addition of acid or base is a relatively simple process which can be made--but should not be made--very complicated. The key to keeping it simple is to think of the buffer mixture as only an acid or a base (depending on what the weak electrolyte is).

Using our hypothetical acid, HA, adding additional acid ( $H_3O^+$ ) will shift the equilibrium below to the left:



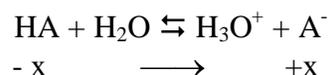
since there is a strong tendency for  $H_3O^+$  to donate protons to  $A^-$ , the conjugate base of the weak acid HA. The amount "x" is the number of moles of acid added.

We use moles because the volume of the mixture will typically change since most added acids or bases will be in aqueous form and that will necessitate a recalculation of the Molarities of HA and A<sup>-</sup>, or it *would* except that this new volume will cancel in the K<sub>a</sub> expression!

$$K_a = \frac{[\text{H}_3\text{O}^+](\text{moles A}^- - x)/V}{(\text{moles HA} + x)/V}$$

From the expression above it is clear that *the change in the ratio of A<sup>-</sup> to HA is altering the pH*. As long as "x" is small compared to the moles of A<sup>-</sup> and HA, the change in pH will be small.

A similar, but opposite, analysis applies to the case of adding base. HA will react with base in a neutralization reaction. The situation is:



$$K_a = \frac{[\text{H}_3\text{O}^+](\text{moles A}^- + x)/V}{(\text{moles HA} - x)/V}$$

This kind of approach requires learning no "magic" formulas and uses the general principles that govern equilibrium and simple neutralization reactions.

Preparing a buffer solution of a particular pH would now seem to be a fairly simple process. After consulting a table of K values, an acid (or base) with a pK close to the desired pH is selected and then the ratio of conjugate to acid (or base) is adjusted to achieve the desired pH value. When this is done in the lab [as in this experiment], the results are only approximate. Why?

The careful student looking back over the previous discussion will notice that several approximations have been made. For example, there is *some* decrease in [HA] due to dissociation and the concentration of conjugate is not *solely* determined by the added common ion. These are relatively obvious places to attempt to tighten up the calculations but the additional mathematical rigor does very little to improve the laboratory result. The real problem lies with more fundamental assumptions about the nature of solutions.

The general treatment of ionic equilibria in solution assumes that ions do not interact. The assumptions used are analogous to those used when describing ideal gases. Not surprisingly, such solutions better approximate ideal behavior as they approach infinite dilution (just as gases approach ideal behavior at very low pressures). Evidence for this goes back to the beginnings of ionic theory with Arrhenius in the 1870's. The freezing points for ionic solutions such as sodium chloride were not exactly what would be predicted based on the assumption that every sodium and chloride ion acted independently. A 1.0 molal solution of NaCl would be expected to freeze at -3.72°C but it actually freezes at -3.37°C. The agreement of calculation with experiment improves as the solution is diluted. For a given concentration a factor can be experimentally determined which "fudges" the numbers. This is the van't Hoff factor, "i", named after the Dutch chemist, and it is often given in the expressions for colligative behavior such as freezing point depression ( $\Delta T_f = iK_fm$ ). For 0.05 m NaCl *i* should be 2 but is found by experiment to be 1.9.

The recognition that typical laboratory solutions rarely behave ideally (in fact, they deviate from ideal behavior far more than gases under usual laboratory conditions) is important even though the effects of this behavior are generally only seen when careful measurements must be made, such as the determination of K values for weak electrolytes or--in the case of this experiment--the preparation of a buffer solution with a designated pH.

In 1923 an attempt was made to describe and account for the important factors which contribute to non-ideal behavior in ionic solutions. *Debye-Hückel Theory* states that there are four major factors which contribute to non-ideal behavior in solution:

- ionic charge
- dielectric constant of the solvent
- temperature
- ionic concentration

The first factor is important because ions of opposite charge will attract each other while ions of the same charge will repel. Ions can thus develop "spheres of influence" which make them behave as much larger particles than they are. The effect increases as the ion charge increases. Smaller ions tend to magnify the effect also since charge is more highly concentrated on them.

The dielectric constant of a solvent is related to its ability to ionize a solute or to support the formation of ions. Water has a value of 80 while ethanol is 25. Higher dielectric constants lead to fewer ionic interactions but more ion-solvent interactions. Ions are surrounded by solvent molecules and are less likely to recombine.

Solutions behave more ideally at higher temperatures rather than lower simply because the additional kinetic energy decreases the likelihood of ion electrostatic interaction.

The final factor is also related to electrostatics. Ions which are more dispersed interact more weakly than ions which are crowded together.

*The net effect of these factors is to make ions seem to have an effective concentration which is less than that calculated based on moles and volumes. The name activity (a) is given to this apparent concentration. The activity coefficient ( $\gamma$ ) is the factor which "fudges" the calculated concentration of an ion (usually expressed in molality) to give the activity:*

$$a = \gamma m$$

[in this experiment we will--as is often done--substitute Molarity for molality for the sake of convenience; the substitution is appropriate at the concentrations used in the experiment]

As the solution approaches infinite dilution,  $\gamma$  approaches 1.

Activity coefficients are not easily measured in the lab but they can be calculated by the **Debye-Hückel Limiting Law**:

$$\log \gamma = -A z^2 \sqrt{I}$$

where  $A$  is an empirical constant for the solvent at a given temperature (0.5091 for water at 298 K),  $z$  is the charge on the ion, and  $I$  is a quantity known as the *ionic strength* of a solution:

$$I = \frac{1}{2} \sum c_i z_i^2$$

where  $c$  is the concentration of the ion expressed in molality [Molarity for us] and  $z$  is again the ion charge. This expression includes ALL of the ions in a mixture, whether they are spectators or not.

Unfortunately, there is a reason this is known as the "Limiting Law". It generally gives good agreement with laboratory observations in only very dilute solutions [one author has referred to these solutions as "slightly contaminated distilled water"]. When concentrations begin to exceed about 0.0010 m, this simple expression gradually fails to "fudge" the numbers sufficiently. The **Extended Debye-Hückel Law** covers solutions with concentrations up to about 0.10 m:

$$\log \gamma = \frac{-A z^2 \sqrt{I}}{1 + B\alpha\sqrt{I}}$$

where  $B$  is an empirical constant and  $\alpha$  is the effective diameter of the hydrated ion. For many common ions such as potassium, chloride, nitrate, etc. the product of  $B$  and  $\alpha$  is nearly 1 and so the expression could be written (with numerical constants included) as:

$$\log \gamma = \frac{-0.5091 z^2 \sqrt{I}}{1 + \sqrt{I}}$$

How is this used to determine the actual pH that will result when the buffer solution is prepared? The  $K_a$  expression for our hypothetical acid HA could be rewritten in terms of *activities* (indeed, this is actually the way equilibrium constants are defined):

$$K_a = \frac{(a_{\text{H}_3\text{O}^+})(a_{\text{A}^-})}{(a_{\text{HA}})}$$

and the pH could be defined in terms of the activity of the hydronium ion as well:  $\text{pH} = -\log (a_{\text{H}_3\text{O}^+})$ .

Recall that the activity of an ion is equal to the activity coefficient multiplied by the concentration:

$$a = \gamma m \text{ (or } \gamma M)$$

Measured masses and volumes can therefore be used to determine the concentrations of the various ions and the expression given above for the adapted Extended Debye-Hückel Law can be used to determine  $\gamma$  for HA and A<sup>-</sup>. Once  $\gamma$  is known, activities can be calculated and used in the K<sub>a</sub> expression to determine the activity of the hydronium ion and the pH.

There's only one problem (besides the number of calculations needed): HA is not an ion.

The buffer system chosen for *this* experiment consists solely of ionic species. The equilibrium involved may be written as:



These ions (which are species derived from phosphoric acid) can be obtained as potassium and sodium salts. The value of K<sub>a</sub> suggests a reasonable target pH range for this buffer system of about 6.90 to 7.50.

[this is a good time to review the rules for significant digits and logs]

You will be assigned a pH target for this system. Your first task is to calculate the amount of the available salts that should be used to prepare 250 mL of the buffer. The salts include:

Salt	Molar mass, g/mol
KH <sub>2</sub> PO <sub>4</sub>	136.09
NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O	137.99
Na <sub>2</sub> HPO <sub>4</sub> ·7 H <sub>2</sub> O	268.09
Na <sub>2</sub> HPO <sub>4</sub> ·12 H <sub>2</sub> O	385.17

To keep the concentration of ions within the range applicable to the Debye-Hückel expression used in this experiment, **you should assume that the more dilute concentration in the ratio of conjugate base to acid is fixed at 0.0200 M.**

Once the solution is prepared the pH can be measured in the usual fashion. The "capacity" of the buffer can also be checked by calculating the volume of 0.10 M HCl or NaOH needed to change the pH **of a 50 mL sample** by 0.10 unit and then observing the result when this is done in the lab.

A few additional tests on the buffer solution complete the experiment.

Finally, it should be said that in practice laboratory chemists do not do these kind of calculations before preparing buffer solutions. Buffer solutions with integer pH values are readily available commercially (someone else has done all of the calculations!). When buffers with non-integer pH values are required, approximate solutions are prepared and additional strong acid or base is carefully added while monitoring the pH of the mixture with a calibrated pH electrode to achieve the desired pH.

## The Experiment

There are four parts to this experiment:

- preparation of the buffer solution for the assigned pH
- testing the buffer "capacity" with HCl and NaOH
- determining the effect on the pH of diluting the buffer
- comparing the behavior of the buffer with distilled water

The following non-locker materials will be provided:

- 250 mL volumetric flask
- CBL w/pH electrode, amplifier and power supply
- pH 6 and 8 buffers
- 25 and 50 mL pipets w/large bulb
- 0.10 M HCl
- 0.10 M NaOH
- micropipettor w/tips
- salts listed in the table in the previous section

## The Chemicals

*Sodium hydroxide* is commonly known as lye or caustic soda. It is a very hygroscopic white solid (absorbs water from the air rapidly) and also absorbs CO<sub>2</sub>. It is very corrosive to vegetable and animal matter and aluminum metal, especially in the presence of moisture. Dissolving NaOH in water generates considerable heat.

Besides its use in the laboratory, sodium hydroxide is used in commercial drain cleaner preparations, to treat cellulose in the manufacture of rayon and cellophane and in the manufacture of some soaps. It is corrosive to all tissues and can be detected on skin by the "slimy" feeling associated with bases. It should be rinsed off thoroughly upon contact. It can damage delicate eye tissues and cause blindness.

*Hydrochloric acid* is also known as muriatic acid. It is the same liquid acid that is often used in controlling the pH of swimming pool water. It is sometimes colored yellow by iron impurities, traces of chlorine and organic matter. Reagent grade HCl contains about 38% hydrogen chloride gas, close to the limit of its solubility at room temperature.

Hydrochloric acid in concentrated form (12 M) has the sharp, choking odor of hydrogen chloride. It is used in the production of other chlorides and in refining some ores (tin and tantalum), cleaning metal products, removing scale from boilers and heat-exchange equipment, and as an important laboratory reagent (often in diluted form).

Concentrated solutions cause severe burns; permanent visual damage may occur. Inhalation causes coughing, choking; inflammation and ulceration of the respiratory tract may occur. Ingestion can be fatal.

*Potassium dihydrogen phosphate* (or potassium biphosphate, potassium acid phosphate, etc.) consists of colorless crystals or a white powder. The pH of a 0.1 M solution ranges from 4.4-4.7. It is used for buffers and has been used as a urinary acidifier.

*Sodium dihydrogen phosphate monohydrate* (or sodium biphosphate, etc.) consists of white or colorless crystals which are slightly deliquescent. Freely soluble in water. The pH of a 0.1 M solution is 4.5. It is used in baking powders and as a dry acidulant for food.

*Sodium monohydrogen phosphate heptahydrate* (or dibasic sodium phosphate, etc.) is generally in the form of crystals or a granular powder which is stable in air. It is soluble in 4 parts water and gives an alkaline solution, pH = 9.5. Used as a mordant in dyeing, in tanning leather, as a soldering flux agent as a reagent in analytical chemistry.

*Sodium monohydrogen phosphate dodecahydrate* is similar to the compound above but the crystals readily lose 5 moles of water on exposure to air at ordinary temperatures.

### **Technique Discussion**

A larger-than-needed quantity of buffer solution is prepared to allow the use of the centigram balances without compromising the precision of the experiment. Nonetheless, care should be exercised in the measurement of the solids and the mixing of the solution. Quantitative transfer techniques should be used.

With the pH electrode calibrated using 6 and 8 buffers, a sample of the prepared buffer should be poured into a small beaker and the pH carefully measured. 25 mL of the buffer solution should be pipetted into a clean, dry beaker and mixed with an equal pipetted volume of distilled water. A pH measurement of this solution will give some idea of the effect of diluting the buffer.

The "capacity" measurements should be made with 50 mL pipetted samples of buffer, using a micropipet to add the calculated volumes of HCl and NaOH. Since these volumes are relatively small, thorough mixing is important.

Finally, repeat the additions of HCl and NaOH but use 50 mL of distilled water rather than the buffer solution. A quick pH measurement of the distilled water itself completes the experimental work.

## The Report

Your initial calculations should include:

1. The ionic strength (I) of your buffer solution [don't forget the spectator ions!!]
2. The activity coefficients ( $\gamma$ ) for  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  in the mixture
3. The activities (a) of  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  in the mixture [assume  $m = M$ ]
4. The expected pH value based on the activities rather than Molar concentrations [relative error]

Your conclusion to this experiment should include a brief discussion of any obvious errors as well as an explanation for the pH of the diluted buffer (what should it be and why?). Is your buffer "centered"? If not, can it absorb more acid or more base? Also comment on the measured pH of distilled water.

If you had access to only  $\text{KH}_2\text{PO}_4$  and some sodium hydroxide, could you prepare an equivalent buffer? Explain.