How does temperature affect the buffer capacity of an acidic buffer?

Introduction

A buffer solution is a solution which resists changes in the pH value when a small amount of an acid or an alkali is added. Buffers solutions are useful especially in living organisms due to their pH resistive properties. Buffering is essential in living organisms because they need to maintain a fairly constant internal environment. Your blood is a buffer for example, since it needs to regulate it's pH, it can't become too acidic or alkaline. I am interested in biochemistry and medicine, which is why this topic was appealing to me because it has plenty of medical applications. I will be investigating the relationship between the buffer capacity of an acidic buffer, composed of ethanoic acid and sodium ethanoate, and temperature.

Theory

The pH value is a measurement of the hydrogen ion concentration of a solution. Acids are typically hydrogen ion donors whereas bases are typically hydroxide ion donors or proton acceptors. When a base is dissolved in water, it is referred to as an alkali. Therefore, alkalis are soluble bases. Coming back to buffer solutions, an acidic buffer is a one which has a pH lower than 7. There are basic buffers also, which have a pH of higher than 7 but we will be concentrating on acidic buffers only. An acidic buffer solution consists of a weak acid and the salt of the weak acid with a strong base, typically a sodium salt.

In order to understand why a buffer solution resists changes in pH when an acid or an alkali is added, I will be giving an example using an acidic buffer solution of **Ethanoic acid and Sodium Ethanoate**, the acidic buffer solution which I used for this experiment. The dissociation of the Ethanoic acid in water is given in **equation 1.**

Equation 1:
$$
CH_3CHOOH_{(aq)} \rightleftharpoons CH_3COO_{(aq)}^+ + H_{(aq)}^+
$$

So the dissociation of Ethanoic acid gives us the Ethanoate ion and a hydrogen ion. Since Ethanoic acid is a very weak acid, it will only partially dissociate. So most of the Ethanoic acid is left undissociated. Weak acids are in fact very strong in terms of keeping their protons.

Now let's say we add a base, for example Sodium Hydroxide, the same base which I also used in the experiment in order to change the pH of my acidic buffer by 1. The dissociation of Sodium Hydroxide in water is given in **equation 2**.

$$
\text{Equation 2:}\quad NaOH_{(aq)} \rightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)}
$$

This is a typical strong base which gives hydroxide ions. When we add small amounts of Sodium Hydroxide into our buffer solution, the hydroxide and sodium ions from **equation 2** tend to bond with the hydrogen and ethanoate ions, from **equation 1**, to form water and salt. The salt produced in this case is Sodium Ethanoate. This shifts our equilibrium of **equation 1** to the left as the dissociated ions tends to get used up. However, since it is a weak acid and most of it remained undissociated, it can simply dissociate more and replace the used up ethonate and hydrogen ions. This results in the equilibrium staying stable and the pH remaining unaltered.

Now, how is temperature related to Buffer Capacity? Well there are 2 main factors influencing the pH of a Buffer Solution (1) :

- 1) The pKa or the pKb of it's acid or base
- 2) The ratio of the initial concentrations of acid and salt, or base and salt, used in it's preparation.

Temperature does affect the pKa or the pKb value. The pKa value also has a logarithmic relationship with the Ka value. This relationship is as follows :

 P ka = $-log(Ka)$

Ka is simply the dissociation constant for an acid. The relationship between pKa and pH can be shown by the Henderson-Hasselbalch equation, **equation 3**.

$$
\text{Equation 3:} \quad pH = pKa + \log(\underbrace{\begin{bmatrix} A^{-} \\ \overline{H}A \end{bmatrix}}) \quad
$$

The square brackets in this equation above, represent the concentrations. The A- represents the conjugate base and the HA represents our weak acid. Relative to the example of the buffer solution which we had previously used as an example, our A⁻ would be the Ethanoate ion and our HA would be the Ethanoic acid. In our case, both of these have high concentrations and are both 1 mol/dm^{3.} Therefore, by substituting these values into the **equation 3**, we get **equation 4.**

Equation 4 :
$$
pH = pKa + log(\frac{1}{1})
$$

Since $Log(1/1) = Log(1)$ and $Log(1) = 0$. The following relationship can be established, **pH = pKa.** Since temperature typically increases the Ka value, it inherently affects the pKa value since P ka = $-log(Ka)$. This means if Ka rises, then pKa decreases, resulting in the pH decreasing. So I hypothesise that the pH and the buffer capacity will decrease as the temperature increases. **Equation 5** shows how to calculate buffer capacity.

Buffer Capacity = $\frac{\text{Base added per volume litre}}{\text{CI}}$ **Equation 5 :** Buffer Capacity = $\frac{2\pi\epsilon_0}{\epsilon_0}$ Change in pH

Equipment List

- 200 ml of 1 mol/dm³ Buffer Solution of Ethanoic Acid and Sodium Ethanoate
- 100 ml of 1 mol/dm³ Sodium Hydroxide
- 1 pH Meter (SPARKvue) (+/- 1)
- 1 Heater
- 1 Thermometer $(+/-0.1^{\circ})$
- 1 150ml measuring cylinder
- 1 Burette (+/-0.05)
- -1150 ml beaker $(+/-1)$
- 2 Tampon Buffers

Method

1) Dilution of the solution : Pour 10 ml of the 1 mol/dm³ buffer solution into the measuring cylinder and add 90 ml of water in order to dilute it to 0.1 mol/dm³ Solution.

- 2) Repeat step 1 with Sodium Hydroxide and dilute it to 0.1 Molar also.
- 3) Pour the 30 ml of the buffer solution into the beaker and place the beaker on the heater.
- 4) Pour 50 ml of the Sodium Hydroxide into the burette and place it directly above the beaker which is on the heater.
- 5) Place the thermometer in the beaker.
- 6) Attach the pH meter to your computer. Then calibrate it using buffer solutions of pH 4 and pH 7 on Sparkvue (2).
- 7) Once calibrated, place the pH meter in the beaker.
- 8) Then turn the heater on and wait till the thermometer reading reaches your desired temperature, 40°C for example.
- 9) Once the desire temperature has been reached, very slowly start pouring the sodium hydroxide into the beaker.
- 10) Once the pH has changed by 1. Stop adding the Sodium Hydroxide immediately. Note down the volume of Sodium Hydroxide required to increase the pH of the buffer by 1.
- 11) Repeat steps 3 to 10 with different temperatures.

Variables

Independant Variables : The temperature

Dependant Variables : The Buffer capacity

Controlled variables : The concentration of the Buffer solution, the concentration of the Sodium hydroxide and the amount of the Buffer solution used for each titration.

Safety Concerns

- Wear protective glasses in order to avoid any solution from getting into your eyes, since it can be mildly corrosive.
- Wear a buttoned up lab coat from any solutions possibly staining your clothes.
- Handle the solutions extremely cautiously, since you will be using electronic equipments which can potentially be damaged if any solution fell on them.

Raw Data (Table 1)

Table 1 : Volume of Sodium Hydroxide used to change the pH of the buffer at different temperatures

Data Processing

This section is divided into 4 sub sections, going chronologically, converting the volume of sodium hydroxide into moles. Then converting the moles relative to 1 litre of the acidic buffer, which will be deriving the buffer capacity. Moreover, calculating the uncertainty of the buffer capacity. At last, I will be providing the final tables and graphs of processed data. I will be using the first data point from **table 1** for the example calculations.

Data Processing 1 : Converting the volume of sodium hydroxide in moles

In order to find out the amount of moles of sodium hydroxide used, one must multiply the volume by the concentration :

When Volume $= 9.5$ ml

We need to convert the volume, in millilitres, into decimetre³ by diving the volume in millilitres by 1000 so :

$-$ > 9.5/1000 = 0.0095

Then we must multiply the volume by the concentration, 0.1 mol/dm^{3,} so:

-> 0.0095 x 0.1 = **0.00095 moles of sodium hydroxide used**

So the final answer would be, for 9.5 millilitres of Sodium Hydroxide, the amount of moles is 0.00095 of Sodium Hydroxide is used to change the pH of the acidic buffer by 1.

Data Processing 2 : Calculating the buffer capacity

The volume of the acidic buffer solution used for all of these titrations is (30+/-1) ml. So one must give the moles of Sodium Hydroxide required to change the pH by 1 of the acidic buffer of *1 litre.* In order to do this we must convert the volume of the acidic buffer from millilitres into decimetres :

\rightarrow 1000/30 = 33.33

Then multiply 33.33 by the amount of moles of sodium hydroxide originally calculated in the previous sub section :

 $-$ 0.00095 x 33.33 = 0.0317 moles of NaOH

The buffer capacity is 0.0317 divided by the change in pH, which is 1 :

$-$ > 0.0317/1 = 0.0317 is the buffer capacity

Data Processing 3 : Calculating the uncertainty of the buffer capacity

First of all, we must convert the absolute uncertainty of the volume of sodium hydroxide into percentage uncertainty, the absolute uncertainty is $(9.5 +/- 0.05)$ ml.

 \rightarrow (0.05/9.5) x 100 = \div -0.526%

Then we must convert the absolute uncertainty of the buffer solution into percentage uncertainty, the absolute uncertainty is (30 +/- 1) ml :

 \rightarrow (1/30) x 100 = \pm /-3.33%

Now we must convert the absolute uncertainty of the pH, 1+/- 0.1, into percentage uncertainty :

 \rightarrow (0.1/1) x 100 = \rightarrow -/- 10%

Furthermore, we add the 3 different percentage uncertainties together :

 \rightarrow 0.526 + 3.33 + 10 = \pm /- 13.86%

Then we need to convert the percentage uncertainty into absolute uncertainty from the final value of the buffer capacity obtained in the previous sub section :

\rightarrow (13.86/100) x 0.0317 = +/-0.004

 $\frac{1}{\alpha}$

So the buffer capacity of the acidic buffer is **(0.03+/-0.004)** moles of sodium hydroxide as that is the amount of moles required to change the pH of 1 litre of the acidic buffer of concentration 0.1 Molar by 1, at a temperature of 20°C. The final value is rounded to 1 significant figure because absolute uncertainties are always rounded to 1 significant figure and so the value itself must also be rounded to 1 significant figure.

Data Processing 4 : Final Tables and Graphs

The graph for the initial pH against temperature is given on **graph 1.** The buffer capacity with change in temperature is given in **table 2.** The graph for table 2 is given in **graph 2.**

Graph 1 : Relationship between pH of the acidic buffer with temperature

Temperature (°C)

Table 2 : Buffer Capacity with change in temperature

Graph 2 : Buffer Capacity with change in temperature

Temperature (°C)

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Conclusion

As we can see from **graph 1**, the relationship between pH and temperature seems to be negative as I originally hypothesised, meaning that the Ka value, the dissociation constant of the acid, is increasing. However, judging by **graph 2**, the relationship between the buffer capacity and the temperature seems to be the opposite to what I hypothesised. I expected it to be negative, and it seems to be fairly positive, despite the majority of the values for the Buffer capacity being 0.04, around the middle. The last data point seems to be off, so it can be considered an anomaly. This positive relationship can be justified in a number of ways. Since the relationship is opposite, it can't be due to random error, it can be a systematic error in the investigation itself, which I discuss further in the limitations section. Another possible justification can be due to the buffer range of the buffer solution. **Graph 3** (3) will help me elaborate further, keeping in mind that our buffer solution is composed of a weak acid, ethanoic acid, and we're adding a strong base, sodium hydroxide. The buffer regions for weak acids vary slightly but are roughly the same.

Graph 3 : Titration of a weak acid with a strong base

The region right before where the graph shoots up and is rather flat, is considered the buffer region. It is referred to as the buffer region due to the fact that adding more moles of the base in this region has very little, if any effect on the pH. Now referring back to **graph 1**, we started with a pH of 4.2 and went down to a pH

of 3.8 as the temperature was increased. So the pH decreased, meaning we went further down the buffer region. So if we are on the green dot in the buffer region where it's a pH of 4.2, we went down to the red dot in the buffer region, where it's a pH of 3.8 as the temperature rose. This could result in a increase in the buffering capacity of the buffer solution due to the very gentle, almost horizontal gradient of the graph at the buffer region. As we go down the buffer region, caused by the decrease in pH as the temperature rises, the more moles of sodium hydroxide we would need in order to make a change in pH by 1. A gradient is defined in the following way :

Δ*y*

Δ*x*

So the gentle gradient at the buffer region means that the gradient has a very low value, a big change in the X axis, moles of sodium hydroxide, will give a very small change in the Y axis, pH. Therefore, as we go further down the buffer region, we will naturally have more of the buffer region ahead of us, so the more difficult it will be to make a change in pH by 1, so the more moles of sodium hydroxide we would need in order to change the pH by 1, resulting in an increase in the buffer capacity as the pH decreases and as the temperature increases.

On top of which, there is also Sodium ethanoate already present in the Buffer solution, which further helps resists changes in the pH. Lastly, as for qualitative observations, there weren't really any to make. Apart from the slight steam forming around the inside of the beaker while being heated. The rest of the 'qualitative observations' were simply observing the temperature on the thermometer and looking at the change in pH on Sparkvue.

Limitations and Improvements

One of the most major limitations in this investigation lies in the titration. When I was adding the Sodium hydroxide, despite me doing it very slowly and cautiously. I would stop the titration after a change in pH by 1 but then after a minute or so, the pH would start rising even more to a certain extent despite me having stopped adding the Sodium hydroxide and the pH change being steady at 1 for a while. This could be caused due to impurities in the NaOH solution. Possibly, there could have been little solid chunks of NaOH in the solution which dissolved after a while of me adding it, resulting in the increase in pH in such a manner. The solution to this would be to simply get a purer solution of the NaOH.

Another drastic improvement in the methodology of this experiment can be achieved by keeping the temperature constant, since I struggled with that and my temperature kept decreasing for the majority of the titrations. This could be improved by the use of a water bath instead of a heater. The fundamental issue here is that, when reaching the equivalence point, less than half a drop of a strong base can make a dramatical change in the pH of an acidic buffer. Therefore, when doing the titration, one must add the Sodium Hydroxide very slowly, this results in the temperature fluctuating as one's waiting for the titration to finish, the temperature itself decreases due to the loss of the average kinetic energy in the molecules of the solution to it's surroundings, as the surrounding temperature around the beaker was much lower than that of the beaker.

In order to maintain the temperature, one could place the beaker with the acidic buffer, in a water bath then heat up the whole water bath itself. If the water surrounding the beaker is the same temperature as the solution in the beaker, then it will take significantly longer for the solution in the beaker to lose it's average kinetic energy to it's surroundings and it's temperature decreasing. One could also perhaps increase the range of temperature with which the buffer capacity was tested by going up to 100°C or by going down to 0°C, giving a wider range of data. Some of the buffer solution could have potentially evaporated while being eaten also, being a potential source of error. One could use a cover over the top of the beaker to prevent this.

Extension of the experiment

There are plenty of possible extensions of this experiment as buffer solutions have a multitude of variables which could potentially be tested. One could change the independent variable from temperature to the concentration of the buffer capacity. Another extension to this investigation could be doing this exact same experiment but with an organic buffer instead of an inorganic buffer. Since Buffer solutions are heavily integrated in Biology and in the human physiology, there could be many different kinds of approaches when it comes to experimenting with buffer solutions.

Bibliography

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