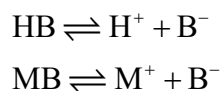


# On the rate of failure of a buffer solution

**Rationale:** In this paper, I derive the equation for the pH curve of a buffer solution with the addition of acid by setting up a system of differential equations for the concentration of the different chemical ions and compounds present in the solution as acid is added. From this result, I define a quantity called the “rate of buffer failure”, and hypothesise (based on the solution to these differential equations) that it is the reciprocal of the rate constant of backwards reaction of the acid dissociation. Following this, I demonstrate an experimental test of this hypothesis with a buffer comprised of sodium acetate and acetic and evaluate its accuracy by measuring the empirical rate of buffer failure. The motivation for the project was that I was troubled by the lack of predictivity of the standard algebraic approach to reaction rate theory, which is why I decided to model it with differential equations.

## 1. Introduction

A buffer solution comprises of either a weak acid and its salt, or a weak base and its corresponding salt. The functioning of the former – an acidic buffer – generally depends on two reversible reactions: the dissociation/re-association of an acid and the solution/precipitation of a salt.



When  $\text{H}^+$  ions are added to the solution, the first equilibrium shifts to the left, and the re-association of the acid  $\text{HB}$  is encouraged, constraining the increase in proton concentration – in addition, the consumption of  $\text{B}^-$  ions shifts the second equilibrium to the right and encourages the dissolution of the salt  $\text{MB}$ , replenishing the conjugate base. When  $\text{OH}^-$  ions are added to the system, they react with the  $\text{H}^+$  ions, shifting the first equilibrium to the right and replenishing the proton concentration.

While the amount of dissociation can be calculated algebraically via the  $K_a$  value for the acid when the environment is free of other compounds, the presence of the salt increases the rate of re-association of the acid by producing a larger quantity of the conjugate base. Meanwhile, the presence of the acid also affects the position of the equilibrium of the salt solution reaction. This system of cross-feedback necessitates a system of differential equations, specifically the following.

$$\left. \begin{aligned} \frac{d[\text{HB}]}{dt} &= -\frac{d[\text{H}^+]}{dt} = -p[\text{HB}] + q[\text{B}^-][\text{H}^+] \\ \frac{d[\text{MB}]}{dt} &= -\frac{d[\text{M}^+]}{dt} = -r[\text{MB}] + s[\text{B}^-][\text{M}^+] \\ \frac{d[\text{B}^-]}{dt} &= \frac{d[\text{M}^+]}{dt} + \frac{d[\text{H}^+]}{dt} \end{aligned} \right\} \quad (1)$$

Where  $[HB]$ ,  $[B^-]$ ,  $[H^+]$ ,  $[HM]$ ,  $[M^+]$  represent the concentrations of acid, conjugate base, hydrogen ions, salt and metal ions respectively, and  $p$ ,  $q$ ,  $r$ ,  $s$  are the rate constants for the acid dissociation, acid re-association, salt solution and salt precipitation reactions respectively. The external addition of  $H^+$  or  $OH^-$  ions (in the usage of the buffer, which is what we are interested in) further complicates the system, but since it doesn't matter if the ions are added after the system reaches equilibrium or before, we may mathematically consider the ions to be an addition to the initial conditions of the set-up. The differential equations therefore remain the same, but the initial conditions depend on the amount of acid or base added.

By solving these differential equations, we will formulate a precise hypothesis for how rapidly the proton concentration changes with respect to further addition of acid to the buffer upon reaching buffer capacity.

## 2. Formulation of hypothesis

A system of 5 differential equations that depend on each other is quite complicated to solve, therefore we will make the following approximations:

$$p \approx 0$$

$$s \approx 0$$

This is reasonable, as the acid is weak (hence dissociation is small) and being a soluble salt, the proportion of undissolved salt at equilibrium is negligible. We will also only consider the addition of  $H^+$  ions, as its dynamics are simpler, and we will see that it has more practical use.

Then (1) becomes:

$$\left. \begin{aligned} \frac{d[HB]}{dt} &= q[B^-][H^+] \\ \frac{d[H^+]}{dt} &= -q[B^-][H^+] \\ \frac{d[MB]}{dt} &= -r[MB] \\ \frac{d[M^+]}{dt} &= r[MB] \\ \frac{d[B^-]}{dt} &= r[MB] - q[B^-][H^+] \end{aligned} \right\} \quad (2)$$

Here, the differential equation in  $[H^+]$  does not depend, even indirectly, on  $[HB]$  and  $[M^+]$  – although we will eventually need to use the conditions on these concentrations to determine the values of some constants of integration, we may ignore their equations when solving for the evolution of  $[H^+]$ . Also, the differential equation for  $[MB]$  is independent of the system and can be solved independently.

$$[MB] = c_1 e^{-rt}$$

(2) then becomes:

$$\left. \begin{aligned} \frac{d[H^+]}{dt} &= -q[B^-][H^+] \\ \frac{d[B^-]}{dt} &= rc_1e^{-rt} - q[B^-][H^+] \end{aligned} \right\} \quad (3)$$

Which is a system of only two differential equations in only two functions. We transform this system into a workable form as follows:

$$\begin{aligned} \frac{d[B^-]}{dt} &= rc_1e^{-rt} + \frac{d[H^+]}{dt} \\ \frac{d([B^-] - [H^+])}{dt} &= rc_1e^{-rt} \\ [B^-] - [H^+] &= \int rc_1e^{-rt} dt \\ \Rightarrow [B^-] &= [H^+] - c_1e^{-rt} - c_2 \end{aligned}$$

Note that as  $c_1, c_2$  are arbitrary constants of integration, it is acceptable to use the same symbols to represent transformed versions of the constants as long as the transformation transforms the constant space to itself – e.g.  $c_2 \rightarrow -c_2$  in this case.

Now that there is an algebraic relationship between  $[H^+]$  and  $[B^-]$ , we may substitute this into the differential equation in  $[H^+]$ , simplifying to

$$\frac{d[H^+]}{dt} - q(c_1e^{-rt} + c_2)[H^+] = q[H^+]^2 \quad (4)$$

This is the differential equation we must solve.

(4) is a special kind of differential equation called a “Bernoulli Differential Equation”<sup>1</sup>. In general, the Bernoulli differential equation takes the form

$$dH(t) / dt + p(t)H(t) = q(t)H(t)^n$$

Where  $n \neq 1$ , and its solution is:

$$H(t) = \left[ \frac{(1-n) \int e^{(1-n) \int p(t) dt} q(t) dt + c_3}{e^{(1-n) \int p(t) dt}} \right]^{\frac{1}{1-n}}$$

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<sup>1</sup> Weisstein, E. (2015). *Bernoulli Differential Equation*. Retrieved from Wolfram Mathworld: <http://mathworld.wolfram.com/BernoulliDifferentialEquation.html>

In our case,

$$\begin{aligned} p(t) &= -q(c_1 e^{-rt} + c_2) \\ q(t) &= q \\ n &= 2 \end{aligned}$$

Importantly,

$$\begin{aligned} \int p(t) dt &= -q(c_2 - c_1 e^{-rt} / r + c_4) \\ e^{(1-n) \int p(t) dt} &= e^{q(c_2 - c_1 \exp(-rt) / r + c_4)} \end{aligned}$$

So that the solution to our differential equation is:

$$[H^+] = \frac{c_4 e^{c_2 t} e^{-c_1 \exp(-rt)}}{c_3 + q c_4 \int e^{c_2 t} e^{-c_1 \exp(-rt)} dt}$$

Where we transformed  $c_1 \rightarrow (r/q)c_1$ ,  $c_4 \rightarrow \ln c_4$ ,  $c_2 \rightarrow c_2/q$ .

We now wish to enforce initial conditions to find the value of the constants  $c_1, \dots, c_5$ . To get the full range of initial conditions, we must solve for  $[B^-]$ ,  $[MB]$ ,  $[HB]$  and  $[M^+]$  to enforce the initial state information we know about each.

We already know that

$$\begin{aligned} [B^-] &= [H^+] - c_1 e^{-rt} - c_2 \\ [MB] &= \frac{-r}{q} c_1 e^{-rt} \end{aligned}$$

With regards to  $[M^+]$ , we solve the differential equation  $\frac{d[M^+]}{dt} = r[MB]$  so that:

$$[M^+] = c_1 c_5 - [MB]$$

Similarly  $\frac{d[HB]}{dt} = q[B][H^+]$  so that

$$[HB] = q \int [H^+]^2 dt - q \int [H^+][MB] dt - q c_2 \int [H^+] dt$$

The following are our initial conditions:

$$[H^+] \Big|_{t=0} = H_0, [B^-] \Big|_{t=0} = 0, [MB] \Big|_{t=0} = S_0, [M^+] \Big|_{t=0} = 0 \quad (5)$$

Note that the constant of integration from  $\int e^{c_2 t} e^{-c_1 \exp(-rt)} dt$  does not produce any new constants to solve for as it can be proportionately accounted for in the values of  $c_3$  and  $c_4$ . So we set the constant of integration so that the initial value of  $\int e^{c_2 t} e^{-c_1 \exp(-rt)} dt$  is 0, i.e. we take the integral from 0 to  $t$ . Then we may solve for the arbitrary constants,

$$\frac{c_4}{c_3} = H_0 e^{q/r S_0}, \quad c_2 = H_0 - S_0, \quad c_1 = -\frac{q}{r} S_0, \quad c_5 = -r/q \quad (6)$$

And substitute them into the expression for  $[H^+]$ .

$$[H^+] = \frac{H_0 e^{q/r S_0} e^{(H_0 - S_0)t} e^{-q/r S_0 \exp(-rt)}}{1 + q H_0 e^{q/r S_0} \int e^{(H_0 - S_0)t} e^{-q/r S_0 \exp(-rt)} dt} \quad (7)$$

(7) fully encodes the behavior of the proton concentration of a Buffer solution when protons are added. However, we are interested only in the value of this function at equilibrium, i.e. its steady-state (long-term) behavior. To do so, we take the limit  $t \rightarrow \infty$ .

$$\begin{aligned} [H^+]_{\text{eq}} &= \lim_{t \rightarrow \infty} \frac{H_0 e^{q/r S_0} e^{(H_0 - S_0)t} e^{-q/r S_0 \exp(-rt)}}{1 + q H_0 e^{q/r S_0} \int e^{(H_0 - S_0)t} e^{-q/r S_0 \exp(-rt)} dt} \\ &= \lim_{t \rightarrow \infty} \frac{H_0 e^{q/r S_0} e^{(H_0 - S_0)t}}{1 + q H_0 e^{q/r S_0} \int e^{(H_0 - S_0)t} dt} \\ &= \lim_{t \rightarrow \infty} \frac{H_0 e^{q/r S_0} e^{(H_0 - S_0)t}}{1 + q H_0 e^{q/r S_0} \frac{e^{(H_0 - S_0)t}}{H_0 - S_0}} \\ &= \lim_{t \rightarrow \infty} \frac{(H_0 - S_0) H_0 e^{q/r S_0} e^{(H_0 - S_0)t}}{H_0 - S_0 + q H_0 e^{q/r S_0} e^{(H_0 - S_0)t}} \end{aligned}$$

If we divide this into two cases based on whether buffer capacity has been reached, we see that

$$[H^+]_{\text{eq}} = \begin{cases} 0 & \text{if } H_0 < S_0 \\ \frac{H_0 - S_0}{q} & \text{if } H_0 > S_0 \end{cases} \quad (8)$$

However, this excludes the dissociation of water, which due to water's weak function as either an acid or a base, has negligible influence on the reaction itself, and can be treated separately from the calculations. Hence, we add  $10^{-\nu}$  (where  $\nu$  is the neutral pH, a function of temperature) to the equation and apply  $\text{pH} = -\log[H^+]$  to obtain our grand result:

$$\text{pH}_{\text{eq}} = \begin{cases} \nu & \text{if } H_0 < S_0 \\ -\log \left[ 10^{-\nu} + \frac{H_0 - S_0}{q} \right] & \text{if } H_0 > S_0 \end{cases} \quad (9)$$

This gives us a precise prediction of the pH curve of a buffer solution as acid is added to it, which is our hypothesis. An unfortunate result of our approximations is that the dissociation of the acid has been understated to the degree that the buffer pH is predicted to be neutral, whereas the actual pH of an acidic buffer will be lower than  $\nu$ . We will call  $d[H^+]_{\text{eq}} / dH_0$  the “rate of buffer failure”. We thus formulate our **hypothesis** precisely as follows: **the rate of buffer failure when acid is added to a buffer equals  $1/q$ , the inverse of the rate constant of acid re-association.**

It is interesting to note that our equation does not depend on the rate constant of dissociation of acid at all, only the rate of re-association. It is possible, though, that in the absence of our approximation that  $p \approx 0$ ,  $p$  might appear in the equation, e.g. replacing  $q$  with  $q - p$ . The impact of this difference, however, would probably be too small to confirm with our set-up.

### 3. Empirical testing

To empirically verify my hypothesis, I decided to conduct a simple experiment with the aim of finding the equation of the pH curve, comparing it with our prediction.

**Research Question:** At what rate does the pH of a buffer solution decrease due to the addition of Hydrochloric Acid after buffer capacity is reached?

#### Variables

- *Independent* – volume of HCl added to buffer
- *Dependent* – pH of mixture
- *Controlled* – amount (by moles) of sodium acetate and acetic acid in the buffer, concentration of sodium acetate and acetic acid in the buffer solution, temperature of mixture, concentration of HCl used

#### Apparatus

- Acetic acid (100 cc, 1.0 M)
- Sodium Acetate solution (100 cc, 1.0 M)
- Hydrochloric acid solution (25 cc, 12.0 M)
- Hot water bath (range: at least 25°C to 70°C)
- Digital thermometer (least count: 0.1°C)
- Measuring cylinder (100cc, least count: 1 cc)
- Beaker (250cc)
- Pipette (least count: 0.01 cc)
- pH probe (least count: 0.01) with datalogger

## Procedure

1. Measure 100.0cc of 1.0M acetic acid and 100.0cc of 1.0M sodium acetate solution with the measuring cylinder and mix them in the beaker.
2. Place beaker in hot water bath – set temperature to 25.0°C and confirm via thermometer.
3. Immerse pH probe in mixture and record pH.
4. Measure 0.900 cc of 12.0M hydrochloric acid with a pipette and add it to the mixture.
5. Record pH.
6. Repeat step 3 a total of 22 times with HCl drops of the same volume and draw pH curve.
7. Repeat Steps 1-5 for a total of three trials.

*Safety, ethical and environmental concerns* – Protective wear such as latex gloves, laboratory goggles and a labcoat were used while handling the 12.0 M Hydrochloric acid. The amount of HCl used was monitored to prevent wastage of a socially valuable resource. The HCl-containing mixture was handed to a chemical waste disposal service to minimise environmental damage.

## Data collection

Table 1: Raw data -- pH of solution vs. volume of HCl added

Volume of HCl /cc ( $\pm 0.005$ )	pH of mixture ( $\pm 0.01$ )		
	Trial 1	Trial 2	Trial 3
0.000	5.89	5.93	5.92
0.900	5.88	5.94	5.92
1.800	5.89	5.91	5.90
2.700	5.88	5.92	5.89
3.600	5.87	5.91	5.86
4.500	5.87	5.91	5.92
5.400	5.88	5.92	5.90
6.300	5.88	5.90	5.90
7.200	5.87	5.91	5.88
8.100	5.87	5.91	5.89
9.000	5.35	5.37	5.36
9.900	5.00	5.02	5.01
10.800	4.81	4.83	4.82
11.700	4.70	4.72	4.72
12.600	4.59	4.61	4.60
13.500	4.50	4.52	4.51
14.400	4.41	4.45	4.43
15.300	4.35	4.37	4.38
16.200	4.31	4.31	4.32
17.100	4.28	4.30	4.30
18.000	4.23	4.23	4.23
18.900	4.19	4.19	4.19
19.800	4.15	4.15	4.15

*Qualitative observations:* Beaker felt cooler as more HCl was added. No visual change.

Sample calculation

$$\text{Average pH} = (\text{Trial 1} + \text{Trial 2} + \text{Trial 3}) / 3 = (5.88 + 5.94 + 5.92) / 3 = 5.91$$

$$\text{Amount of HCl} = 0.900\text{cc} \times 1\text{dm}^3 / 1000\text{cc} \times 12.0\text{ mol dm}^{-3} = 0.0108\text{ mol}$$

$$[H^+] = 10^{-\text{pH}} = 10^{-5.91} \approx 1.23 \times 10^{-6}$$

Propagation of error

$$\text{Uncertainty in amount of HCl} = \frac{0.0108\text{ mol}}{1000} \left( \frac{0.005\text{cc}}{0.900\text{cc}} + \frac{0.0005\text{ mol dm}^{-3}}{12.0\text{ mol dm}^{-3}} \right) \approx 0.0000006\text{ mol}$$

$$\text{Via differentiation for small } \Delta\text{pH}, \Delta[H^+] = 10^{-\text{pH}} \ln 10 \Delta\text{pH} = 0.01 \times \ln 10 [H^+] = 2.83 \times 10^{-8}$$

Table 2: Processed Data -- pH of mixture vs. moles of HCl added, predicted and empirical

Amount of HCl/mol	Uncertainty in amount/mol	pH of mixture ( $\pm 0.01$ )	$[H^+]$ / $10^{-6}$ mol dm <sup>-3</sup>	Uncertainty in $[H^+]$ / $10^{-8}$ mol dm <sup>-3</sup>
0.0000	0.0000000	5.91	1.23	2.83
0.0108	0.0000006	5.91	1.23	2.83
0.0216	0.0000006	5.90	1.26	2.90
0.0324	0.0000006	5.90	1.26	2.90
0.0432	0.0000006	5.89	1.29	2.97
0.0540	0.0000006	5.89	1.29	2.97
0.0648	0.0000006	5.90	1.26	2.90
0.0756	0.0000006	5.89	1.29	2.97
0.0864	0.0000006	5.89	1.29	2.97
0.0972	0.0000006	5.89	1.29	2.97
0.1080	0.0000006	5.36	4.38	10.05
0.1188	0.0000006	5.01	9.77	22.50
0.1296	0.0000006	4.82	15.14	34.85
0.1404	0.0000006	4.71	19.50	44.90
0.1512	0.0000006	4.60	25.12	57.84
0.1620	0.0000006	4.51	30.90	71.16
0.1728	0.0000006	4.43	37.15	85.55
0.1836	0.0000006	4.36	43.65	100.51
0.1944	0.0000006	4.31	48.98	112.78
0.2052	0.0000006	4.29	51.29	118.09
0.2160	0.0000006	4.23	58.88	135.59
0.2268	0.0000006	4.19	64.57	148.67
0.2376	0.0000006	4.15	70.79	163.01



## 4. Data Analysis

Figure 1: pH curve

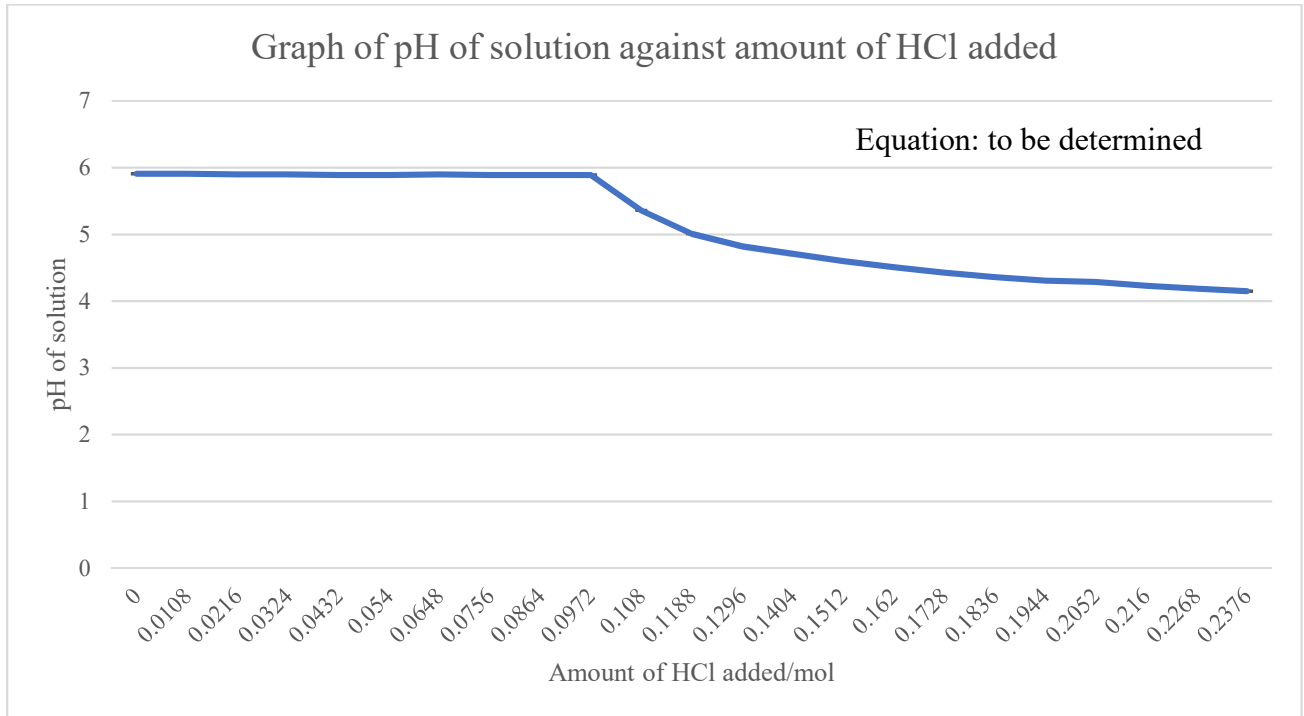
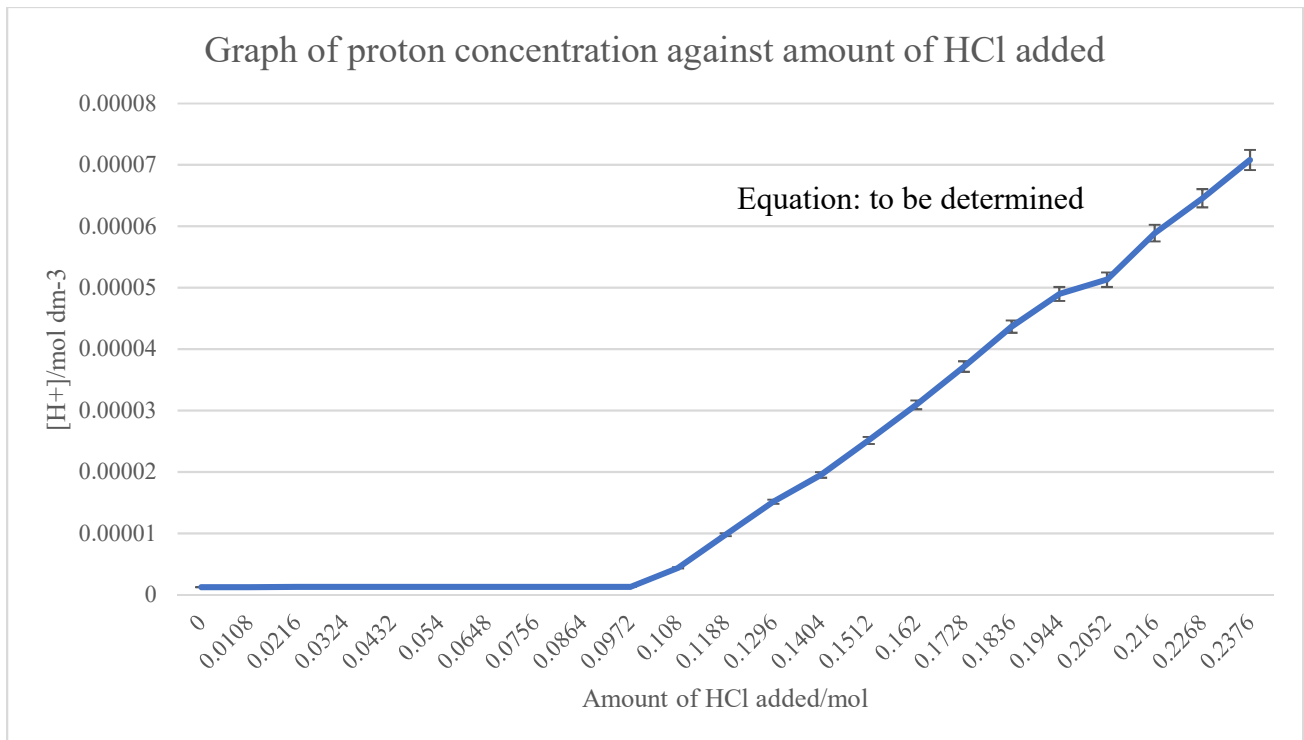


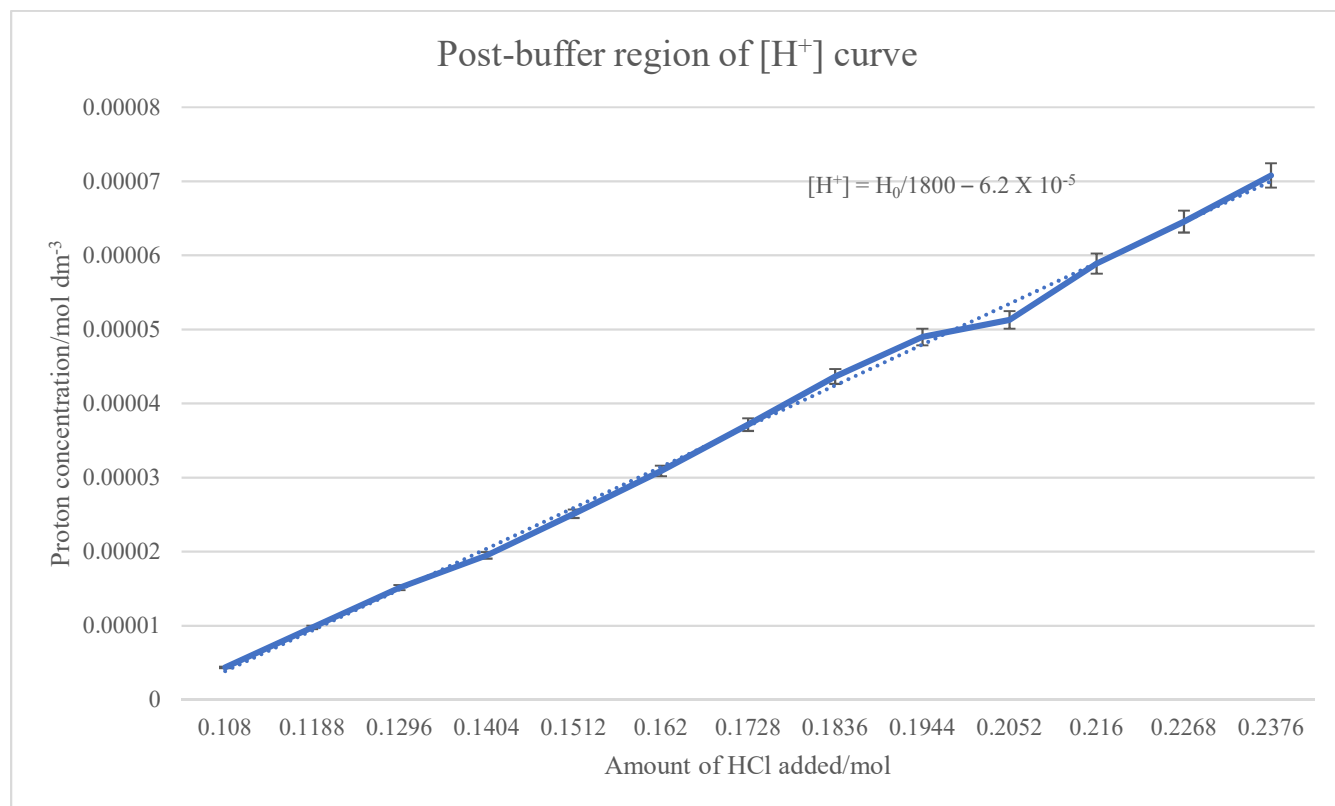
Figure 2: pH curve -- linearised



Note: the error bars are often too small to be seen in the graphs above, but are present in both.

Considering  $H_0 > S_0$  occurs when there are more moles of acid than there are of salt (since they are both present in the same volume of mixture) and there are  $0.1 \text{ dm}^3 \times 1.0 \text{ mol dm}^{-3} = 0.1 \text{ mol}$  of salt, we expect the trendline to shift from a horizontal line to a straight, positive-sloping line at the point 0.1 mol, which is precisely what is observed.

Figure 3: Post-buffer region of proton concentration curve



The equation for the piecewise linear best-fit of our curve is then:

$$[H^+] / \text{mol dm}^{-3} = \begin{cases} 1.23 \times 10^{-6} & \text{if } H_0 < S_0 \\ \frac{1}{1800} H_0 - 6.2 \times 10^{-5} & \text{if } H_0 > S_0 \end{cases}$$

While the  $6.2 \times 10^{-5}$  term would, according to our hypothesis, be a combination of the  $-S_0 / q$  term and the proton concentration of the buffer and water itself, the coefficient on  $H_0$  is the empirical rate of buffer failure. Therefore we can say that the empirical rate of buffer failure is  $1/1800$ .

The uncertainty in the rate of failure can be calculated as:

$$\frac{(0.2376 + 0.0000006) - (0.1080 - 0.0000006)}{(7.07946 \times 10^{-5} - 1.63011 \times 10^{-6}) - (1.23027 \times 10^{-6} + 2.8328 \times 10^{-8})} - \frac{(0.2376 - 0.0000006) - (0.1080 + 0.0000006)}{(7.07946 \times 10^{-5} + 1.63011 \times 10^{-6}) - (1.23027 \times 10^{-6} - 2.8328 \times 10^{-8})} \approx 0.000026$$

Which is an uncertainty of 4.7%, indicating a reasonable level of precision. According to Harned & Ehlers (1933)<sup>2</sup>, the rate constant of dissociation of acetic acid is  $8.85 \times 10^{-9} \text{ dm}^3 \text{ s}^{-1}$ , and we also know<sup>3</sup> that the  $K_a$  value of acetic acid is  $1.77 \times 10^{-5} \text{ mol dm}^{-3}$ . Therefore according to our calculations, the rate of buffer failure is  $1/q$ , which is:

$$\frac{8.85 \times 10^{-9} \text{ dm}^3 \text{ s}^{-1}}{1.77 \times 10^{-5} \text{ mol dm}^{-3}} \approx \frac{1}{2000} \text{ mol}^{-1} \text{ dm}^6 \text{ s}^{-1}$$

The absolute error in the value of  $1/q$  is therefore

$$\left( \frac{1}{1800} - \frac{1}{2000} \right) \text{ mol dm}^{-6} \text{ s} = \frac{1}{18000} \text{ mol dm}^{-6} \text{ s}$$

Which is an 11.1% error margin. This is relatively small, indicating a relatively high accuracy in our result.

## 5. Conclusion

We hypothesized that the pH of a buffer solution as  $H^+$  ions are added behaves as equation (9) predicts, implying a “rate of buffer failure” (defined as the rate at which equilibrium proton concentration increases with an addition to the concentration of acid added to the buffer) of  $1/q$ , where  $q$  is the rate constant of the backward reaction for acid dissociation. The empirical pH curve we obtained does indeed follow this trend in the case of a buffer comprised of sodium acetate and acetic acid, and the empirical rate of buffer failure,  $1/1800 \text{ mol}^{-1} \text{ dm}^6 \text{ s}^{-1}$  (random uncertainty of 4.7%), a systematic error of only 11% away from the prediction made by our calculations, which is  $1/2000 \text{ mol}^{-1} \text{ dm}^6 \text{ s}^{-1}$ .

While this calculation was made by solving a system of differential equations, the result can be understood rather intuitively – once the amount of acid being added exceeds the amount of weak acid (or of salt, whichever is lower) in the buffer, there is no amount of the conjugate base that could possibly neutralize it – this is similar to the equivalence point of a titration curve. Beyond this point, the proton concentration will increase proportionately to the acid added, limited primarily by the re-association of the acidic compound, a reaction whose rate constant is  $q$ . Some

<sup>2</sup> Harned, H., & Ehlers, R. (1933). The Dissociation Constant of Acetic Acid from 0 to 60° Centigrade. *Journal of the American Chemical Society*, 652-656.

<sup>3</sup> Reusch, W. (2012). *Ionization Constants of Heteroatom Organic Acids*. Retrieved from the Michigan State University Website: <https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/acidity2.htm>

research has been done into related measurements of buffer capacity, such as the buffer index<sup>4</sup>, but there is little exploration into the “rate of buffer failure” approach I adopt in this paper.

Our result has several practical implications in industries where the pH of a certain buffer environment cannot fall below a certain limit, yet the industry seeks to minimize costs by minimizing the amount of buffer solution necessary. An example would be preventing milk from souring<sup>5</sup>.

### Evaluation

Our exploration of the rate of buffer failure  $d[H^+]_{\text{eq}} / dH_0$  has the strength of being directly applicable in any practical setting where a certain minimum pH must be maintained – however, the definition may be seen as somewhat arbitrary or contrived for usage in further theoretical research compared to the buffer index.

There are several ways in which our exploration could have been improved. For starters, the approximations made in solving the system of differential equations caused some inaccuracies in the prediction, such as predicting the pH of a buffer as neutral before buffer capacity is reached. A full solution to the 5-variable differential equation without the approximations should be done, perhaps by numerical approximations or with the help of a computer.

A significant source of error was the increase in volume of the mixture as HCl was added, hence changing the concentration of both buffer components and the acid in differently from what was recorded – this was un-accounted for in the calculation as a changing concentration would bring several complications into the differential equations.

A more controlled temperature environment was needed, as the rates of reaction and dissociation constant of water are both temperature-dependent. In particular, neutralization is itself an exothermic reaction – this factor either needs to be controlled very precisely via thermostats (which would be very expensive and might introduce several other sources of error into the experiment), accounted for in the calculations (which would complicate the differential equation system further) or mitigated by adding the acid at a very slow rate and letting the system cool back to its initial temperature before making any measurements. The latter option appears to be the most practical.

The research can also be extended to include adding  $\text{OH}^-$  ions and to consider basic buffers. Both kinds of buffers work with the addition of either  $\text{H}^+$  or  $\text{OH}^-$  ions, but their exact functioning is somewhat different. For instance, the addition of  $\text{OH}^-$  ions to an acidic buffer introduces an entirely new variable,  $[\text{OH}^-]$ , into the differential equation set-up, further complicating the mathematics.

Studying these four set-ups (addition of acid/base to an acidic/basic buffer) and extending our calculations to non-monoprotic acids would lead to a sort of “unified theory” for buffer failure.

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<sup>4</sup> Sandell, E. B., & West, T. S. (1969). *Recommended Nomenclature for Titrimetric Analysis*. Durham: International Union of Pure and Applied Chemistry.

<sup>5</sup> Schaffner, D. (1999). *What is the pH of spoilt milk?* Retrieved from MadSci Network: <http://www.madsci.org/posts/archives/1999-06/929768711.Ch.r.html>

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