A Buffer Does Not Hold the pH; It Holds Only the Neighbourhood of Its pKa

— At a total concentration of **0.1** M and a pKa of **4.76**, the buffer capacity is **0.057565** mol/(L·pH) exactly at the pKa, falls to **0.330579** of that one unit away and to **0.039212** two units away — the separator is whether the system is closed or open — [Paper 679]

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— From thinking to syncing. —

Abstract

A buffer is described as something that holds the pH. But it holds only the neighbourhood of its pKa, and one unit away its capacity has fallen to a third.How far it holds is marked off here with the buffer capacity.No new theorem or law is claimed. First, and this is the core. The capacity peaks at the pKa and falls steeply on both sides——at 0.1 M total and a pKa of 4.76, the 0.057565 mol/(L·pH) at the pKa becomes 0.330579 of that one unit away and 0.039212 two units away (Section 2). **Second, the shape of that fall belongs to no substance——the ratio one unit away is 40/121, matching the measured 0.330579 to ten digits, and neither the total concentration nor the pKa appears in it** (Section 2). **Third, only the total concentration sets the height of the peak——it is $2.302585C/4$, giving 0.057565 mol/(L·pH) at 0.1 M. Nothing but concentration raises it** (Section 2). **Fourth, blood appears to break this rule——it holds pH 7.4 on a system whose pKa is 6.1, that is 1.3 units away, where a closed-system capacity would be only 0.002637 mol/(L·pH)** (Section 3). **Fifth, it breaks nothing; the system is simply not closed——in an open system that can exhale carbon dioxide the capacity is 0.055262 mol/(L·pH), 20.952623 times the closed value** (Section 3). **Sixth, the separator is whether the system is closed or open——at the same concentration, pKa and pH, being able to discard one component to the outside is worth a factor of twenty** (Section 4). **Keywords**: buffer capacity, pKa, Henderson--Hasselbalch relation, bicarbonate buffer, open system, weak acid and conjugate base.

Scope of this paper (scope note): **No new theorem or law is claimed——the Henderson--Hasselbalch relation, the Van Slyke buffer capacity and open-system bicarbonate buffering are all standard (Atkins and de Paula 2014, Harris 2015, Boron and Boulpaep 2016).Polyprotic acids are not treated——acids with more than one dissociation, and mixtures of several buffer systems, are left out. Only a single weak acid is examined.Physiological regulation is not discussed——active control by the kidney and by breathing, and the clinical picture of acidosis, are not the subject; only the single fact of an open system is used.Activity coefficients are not included——concentrations are used and ionic strength is ignored.No recipes are given——how to prepare a buffer, and which reagents to choose, are not treated.Relation to earlier papers**: **Paper 573 showed that the pH 5.6 line of acid rain is a property of the rain, while the damage is a property of what receives it——there the dividing fact was whether the receiver could bear it; here the receiver's side is entered and that bearing is counted as one quantity.**What is added is **tabulating the capacity against distance from the pKa**, **showing the ratio one unit away to be $40/121$, a number belonging to no substance**, **showing that a closed-system count leaves blood short**, **putting the open-to-closed ratio at $\mathbf{20.952623}$**, and **placing the separator on whether the system is closed or open**.

1. Notation and the Question

Setting: **take a weak acid and its conjugate base at total concentration C. The buffer capacity is the amount of strong base needed to move the pH by one unit.**

$$\beta = 2.302585\,C\,\frac{K_a[\mathrm{H^+}]}{(K_a+[\mathrm{H^+}])^2}, \qquad \beta_{\max} = \frac{2.302585\,C}{4}, \qquad \frac{\beta}{\beta_{\max}} = \frac{4\cdot 10^{\delta}}{(1+10^{\delta})^2}$$

Here δ is the difference between pH and pKa. Note that neither C nor K_a survives into the rightmost expression.

Question: **how far does a buffer hold?**

2. The Peak and How It Falls

Computation 2.1: **the capacity was derived at each distance from the pKa, for 0.1 M total and a pKa of 4.76.**

distance from pKa	capacity	against the maximum
0	0.057565	1.000000
0.5	0.042029	0.730126
1	0.019030	0.330579
1.5	0.006842	0.118855
2	0.002257	0.039212

All capacities are in mol/(L·pH).

> **Observation 2.2**
>
> this is the core: the subject of “holds the pH” is not the solution but a place, the neighbourhood of the pKa.One unit away it is down to a third, two units away to nearly a twenty-fifth——choosing a buffer is not choosing a pH to hold but choosing an acid whose pKa lies near it.

Computation 2.3: one unit away the closed form gives $4 \cdot 10/(1+10)^2 = 40/121$, and the computed 0.330579 agrees with it to ten digits.

> **Observation 2.4**
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> the fall is not a property of the substance.Neither the total concentration nor the dissociation constant survives into the ratio, so any weak acid at any concentration is at $40/121$ one unit away——what can be changed is the height of the peak, never its shape.

3. Blood Breaks Nothing; It Is Simply Not Closed

Computation 3.1: in blood the bicarbonate system has a pKa of 6.1, the bicarbonate concentration is 0.024 M and the pH is 7.4, giving a total of 0.025203 M. Counted as a closed system by the relation above, the capacity is 0.002637 mol/(L·pH).

> **Observation 3.2**
>
> seen as a closed system, this is a poor arrangement.It sits 1.3 units from the pKa, where the capacity has fallen to about four hundredths of the peak——chosen by the textbook rule, an acid with a pKa near 7.4 should have been used.

Computation 3.3: but the acid side leaves as a gas through the lungs. Where the partial pressure of carbon dioxide is held fixed, the capacity becomes $2.302585 \times [\mathrm{HCO_3^-}]$, that is 0.055262 mol/(L·pH), which is 20.952623 times the closed value.

> **Observation 3.4**
>
> being open more than makes up for the poor position.When acid is added, the carbonic acid formed leaves as a gas, so one side of the ratio does not fall——the closed-system relation is right to say that 1.3 units away will not do, and it does not apply, because the system is not closed.

4. The Separator

> **Observation 4.1**
>
> the separator is whether the system is closed or open.At the same concentration, the same pKa and the same pH, being able to discard one component to the outside is worth 20.952623——the single phrase “buffer capacity” carries a boundary condition inside it.

> **Observation 4.2**
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> beside Paper 573.Paper 573 showed that the pH 5.6 line of acid rain belongs to the rain, and that the same rain does different damage according to what receives it——there the difference between receivers was the conclusion; here the receiver’s side is entered, its power to bear is counted, and that power is found to exist only near the pKa.

> **Observation 4.3**
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> **what is not said.Polyprotic acids and superposed systems are not treated, and active regulation by kidney and lung is left out——what is shown is that the shape of the capacity belongs to no substance, and why an open system escapes that shape.**

5. Roll Call and Closing

1. **peak 0.057565 mol/(L·pH)** (Computation 2.1): **equal to $2.302585C/4$.**
2. **0.330579 one unit away** (Computation 2.1): **the core.**
3. **0.039212 two units away** (Computation 2.1): **nearly a twenty-fifth.**
4. **0.730126 at half a unit** (Computation 2.1): **the peak is sharp.**
5. **$40/121$ to ten digits** (Computation 2.3): **the shape belongs to no substance.**
6. **blood sits 1.3 from its pKa** (Computation 3.1): **a poor position.**
7. **closed system gives 0.002637** (Computation 3.1): **not enough.**
8. **open system gives 0.055262** (Computation 3.3): **the lungs discard one side.**
9. **a factor of 20.952623** (Computation 3.3): **the position is bought back.**
10. **closed or open** (Observation 4.1): **the separator; Paper 573.**

Closing: **A buffer does not hold the pH.It holds only the neighbourhood of its pKa: one unit away the capacity is 0.330579 of the peak, two units away 0.039212.That fall is fixed by $40/121$, a number belonging to no substance, and changing the total concentration only raises or lowers the peak of 0.057565 mol/(L·pH) without changing the shape——choosing a buffer means choosing a pKa.Blood holds pH 7.4 on a pKa of 6.1, where a closed system would give only 0.002637 mol/(L·pH).In an open system that can exhale carbon dioxide it is 0.055262 mol/(L·pH), a factor of 20.952623——no rule is broken; the system is not closed.The separator is whether the system is closed or open.Placed among the earlier papers——Paper 573 showed the damage to be a property of the receiver; here the receiver's power to bear is counted.To be honest——polyprotic acids and active regulation are not treated, and only a single weak acid was examined.**

References

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