Approximation of pH Values *

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Approximated pH of Strong Acids and Bases

Given an aqueous solution of N strong acids and M strong bases, with known concentrations, we can define a set of acids $\mathcal{A} = \{\mathrm{H}\alpha\}$, $|\mathcal{A}| = N$, and a set of bases $\mathcal{B} = \{\beta\}$, $|\mathcal{B}| = M$, which we will use to compute an approximation for the equilibrium $\mathrm{H_3O^+}$ concentration.

We start laying out the possible reactions in a system of strong acids and bases

$$\mathrm{H}\alpha + \mathrm{H_2O} \rightarrow \mathrm{H_3O^+} + \alpha^-, \qquad \mathrm{H}\alpha \in \mathcal{A}, \tag{1}$$

$$\beta + \mathrm{H_2O} \rightarrow \mathrm{H}\beta^+ + \mathrm{OH^-}, \qquad \beta \in \mathcal{B}, \tag{2}$$

$$2\mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{OH^-}, \tag{3}$$

a system with a reaction for each different acid $\mathrm{H}\alpha \in A$, a reaction for each base $\beta \in B$, and an additional reaction for the water dissociation and association. As we assume that all acids and bases are strong, we just take into account their dissociation reaction. Thus, at equilibrium, we expect all acids and bases to be fully dissociated (meaning $\mathrm{H}\alpha = 0$, $\forall \mathrm{H}\alpha \in \mathcal{A}$, and $\beta = 0$, $\forall \beta \in \mathcal{B}$).

As those reactions only imply association and dissociation, we can simply write our mass balance equations at any time as

$$[\mathrm{H}\alpha]_0 = [\mathrm{H}\alpha] + [\alpha^-], \qquad \mathrm{H}\alpha \in \mathcal{A},$$

$$[\beta]_0 = [\beta] + [\mathrm{H}\beta^+], \qquad \beta \in \mathcal{B},$$

where $[\mathrm{H}\alpha]_0$ and $[\beta]_0$ are the initial acid and base concentrations. The conserved constant is thus the sum of the dissociated and undissociated

*This is just a rough draft, expect bad typography, typos, spelling errors and more.

chemical species derived from the initial acids and bases, serving as a form of mass conservation.

The total charge in the solution should also be preserved. Therefore,

$$[\mathrm{H_3O^+}] + \sum_{j=0}^{M}[\mathrm{H}\beta^+] = [\mathrm{OH^-}] + \sum_{i=0}^{N}[\alpha^-], \qquad \mathrm{H}\alpha \in \mathcal{A}, \qquad \beta \in \mathcal{B},$$

the equality between negative-charged and positive charged chemical species must be maintained. In this context, neutral charged species are not considered, though they are still included in the mass balance equation.

Given the constraints dictated by the reactions and mass conservation, we can rearrange the charge conservation equality to obtain

$$\frac{K_\mathrm{w}}{[\mathrm{H_3O^+}]} + \sum_{\mathrm{H}\alpha\in\mathcal{A}}[\alpha^-] - [\mathrm{H_3O^+}] - \sum_{\beta\in\mathcal{B}}[\mathrm{H}\beta^+] = 0,$$

which is a quadratic equation with two possible solutions: one positive, and one negative. As hydronium concentration cannot be negative, the only possible solution would be the positive one.

We can rearrage the expression as

$$-[\mathrm{H_3O^+}]^2 + (A-B)[\mathrm{H_3O^+}] + K_\mathrm{w} = 0, \quad A = \sum_{\mathrm{H}\alpha\in\mathcal{A}}[\alpha^-], \quad B = \sum_{\beta\in\mathcal{B}}[\mathrm{H}\beta^+],$$

the sum of all concentrations of acids and bases respectively.

The positive root of this equation is an approximation of the concentration of free $\mathrm{H_3O^+}$ ions in an aqueous solution, which can be "easily" computed using the quadratic formula as follows

$$[\mathrm{H_3O^+}] = \frac{A - B \pm \sqrt{(A-B)^2 + 4K_\mathrm{w}}}{2},$$

or by using root-finding algorithms.

Numerical instabilities in the quadratic formula

Given the quadratic formula for the approximate pH

$$[\mathrm{H_3O^+}] = \frac{A - B \pm \sqrt{(A-B)^2 + 4K_\mathrm{w}}}{2},$$

when numerically solving for $[\mathrm{H_3O^+}]$, and considering $K_\mathrm{w} \approx 10^{-14}$ as the standard value, numerical instabilities can araise. This is due to the fact that K_w can be significantly smaller than $A - B$. Thus, the subtraction in the numerator can potentially involve two similar values, potentially resulting in numerical instabilities. [1]

A quadratic equation with real coefficients a, b, and c, generally represented as

$$0 = a \cdot x^2 + b \cdot x + c,$$

can be solved using two different methods. The widely known solution is

$$x = \frac{-b \pm \sqrt{b^2 - 4 \cdot a \cdot c}}{2 \cdot a},$$

and an alternate, yet equivalent, form known as the "citardauq" formula is

$$x = \frac{2 \cdot c}{-b \pm \sqrt{b^2 - 4 \cdot a \cdot c}},$$

which provides the same roots, assuming $ac \neq 0$.

Both expressions may cause difficulties when a or c (or both) are small relative to b. Under such circumstances, one of the roots will require subtracting b from a value that is nearly equal to it, a process that often leads to significant numerical inaccuracies.

This issue can be circumvented by calculating the root that does not necessitate the subtraction of b using the appropriate formula.

An analogous numerical recipe is to compute

$$q \equiv -\frac{1}{2} \cdot \left[b + \operatorname{sgn}(b) \cdot \sqrt{b^2 - 4 \cdot a \cdot c} \right],$$

with

$$\operatorname{sgn}(u) = \begin{cases} -1 & \text{if } u < 0, \\ +1 & \text{if } u \geq 0, \end{cases}$$

a version of the the signum function with the indeterminacy at zero removed, restricting the point to be grouped with either the positive or the negative numbers.

Then the two roots are

$$x_1 = \frac{q}{a}, \qquad x_2 = \frac{c}{q}.$$

However, this approach encounters issues if $a = 0$, although this is not a concern since the use of a quadratic solver is redundant in such a scenario.

[1] This is commonly known as "catastrophic cancellation" in floating-point number systems with subnormal numbers like IEEE 755. Check [1].

Approximated pH of Weak Acids and Bases

Suppose a mixture of a weak acid $H\alpha$ and a weak base β, with known initial concentrations in an aqueous solution. (Although it can be easily generalized for any number of acids and bases.)

We have the following reactions and their respective equilibria

$$\mathrm{H}\alpha + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \alpha^-, \qquad K_\mathrm{a} = \frac{[\mathrm{H_3O^+}]\cdot[\alpha^-]}{[\mathrm{H}\alpha]},$$

$$\beta + \mathrm{H_2O} \rightleftharpoons \mathrm{H}\beta^+ + \mathrm{OH^-}, \qquad K_\mathrm{b} = \frac{[\mathrm{H}\beta^+]\cdot[\mathrm{OH^-}]}{[\beta]},$$

$$2\mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{OH^-}, \qquad K_\mathrm{w} = [\mathrm{H_3O^+}]\cdot[\mathrm{OH^-}].$$

Simulations of this set of reactions can be performed to recreate paths leading to the global equilibria, but we are able to find an approximation to the equilibrium with some additional restrictions.

Following the same procedure as in the strong acids and bases case, the concentration of each chemical species must be preserved. Thus,

$$[\mathrm{H}\alpha]_0 = [\mathrm{H}\alpha] + [\alpha^-],$$

$$[\beta]t_0 = [\beta] + [\mathrm{H}\beta^+].$$

As in the previous case, total charge must also be preserved

$$[\mathrm{H_3O^+}] + [\mathrm{H}\beta^+] = [\mathrm{OH^-}] + [\alpha^-].$$

Thus, we can compute the amount of free hydronium from the previous constrains as

$$\frac{K_\mathrm{w}}{[\mathrm{H_3O^+}]} + \frac{K_\mathrm{a}\cdot[\mathrm{H}\alpha]_0}{[\mathrm{H_3O^+}]+K_\mathrm{a}} - \frac{K_\mathrm{b}\cdot[\beta]_0}{\frac{K_\mathrm{w}}{[\mathrm{H_3O^+}]}+K_\mathrm{b}} - [\mathrm{H_3O^+}] = 0.$$

Although a closed-form expression exists to solve this problem, it is quite large and involved. Therefore, it is highly recommended to instead employ a root-finding algorithm with fine tolerances to solve numerically.

Daisyworld: pH homeostasis by engineered bacterial communities

For the sake of simplicity, we will adopt an approximation wherein we assume complete dissociation of all acids and bases. Consequently, our focus will be solely on strong acids and strong bases. Although this is not realistic and bacteria typically produce weaker acids and bases, the interesting dynamics showcased by the model are preserved.

The model draws inspiration from Daisyworld, a conceptual model featuring a hypothetical planet where two types of daisies—black and white—coexist and interact with their environment. This planet begins with a barren surface, with daisies being the sole life form introduced. A crucial aspect is that the daisies are assumed to significantly affect the planet's albedo, thereby influencing its temperature and playing a pivotal role in global climate regulation.

In this scenario, black daisies absorb more sunlight, leading to a slight increase in their local temperature, whereas white daisies reflect more sunlight, contributing to a slight decrease in their local temperature. The overall temperature of Daisyworld is affected by the impact on albedo from both the black and white daisies.

In our scenario, we have two distinct strains of bacteria, genetically modified to consistently produce either an acid or a base, cultivated within a chemostat. This setup parallels Daisyworld, but instead of temperature, we focus on pH. The acid-producing bacteria protonate their surroundings, leading to a slight acidification in the pH sensing pathways (which is a result of both the remaining acid inside the cell, and the acid in the immediate environment). Conversely, the base-producing bacteria deprotonate their surroundings, leading to a slight alkalinization in the pH sensing pathways.

Cell dynamics

This can be naively modeled using a system of differential equations as follows

$$\frac{\mathrm{d}u_a}{\mathrm{d}t} = [\phi \cdot \beta(\mathrm{pH}_a) - \delta] \cdot u_a,$$
$$\frac{\mathrm{d}u_b}{\mathrm{d}t} = [\phi \cdot \beta(\mathrm{pH}_b) - \delta] \cdot u_b,$$

where u_a is the concentration of the acid-producer strain, u_b is the concentration of the base-producer strain, $\phi = 1 - (u_a + u_b)$ is a simple logistic term used to limit cell growth, and δ is the dilution rate of the chemostat. The function $\beta(\mathrm{pH}_x)$ characterizes the maximum growth rate achievable at a specific pH. It aggregates various pH-dependent factors influencing cell growth, including nutrient availability. A simplified version of this function can be represented as a parabola, defined as

$$\beta(\mathrm{pH}_x) = \frac{\mathrm{pH}_{\mathrm{opt}} - \mathrm{pH}_x}{\mathrm{pH}_{\mathrm{opt}} - \mathrm{pH}_{\mathrm{lim}}},$$

where $\mathrm{pH}_{\mathrm{opt}}$ is the optimal pH for growth, $\mathrm{pH}_{\mathrm{lim}}$ represents the maximum deviation from the optimum pH that still permits bacterial growth, and pH_x is the pH level sensed by the strain u_x. This function exhibits a single peak at the optimal pH, and decreases as the pH deviates from this optimum.

The typical definiton for pH for conversion from $\mathrm{H_3O^+}$ is used:

$$\mathrm{pH}([H_3O^+]) = -\log_{10}\left(\frac{[H_3O^+]}{1\ \mathrm{M}}\right).$$

Molecular dynamics

Appart from cell dynamics, we also should model the pH change over time. Bacteria create an acid (or a base) at a constant rate, and the molecules are exported through the membrane as

$$\emptyset \xrightarrow{\gamma} a_i \underset{k_2}{\overset{k_1}{\rightleftharpoons}} a_e \xrightarrow{\delta} \emptyset, \qquad \emptyset \xrightarrow{\gamma} b_i \underset{k_4}{\overset{k_3}{\rightleftharpoons}} b_e \xrightarrow{\delta} \emptyset,$$

where a_i and b_i are the internal acid and base concentrations, and a_e and b_e are the external acid and base concentrations. The equivalent differential equations are

$$\begin{aligned}
\frac{\mathrm{d}a_i}{\mathrm{d}t} &= \gamma - k_1 \cdot a_i + k_2 \cdot a_e \\
\frac{\mathrm{d}a_e}{\mathrm{d}t} &= k_1 \cdot a_i - k_2 \cdot a_e - \delta \cdot a_e \\
\frac{\mathrm{d}b_i}{\mathrm{d}t} &= \gamma - k_e \cdot b_i + k_4 \cdot b_e \\
\frac{\mathrm{d}b_e}{\mathrm{d}t} &= k_3 \cdot b_i - k_4 \cdot b_e - \delta \cdot b_e
\end{aligned}$$

It can be assumed that those reactions, happening at the molecular level, are in fact much faster than the population dynamics of interest. Therefore, by applying the fast-relaxation assumption, we have

$$\begin{aligned}
a_i^* &= \frac{\gamma(k_2 - \delta)}{\delta \cdot k_1}, & a_e^* &= \frac{\gamma}{\delta}, \\
b_i^* &= \frac{\gamma(k_4 - \delta)}{\delta \cdot k_3}, & b_e^* &= \frac{\gamma}{\delta}.
\end{aligned}$$

We can then compute the environmental pH from the approximated H_3O^+ from the mix of acids and bases in the media as previously discussed

$$H_f(A,\, B) = \frac{A - B \pm \sqrt{(A-B)^2 + 4 \cdot K_\mathrm{w}}}{2},$$

where $A := u_a \cdot a_e + A_0$, and $B := u_b \cdot b_e + B_0$. Here, A_0 and B_0 represent the concentrations of acid and base, respectively, in the supplied media.

With this information, we can also compute pH_a and pH_b as

$$\begin{aligned} \mathrm{pH}_a &:= -\log_{10}\left(H_a\right), & H_a &:= H_f(A + \omega_a \cdot a_e,\, B), \\ \mathrm{pH}_b &:= -\log_{10}\left(H_b\right), & H_b &:= H_f(A,\, B + \omega_b \cdot b_e), \end{aligned}$$

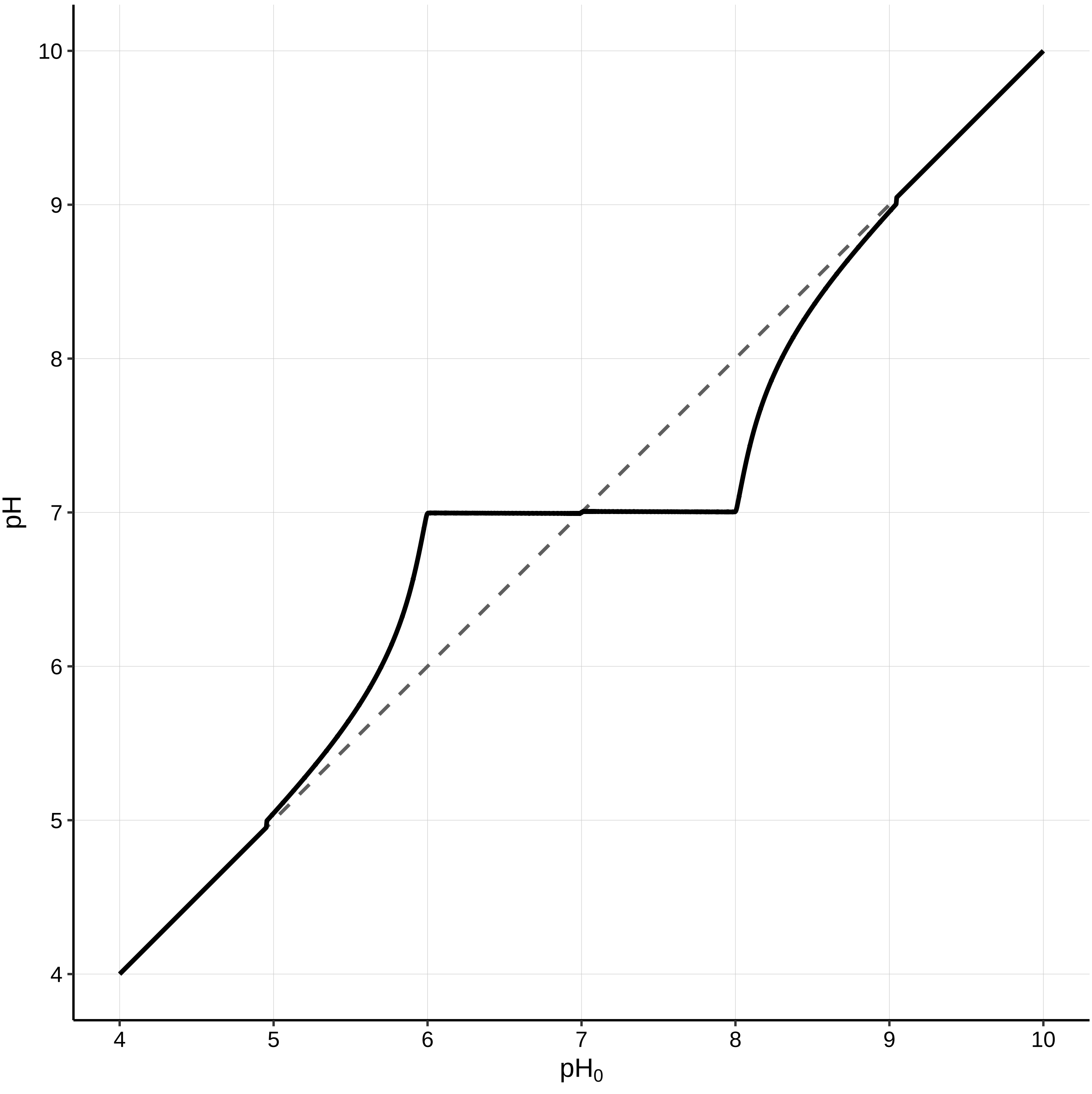
where ω_x is a parameter modeling the sensitivity of the strains to the molecule being produced. It is assumed to be a parameter depending on the amount of internal and external molecule in a generic form

$$\begin{aligned} \omega_a \cdot a_e &= c_1 \cdot (c_2 \cdot a_i + c_3 \cdot a_e) = c_1 \cdot \left(c_2 \cdot \frac{k_2 - \delta}{k_1} + c_3\right) \cdot a_e, \\ \omega_b \cdot b_e &= c_4 \cdot (c_5 \cdot b_i + c_6 \cdot b_e) = c_4 \cdot \left(c_5 \cdot \frac{k_4 - \delta}{k_3} + c_6\right) \cdot b_e, \end{aligned}$$

where c_i, $i \in \{1, 2, 3, 4, 5, 6\}$, are parameters that control the extent to which the acid or base disrupts the internal pH homeostasis or the local external pH.

References

[1] Jean-Michel Muller, Nicolas Brunie, Florent de Dinechin, Claude-Pierre Jeannerod, Mioara Joldes, Vincent Lefèvre, Guillaume Melquiond, Nathalie Revol, and Serge Torres. *Handbook of Floating-Point Arithmetic.* Springer International Publishing, 2018.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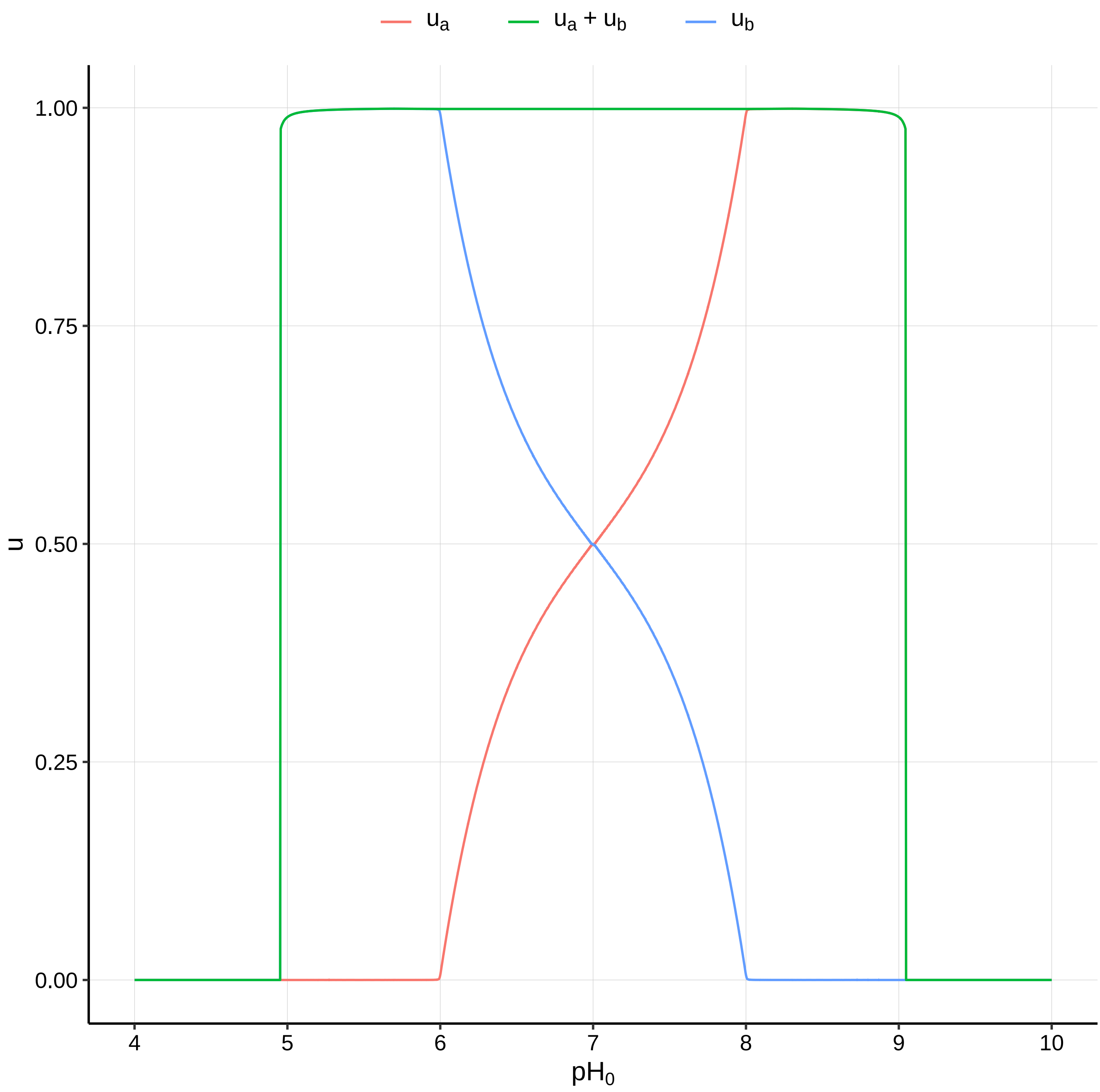

u_a
u_a + u_b
u_b
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0.25
0.00
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5
6
7
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9
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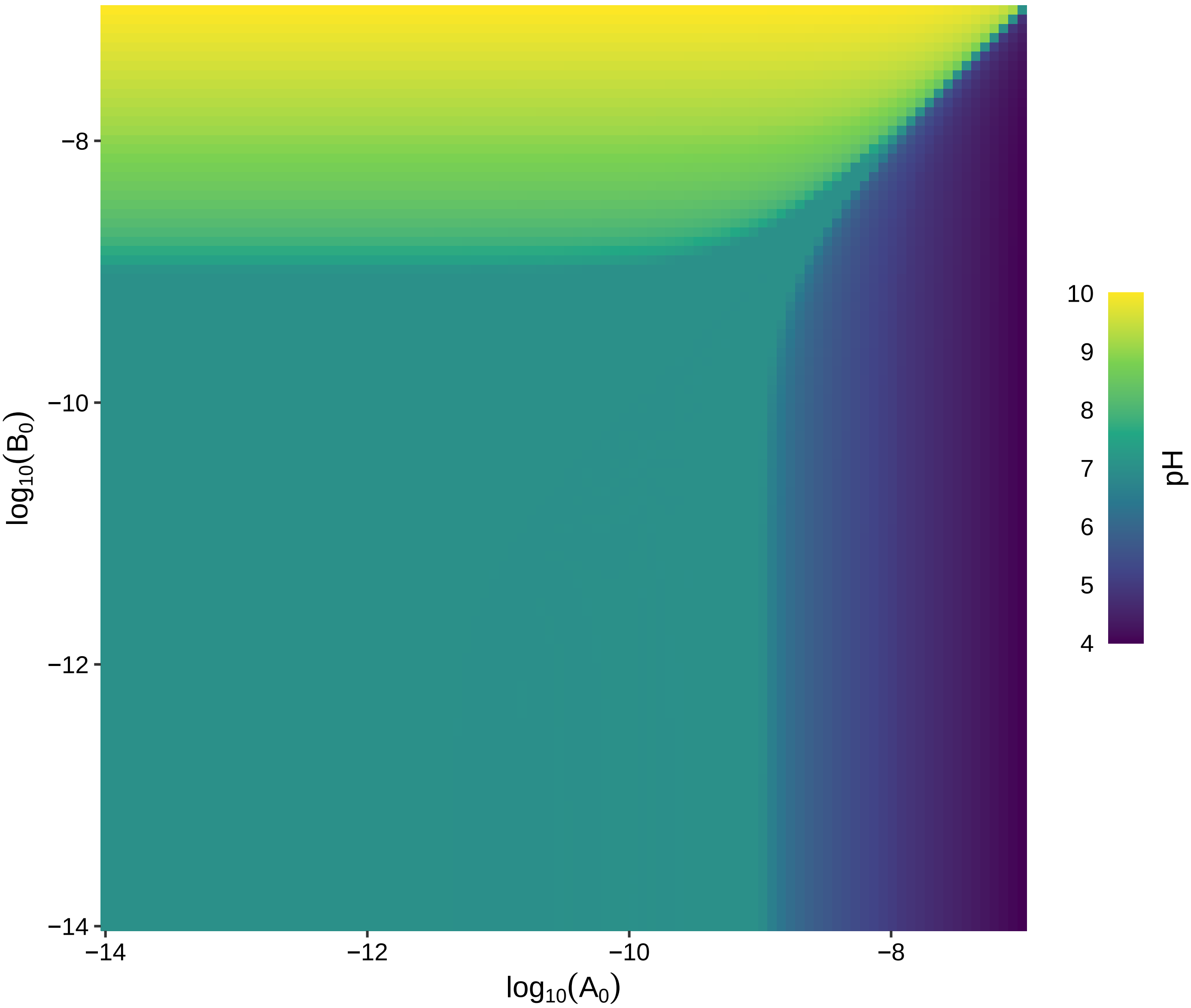
pH_0



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$\log_{10}(B_0)$
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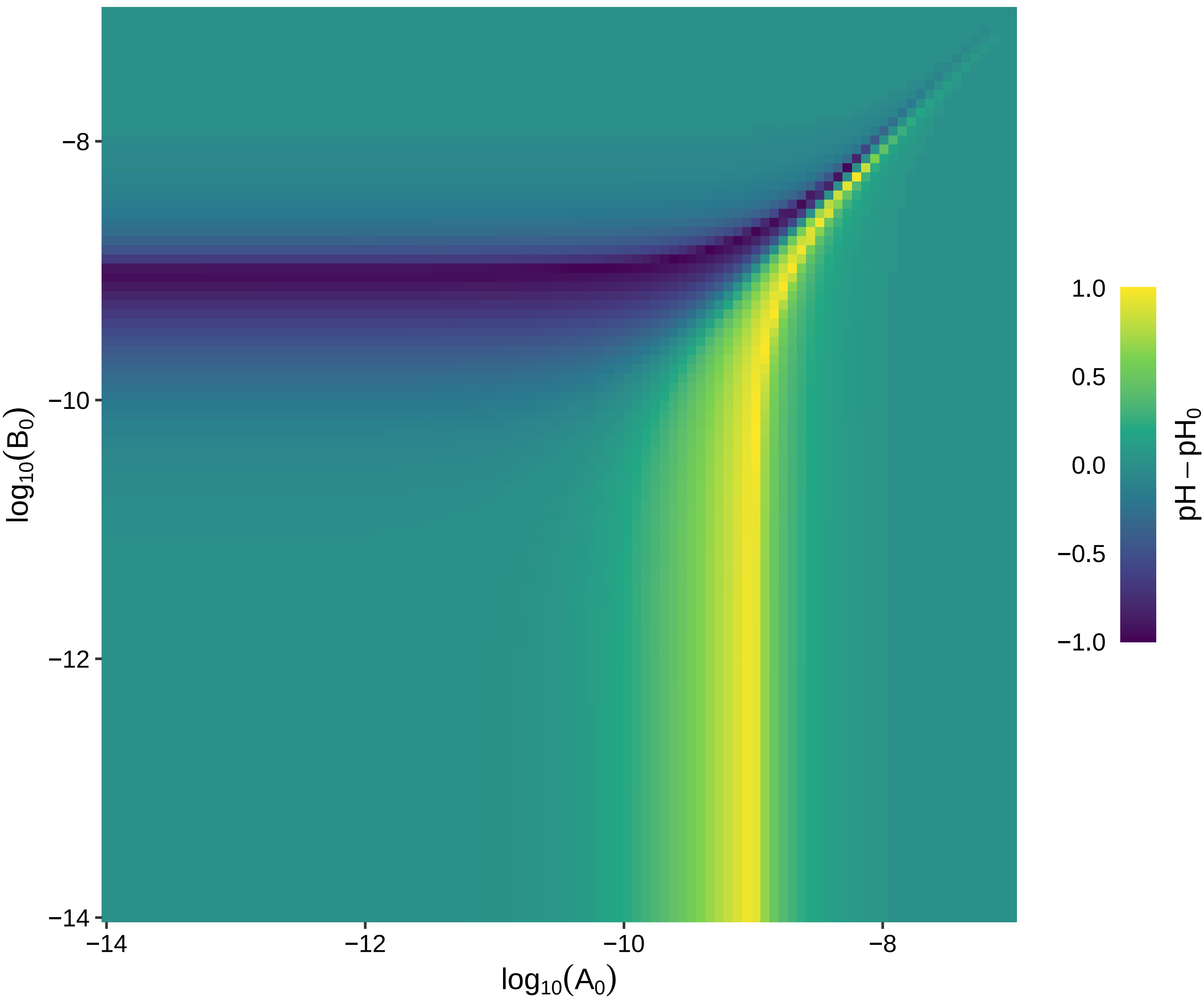
pH



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