Supplementary Material to

"SolveSAPHE-r2: revisiting and extending the Solver Suite for Alkalinity-PH Equations for usage with CO_2, HCO_3^- or CO_3^{2-} input data"

Mathematical and Technical Details

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Abstract

We provide additional theoretical and technical developments.

Contents

1 Asymptotes for $\mathrm{Alk_{nW}}$

The expression for the contribution of the dissociation products of an acid $\mathrm{H_nA}$ to total alkalinity writes (Munhoven, 2013, eq. (4))

$$\mathrm{Alk_A}([\mathrm{H}^+]) = [\Sigma\mathrm{A}] \left(\frac{\sum\limits_{j=0}^{n} j\Pi_j [\mathrm{H}^+]^{n-j}}{\sum\limits_{j=0}^{n} \Pi_j [\mathrm{H}^+]^{n-j}} - m \right) = [\Sigma\mathrm{A}] \left(\frac{D_1}{D} - m \right)$$

where m is the zero-proton level of the acid, $\Pi_j = \prod_{i=1}^{j} K_i$, with $K_1, \ldots, K_n$ being the successive dissociation constants of $\mathrm{H_nA}$, and $\Pi_0 = 1$ and where we have introduced the shorthands D_1 and D for the numerator and the denominator of the fraction, resp. Here we are going to show that

1. $a_n([\mathrm{H}^+]) = \frac{D_1}{[H^+]^n}$ is an asymptote for $\frac{D_1}{D}$ as $[\mathrm{H}^+] \to +\infty$, which means that

$$\lim_{[\mathrm{H}^+] \to +\infty} \left(\frac{D_1}{D} - \frac{D_1}{[H^+]^n} \right) = 0.$$

2. the partial sums of the leading terms of $a_n([H^+])$, $a_1([H^+]) = \frac{K_1}{[\mathrm{H}^+]}$ are also a asymptotes for $\frac{D_1}{D}$ as $[\mathrm{H}^+] \to +\infty$ for common naturally occurring acids – here we consider $a_1([\mathrm{H}^+]) = \frac{\Pi_1}{[\mathrm{H}^+]}$ and $a_2([\mathrm{H}^+]) = \frac{\Pi_1}{[\mathrm{H}^+]} + 2\frac{\Pi_2}{[\mathrm{H}^+]^2}$.

In addition,

$$\mathrm{Alk_A}([\mathrm{H}^+]) < \mathrm{Alk_{Ainf}} + [\Sigma\mathrm{A}] \times a([\mathrm{H}^+])$$

where a stands for either one of a_1, a_2 or a_n.

1.1 The universal asymptote: a_n

In order to establish the quality of a_n as an asymptote for $\frac{D_1}{D}$, we need to analyse the difference Δ_n between the two as $[\mathrm{H}^+] \to +\infty$:

$$\Delta_n = \frac{D_1}{[\mathrm{H}^+]^n} - \frac{D_1}{D} = \frac{D_1}{D} \left(\frac{D}{[\mathrm{H}^+]^n} - 1 \right).$$

Since D is a sum of strictly positive terms (assuming that $[\mathrm{H}^+] > 0$), D is lower than any sub-sum of its terms and thus also of any single term of the sum. Hence $\frac{D}{[\mathrm{H}^+]} > 1$ and therefore $\Delta_n > 0$. The factor in brackets is

$$\frac{D}{[\mathrm{H}^+]^n} - 1 = \frac{1}{[\mathrm{H}^+]^n} \sum_{j=0}^{n} \Pi_j [\mathrm{H}^+]^{n-j} - 1 = \sum_{j=0}^{n} \Pi_j \frac{1}{[\mathrm{H}^+]^j} - 1 = \sum_{j=1}^{n} \Pi_j \frac{1}{[\mathrm{H}^+]^j}$$

since $\Pi_0 = 1$. With the index change $i = j - 1$, this latter sum can be rewritten and we find that

$$\frac{D}{[\mathrm{H}^+]^n} - 1 = \frac{1}{[\mathrm{H}^+]} \sum_{i=0}^{n-1} \Pi_{i+1} \frac{1}{[\mathrm{H}^+]^i}.$$

We furthermore have

$$\begin{aligned} D_1 &= \sum_{j=0}^{n} j\Pi_j [\mathrm{H}^+]^{n-j} = \sum_{j=1}^{n} j\Pi_j [\mathrm{H}^+]^{n-j} = \sum_{j=0}^{n-1} (j+1)\Pi_{j+1} [\mathrm{H}^+]^{n-j-1} \\ &= \frac{1}{[\mathrm{H}^+]} \sum_{j=0}^{n-1} (j+1)\Pi_{j+1} [\mathrm{H}^+]^{n-j}. \end{aligned}$$

The assembly of these two pieces leads to

$$\Delta_n = \frac{D_1}{D}\left(\frac{D}{[\mathrm{H}^+]^n} - 1\right) = \frac{1}{[\mathrm{H}^+]^2} \frac{\left(\sum\limits_{j=0}^{n-1}(j+1)\Pi_{j+1}[\mathrm{H}^+]^{n-j}\right) \times \left(\sum\limits_{j=0}^{n-1}\Pi_{j+1}\frac{1}{[\mathrm{H}^+]^j}\right)}{\sum\limits_{j=0}^{n}\Pi_j[\mathrm{H}^+]^{n-j}}$$

$$= \frac{1}{[\mathrm{H}^+]^2} \frac{\left(\sum\limits_{j=0}^{n-1}(j+1)\Pi_{j+1}\frac{1}{[\mathrm{H}^+]^j}\right) \times \left(\sum\limits_{j=0}^{n-1}\Pi_{j+1}\frac{1}{[\mathrm{H}^+]^j}\right)}{\sum\limits_{j=0}^{n}\Pi_j\frac{1}{[\mathrm{H}^+]^j}}.$$

This demonstrates that $\Delta_n = O(\frac{1}{[\mathrm{H}^+]^2})$ as $[\mathrm{H}^+] \to +\infty$, and thus $\lim_{[\mathrm{H}^+]\to+\infty} \Delta_n = 0$. Accordingly,

$$\mathrm{Alk_A}([\mathrm{H}^+]) = [\Sigma\mathrm{A}]\left(\frac{D_1}{D} - m\right) = \mathrm{Alk_{Ainf}} + [\Sigma\mathrm{A}]\frac{D_1}{D} = \mathrm{Alk_{Ainf}} + [\Sigma\mathrm{A}](a_n([\mathrm{H}^+]) - \Delta_n)$$

which allows us to conclude:

$$\mathrm{Alk_A}([\mathrm{H}^+]) < \mathrm{Alk_{Ainf}} + [\Sigma\mathrm{A}]\; a_n([\mathrm{H}^+]).$$

1.2 The practical asymptote: a_1

The asymptote a_n is unconditionally valid. For a_1 to be an asymptote, it will be shown below that it is sufficient that the successive dissociation constants of H_nA fulfil a condition on their magnitude, which is nevertheless generally fulfilled. Similarly to above, we need to analyse the distance between $\frac{D_1}{D}$ and a_1. The general developments are only valid for $n > 1$ (as for a_n) and we therefore address the case $n = 1$ separately:

$$\Delta_1 = \frac{K_1}{[\mathrm{H}^+]} - \frac{D_1}{D} = \frac{K_1}{[\mathrm{H}^+]} - \frac{K_1}{[\mathrm{H}^+] + K_1} = \frac{K_1^2}{[\mathrm{H}^+] + K_1}$$

which is sufficient to conclude and furthermore shows that valid without conditions.

For $n > 1$, we proceed as above. To start,

$$\Delta_1 = \frac{K_1}{[\mathrm{H}^+]} - \frac{D_1}{D} = \frac{\frac{K_1}{[\mathrm{H}^+]}D - D_1}{D}$$

The expression at the numerator can be developed as follows:

$$\frac{K_1}{[\mathrm{H}^+]}D - D_1 = \frac{K_1}{[\mathrm{H}^+]}\sum_{j=0}^{n}\Pi_j[\mathrm{H}^+]^{n-j} - \sum_{j=1}^{n} j\Pi_j[\mathrm{H}^+]^{n-j}$$
$$= \sum_{j=0}^{n} K_1\Pi_j[\mathrm{H}^+]^{n-j-1} - \sum_{j=1}^{n} j\Pi_j[\mathrm{H}^+]^{n-j}$$

In order to merge the two sums, we operate an index change $i = j - 1$ in the second one. For the sake of clarity we also rename the index j to i in the first one. As a result, we get

$$\frac{K_1}{[\mathrm{H}^+]}D - D_1 = \sum_{i=0}^{n} K_1\Pi_i[\mathrm{H}^+]^{n-i-1} - \sum_{i=0}^{n-1}(i+1)\Pi_{i+1}[\mathrm{H}^+]^{n-i-1}$$
$$= \frac{K_1\Pi_n}{[\mathrm{H}^+]} + \sum_{i=0}^{n-1}(K_1\Pi_i - (i+1)\Pi_{i+1})[\mathrm{H}^+]^{n-i-1}$$
$$= \frac{1}{[\mathrm{H}^+]}\left(K_1\Pi_n + \sum_{i=0}^{n-1}\Pi_i(K_1 - (i+1)\frac{\Pi_{i+1}}{\Pi_i})[\mathrm{H}^+]^{n-i}\right)$$
$$= \frac{1}{[\mathrm{H}^+]}\left(K_1\Pi_n + \sum_{i=1}^{n-1}\Pi_i(K_1 - (i+1)K_{i+1})[\mathrm{H}^+]^{n-i}\right)$$

where we have taken into account that $\Pi_{i+1} = K_{i+1}\Pi_i$ and omitted the term for $i = 0$ from the sum, as it is zero. We operate again an index change $j = i - 1$ on the sum and get

$$\begin{aligned}
\frac{K_1}{[\mathrm{H}^+]}D - D_1 &= \frac{1}{[\mathrm{H}^+]}\left(K_1\Pi_n + \sum_{j=0}^{n-2}\Pi_{j+1}(K_1 - (j+2)K_{j+2})[\mathrm{H}^+]^{n-j-1}\right) \\
&= \frac{1}{[\mathrm{H}^+]^2}\left(K_1\Pi_n[\mathrm{H}^+] + \sum_{j=0}^{n-2}\Pi_{j+1}(K_1 - (j+2)K_{j+2})[\mathrm{H}^+]^{n-j}\right)
\end{aligned}$$

If $K_1 - (j+2)K_{j+2} \geq 0$, i.e., if $K_{j+2} < \frac{K_1}{j+2}$ for $j = 0, \ldots, n-2$, then $\frac{K_1}{[\mathrm{H}^+]}D - D_1 > 0$ from which we may conclude that $\Delta_1 > 0$. This is normally the case, as consecutive dissociation constants are orders of magnitude and not only a factor of two to four apart as would be the case with the common acid-base systems contributing to total alkalinity. Finally

$$\begin{aligned}
\Delta_1 &= \frac{\frac{K_1}{[\mathrm{H}^+]}D - D_1}{D} \\
&= \frac{1}{[\mathrm{H}^+]}\,\frac{K_1\Pi_n[\mathrm{H}^+] + \sum\limits_{j=0}^{n-1}\Pi_{j+1}(K_1 - (j+2)K_{j+2})[\mathrm{H}^+]^{n-j}}{\sum\limits_{j=0}^{n}\Pi_j[\mathrm{H}^+]^{n-j}} \\
&= \frac{1}{[\mathrm{H}^+]^2}\,\frac{\frac{K_1\Pi_n}{[\mathrm{H}^+]^{n-1}} + \sum\limits_{j=0}^{n-1}\Pi_{j+1}(K_1 - (j+2)K_{j+2})\frac{1}{[\mathrm{H}^+]^j}}{\sum\limits_{j=0}^{n}\Pi_j\frac{1}{[\mathrm{H}^+]^j}}
\end{aligned}$$

We may therefore conclude that if $K_j < \frac{K_1}{j}$, for $j = 2, \ldots, n$,

1. $\Delta_1 > 0$ for any positive value of $[\mathrm{H}^+]$;
2. $\Delta_1 = O(\frac{1}{[\mathrm{H}^+]^2})$ as $[\mathrm{H}^+] \to +\infty$, and thus $\lim_{[\mathrm{H}^+]\to+\infty}\Delta_1 = 0$.

Using the same reasoning as above, we finally find that

$$\mathrm{Alk_A}([\mathrm{H}^+]) = \mathrm{Alk_{Ainf}} + [\Sigma\mathrm{A}]\frac{D_1}{D} = \mathrm{Alk_{Ainf}} + [\Sigma\mathrm{A}](a_1([\mathrm{H}^+]) - \Delta_1)$$

which allows us to conclude:

$$\mathrm{Alk_A}([\mathrm{H}^+]) < \mathrm{Alk_{Ainf}} + [\Sigma\mathrm{A}]\; a_1([\mathrm{H}^+]).$$

which establishes the asymptotic role of $[\Sigma\mathrm{A}]\frac{K_1}{[\mathrm{H}^+]}$ for $\mathrm{Alk_A}([\mathrm{H}^+])$ as $[\mathrm{H}^+] \to +\infty$.

The summation over all the non-water related acid-base system contributions then leads to

$$\mathrm{Alk_{nW}}([\mathrm{H}^+]) < \mathrm{Alk_{nWinf}} + \frac{\sum_i[\Sigma\mathrm{A}_{[i]}]K_{1,[i]}}{[\mathrm{H}^+]}, \tag{1}$$

providing a stronger upper limit on $\mathrm{Alk_{nW}}([\mathrm{H}^+])$ than $\mathrm{Alk_{nWsup}}$ when $[\mathrm{H}^+]$ is sufficiently large, i. e., when

$$[\mathrm{H}^+] > \frac{\sum_i[\Sigma\mathrm{A}_{[i]}]K_{1,[i]}}{\mathrm{Alk_{nWsup}} - \mathrm{Alk_{nWinf}}}.$$

This could also possibly be used to determine a tighter upper bound for the root of the original SOLVESAPHE, but it is not clear whether the calculation of that tighter upper bound would actually be compensated by a reduced number of iterations.

1.3 Another (slightly less) practical asymptote: a_2

For a_2 to be an asymptote, it will be shown below that it is sufficient that the successive dissociation constants of H_nA fulfil a condition on their magnitude, which is nevertheless generally fulfilled. Similarly to above, we need to analyse the distance between $\frac{D_1}{D}$ and a_2

$$\Delta_2 = \frac{\Pi_1}{[\mathrm{H}^+]} + \frac{2\Pi_2}{[\mathrm{H}^+]^2} - \frac{D_1}{D} = \frac{\left(\frac{\Pi_1}{[\mathrm{H}^+]} + \frac{2\Pi_2}{[\mathrm{H}^+]^2}\right) D - D_1}{D}$$

Developments are analogue to the previous case, and we therefore only report the final result here

$$\begin{aligned}
&\left(\frac{\Pi_1}{[\mathrm{H}^+]} + \frac{2\Pi_2}{[\mathrm{H}^+]^2}\right) D - D_1 \\
&\quad = \frac{\Pi_1}{[\mathrm{H}^+]} \sum_{j=0}^{n} \Pi_j [\mathrm{H}^+]^{n-j} + \frac{2\Pi_2}{[\mathrm{H}^+]^2} \sum_{j=0}^{n} \Pi_j [\mathrm{H}^+]^{n-j} - \sum_{j=1}^{n} j\Pi_j [\mathrm{H}^+]^{n-j} \\
&\quad = \frac{2\Pi_2\Pi_{n-1}}{[\mathrm{H}^+]} + \frac{2\Pi_2\Pi_n}{[\mathrm{H}^+]^2} + \frac{\Pi_1\Pi_n}{[\mathrm{H}^+]} + \frac{1}{[\mathrm{H}^+]^2} \sum_{j=0}^{n-2} \Pi_{j+1}(K_1 + \frac{2\Pi_2}{K_{j+1}} - (j+2)K_{j+2})[\mathrm{H}^+]^{n-j}
\end{aligned}$$

Again, the condition that $K_j < \frac{K_1}{j}$ for $j = 2, \ldots, n$ is sufficient to guarantee that $\Delta_2 > 0$ for all $[\mathrm{H}^+] > 0$. Finally,

$$\begin{aligned}
\Delta_2 &= \frac{\left(\frac{\Pi_1}{[\mathrm{H}^+]} + \frac{2\Pi_2}{[\mathrm{H}^+]^2}\right) D - D_1}{D} \\
&= \frac{1}{[\mathrm{H}^+]^2} \frac{\frac{2\Pi_2\Pi_{n-1} + \Pi_1\Pi_n}{[\mathrm{H}^+]^{n-1}} + \frac{2\Pi_2\Pi_n}{[\mathrm{H}^+]^n} + \sum_{j=0}^{n-2} \Pi_{j+1}(K_1 + \frac{2\Pi_2}{K_{j+1}} - (j+2)K_{j+2})\frac{1}{[\mathrm{H}^+]^j}}{\sum_{j=0}^{n} \Pi_j \frac{1}{[\mathrm{H}^+]^j}}.
\end{aligned}$$

In conclusion, if $K_j < \frac{K_1}{j}$, for $j = 2, \ldots, n$,

1. $\Delta_2 > 0$ for any positive value of $[\mathrm{H}^+]$;
2. $\Delta_2 = O(\frac{1}{[\mathrm{H}^+]^2})$ as $[\mathrm{H}^+] \to +\infty$, and thus $\lim_{[\mathrm{H}^+] \to +\infty} \Delta_2 = 0$.

and

$$\mathrm{Alk_A}([\mathrm{H}^+]) < \mathrm{Alk_{Ainf}} + [\Sigma\mathrm{A}]\, a_2([\mathrm{H}^+]).$$

$[\Sigma\mathrm{A}](\frac{K_1}{[\mathrm{H}^+]} + \frac{2K_1K_2}{[\mathrm{H}^+]^2})$ is thus an asymptote for $\mathrm{Alk_A}([\mathrm{H}^+])$ as $[\mathrm{H}^+] \to +\infty$.

2 Second derivative of the alkalinity fraction

From Munhoven (2013), we know that

$$\mathrm{Alk_A} = [\Sigma\mathrm{A}]\left(\frac{D_1}{D} - m\right),$$

with

$$D = \sum_{j=0}^{n} \Pi_j H^{n-j} \quad \text{and} \quad D_1 = \sum_{j=0}^{n} j\Pi_j H^{n-j}.$$

More generally, we define

$$D_k = \sum_{j=0}^{n} j^k \Pi_j H^{n-j}.$$

It is straightforward to show that

$$\frac{dD}{dH} = \frac{1}{H}(nD - D_1) \quad \text{and} \quad \frac{dD_k}{dH} = \frac{1}{H}(nD_k - D_{k+1}), \text{ for } k \geq 1.$$

Munhoven (2013) has shown that

$$\frac{d}{dH}\left(\frac{D_1}{D}\right) = -\frac{1}{H}\frac{DD_2 - D_1^2}{D^2}$$

and that this derivative is strictly negative for $H > 0$. Here, we analyse the second derivative of $\frac{D_1}{D}$. To start, we notice that

$$\frac{d^2}{dH^2}\left(\frac{D_1}{D}\right) = \frac{1}{H^2D^2}(DD_2 - D_1^2) - \frac{1}{HD^2}\frac{d}{dH}(DD_2 - D_1^2) + \frac{2}{HD^3}(DD_2 - D_1^2)\frac{dD}{dH}.$$

The first term at the right-hand side will in a first stage be left as is. The second one is developed as

$$\begin{aligned}
-\frac{1}{HD^2}\frac{d}{dH}(DD_2 - D_1^2) &= -\frac{1}{HD^2}\left(\frac{dD}{dH}D_2 + D\frac{dD_2}{dH} - 2D_1\frac{dD_1}{dH}\right) \\
&= -\frac{1}{H^2D^2}\Big(2n(DD_2 - D_1^2) + D_1D_2 - DD_3\Big)
\end{aligned}$$

Similarly, the third term becomes

$$\begin{aligned}
\frac{2}{HD^3}(DD_2 - D_1^2)\frac{dD}{dH} &= \frac{2}{H^2D^3}(DD_2 - D_1^2)(nD - D_1) \\
&= \frac{1}{H^2D^3}(2nD(DD_2 - D_1^2) - 2D_1(DD_2 - D_1^2)
\end{aligned}$$

Hence

$$\begin{aligned}
\frac{d^2}{dH^2}\left(\frac{D_1}{D}\right) &= \frac{1}{H^2D^3}\Big(D(DD_2 - D_1^2) - D(D_1D_2 - DD_3) - 2D_1(DD_2 - D_1^2)\Big) \\
&= \frac{1}{H^2D^3}\Big((D - 2D_1)(DD_2 - D_1^2) - D(D_1D_2 - DD_3)\Big). \qquad (2)
\end{aligned}$$

We know that (Munhoven, 2013)

$$\begin{aligned}
DD_2 - D_1^2 &= \left(\sum_{i=0}^{n}\Pi_i H^{n-i}\right)\left(\sum_{j=0}^{n} j^2\Pi_j H^{n-j}\right) - \left(\sum_{k=0}^{n} k\Pi_k H^{n-k}\right)^2 \\
&= \tfrac{1}{2}\sum_{i=0}^{n}\sum_{j=0}^{n}(i-j)^2\Pi_i\Pi_j H^{2n-i-j}.
\end{aligned}$$

according to Lagrange's identity, which helped to establish that $DD_2 - D_1^2 > 0$. A similar formula can be developed for $D_1D_2 - DD_3$. We have

$$\begin{aligned}
D_1D_2 - DD_3 &= \left(\sum_{i=0}^{n} i\Pi_i H^{n-i}\right)\left(\sum_{j=0}^{n} j^2\Pi_j H^{n-j}\right) - \left(\sum_{i=0}^{n}\Pi_i H^{n-i}\right)\left(\sum_{i=0}^{n} j^3\Pi_j H^{n-j}\right) \\
&= \sum_{i=0}^{n}\sum_{j=0}^{n}(ij^2 - j^3)\Pi_i\Pi_j H^{2n-i-j} \\
&= \sum_{i=0}^{n}\sum_{j=0}^{n} j^2(i-j)\Pi_i\Pi_j H^{2n-i-j}.
\end{aligned}$$

By respective permutations of i and j in the two terms, we get the following four expressions for $D_1D_2 - DD_3$:

$$D_1D_2 - DD_3 = \sum_{i=0}^{n}\sum_{j=0}^{n} j^2(i-j)\Pi_i\Pi_j H^{2n-i-j}$$
$$D_1D_2 - DD_3 = \sum_{i=0}^{n}\sum_{j=0}^{n} j(i^2-j^2)\Pi_i\Pi_j H^{2n-i-j}$$
$$D_1D_2 - DD_3 = \sum_{i=0}^{n}\sum_{j=0}^{n} i^2(j-i)\Pi_i\Pi_j H^{2n-i-j}$$
$$D_1D_2 - DD_3 = \sum_{i=0}^{n}\sum_{j=0}^{n} i(j^2-i^2)\Pi_i\Pi_j H^{2n-i-j}$$

By taking the average of the four expressions, one gets an expression for $D_1D_2 - DD_3$ that is symmetric in i and j. The resulting multiplier of $\Pi_i\Pi_j H^{2n-i-j}$ then becomes

$$\begin{aligned}&\tfrac{1}{4}(j^2(i-j) + j(i^2-j^2) + i^2(j-i) + i(j^2-i^2))\\&= -\tfrac{1}{2}(i-j)^2(i+j).\end{aligned}$$

so that
$$D_1D_2 - DD_3 = -\frac{1}{2}\sum_{i=0}^{n}\sum_{j=0}^{n}(i-j)^2(i+j)\Pi_i\Pi_j H^{2n-i-j}.$$

Accordingly,

$$\begin{aligned}&(D-2D_1)(DD_2 - D_1^2) - D(D_1D_2 - DD_3)\\&= \frac{1}{2}\left(\sum_{k=0}^{n}(1-2k)\Pi_k H^{n-k}\right)\left(\sum_{i=0}^{n}\sum_{j=0}^{n}(i-j)^2\Pi_i\Pi_j H^{2n-i-j}\right)\\&\quad+\frac{1}{2}\left(\sum_{k=0}^{n}\Pi_k H^{n-k}\right)\left(\sum_{i=0}^{n}\sum_{j=0}^{n}(i-j)^2(i+j)\Pi_i\Pi_j H^{2n-i-j}\right)\\&= \frac{1}{2}\left(\sum_{i=0}^{n}\sum_{j=0}^{n}\sum_{k=0}^{n}(i-j)^2(i+j-2k+1)\Pi_i\Pi_j\Pi_k H^{3n-i-j-k}\right).\end{aligned}$$

The previous expression is symmetric in i and j: the summands are identical for i and j permuted. It is therefore sufficient to consider the terms for $i < j$ and drop the $\frac{1}{2}$. Since the terms for $i = j$ are furthermore equal to 0, we may write that

$$\begin{aligned}&(D-2D_1)(DD_2 - D_1^2) - D(D_1D_2 - DD_3)\\&= \sum_{i=0}^{n-1}\sum_{j=i+1}^{n}\sum_{k=0}^{n}(i-j)^2(i+j-2k+1)\Pi_i\Pi_j\Pi_k H^{3n-i-j-k}.\end{aligned} \tag{3}$$

Whereas $\frac{d}{dH}(\frac{D_1}{D}) > 0$ for any set of positive Π_i ($i = 1, \ldots, n$) — see Munhoven (2013, Appendix A) — it is not possible to draw a similarly clear conclusion for $\frac{d^2}{dH^2}(\frac{D_1}{D})$. However, it is possible to derive sufficient conditions, which are fulfilled for naturally occurring acid-base base systems, such that
$$\frac{d^2}{dH^2}(\frac{D_1}{D}) > 0.$$

The program `sdt_iconstraints.f90` can be used to characterise the individual terms of the series above for a given n, and for all i, j and k.

2.1 Signs of the aggregated terms of the sum

The actual coefficients for a given H^m in the sum in eq. (3) generally result from several terms, obtained by sets of (i, j, k) triplets, such that $i + j + k = 3n - m$. There are subsets in these sets that are obtained by permutations of the three indices. We first deal with these latter.

We consider a $\Pi_a \Pi_b \Pi_c$ product, where a, b and c are ordered such that $a \leq b \leq c$. There are actually only three cases to consider since i, j and k are such that

- $0 \leq i \leq n - 1$
- $i + 1 \leq j \leq n$
- $0 \leq k \leq n$

We therefore know that it is not possible to have $a = b = c$ and the only cases to distinguish are

1. $a = b < c$
2. $a < b = c$
3. $a < b < c$

The coefficient h_m of a H^m in the sum is obtained from

$$h_m = \sum_{a+b+c=3n-m} f_{abc} \Pi_a \Pi_b \Pi_c$$

where $a \leq b \leq c$ and $a < c$.

2.1.1 Case $a = b < c$

Since $i < j$, there is only one (i, j, k) triplet that is compatible with this case: $i = a$, $j = c$ and $k = b = a$. The corresponding term in the sum is thus

$$(i - j)^2 (i + j - 2k + 1) \Pi_i \Pi_j \Pi_k H^{3n-i-j-k}$$

and it is the coefficient of $\Pi_i \Pi_j \Pi_k$ that sets the sign of the term. In this given case, the coefficient of $\Pi_a \Pi_b \Pi_c$ simplifies to

$$(c - b)^2 (b + c - 2b + 1) = (c - b)^2 (c - b + 1)$$

or, by introducing $\delta_b = c - b$,

$$f_{abc} = \delta_b^2 (\delta_b + 1) \tag{4}$$

which is always strictly positive.

2.1.2 Case $a < b = c$

Similarly to the first case, there is only one (i, j, k) triplet that is compatible with this case: $i = a$, $j = b = c$ and $k = c = b$. The coefficient of $\Pi_a \Pi_b \Pi_c$ simplifies to

$$(b - a)^2 (a + b - 2b + 1) = -(b - a)^2 (b - a - 1)$$

which can be rewritten as

$$f_{abc} = -\delta_a^2 (\delta_a - 1) \tag{5}$$

by introducing $\delta_a = b - a$. f_{abc} is

- equal to 0 if $\delta_a = 1$;
- strictly negative if $\delta_a > 1$.

2.1.3 Case $a < b < c$

Since $i < j$, there are three (i, j, k) triplets that contribute to the term in $\Pi_a \Pi_b \Pi_c H^{3n-a-b-c}$:

- $(i, j, k) = (a, b, c)$
- $(i, j, k) = (b, c, a)$
- $(i, j, k) = (a, c, b)$

The sum of factors in these three terms is

$$\begin{aligned} f_{abc} &= (a-b)^2(a+b-2c+1) + (b-c)^2(b+c-2a+1) + (a-c)^2(a+c-2b+1) \\ &= (b-a)^2(a+b-2c+1) + (c-b)^2(b+c-2a+1) \\ &\quad + \big((c-b)+(b-a)\big)^2(a+c-2b+1) \end{aligned}$$

Using the same $\delta_a = b - a$ and $\delta_b = c - b$ as already introduced above and furthermore noticing that $c - a = \delta_a + \delta_b$, we get

$$\begin{aligned} f_{abc} &= (a-b)^2(a+b-2c+1) + (b-c)^2(b+c-2a+1) + (a-c)^2(a+c-2b+1) \\ &= -2\delta_a^3 - (3\delta_b - 2)\delta_a^2 + \delta_b(3\delta_b + 2)\delta_a + 2\delta_b^2(\delta_b + 1). \end{aligned}$$

The sign of f_{abc} as a function of δ_a and δ_b is difficult to predict from this expression. That information can nevertheless be derived by expressing it in terms of δ_b and $x = \delta_a/\delta_b$ instead. With $\delta_a = x\delta_b$, the previous expression becomes

$$\begin{aligned} f_{abc}(x) &= -2\delta_a^3 - (3\delta_b - 2)\delta_a^2 + \delta_b(3\delta_b + 2)\delta_a + 2\delta_b^2(\delta_b + 1) \\ &= -2\delta_b^3 x^3 - (3\delta_b - 2)\delta_b^2 x^2 + \delta_b^2(3\delta_b + 2)x + 2\delta_b^2(\delta_b + 1) \\ &= -\delta_b^2\big(2\delta_b x^3 + (3\delta_b - 2)x^2 - (3\delta_b + 2)x - 2(\delta_b + 1)\big). \end{aligned}$$

Since and $\delta_b \geq 1$ (and $\delta_a \geq 1$ as well), we may conclude that

$$\begin{aligned} f_{abc}(0) &= 2\delta_b^2(\delta_b + 1) > 0 \\ f_{abc}(1) &= 6\delta_b^2 > 0 \\ f_{abc}(2) &= -\delta_b^2(20\delta_b - 14) < 0 \end{aligned}$$

The derivative of f is

$$f'_{abc}(x) = -\delta_b^2\big(6\delta_b x^2 + 2(3\delta_b - 2)x - (3\delta_b + 2)\big)$$

$$\begin{aligned} f'_{abc}(0) &= \delta_b^2(3\delta_b + 2) > 0 \\ f'_{abc}(1) &= -\delta_b^2(9\delta_b - 6) < 0 \end{aligned}$$

The equation $f'_{abc}(x) = 0$ always has one strictly positive and one strictly negative solution, since the constant term is strictly negative. The reduced discriminant of this equation is

$$\begin{aligned} \Delta' &= (3\delta_b - 2)^2 + 6\delta_b(3\delta_b + 2) \\ &= 9\delta_b^2 - 12\delta_b + 4 + 18\delta_b^2 + 12\delta_b \\ &= 27\delta_b^2 + 4 > 0. \end{aligned}$$

The positive root, where f has a local maximum, is at

$$x'_0 = \frac{-3\delta_b + 2 + \sqrt{\Delta'}}{6\delta_b} = \frac{3\delta_b + 2}{(3\delta_b - 2) + \sqrt{\Delta'}} > 0$$

It is straightforward to show that $0 < x'_0 < 1$, for any $\delta_b \geq 1$. Hence

- $f'_{abc}(x) < 0$ for $x > x'_0$ and $f'(x) > 0$ for $0 < x < x'_0$;
- $f_{abc}(x)$ is strictly decreasing for $x > x'_0$;
- $f_{abc}(x)$ is strictly increasing for $0 < x < x'_0$
- $f_{abc}(x) = 0$ has exactly one root x_0 that is greater then x'_0;
- x_0 is bracketed by $1 < x_0 < 2$.

Accordingly

- $f_{abc}(x) > 0$ for $0 < x < x_0$
- $f_{abc}(x) < 0$ for $x > x_0$

and thus for any given $a < b < c$, we may calculate $x_0 = x_0(\delta_b)$ and depending on $x = \delta_a/\delta_b$ decide whether the corresponding term $f_{abc}\Pi_a\Pi_b\Pi_c H^{3n-a-b-c}$ which includes the contribution of all possible permutations of a, b and c represents a net positive or a net negative contribution to the sum.

2.1.4 Lemma

For $a < b < c$, we have

$$f_{abc} = -2\delta_a^3 - (3\delta_b - 2)\delta_a^2 + \delta_b(3\delta_b + 2)\delta_a + 2\delta_b^2(\delta_b + 1)$$

If $b + 1 \neq c$

$$f_{a-1,b+1,c} = -2(\delta_\alpha)^3 - (3\delta_\beta - 2)(\delta_\alpha)^2 + \delta_\beta(3\delta_\beta + 2)\delta_\alpha + 2(\delta_\beta)^2(\delta_\beta + 1)$$

with $\delta_\alpha = (b+1) - (a-1) = \delta_a + 2$ and $\delta_\beta = c - (b+1) = \delta_b - 1$. Hence, if $b \neq c$ we get

$$\begin{aligned} f_{a-1,b+1,c} &= -2(\delta_a + 2)^3 - (3(\delta_b - 1) - 2)(\delta_a + 2)^2 \\ &\quad + (\delta_b - 1)(3(\delta_b - 1) + 2)(\delta_a + 2) + 2(\delta_b - 1)^2\delta_b \\ &= f_{abc} - 3(\delta_a + 1)(6\delta_b + 3\delta_a - 2) \end{aligned}$$

Hence, $f_{a-1,b+1,c} < f_{abc}$ and if δ_a and δ_b are sufficiently large, $f_{a-1,b+1,c}$ becomes negative.

If $b + 1 = c$, then

$$f_{a-1,b+1,c} = (\delta_a + 2)^2(1 - (\delta_a + 2)) = -(\delta_a + 1)(\delta_a + 2)^2$$

This means, however, that $\delta_b = 1$, and so

$$f_{abc} = -2\delta_a^3 - \delta_a^2 + 5\delta_a + 4 = -(\delta_a + 1)(2\delta_a^2 - \delta_a - 4)$$

Hence,

$$\begin{aligned} f_{a-1,b+1,c} - f_{abc} &= f_{a-1,c,c} - f_{a,c-1,c} \\ &= (\delta_a + 1)(\delta_a - \frac{5 - \sqrt{57}}{2})(\delta_a - \frac{5 + \sqrt{57}}{2}) \\ &\simeq (\delta_a + 1)(\delta_a + 1.2749)(\delta_a - 6.2749) \end{aligned}$$

For a given exponent m, we may fix c such that $c > 0$, $c \leq n$ and $c < 3n - m - 1$. As a result, $a + b = 3n - m - c$. The maximum and minimum values of a and b respectively depend on whether $3n - m - c$ is even or odd:

- if $3n - m - c$ is even, the maximum of a is $(3n - m - c)/2$ and the minimum value of b is the same. Accordingly, we have $a = b < c$ in this case and $f_{abc} > 0$.

- if $3n-m-c$ is odd, the maximum of a is $(3n-m-c-1)/2$ and the minimum of b is $(3n-m-c+1)/2$. Hence, $\delta_a = 1$. If $b = c$, then $f_{abc} = 0$; if $b < c$, then $f_{abc} = \delta_b(2\delta_b + 5\delta_b - 1) > 0$ because $\delta_b \geq 1$ in this case.

If we order the terms of the subseries $\sum_{a+b=3n-m-c} f_{abc}\Pi_a\Pi_b\Pi_c$ by decreasing a values, the leading term is thus always strictly positive, which allows us to derive sufficient conditions to ensure that $f_{abc}\Pi_a\Pi_b\Pi_c + f_{a-1,b+1,c}\Pi_{a-1}\Pi_{b+1}\Pi_c > 0$, even if $f_{a-1,b+1,c} < 0$. We may indeed write that

$$\begin{aligned}
f_{abc}\Pi_a\Pi_b\Pi_c + f_{a-1,b+1,c}\Pi_{a-1}\Pi_{b+1}\Pi_c &= \Pi_{a-1}\Pi_b\Pi_c(f_{abc}\Pi_a/\Pi_{a-1} + f_{a-1,b+1,c}\Pi_{b+1}/\Pi_b) \\
&= \Pi_{a-1}\Pi_b\Pi_c(f_{abc}K_a + f_{a-1,b+1,c}K_{b+1})
\end{aligned}$$

Hence, if $K_a > (-f_{a-1,b+1,c}/f_{abc})K_{b+1}$ the sum of these two terms, which contribute to the same H^m is positive.

2.1.5 Sufficient conditions

For $a = 1, \ldots, n-1$, the coefficient for $H^{3n-3a-1}$ includes a subset for $c = a-1$ that reads

$$f_{a,a,a+1}\Pi_a\Pi_a\Pi_{a+1} + f_{a-1,a+1,a+1}\Pi_{a-1}\Pi_{a+1}\Pi_{a+1}$$

Both f factors are special cases:

- $f_{a,a,a+1}$ has $\delta_b = 1$ and $f_{a,a,a+1} = 2$
- $f_{a-1,a+1,a+1}$ has $\delta_a = 2$ and $f_{a-1,a+1,a+1} = -4\Pi_{a+1}$

Hence

$$\begin{aligned}
&f_{a,a,a+1}\Pi_a\Pi_a\Pi_{a+1} + f_{a-1,a+1,a+1}\Pi_{a-1}\Pi_{a+1}\Pi_{a+1} \\
&= 2\Pi_a\Pi_a\Pi_{a+1} - 4\Pi_{a-1}\Pi_{a+1}\Pi_{a+1} \\
&= 2\Pi_{a-1}\Pi_a\Pi_{a+1}(\frac{\Pi_a}{\Pi_{a-1}} - 2\frac{\Pi_{a+1}}{\Pi_a}) \\
&= 2\Pi_{a-1}\Pi_a\Pi_{a+1}(K_a - 2K_{a+1})
\end{aligned}$$

A first condition to check would thus be

$$K_{a+1} < \frac{K_a}{2}, \text{ for } a = 1, \ldots, n-1$$

2.2 Chain structure

As mentioned before, the coefficient of the H^m in the sum at the numerator of $\frac{d^2}{dH^2}\frac{D_1}{D}$ is obtained by $\sum_{a,b,c} f_{abc}\Pi_a\Pi_b\Pi_c$, where $a+b+c = 3n-m$, $0 \leq a \leq b \leq c$, but $a \neq c$.

To show that the test condition mentioned above is sufficient to guarantee that $\frac{d^2}{dH^2}\frac{D_1}{D} > 0$, we analyse the H^m terms individually, and in the calculation of the coefficient d_m of H_m, the various sub-sums for each possible c:

$$h_m = \sum_c h_{m,c}$$

and

$$h_{m,c} = \sum_{a,b} f_{abc}\Pi_a\Pi_b\Pi_c$$

with $a+b = 3n-m-c$, and, as above $0 \leq a \leq b \leq c$ but $a \neq c$. The (a,b,c) triplets of this sum can be ordered by increasing b (and thus decreasing a, since $a+b = 3n-m-c$ is constant for given m and c. There are thus several types of chains of (a,b,c) triplets terms contributing to $d_{m,c}$ that may arise. There are two types of starting values for these chains:

- (b,b,c), with $0 \leq b < c$

- $(b-1, b, c)$, with $0 < b \leq c$.

As before, we denote $\delta_b = c - b$. However, we consider in this section that δ_b is a characteristic of the chain. The corresponding chains then respectively start as follows

$$(b, b, c),\ (b-1, b+1, c), \ldots,\ (b-j, b+j, c), \ldots \tag{6}$$

$$(b-1, b, c),\ (b-2, b+1, c), \ldots,\ (b-1-j, b+j, c), \ldots \tag{7}$$

We consider the two cases separately. It has been shown before that

$$f_{\alpha,\beta,c} = -2\delta_\alpha^3 - (3\delta_\beta - 2)\delta_\alpha^2 + \delta_\beta(3\delta_\beta + 2)\delta_\alpha + 2\delta_\beta^2(\delta_\beta + 1) \tag{8}$$

for $0 \leq \alpha < \beta < c$ and where $\delta_\alpha = \beta - \alpha$ and $\delta_\beta = c - \beta$. In addition, if $0 \leq \alpha - 1 < \beta + 1 < c$ then

$$f_{\alpha-1,\beta+1,c} = f_{\alpha,\beta,c} - 3(\delta_\alpha + 1)(6\delta_\beta + 3\delta_\alpha - 2). \tag{9}$$

2.2.1 (*b*,*b*,*c*) chains

This triplet always leads to the initial term $f_{bbc}\Pi_b^2\Pi_c$ with $f_{bbc} = \delta_b^2(\delta_b + 1)$, independent of the actual values of b and c. There are a few trivial cases that can be considered.

1. If $b = 0$, i. e., $\delta_b = c$, the chain reduces to the single element $(0, 0, c)$. This element can only be part of $h_{m,c}$ for which $c = 3n - m$ and this $d_{m,c}$ reduces to a single term: $d_{m,c} = f_{00c}\Pi_0^2\Pi_c = \delta_b^2(\delta_b + 1)$, which is always strictly positive.
2. If $\delta_b = 1$, the chain has two elements $(c-1, c-1, c)$ and $(c-2, c, c)$ and

$$h_{m,c} = f_{c-1,c-1,c}\Pi_{c-1}^2\Pi_c + f_{c-2,c,c}\Pi_{c-2}\Pi_c^2 = 2\Pi_{c-1}^2\Pi_c - 4\Pi_{c-2}\Pi_c^2$$

In the following, we thus suppose that $b > 0$ and $\delta_b > 1$
We already have

$$f_{bbc} = \delta_b^2(\delta_b + 1)$$

For stage $j > 0$, where we need to calculate $f_{b-j,b+j,c}$, we may use eq. (8) with $\delta_\beta = c - (b+j) = \delta_b - j$ and $\delta_\alpha = 2j$:

$$\begin{aligned}
f_{b-j,b+j,c} &= -2(2j)^3 - (3(\delta_b - j) - 2)(2j)^2 \\
&\quad + (\delta_b - j)(3(\delta_b - j) + 2)2j \\
&\quad + 2(\delta_b - j)^2((\delta_b - j) + 1) \\
&= -16j^3 - (12\delta_b - 12j - 8)j^2 + (\delta_b - j)(6\delta_b - 6j + 4)j \\
&\quad + (\delta_b^2 - 2j\delta_b + j^2)(2\delta_b - 2j + 2) \\
&= -16j^3 - 12j^2\delta_b + 12j^3 + 8j^2 + 6j\delta_b^2 - 6j^2\delta_b + 4j\delta_b - 6j^2\delta_b + 6j^3 - 4j^2 \\
&\quad + 2\delta_b^3 - 2j\delta_b^2 + 2\delta_b^2 - 4j\delta_b^2 + 4j^2\delta_b - 4j\delta_b + 2j^2\delta_b - 2j^3 + 2j^2 \\
&= (-18\delta_b + 6)j^2 + 2\delta_b^3 + 2\delta_b^2 \\
&= -6j^2(3\delta_b - 1) + 2\delta_b^2(\delta_b + 1) \\
&= 2f_{bbc} - 6j^2(3\delta_b - 1)
\end{aligned}$$

The difference between the two first elements is

$$\begin{aligned}
f_{b-1,b+1,c} - f_{bbc} &= f_{bbc} - 6(3\delta_b - 1) \\
&= \delta_b^3 + \delta_b^2 - 18\delta_b + 6
\end{aligned}$$

This difference is negative for $\delta_b < 4$ and positive for $\delta_b \geq 4$. The difference between successive elements $j-1$ and j ($j > 1$) can be calculated from eq. (9) with $\delta_\alpha = 2(j-1)$ and $\delta_\beta = c - (b + (j-1)) = \delta_b - j + 1$:

$$\begin{aligned} f_{b-j,b+j,c} - f_{b-(j-1),b+(j-1),c} &= -3(2(j-1)+1)(6(\delta_b - j + 1) + 3 \cdot 2(j-1) - 2) \\ &= -6(2j-1)(3\delta_b - 1) \end{aligned}$$

The difference between consecutive members is thus always negative, and increasing in absolute value with j.

This recursion on j is valid as long as $j \leq b$ and $j < \delta_b$. The end of the chain thus depends on how b and δ_b compare.

- If $b < \delta_b$, $b - j$ reduces to 0 before $b + j$ increases to c. The recursion thus remains valid for all $1 \leq j \leq b$.
- If $b >= \delta_b$, the last term in the chain is $f_{b-\delta_b,c,c}$ for which (8) is not applicable and eq. (5) must be used instead

  $$f_{b-\delta_b,c,c} = -(c - (b - \delta_b))^2(c - (b - \delta_b) - 1) = -4\delta_b^2(2\delta_b - 1).$$

  The second but last member of the chain is obtained for $j = \delta_b - 1$. Accordingly,

  $$\begin{aligned} & f_{b-\delta_b,c,c} - f_{b-\delta_b+1,c-1,c} \\ &= -4\delta_b^2(2\delta_b - 1) - 2\delta_b^2(\delta_b + 1) + 6(\delta_b - 1)^2(3\delta_b - 1) \\ &= -6(2\delta_b - 1)(3\delta_b - 1) + 4\delta_b^2(2\delta_b - 1) \end{aligned}$$

  The difference between the last two elements in the chain is thus greater than the regular difference, which would be $-6(2\delta_b - 1)(3\delta_b - 1)$ for $j = \delta_b$. The nominal difference is augmented by the absolute value of the last element in the chain.

2.2.2 (*b-1,b,c*) chains

There are three trivial cases to consider for $(b-1, b, c)$ chains.

1. If $b = c$, the chain reduces to the single element $(c-1, c, c)$, with $f_{c-1,c,c} = 0$.
2. if $b = 1$, the chain reduces to the single element $(0, 1, c)$. For this element, $\delta_a = 1$ and $\delta_b = c - 1$.

   $$f_{0,1,c} = \delta_b(2\delta_b^2 + 5\delta_b - 1).$$

   If furthermore $c = 1$, this becomes a special case of the previous one. Since $c > 1$ we know that $f_{0,1,c} > 0$.
3. With $b = 2$ and $c = 3$, the chain has only two elements: $(1, 2, 3)$ and $(0, 3, 3)$, with $f_{1,2,3} = 6$ and $f_{0,3,3} = -18$.

In the following we assume that $1 < b < c$. As before, we have

$$f_{b-1,b,c} = \delta_b(2\delta_b^2 + 5\delta_b - 1).$$

The recurrence (8) is applicable right from the beginning. To calculate element j, i. e., $f_{b-1-j,b+j,c}$ we use (8) with $\delta_\alpha = 2j + 1$ and $\delta_\beta = \delta_b - j$:

$$\begin{aligned} f_{b-1-j,b+j,c} &= -2(2j+1)^3 - (3(\delta_b - j) - 2)(2j+1)^2 \\ &\quad + (\delta_b - j)(3(\delta_b - j) + 2)(2j+1) + 2(\delta_b - j)^2((\delta_b - j) + 1) \\ &= \delta_b(2\delta_b^2 + 5\delta_b - 1) - 3j(j+1)(6\delta_b + 1) \end{aligned}$$

The difference between successive elements $j-1$ and j ($j > 0$) can be calculated from eq. (9) with $\delta_\alpha = 2j-1$ and $\delta_\beta = \delta_b - j + 1$:

$$\begin{aligned} f_{b-1-j,b+j,c} - f_{b-1-(j-1),b+(j-1),c} &= -3 \cdot 2j \cdot (6(\delta_b - j + 1) + 3(2j-1) - 2) \\ &= -3 \cdot 2j \cdot (6\delta_b + 1) \end{aligned}$$

The difference between consecutive members is thus always negative, and increasing with j in absolute value.

The previous recursions are valid for j as long as $j \leq b-1$ and $j < \delta_b$. The end of the chain thus depends again on how b and δ_b compare.

- If $b-1 < \delta_b$, $b-1-j$ reduces to 0 before $b+j$ increases to c. The recursion thus remains valid for all $1 \leq j \leq b-1$.
- If $b \geq \delta_b + 1$, the last term in the chain is $f_{b-1-\delta_b,c,c}$ for which (8) is not applicable and eq. (5) must be used instead:

  $$\begin{aligned} f_{b-1-\delta_b,c,c} &= -(c-(b-1-\delta_b))^2(c-(b-1-\delta_b)-1) \\ &= -2\delta_b(2\delta_b+1)^2 \end{aligned}$$

  The second but last member of the chain is $f_{b-\delta_b,c-1,c}$, obtained for $j = \delta_b - 1$. Accordingly,

  $$\begin{aligned} &f_{b-\delta_b,c-1,c} - f_{b-1-\delta_b,c,c} \\ &= -2\delta_b(2\delta_b+1)^2 - \delta_b(2\delta_b^2 + 5\delta_b - 1) + 3(\delta_b - 1)\delta_b(6\delta_b + 1) \\ &= -6\delta_b \cdot (6\delta_b + 1) + 2\delta_b(2\delta_b + 1)^2 \end{aligned}$$

  The difference between the last two elements in the chain is again greater than the regular difference, which would be $-6\delta_b \cdot (6\delta_b + 1)$ for $j = \delta_b$. As for the (b, b, c) chain, the last difference is augmented by the absolute value of the last element.

2.2.3 Successive terms and how their sums compare

We analyse the comparative magnitudes of successive terms of the series that define the coefficients of the different coefficients of the polynomial at the numerator of $\frac{d^2}{dH^2}(\frac{D_1}{D})$ under the assumption that $K_{j+1} < \frac{1}{2}K_j$ (and equivalently, $K_j > 2K_{j+1}$), for $j = 1, \ldots, n-1$. This c

In **(*b,b,c*) chains**, successive elements j and $j+1$ write

$$f_{b-j,b+j,c}\Pi_{b-j}\Pi_{b+j}\Pi_c \text{ and } f_{b-j-1,b+j+1,c}\Pi_{b-j-1}\Pi_{b+j+1}\Pi_c.$$

To analyse how the sum of two such element compares with one of the two terms under the assumption of $K_{j+1} < \frac{1}{2}K_j$, we first determine q such that

$$\Pi_{b-j}\Pi_{b+j} - q\Pi_{b-j-1}\Pi_{b+j+1} > 0$$

We successively have

$$\begin{aligned} &\Pi_{b-j}\Pi_{b+j} - q\Pi_{b-j-1}\Pi_{b+j+1} \\ &= \Pi_{b-j-1}\Pi_{b+j}\left(\frac{\Pi_{b-j}}{\Pi_{b-j-1}} - q\frac{\Pi_{b+j+1}}{\Pi_{b+j}}\right) \\ &= \Pi_{b-j-1}\Pi_{b+j}(K_{b-j} - qK_{b+j+1}) \\ &> \Pi_{b-j-1}\Pi_{b+j}(2^j K_b - q2^{-(j-1)}K_b) \\ &= \Pi_{b-j-1}\Pi_{b+j}2^{-(j-1)}K_b(2^{2j+1} - q) \end{aligned}$$

and is thus sufficient to chose $q = 2^{2j+1}$, which leads to

$$\Pi_{b-j}\Pi_{b+j} - 2^{2j+1}\Pi_{b-j-1}\Pi_{b+j+1} > 0. \tag{10}$$

As a consequence, assuming that $f_{b-j,b+j,c} > 0$, we find that

$$\begin{aligned}
&f_{b-j,b+j,c}\Pi_{b-j}\Pi_{b+j}\Pi_c \;+\; f_{b-j-1,b+j+1,c}\Pi_{b-j-1}\Pi_{b+j+1}\Pi_c \\
&= f_{b-j,b+j,c}\Pi_{b-j}\Pi_{b+j}\Pi_c \;-\; 2^{2j+1}f_{b-j,b+j,c}\Pi_{b-j-1}\Pi_{b+j+1}\Pi_c \\
&\quad + 2^{2j+1}f_{b-j,b+j,c}\Pi_{b-j-1}\Pi_{b+j+1}\Pi_c \;+\; f_{b-j-1,b+j+1,c}\Pi_{b-j-1}\Pi_{b+j+1}\Pi_c \\
&> \left(2^{2j+1}f_{b-j,b+j,c} + f_{b-j-1,b+j+1,c}\right)\Pi_{b-j-1}\Pi_{b+j+1}\Pi_c \\
&= \left(2^{2j+1} + \frac{f_{b-j-1,b+j+1,c}}{f_{b-j,b+j,c}}\right) f_{b-j,b+j,c}\Pi_{b-j-1}\Pi_{b+j+1}\Pi_c
\end{aligned}$$

With the index translation $j \to j-1$, the inequality (10) translates to $\Pi_{b-j+1}\Pi_{b+j-1} - 2^{2j-1}\Pi_{b-j}\Pi_{b+j} > 0$, or, equivalently,

$$\Pi_{b-j}\Pi_{b+j} - \frac{1}{2^{2j-1}}\Pi_{b-j+1}\Pi_{b+j-1} < 0. \tag{11}$$

Assuming that $f_{b-j,b+j,c} < 0$ we then find that

$$\begin{aligned}
&f_{b-j+1,b+j-1,c}\Pi_{b-j+1}\Pi_{b+j-1}\Pi_c \;+\; f_{b-j,b+j,c}\Pi_{b-j}\Pi_{b+j}\Pi_c \\
&= f_{b-j+1,b+j-1,c}\Pi_{b-j+1}\Pi_{b+j-1}\Pi_c \;+\; \frac{1}{2^{2j-1}}f_{b-j,b+j,c}\Pi_{b-j+1}\Pi_{b+j-1}\Pi_c \\
&\quad - \frac{1}{2^{2j-1}}f_{b-j,b+j,c}\Pi_{b-j+1}\Pi_{b+j-1}\Pi_c \;+\; f_{b-j,b+j,c}\Pi_{b-j}\Pi_{b+j}\Pi_c \\
&> \left(f_{b-j+1,b+j-1,c} + \frac{1}{2^{2j-1}}f_{b-j,b+j,c}\right)\Pi_{b-j+1}\Pi_{b+j-1}\Pi_c \\
&= \left(\frac{f_{b-j+1,b+j-1,c}}{f_{b-j,b+j,c}} + \frac{1}{2^{2j-1}}\right) f_{b-j,b+j,c}\Pi_{b-j+1}\Pi_{b+j-1}\Pi_c
\end{aligned}$$

In ***(b-1,b,c)* chains**, successive elements j and $j+1$ write

$$f_{b-j-1,b+j,c}\Pi_{b-j-1}\Pi_{b+j}\Pi_c \text{ and } f_{b-j-2,b+j+1,c}\Pi_{b-j-2}\Pi_{b+j+1}\Pi_c$$

Similarly to before, we first determine q such that

$$\Pi_{b-j-1}\Pi_{b+j} - q\Pi_{b-j-2}\Pi_{b+j+1} > 0.$$

We successively have

$$\begin{aligned}
&\Pi_{b-j-1}\Pi_{b+j} - q\Pi_{b-j-2}\Pi_{b+j+1} \\
&= \Pi_{b-j-2}\Pi_{b+j}\left(\frac{\Pi_{b-j-1}}{\Pi_{b-j-2}} - q\frac{\Pi_{b+j+1}}{\Pi_{b+j}}\right) \\
&= \Pi_{b-j-2}\Pi_{b+j}(K_{b-j-1} - qK_{b+j+1}) \\
&> \Pi_{b-j-2}\Pi_{b+j}(2^{j+1}K_b - q2^{-(j+1)}K_b) \\
&= \Pi_{b-j-2}\Pi_{b+j}2^{-(j+1)}K_b(2^{2j+2} - q)
\end{aligned}$$

and it is sufficient to chose $q = 2^{2j+2}$. We thus have

$$\Pi_{b-j-1}\Pi_{b+j} - 2^{2j+2}\Pi_{b-j-2}\Pi_{b+j+1} > 0. \tag{12}$$

As a consequence, assuming that $f_{b-j-1,b+j,c} > 0$, we find that

$$\begin{aligned}
&f_{b-j-1,b+j,c}\Pi_{b-j-1}\Pi_{b+j}\Pi_c \;+\; f_{b-j-2,b+j+1,c}\Pi_{b-j-2}\Pi_{b+j+1}\Pi_c \\
&\quad = f_{b-j-1,b+j+1,c}\Pi_{b-j-1}\Pi_{b+j}\Pi_c \;-\; 2^{2j+2} f_{b-j-1,b+j+1,c}\Pi_{b-j-2}\Pi_{b+j+1}\Pi_c \\
&\qquad +\; 2^{2j+2} f_{b-j-1,b+j,c}\Pi_{b-j-2}\Pi_{b+j+1}\Pi_c \;+\; f_{b-j-2,b+j+1,c}\Pi_{b-j-2}\Pi_{b+j+1}\Pi_c \\
&\quad > (2^{2j+2} f_{b-j-2,b+j,c} + f_{b-j-1,b+j+1,c})\Pi_{b-j-1}\Pi_{b+j+1}\Pi_c
\end{aligned}$$

With the index translation $j \to j-1$, the inequality (12) translates to $\Pi_{b-j}\Pi_{b+j-1} - 2^{2j}\Pi_{b-j-1}\Pi_{b+j} > 0$, or, equivalently,

$$\Pi_{b-j-1}\Pi_{b+j} - \frac{1}{2^{2j}}\Pi_{b-j}\Pi_{b+j-1} < 0. \tag{13}$$

Assuming that $f_{b-j-1,b+j,c} < 0$ we then find that

$$\begin{aligned}
&f_{b-j,b-1+j,c}\Pi_{b-j}\Pi_{b-1+j}\Pi_c \;+\; f_{b-1-j,b+j,c}\Pi_{b-1-j}\Pi_{b+j}\Pi_c \\
&\quad = f_{b-j,b-1+j,c}\Pi_{b-j}\Pi_{b-1+j}\Pi_c \;+\; \frac{1}{2^{2j}} f_{b-1-j,b+j,c}\Pi_{b-j}\Pi_{b-1+j}\Pi_c \\
&\qquad -\; \frac{1}{2^{2j}} f_{b-j-1,b+j,c}\Pi_{b-j}\Pi_{b+j}\Pi_c \;+\; f_{b-j-1,b+j,c}\Pi_{b-j-1}\Pi_{b-1+j}\Pi_c \\
&\quad > \left(f_{b-j,b-1+j,c} + \frac{1}{2^{2j}} f_{b-1-j,b+j,c}\right)\Pi_{b-j}\Pi_{b-1+j}\Pi_c \\
&\quad = \left(\frac{f_{b-j,b-1+j,c}}{f_{b-j-1,b+j,c}} + \frac{1}{2^{2j}}\right) f_{b-1-j,b+j,c}\Pi_{b-1+j}\Pi_c
\end{aligned}$$

2.3 Heuristic determination of sufficient conditions

For the evaluation in this section, the relevant f_{abc} for the different values of n were generated with `secondderivterms.f90`

2.3.1 $n = 1$

e. g., $B(OH_3)$: unconditionally positive

2.3.2 $n = 2$

e. g., H_2CO_3:

- term in H^2, for $c = 2$

$$\begin{aligned}
2\Pi_1^2\Pi_2 - 4\Pi_2^2 &= 2\Pi_1\Pi_2(\Pi_1 - 2\Pi_2/\Pi_1) \\
&= 2\Pi_1\Pi_2(K_1 - 2K_2)
\end{aligned}$$

  Sufficient condition for positivity:

  - $K_2 < \frac{1}{2}K_1$

2.3.3 $n = 3$

e. g., $H_3(PO)_4$:

1. term in H^5, for $c = 2$

$$2\Pi_1^2\Pi_2 - 4\Pi_2^2 = 2\Pi_2\Pi_1(K_1 - 2K_2)$$

   Sufficient condition for positivity:

- $K_2 < \frac{1}{2}K_1$

2. term in H^2, for $c = 3$

$$\begin{aligned} 2\Pi_2^2\Pi_3 - 4\Pi_1\Pi_3^2 &= 2\Pi_1\Pi_2\Pi_3(\Pi_2/\Pi_1 - 2\Pi_3/\Pi_2) \\ &= 2\Pi_1\Pi_2\Pi_3(K_2 - 2K_3) \end{aligned}$$

   Sufficient condition for positivity:

   - $K_3 < \frac{1}{2}K_2$

These two conditions are actually already strong enough for all the remaining negative terms to be compensated by other positives:

- term in H^4, for $c = 3$

$$\begin{aligned} 12\Pi_1^2\Pi_2 - 6\Pi_2^2 &= 6\Pi_1\Pi_2(2\Pi_1 - \Pi_2/\Pi_1) \\ &= 6\Pi_2\Pi_1(2K_1 - K_2) \end{aligned}$$

  Sufficient condition for positivity:

  - $K_2 < 2K_1$, already met by 1. above: $K_2 < \frac{1}{2}K_1 < 2K_1$

- term in H^3, for $c = 3$

$$\begin{aligned} 6\Pi_1\Pi_2\Pi_3 - 18\Pi_3^2 &= 6\Pi_2\Pi_3(\Pi_1 - 3\Pi_3/\Pi_2) \\ &= 6\Pi_2\Pi_3(K_1 - 3K_3) \end{aligned}$$

  Sufficient condition for positivity:

  - $K_3 < \frac{1}{3}K_1$, already met following 1. and 2. above: $K_3 < \frac{1}{2}K_2 < \frac{1}{4}K_1 < \frac{1}{3}K_1$.

2.3.4 $n = 4$

e. g., $H_4(SiO)_4$:

1. term in H^8, for $c = 2$

$$2\Pi_1^2\Pi_2 - 4\Pi_2^2 = 2\Pi_2\Pi_1(K_1 - 2K_2)$$

   Sufficient condition for positivity:

   - $K_2 < \frac{1}{2}K_1$

2. term in H^5, for $c = 3$

$$2\Pi_2^2\Pi_3 - 4\Pi_1\Pi_3^2 = 2\Pi_1\Pi_2\Pi_3(K_2 - 2K_3)$$

   Sufficient condition for positivity:

   - $K_3 < \frac{1}{2}K_2$

3. term in H^2, for $c = 4$

$$\begin{aligned} 2\Pi_3^2\Pi_4 - 4\Pi_2\Pi_4^2 &= 2\Pi_2\Pi_3\Pi_4(\Pi_3/\Pi_2 - 2\Pi_4/\Pi_3) \\ &= 2\Pi_2\Pi_3\Pi_4(K_3 - 2K_4) \end{aligned}$$

   Sufficient condition for positivity:

   - $K_4 < \frac{1}{2}K_3$

These three conditions are again strong enough for all the remaining negative terms to be compensated by other positives:

- term in H^7, for $c = 3$

$$\begin{aligned} 12\Pi_1^2\Pi_3 - 6\Pi_2\Pi_3 &= 6\Pi_1\Pi_3(2\Pi_1 - \Pi_2/\Pi_1) \\ &= 6\Pi_1\Pi_3(2K_1 - K_2) \end{aligned}$$

  Sufficient condition for positivity:

  - $K_2 < 2K_1$, already met following 1. above: $K_2 < \frac{1}{2}K_1 < 2K_1$

- term in H^6, for $c = 3$

$$\begin{aligned} 6\Pi_1\Pi_2\Pi_3 - 18\Pi_3^2 &= 6\Pi_2\Pi_3(\Pi_1 - 3\Pi_3/\Pi_2) \\ &= 6\Pi_2\Pi_3(K_1 - 3K_3) \end{aligned}$$

  Sufficient condition for positivity:

  - $K_3 < \frac{1}{3}K_1$, already met following 1. and 2. above: $K_3 < \frac{1}{2}K_2 < \frac{1}{4}K_1 < \frac{1}{3}K_1$

- term in H^5, for $c = 4$

$$\begin{aligned} 34\Pi_1\Pi_2\Pi_4 - 44\Pi_3\Pi_4 &= 2\Pi_2\Pi_4(17\Pi_1 - 22\Pi_3/\Pi_2) \\ &= 2\Pi_2\Pi_4(17K_1 - 22K_3) \end{aligned}$$

  Sufficient condition for positivity:

  - $K_3 < \frac{17}{22}K_1$, already met following 1. and 2. above: $K_3 < \frac{1}{2}K_2 < \frac{1}{4}K_1 < \frac{17}{22}K_1$

- term in H^4, for $c = 4$

$$\begin{aligned} &12\Pi_2^2\Pi_4 - 6\Pi_1\Pi_3\Pi_4 - 48\Pi_4^2 \\ &= 12\Pi_2^2\Pi_4 - 12\Pi_1\Pi_3\Pi_4 + 6\Pi_1\Pi_3\Pi_4 - 48\Pi_4^2 \\ &= 12\Pi_1\Pi_2\Pi_4(\Pi_2/\Pi_1 - \Pi_3/\Pi_2) + 6\Pi_3\Pi_4(\Pi_1 - 8\Pi_4/\Pi_3) \\ &= 12\Pi_1\Pi_2\Pi_4(K_2 - K_3) + 6\Pi_3\Pi_4(K_1 - 8K_4) \end{aligned}$$

  Sufficient conditions for positivity:

  - $K_3 < K_2$, already met following 2. above: $K_3 < \frac{1}{2}K_2 < K_2$
  - $K_4 < \frac{1}{8}K_1$, already met following 1., 2. and 3. above: $K_4 < \frac{1}{2}K_3 < \frac{1}{4}K_2 < \frac{1}{8}K_1$

- term in H^3, for $c = 4$

$$\begin{aligned} 6\Pi_2\Pi_3\Pi_4 - 18\Pi_1\Pi_4\Pi_4 &= 6\Pi_1\Pi_3\Pi_4(\Pi_2/\Pi_1 - 3\Pi_4/\Pi_3) \\ &= 6\Pi_3\Pi_4(K_2 - 3K_4) \end{aligned}$$

  Sufficient condition for positivity:

  - $K_4 < \frac{1}{3}K_2$, already met by 2. and 3. above: $K_4 < \frac{1}{2}K_3 < \frac{1}{4}K_2 < \frac{1}{3}K_2$

2.3.5 $n > 4$

The program `sdt_iconstraints.f90` calculates for a given n, the coefficients of the polynomial at the numerator of $\frac{d^2}{dH^2}(\frac{D_1}{D})$, and the coefficients of the minoring polynomial based upon the hypothesis that $K_{j+1} < \frac{1}{2}K_j$ ($j = 1, \ldots, n-1$), using the inequalities (10) and (12). For up to $n = 12$, we have checked that all the coefficients of the so defined minoring polynomial are positive.[1] We may thus reasonably assume that $\frac{d^2}{dH^2}(\frac{D_1}{D}) > 0$ for naturally occurring acid systems. Accordingly, we can be sure that the minimization problem from section 2.3 (part $\gamma > 0$) has exactly one solution at least for $n \leq 12$.

[1] Please notice though that all the arithmetic in `sdt_iconstraints.f90` is done in `INTEGER` type. For $n > 9$, the calculations suffer from overflows. For calculations exceeding $n > 9$, the program must be compiled with adequate options to use a 64-bit wide `INTEGER` type by default (for GFORTRAN, the required option is `-fdefault-integer-8`).

3 Initialisation of the iterative solvers

3.1 Fundamental rationale

Since we have bracketing intervals for each root and, in case there are two roots, these are non-overlapping, we may always use the fall-back initial value $H_0 = \sqrt{H_{\text{inf}} H_{\text{sup}}}$. This value is, however, often far from optimal. The efficient initialisation strategy of Munhoven (2013) can be generalized and adapted to each of the three pairs. For each case, we chose the most complex Alk_T approximation that leads to a cubic equation. If the cubic polynomial behind that equation has does not have a local minimum and a local maximum, we use the fall-back value. If such local minimum and maximum exist, we use the quadratic Taylor expansion around the relevant extremum — this will normally be the maximum if the coefficient of the cubic term is negative, and the minimum if that coefficient is positive. If that quadratic does not have any positive roots, the fall-back initial value is used. The roots for that quadratic are then determined. For problems that have only one positive $[\text{H}^+]$ solution (Alk_T & CO_2, Alk_T & HCO_3^- and the Alk_T & CO_3^{2-} with $\gamma < 0$), we consider that root of the quadratic expansion that is greater than the greatest location of the two extrema: if that root is lower than H_{inf}, we use $H_0 = H_{\text{inf}}$; if it is greater than H_{sup}, we set $H_0 = H_{\text{inf}}$. For problems that have two positive $[\text{H}^+]$ solutions (Alk_T & CO_3^{2-} with $\gamma > 0$ and sufficiently great Alk_T), the initial value for determining the greater of the two $[\text{H}^+]$ solutions can be chosen exactly the same way; the initial value required to calculate the lower of the two $[\text{H}^+]$ solutions may be more tricky. If the location of the right-hand side extremum is too close to 0, the estimated root of the cubic may be negative. In this case, the quadratic fitted to left-hand extremum should be considered as well and the greater of its roots tested. Because of the symmetries of a cubic, that root can be calculated with a few extra additions only.

3.2 Alk_T & CO_2

We call upon the Alk_CB approximation, which in terms of $[\text{CO}_2]$ instead of C_T reads

$$\begin{aligned}\text{Alk}_\text{CB} &= [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] \\ &= \left(\frac{K_1}{[\text{H}^+]} + \frac{2K_1K_2}{[\text{H}^+]^2}\right)[\text{CO}_2] + \frac{K_\text{B}}{K_\text{B} + [\text{H}^+]} B_\text{T}.\end{aligned} \tag{14}$$

As the right-hand side is a monotonously decreasing function of $[\text{H}^+]$, we conclude that $\text{Alk}_\text{CB} > 0$ for a given $[\text{CO}_2]$. For a given Alk_CB, the definition (14) leads to a cubic equation in $[\text{H}^+]$, namely

$$P_\text{CB}([\text{H}^+]) \equiv c_3[\text{H}^+]^3 + c_2[\text{H}^+]^2 + c_1[\text{H}^+] + c_0 = 0,$$

where

$$\begin{aligned}c_3 &= \frac{\text{Alk}_\text{CB}}{[\text{CO}_2]} \\ c_2 &= -K_1 + K_\text{B}\left(\frac{\text{Alk}_\text{CB}}{[\text{CO}_2]} - \frac{B_\text{T}}{[\text{CO}_2]}\right) \\ c_1 &= -(K_1K_\text{B} + 2K_1K_2) \\ c_0 &= -2K_1K_2K_\text{B}.\end{aligned}$$

Since $c_3 > 0$, $P_\text{CB}(0) = c_0 < 0$ and $P'_\text{CB}(0) = c_1 < 0$, $P_\text{CB}([\text{H}^+])$ has a local minimum with a negative value for $[\text{H}^+] > 0$ and a single positive root. The minimum is located at

$$H_\text{min} = \frac{\sqrt{c_2^2 - 3c_1c_3} - c_2}{3c_3}$$

As proposed above, we use the quadratic Taylor expansion of the cubic around (H_min) and we chose the greater of its two roots as the initial value H_0 for the iterative solution of the Alk_T-$[\text{CO}_2]$

problem:

$$H_0 = H_{\min} + \sqrt{-\frac{P_{\mathrm{CB}}(H_{\min})}{\sqrt{c_2^2 - 3c_1c_3}}}.$$

The calculated H_0 has nevertheless to fulfil an additional constraint. $\mathrm{Alk}_{\mathrm{CB}}$ actually has the upper limit $2C_{\mathrm{T}} + B_{\mathrm{T}}$ (see Munhoven (2013)). Although C_{T} is unknown at this stage, as it will have to be calculated from the given $[\mathrm{CO_2}]$ and the $[\mathrm{H^+}]$ solution of the $\mathrm{Alk_T}$-$[\mathrm{CO_2}]$ problem, we can use the relationship between C_{T} and $[\mathrm{CO_2}]$

$$[\mathrm{CO_2}] = \frac{[\mathrm{H^+}]^2}{[\mathrm{H^+}]^2 + K_1[\mathrm{H^+}] + K_1K_2}\, C_{\mathrm{T}}$$

to restrain the range of possible values for $[\mathrm{H^+}]$. In order to have $\mathrm{Alk}_{\mathrm{CB}} < 2C_{\mathrm{T}} + B_{\mathrm{T}}$, it is necessary that

$$\mathrm{Alk}_{\mathrm{CB}} < 2\frac{[\mathrm{H^+}]^2 + K_1[\mathrm{H^+}] + K_1K_2}{[\mathrm{H^+}]^2}\,[\mathrm{CO_2}] + B_{\mathrm{T}}$$

or

$$\left(2 - \frac{\mathrm{Alk}_{\mathrm{CB}}}{[\mathrm{CO_2}]} + \frac{B_{\mathrm{T}}}{[\mathrm{CO_2}]}\right)[\mathrm{H^+}]^2 + 2K_1[\mathrm{H^+}] + 2K_1K_2 > 0.$$

Let us denote the reduced discriminant of this quadratic by $\Delta' = 1 - \frac{2K_2}{K_1}\left(2 - \frac{\mathrm{Alk}_{\mathrm{CB}}}{[\mathrm{CO_2}]} + \frac{B_{\mathrm{T}}}{[\mathrm{CO_2}]}\right)$. We need to distinguish two cases.

- If $2 - \frac{\mathrm{Alk}_{\mathrm{CB}}}{[\mathrm{CO_2}]} + \frac{B_{\mathrm{T}}}{[\mathrm{CO_2}]} < 0$ this quadratic has one positive and one negative root. The positive root is $H_2 = \frac{K_2}{\sqrt{\Delta'} - 1}$ and the inequality is only fulfilled for $[\mathrm{H^+}] < H_2$.
- If $2 - \frac{\mathrm{Alk}_{\mathrm{CB}}}{[\mathrm{CO_2}]} + \frac{B_{\mathrm{T}}}{[\mathrm{CO_2}]} \geq 0$ then, the right-hand expression of the inequality does not have real positive roots: the inequality is fulfilled for all $[\mathrm{H^+}] > 0$

In practice, we will set $\mathrm{Alk}_{\mathrm{CB}} = \mathrm{Alk}_{\mathrm{T}}$. If $\mathrm{Alk}_{\mathrm{T}} > 0$ and the calculated H_0 falls within the ranges just derived that guarantee that $\mathrm{Alk}_{\mathrm{CB}} < 2C_{\mathrm{T}} + B_{\mathrm{T}}$, we use it; in all other cases we set $H_0 = \sqrt{H_{\inf} H_{\sup}}$.

3.3 $\mathrm{Alk_T}$ & $\mathrm{HCO_3^-}$

This time, we may call upon the $\mathrm{Alk}_{\mathrm{CBW}}$ approximation, which in terms of $[\mathrm{HCO_3^-}]$ instead of C_{T} reads

$$\mathrm{Alk}_{\mathrm{CBW}} = \left(1 + \frac{2K_2}{[\mathrm{H^+}]}\right)[\mathrm{HCO_3^-}] + \frac{K_{\mathrm{B}}}{K_{\mathrm{B}} + [\mathrm{H^+}]}B_{\mathrm{T}} + \frac{K_{\mathrm{W}}}{[\mathrm{H^+}]} - \frac{[\mathrm{H^+}]}{s} \tag{15}$$

For a given $[\mathrm{HCO_3^-}] > 0$, $\mathrm{Alk}_{\mathrm{CBW}}([\mathrm{H^+}])$ decreases monotonously from $+\infty$ in $[\mathrm{H^+}] = 0^+$ to $-\infty$ as $[\mathrm{H^+}] \to \infty$. For a given $[\mathrm{HCO_3^-}]$ and $\mathrm{Alk}_{\mathrm{CBW}}$, the definition (15) defines an equation in $[\mathrm{H^+}]$, that has exactly one positive root. Eq. (15) can be converted into a cubic equation

$$P_{\mathrm{CBW}}([\mathrm{H^+}]) \equiv c_3[\mathrm{H^+}]^3 + c_2[\mathrm{H^+}]^2 + c_1[\mathrm{H^+}] + c_0 = 0$$

where

$$\begin{aligned}
c_3 &= \frac{1}{s[\mathrm{HCO_3^-}]} \\
c_2 &= \frac{\mathrm{Alk}_{\mathrm{CBW}}}{[\mathrm{HCO_3^-}]} + \frac{K_{\mathrm{B}}}{s[\mathrm{HCO_3^-}]} - 1 \\
c_1 &= K_{\mathrm{B}}\left(\frac{\mathrm{Alk}_{\mathrm{CBW}}}{[\mathrm{HCO_3^-}]} - \frac{B_{\mathrm{T}}}{[\mathrm{HCO_3^-}]} - 1\right) - \frac{K_{\mathrm{W}}}{[\mathrm{HCO_3^-}]} - 2K_2 \\
c_0 &= -K_{\mathrm{B}}\left(\frac{K_{\mathrm{W}}}{[\mathrm{HCO_3^-}]} + 2K_2\right)
\end{aligned}$$

Since P_{CBW} differs from eq. (15) by multiplication with the strictly positive factor $[\text{H}^+]([\text{H}^+] + K_\text{B})$, both equations have exactly the same positive roots. As outlined above, we are first checking whether P_{CBW} has local extrema. The derivative of $P_{\text{CBW}}([\text{H}^+])$ writes

$$P'_{\text{CBW}}([\text{H}^+]) = 3c_3[\text{H}^+]^2 + 2c_2[\text{H}^+] + c_1.$$

P'_{CBW} does not have any roots and thus no local extrema if $\Delta = c_2^2 - 3c_1c_3 < 0$. In this case, we use the fall-back initial value $H_0 = \sqrt{H_{\text{inf}}\, H_{\text{sup}}}$. If $\Delta \geq 0$, P_{CBW} has a local minimum for $H_{\text{min}} = \frac{\sqrt{\Delta}-c_2}{3c_3}$ and a local maximum for $H_{\text{max}} = -\frac{\sqrt{\Delta}+c_2}{3c_3}$. Since $c_3 > 0$, we have $H_{\text{max}} < H_{\text{min}}$. We now have to distinguish two cases:

1. If $P_{\text{CBW}}(H_{\text{min}}) < 0$, we use the quadratic Taylor expansion of P_{CBW} in H_{min}:

   $$Q_{\text{min}}(H) = P_{\text{CBW}}(H_{\text{min}}) + \sqrt{\Delta}(H - H_{\text{min}})^2.$$

   The greater of the two roots of Q_{min} is then chosen as H_0:

   $$H_0 = H_{\text{min}} + \sqrt{-\frac{P_{\text{CBW}}(H_{\text{min}})}{\sqrt{\Delta}}}.$$

2. If $P_{\text{CBW}}(H_{\text{min}}) > 0$, then the positive root of P_{CBW} is necessarily lower than H_{max}. In this case, we use the quadratic Taylor expansion of P_{CBW} in H_{max}, which would write $Q_{\text{max}}(H) = P_{\text{CBW}}(H_{\text{max}}) - \sqrt{\Delta}(H - H_{\text{max}})^2$. The lower of the two roots of this quadratic may, however, be negative, making its useless for deriving a H_0. We therefore modify the parabola Q_{max} such that it still has its maximum in $(H_{\text{max}}, P_{\text{CBW}}(H_{\text{max}}))$, but that it passes through $(0, c_0)$, remembering that $c_0 < 0$:

   $$\tilde{Q}_{\text{max}}(H) = P_{\text{CBW}}(H_{\text{max}}) - \frac{P_{\text{CBW}}(H_{\text{max}}) - c_0}{H_{\text{max}}^2}(H - H_{\text{max}})^2.$$

   The lower of the two roots of this $\tilde{Q}_{\text{max}}$ can then be used as H_0:

   $$H_0 = H_{\text{max}} - H_{\text{max}}\sqrt{\frac{P_{\text{CBW}}(H_{\text{max}})}{P_{\text{CBW}}(H_{\text{max}}) - c_0}}$$

Please notice that $P_{\text{CBW}}(H_{\text{min}})$ can never be equal to zero, as this would imply that P_{CBW} has a double root at H_{min}, which is not possible. In practice, we will set $\text{Alk}_{\text{CBW}} = \text{Alk}_\text{T}$ and use the above as is.

3.4 Alk_T & CO_3^2-

We use again the Alk_{CBW} approximation. In terms of $[\text{CO}_3^{2-}]$ instead of C_T it reads

$$\text{Alk}_{\text{CBW}} = \gamma[\text{H}^+] + \frac{K_\text{W}}{[\text{H}^+]} + 2[\text{CO}_3^{2-}] + \frac{K_\text{B}}{K_\text{B} + [\text{H}^+]}B_\text{T}. \tag{16}$$

Eq. (16) can be converted into a cubic equation

$$P_{\text{CBW}}([\text{H}^+]) \equiv c_3[\text{H}^+]^3 + c_2[\text{H}^+]^2 + c_1[\text{H}^+] + c_0 = 0 \tag{17}$$

where

$$\begin{aligned}
c_3 &= \frac{\gamma}{[\text{CO}_3^{2-}]} \\
c_2 &= -\left(K_\text{B}\frac{\gamma}{[\text{CO}_3^{2-}]} + \frac{\text{Alk}_{\text{CBW}}}{[\text{CO}_3^{2-}]} - 2\right) \\
c_1 &= -K_\text{B}\left(\frac{\text{Alk}_{\text{CBW}}}{[\text{CO}_3^{2-}]} - \frac{B_\text{T}}{[\text{CO}_3^{2-}]} - 2\right) + \frac{K_\text{W}}{[\text{CO}_3^{2-}]} \\
c_0 &= K_\text{B}\frac{K_\text{W}}{[\text{CO}_3^{2-}]}
\end{aligned}$$

The complete analysis from section 2.3 in the main paper remains valid for this approximation: Alk_{ncW} reduces to borate alkalinity, i. e., $\text{Alk}_{\text{ncW}}([\text{H}^+]) = \frac{K_\text{B}}{K_\text{B}+[\text{H}^+]} B_\text{T}$ and thus $\text{Alk}_{\text{nWCinf}} = 0$ and $\text{Alk}_{\text{nWCsup}} = B_\text{T}$.

There is not much that can be said a priori about the overall shape of this cubic function. as the signs of the coefficients c_2 and c_1 are difficult to predict. It is only clear that $P_{\text{CBW}}(0) = c_0 > 0$.

Case $\gamma = 0$

The cubic equation degenerates to the quadratic

$$-\left(\frac{\text{Alk}_{\text{CBW}}}{[\text{CO}_3^{2-}]} - 2\right)[\text{H}^+]^2 + c_1[\text{H}^+] + c_0 \tag{18}$$

The analysis in section 2.3 revealed that eq. (18) does not have any roots if $\text{Alk}_{\text{CBW}} - \text{Alk}_{\text{nWCinf}} \leq 2[\text{CO}_3^{2-}]$, i. e., if $\frac{\text{Alk}_{\text{CBW}}}{[\text{CO}_3^{2-}]} \leq 2$. We therefore assume that $\frac{\text{Alk}_{\text{CBW}}}{[\text{CO}_3^{2-}]} > 2$. Eq. (18) then has a negative and a positive root (their product is equal to c_0/c_2, which is negative). The positive root can be used as a starting value for the iterative solvers.

For $\gamma \neq 0$, our initial value selection scheme revolves around the characteristics of the derivative of $P_{\text{CBW}}([\text{H}^+])$. If $c_2^2 - 3c_1c_3 \leq 0$, the cubic does hence not present any local minimum and maximum. We use the default H_0.

Case $\gamma < 0$

For $\gamma \neq 0$, our initial value selection scheme revolves around the characteristics of the derivative of $P_{\text{CBW}}([\text{H}^+])$. If $c_2^2 - 3c_1c_3 \leq 0$, the cubic does hence not present any local minimum and maximum. We use the default H_0.

The case $\gamma < 0$ is analogous to the Alk_T & HCO_3^- pair, except that the cubic is decreasing, and that $P_{\text{CBW}}(0) > 0$. P_{CBW} has a local minimum for $H_{\min} = \frac{\sqrt{\Delta}-c_2}{3c_3}$ and a local maximum for $H_{\max} = -\frac{\sqrt{\Delta}+c_2}{3c_3}$. Since $c_3 < 0$, we have $H_{\min} < H_{\max}$. We have again to distinguish two cases:

1. If $P_{\text{CBW}}(H_{\max}) > 0$, we use the quadratic Taylor expansion of P_{CBW} in $H_{\max}$:

   $$Q_{\max}(H) = P_{\text{CBW}}(H_{\max}) - \sqrt{\Delta}(H - H_{\max})^2.$$

   The greater of the two roots of $Q_{\max}$ is then chosen as H_0:

   $$H_0 = H_{\max} + \sqrt{\frac{P_{\text{CBW}}(H_{\max})}{\sqrt{\Delta}}}.$$

2. If $P_{\text{CBW}}(H_{\max}) < 0$, then the positive root of P_{CBW} is necessarily lower than $H_{\min}$. In this case, we use the quadratic Taylor expansion of P_{CBW} in $H_{\min}$, which would be written $Q_{\min}(H) = P_{\text{CBW}}(H_{\min}) + \sqrt{\Delta}(H - H_{\min})^2$. In order to avoid that the lower of the two roots of this quadratic is negative, we modify it such that it still has its minimum in $(H_{\min}, P_{\text{CBW}}(H_{\min}))$, but that $Q_{\min}(0) = c_0 > 0$:

   $$\tilde{Q}_{\min}(H) = P_{\text{CBW}}(H_{\min}) - \frac{P_{\text{CBW}}(H_{\min}) - c_0}{H_{\min}^2}(H - H_{\min})^2.$$

   The lower of the two roots of $\tilde{Q}_{\min}$ can then be used as H_0:

   $$H_0 = H_{\min} - H_{\min}\sqrt{\frac{P_{\text{CBW}}(H_{\min})}{P_{\text{CBW}}(H_{\min}) - c_0}}.$$

Case $\gamma > 0$

The case $\gamma > 0$ is slightly more tedious to treat than the previous cases. Here, we only have to handle the case where two $[\mathrm{H}^+]$ solutions are required. The case where there are no roots is of course trivial; the where there is one root has been solved as the tangent point at $[\mathrm{H}^+] = H_{\mathrm{tan}}$ is the solution.

Since $c_3 > 0$, $H_{\mathrm{max}} < H_{\mathrm{min}}$ this time. The only geometrical setting of the cubic that crosses the vertical axis at $c_0 > 0$ and that allows for exactly two positive roots is the one where the local minimum is located at a positive H_{min} and where $P_{\mathrm{CBW}}(H_{\mathrm{min}}) < 0$. Accordingly, if $H_{\mathrm{min}} \leq 0$ or $P_{\mathrm{CBW}}(H_{\mathrm{min}}) \geq 0$, we adopt the respective default initial values for the two roots.

For **the greater of the two roots**, the quadratic expansion around the local minimum is used and the greater of its two roots adopted:

$$H_0 = H_{\mathrm{min}} + \sqrt{-\frac{P_{\mathrm{CBW}}(H_{\mathrm{min}})}{\sqrt{\Delta}}}.$$

The lower of the two roots needs extra attention. There are in general two estimates possible: the lower root of the quadratic expansion around the minimum or the greater of the roots of the quadratic expansion at the local maximum. It should be noticed that the latter is greater than the former and that the actual root of the cubic lies between the two. The inflection point located at $H_{\mathrm{ifl}} = -\frac{c_2}{3c_3}$ provides a criterion to decide which one of the two to retain. Since $H_{\mathrm{max}} < H_{\mathrm{min}}$ for this case, we also have $H_{\mathrm{max}} < H_{\mathrm{ifl}} < H_{\mathrm{min}}$. As we are interested in having $H_0 > 0$, we have to consider different cases depending on the sign of H_{ifl}.

Let us start with the case where $H_{\mathrm{ifl}} \geq 0$.

1. If $P_{\mathrm{CBW}}(H_{\mathrm{ifl}}) > 0$, the root searched for lies between H_{ifl} and H_{min}. To make sure the estimated H_0 remains within this interval, we modify — similarly to what has been already done twice before — the quadratic expansion at the minimum so that it passes through the inflection point:

$$\tilde{Q}_{\mathrm{min}}(H) = P_{\mathrm{CBW}}(H_{\mathrm{min}}) + \frac{P_{\mathrm{CBW}}(H_{\mathrm{ifl}}) - P_{\mathrm{CBW}}(H_{\mathrm{min}})}{(H_{\mathrm{ifl}} - H_{\mathrm{min}})^2}(H - H_{\mathrm{min}})^2.$$

   We then adopt the lower root of this $\tilde{Q}_{\mathrm{min}}$ as H_0:

$$H_0 = H_{\mathrm{min}} - (H_{\mathrm{min}} - H_{\mathrm{ifl}})\sqrt{\frac{P_{\mathrm{CBW}}(H_{\mathrm{min}})}{P_{\mathrm{CBW}}(H_{\mathrm{min}}) - P_{\mathrm{CBW}}(H_{\mathrm{ifl}})}}.$$

2. If $P_{\mathrm{CBW}}(H_{\mathrm{ifl}}) < 0$, the root searched for lies between H_{max} and H_{ifl}. To make sure the estimated H_0 remains within this interval, we modify the quadratic expansion at the maximum so that it passes through the inflection point:

$$\tilde{Q}_{\mathrm{max}}(H) = P_{\mathrm{CBW}}(H_{\mathrm{max}}) - \frac{P_{\mathrm{CBW}}(H_{\mathrm{max}}) - P_{\mathrm{CBW}}(H_{\mathrm{ifl}})}{(H_{\mathrm{ifl}} - H_{\mathrm{max}})^2}(H - H_{\mathrm{max}})^2.$$

   We then adopt the greater root of this $\tilde{Q}_{\mathrm{max}}$ as H_0:

$$H_0 = H_{\mathrm{max}} + (H_{\mathrm{ifl}} - H_{\mathrm{max}})\sqrt{\frac{P_{\mathrm{CBW}}(H_{\mathrm{max}})}{P_{\mathrm{CBW}}(H_{\mathrm{max}}) - P_{\mathrm{CBW}}(H_{\mathrm{ifl}})}}.$$

If $H_{\mathrm{ifl}} < 0$, we use the quadratic expansion at the minimum and adapt it to make it go through $(0, c_0)$,

$$\tilde{Q}_{\mathrm{min}}(H) = P_{\mathrm{CBW}}(H_{\mathrm{min}}) - \frac{P_{\mathrm{CBW}}(H_{\mathrm{min}}) - c_0}{H_{\mathrm{min}}^2}(H - H_{\mathrm{min}})^2,$$

and use the lower root of that $\tilde{Q}_{\mathrm{min}}$:

$$H_0 = H_{\mathrm{min}} - H_{\mathrm{min}}\sqrt{\frac{P_{\mathrm{CBW}}(H_{\mathrm{min}})}{P_{\mathrm{CBW}}(H_{\mathrm{min}}) - c_0}}.$$

References

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