

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

Reply to the Referees' Comments

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I thank both referees for their welcoming reviews and the careful reading of my manuscript, and of its Supplement. I greatly appreciate their constructive, thoughtful and thought provoking comments, ideas and supporting calculations that will be very valuable for revising the manuscript.

In General ...

... my reading of the two Anonymous Referees' comments (hereafter resp. AR#1 and AR#2) is that they have essentially three major requests or recommendations to make.

1 Improve the Framing of the Story

AR#2 recommends to make "[...] the paper more appealing to a wider audience" and has given pertinent and precise references to the recent literature for this purpose. These references will be valuable to improve the introduction to the theme. The framing of the study will be amended along the lines suggested by AR#2., i. e., by considering CO_3^{2-} as the fifth measurable besides Alk_T , C_T , $(p)\text{CO}_2$ and $p\text{H}$. Sharp and Byrne (2019) have shown that Alk_T & $[\text{CO}_3^{2-}]$ and C_T & $[\text{CO}_3^{2-}]$ are the most suitable data pairs to use for the carbonate system speciation, given the uncertainties of all the measurables and of all the various parameters that enter these calculations. While the C_T & $[\text{CO}_3^{2-}]$ problem is straightforward to solve as it only requires the solution of a quadratic equation that always has only one positive root, the Alk_T & $[\text{CO}_3^{2-}]$ counterpart is more difficult to address, because of the complications that result from the existence of two physically realistic roots and because it requires an iterative approach. A reliable and fail-safe solution algorithm is therefore of order.

2 Alk_T & CO_3^{2-} : A Tale of Two Solutions

Both AR#1 and AR#2 were concerned about the question which root shall be chosen when there are two of them?

I first of all thank AR#1 for pointing out the little important detail in the solution recipe for the Alk_T & CO_3^{2-} pair in Zeebe and Wolf-Gladrow (2001, pp. 276–277), that had escaped my attention: "Roots: two positive (use the larger one), three negative." Thank you also for the instructive

calculations and the supporting MATLAB code that allowed to see exactly what simplifications were adopted.

I have been convinced for some time already that the existence of two roots had to do with CO_3^{2-} and OH^- swapping their roles as dominant contributors to Alk_T with increasing $p\text{H}$. The calculations and the graph provided in your comment provides a straightforward and simple way to illustrate this.

The observation that the concentration of CO_3^{2-} as a function of $p\text{H}$ (I use $[\text{H}^+]$ here instead), for a given Alk_T goes to 0 at some $p\text{H}$ value is actually universally true. Let us denote the function that describes the evolution of that concentration by $c_3([\text{H}^+]; \text{Alk}_T)$, to distinguish it from any given $[\text{CO}_3^{2-}]$ and also because that function becomes negative above some threshold $p\text{H}$, which would be meaningless for CO_3^{2-} . We have

$$c_3([\text{H}^+]; \text{Alk}_T) = \frac{\text{Alk}_T - \text{Alk}_{\text{nWC}}([\text{H}^+]) - \frac{K_W}{[\text{H}^+]} + \frac{[\text{H}^+]}{s}}{\frac{[\text{H}^+]}{K_2} + 2}, \quad (1)$$

which is to be understood as a parametric function of $[\text{H}^+]$, with Alk_T as a parameter. There are two noteworthy facts about this function:

1. as $[\text{H}^+] \rightarrow +\infty$, $c_3([\text{H}^+]; \text{Alk}_T) \rightarrow \frac{K_2}{s}$, i. e., the value that $[\text{CO}_3^{2-}]$ takes for $\gamma = 0$;
2. as $[\text{H}^+] \rightarrow 0^+$, $c_3([\text{H}^+]; \text{Alk}_T) \rightarrow -\infty$.

Both limits are independent of Alk_T . Accordingly, $c_3([\text{H}^+]; \text{Alk}_T) > 0$ for sufficiently large $[\text{H}^+]$ (i. e., sufficiently low $p\text{H}$) on one hand, while $c_3([\text{H}^+]; \text{Alk}_T) < 0$ for sufficiently low $[\text{H}^+]$ (i. e., sufficiently high $p\text{H}$) on the other hand. The equation $c_3([\text{H}^+]; \text{Alk}_T) = 0$ must therefore have at least one root. It actually has exactly one, for any value of Alk_T , since this simply requires that the numerator at the right-hand side of the definition of c_3 (Eq. (1)) is 0, i. e., that $[\text{H}^+]$ is the solution of a standard alkalinity- $p\text{H}$ equation where $C_T = 0$. Such an equation always has exactly one positive solution, for any physically meaningful set of total concentrations of the different acid-base systems at play and any Alk_T value (Munhoven, 2013).

In the particular case presented by AR#1, where $\text{Alk}_T := [\text{HCO}_3^+] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$, it is normal that there is no solution possible for $p\text{H} > 11$: at sufficiently high $p\text{H}$, OH^- becomes the single most important, if not the only significant, contributor to Alk_T as is illustrated on the graph provided. At this point $\text{Alk}_T \simeq [\text{OH}^-]$, i. e., $\text{Alk}_T \simeq K_W/[\text{H}^+]$. The corresponding $p\text{H}$ value is $p\text{H} = -\log(K_W/\text{Alk}_T)$. With the values adopted by AR#1 ($K_W = 2.3 \times 10^{-14} \text{ mol kg}^{-1}$ and $\text{Alk}_T = 2300 \mu\text{mol (kg-SW)}^{-1}$), we find that this threshold $p\text{H}$ is 11. Not only are there no solutions for $p\text{H} > 11$, but $p\text{H}$ values above 11 are actually incompatible with Alk_T fixed at $2300 \mu\text{mol (kg-SW)}^{-1}$. Unlike shown on the graph by AR#1, $[\text{OH}^-]$ cannot grow beyond the point where $c_3([\text{H}^+]; \text{Alk}_T) = 0$ as it is the only contributor to Alk_T beyond that point. With Alk_T is fixed, $[\text{OH}^-]$ essentially also becomes fixed in this simple configuration once $[\text{CO}_3^{2-}]$ has vanished. So, it is not possible for $p\text{H}$ to increase beyond that point.

This is, however, not only true in the simple example proposed by AR#1, but in general and is reflected by the blank areas in Fig. R2, panels (c) to (e), below (Fig. R2 is the revised version of Fig. 1 from the manuscript).

Following the suggestion of AR#2, I have prepared two graphs similar to that of AR#1 that I am going to include in the revised manuscript.

- The first one is equivalent to that of AR#1, except that it is based upon the results presented in Fig. 1 in the submitted manuscript (see Fig. R2). These results also include borate alkalinity (and actually phosphate and ammonia alkalinities as well, which are, however, too low to yield any discernible contribution on the graph and have therefore been omitted). The range of $p\text{H}$ values has furthermore been extended to match that of Fig. 1, panels (c)–(e), in the manuscript.

- The second one presents the CO_3^{2-} concentrations as a function of $p\text{H}$ at fixed Alk_T for different values of Alk_T . The different curves are thus horizontal cross-sections through the $[\text{CO}_3^{2-}]$ distribution shown in Fig. 1c in the manuscript (Fig. R2e below) at different Alk_T levels.

The two graphs are shown in Fig. R1 in this comment.

There is a noteworthy feature regarding the different c_{O_3} curves shown in Fig. R1b. The locus of their maxima actually has a seemingly simple analytical equation:

$$c_{\text{O}_3\text{max}}(H) = K_2 \left(-\frac{d\text{Alk}_{\text{nWC}}}{dH} + \frac{K_W}{H^2} + \frac{1}{s} \right) \quad (2)$$

where H is used as a shorthand for $[\text{H}^+]$. The derivative of Alk_{nWC} is always negative (Munhoven, 2013) and this expression is thus always positive.

At first sight Eq. (2) might appear to offer an alternative to the A minimisation procedure described in the manuscript to determine the number of roots of the problem for a given Alk_T & CO_3^{2-} data pair as it gives direct access to the maximum of a c_{O_3} curve as a function of $p\text{H}$. Obviously, knowing the characteristics of the maximum of the c_{O_3} obtained for a given Alk_T (i. e., the $p\text{H}$ value that locates the maximum and the maximum value itself) would directly allow to conclude about the number of roots, and, if there are two of them, provide a separation between them. Unfortunately, Eq. (2) somehow has that information only backwards: it provides the maximum value of the curve that has its maximum at a given $p\text{H}$ value, without knowing which Alk_T that curve corresponds to. To find that Alk_T value one has to invert the function, i. e., to calculate the $p\text{H}$ at which a given $c_{\text{O}_3\text{max}}$ is reached. With those two pieces of information, Eq. (1) would then allow to determine the Alk_T corresponding to the curve.

Notwithstanding the complications related to the inversion of $c_{\text{O}_3\text{max}}(H)$ defined by Eq. (2), it should be noticed that minimizing $A([\text{H}^+]; [\text{CO}_3^{2-}])$ as is done in SOLVESAPHE-r2 and maximizing $c_{\text{O}_3}([\text{H}^+]; \text{Alk}_T)$ are actually two completely equivalent problems. Minimising $A([\text{H}^+]; [\text{CO}_3^{2-}])$ presents one important advantage over maximising $c_{\text{O}_3}([\text{H}^+]; \text{Alk}_T)$: negative A values are perfectly acceptable, while they are meaningless when it comes to c_{O_3} . Appropriate algorithms for the maximisation of c_{O_3} would therefore be more complicated to design and implement as they would require additional safeguards.

Remains the burning question:

Which root chose when there are two of them?

First of all, it is difficult to say whether the answer to this question is beyond the scope of this paper (AR#2)—may be it is, may be it is not—but I certainly agree with AR#1 that it is “beyond mathematics.”

There is no universally valid a priori justification to prefer one of the two solutions over the other and additional information, qualitative or quantitative, will be required to chose. This could be a third measurable, but often even qualitative information only about, say, the expected $p\text{H}$ or the C_T range might be sufficient. For natural sea- or freshwater samples, it will generally be the lower of the two $p\text{H}$ solutions that will be the relevant one (in terms of $[\text{H}^+]$, the “use the larger one” advice of Zeebe and Wolf-Gladrow (2001)). The high- $p\text{H}$ solution generally goes together with $C_T \simeq [\text{CO}_3^{2-}]$. For the surface cold conditions at the basis of the results shown in Fig. R2, CO_3^{2-} represents more than 90% of DIC for $p\text{H} > 10$, as can be calculated from Eq. (6) in the manuscript. From Fig. R2, one can see that $c_{\text{O}_3\text{max}} > 0.47 \text{ mmol kg}^{-1}$ for $\text{Alk}_T \geq 1.5 \text{ mmol kg}^{-1}$ and that it is located at $p\text{H} > 10$. Since the larger of the two solutions is always at greater or equal $p\text{H}$ than that maximum, we may conclude that for $[\text{CO}_3^{2-}] < 0.47 \text{ mmol kg}^{-1}$ and $\text{Alk}_T \geq 1.5 \text{ mmol kg}^{-1}$, the greater of the two $p\text{H}$ roots, if it exists, always implies that CO_3^{2-} represents more than 90% of DIC. Accordingly, even a rough estimate of one of the other relevant parameters of the carbonate system might be sufficient to reject one of the two roots.

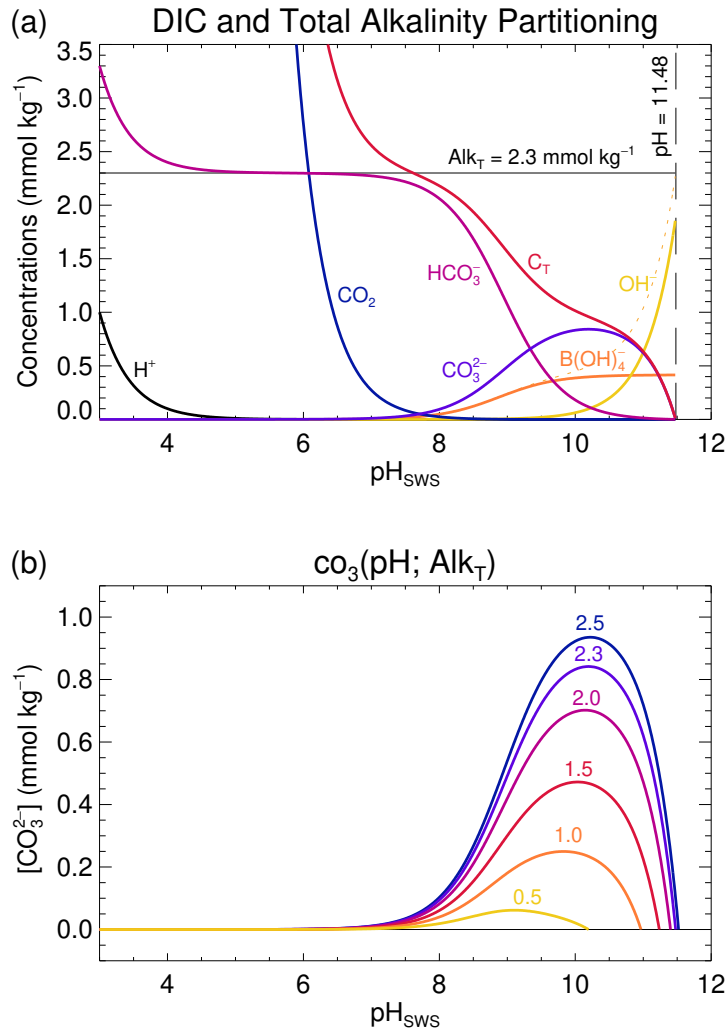


Figure R1: (a) Evolutions of the different species composing Alk_T and C_T as a function of pH, for Alk_T = 2.3 mmol kg⁻¹. C_T and all of its components reduce to 0 at pH = 11.48 (marked by the long-dashed vertical black line) in this example. The short-dashed orange line represents the joint contribution of B(OH)₄⁻ and OH⁻ which are the dominant Alk_T contributors at high pH. (b) co₃([H⁺]; Alk_T) as a function of pH for different Alk_T values (indicated in mmol kg⁻¹ for each curve). Each curve represents a horizontal cross-section at the corresponding Alk_T level through the [CO₃²⁻] distribution depicted in Fig. R2e below.

SOLVESAPHE-r2, which is meant to be universally applicable therefore always determines both roots and leaves it to the user's responsibility to select the relevant one.

In practice, the problem is perhaps not as insurmountable as it might appear at first sight: all the standard procedures for the determination of the total alkalinity of a water sample that I am aware of involve a titration procedure, which requires ... *pH* monitoring, and so it should always be possible to get some information about the sample's *pH*, although it might not always be recorded. Depending on the titration procedure adopted (open- or closed-cell – see, e. g., Dickson et al. (2007)), the titration data possibly also allow to get at least an approximate estimate of the sample's C_T .

3 New Test Case: ABW5

AR#2 suggests to include some other case studies, thinking more specifically about [sediment] pore waters.

I had difficulties to secure sufficiently complete data sets for porewater chemistry to design a realistic representative test case as requested by AR#2. As the purpose was to cover samples where "[...] the concentrations of various acid-base systems may be higher, especially the relative contributions of non-carbonate bases to Alk" I finally resorted to using the data of Yao and Millero (1995) for the anoxic waters of the Framvaren Fjord, Norway, as a starting point. The water column in this fjord is anoxic below 20 m depth, and at depths greater than 100 m, it is characterised by H_2S concentrations between about 4.5 and 5.8 mM, as well as NH_4^+ concentrations between about 1.3 and 1.6 mM. Yao and Millero (1995) provide data for all the acid-systems currently considered in the Fortran 90 implementation of SOLVESAPHE-r2.

For the new test case ABW5, where "ABW" stands for *anoxic brackish water*, I then use average concentrations between 100 and 170 m depth for all components except Alk_T and C_T , for which roughly rounded ranges over that depth interval are adopted: $T = 7.56^\circ C$, $S = 22.82$, $D = 135$ m, $[H_2S] = 5.1$ mmol kg⁻¹, $[PO_4^{3-}] = 0.1$ mmol kg⁻¹, $[NH_4^+] = 1.5$ mmol kg⁻¹, $[SiO_2] = 0.6$ mmol kg⁻¹, $Alk_T = 17 - 20$ mmol kg⁻¹, $C_T = 15 - 17.5$ mmol kg⁻¹. All reported concentrations are assumed to represent total concentrations of their respective acid systems.

In order not to lengthen the manuscript unnecessarily, the results for SW1 will be removed from Figs. 5 and 6 and those for ABW5 included instead. SW1 is a subset of SW2 and their iteration number histograms are broadly similar in terms of frequencies (not absolute numbers, as SW1 is based upon a C_T - Alk_T grid with 600×600 points and SW2 upon one with 1500×1300 points). The results for SW1 are still going to be reported in the "Additional Results" in the Supplement.

Minor Points and Technical Comments

All the typos will be corrected as suggested and I am not mentioning them here.

Anonymous reviewer # 1

Units of alkalinity: I suggest replacing meq (outdated) by mmol (compare, for example, Dickson et al., 2007, Chapter 5, Table 2)

OK, will be amended.

L51 's is a factor to convert from that scale to the free scale': it might be useful to mention that the value of s is close to 1

The sentence at lines 51–52 will be rewritten to read

"s depends on temperature, pressure and salinity of the sample and its value is close to 1 (typically between 1.0 and 1.3)."

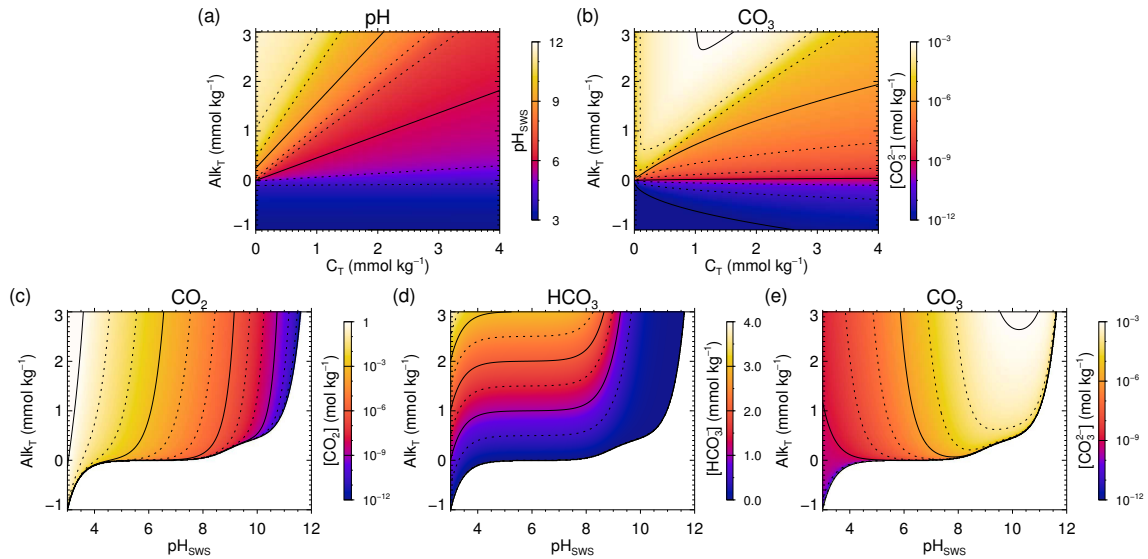


Figure R2: (a) pH isolines; (b) CO_3^{2-} concentration isolines in C_T - Alk_T space; (c) CO_2 , (d) HCO_3^- and (e) CO_3^{2-} and concentration isolines in pH - Alk_T space. These distributions were calculated with SOLVESAPHE version 1.0.3. For (c), (d) and (e), carbonate alkalinity, Alk_C , was derived by using eq. (2) [from the manuscript], combined with eqs. (7), (8) and (9) [from the manuscript] to derive $[CO_2]$, $[HCO_3^-]$, and $[CO_3^{2-}]$, respectively. Blank areas represent the pH - Alk_T combinations that lead to negative Alk_C . Figure 3 in Deffeyes (1965) is similar to (b).

Fig. 1: axes labels (quantities & units) missing, same for color bars; remove titles (numbers); y-axes from 1 to 0 to 3 or from -1 to 3 (??); a bit more explanation/discussion might be in order

The annotations of Fig. 1 in the manuscript were partly lost during the processing of the submitted manuscript file (where the figure was complete) to produce the preprint posted on the GMDD forum. An Author's Comment (AC1) with a reprocessed version of the figure was posted on 9th March 2021 (doi:10.5194/gmd-2020-447-AC1). I reproduce the complete figure here as Fig. R2, in the version that I plan to include in the revised manuscript. It has its colour scheme changed for a colour-blind safe one and the panels in the lower row of the figure have been rearranged so that they are in $CO_2 - HCO_3^- - CO_3^{2-}$ order.

L193 $[H^+] \gg$: something missing here

This was meant to be understood as "for great values of $[H^+]$ ". This will be replaced by "as $[H^+] \rightarrow +\infty$."

L210 $H_1 < H_{\min}$ and $H_2 > H_{\min}$ might be shortened to $H_1 < H_{\min} < H_2$

Yes, this is correct and both forms of course mathematically equivalent. I prefer to leave it as is, to emphasize that H_1 is lower than H_{\min} and that H_2 is greater than H_{\min} .

L229 'exact knowledge determination' ???

"determination" needs to be deleted so that the sentence reads "[...] for which the exact knowledge of H_{\tan} is not indispensable."

L271 API = ???

API is a standard acronym in computer science standing for “Application Programming Interface” – the definition will be added.

L275 *‘In the course of the development s related to ...’ ??? something missing here?*

There is actually a spurious blank between “development” and the “s” that follows. This should read “In the course of the developments related to [...]”

L291 *‘equation function’ ???*

I make a distinction between an equation and the function that defines it, which I then call the equation function (e. g., when it comes to stating that the function defining the equation is monotonous or decreasing – see also line 179). Here “function” can nevertheless be discarded.

Anonymous reviewer # 2

Throughout

“on Fig. *n*” changed to “in Fig. *n*” as suggested repeatedly.

L.10-11: *“longer”/“more time” – > than what exactly?*

There is actually an error on line 11: “while Alk_T & CO_2 requires about four times as much time.” should actually read “while Alk_T & CO_3^{2-} requires about four times as much time.” Lines 10–11 will be rewritten to read:

“The Alk_T & CO_2 pair is numerically the most challenging. With the Newton-Raphson based solver, it takes about five times as long to solve as the companion Alk_T & C_T pair; the Alk_T & CO_3^{2-} pair requires on average about four times as much time as the Alk_T & C_T pair.”

L.12-13: *“It outperforms the Newton-Raphson based one by a factor of four’ – > In terms of what, calculation time?*

In terms of the required number of iterations. This will be reformulated more precisely.

L.15: *“For Alk_T & CO_3^{2-} data pairs” would read better here*

OK – will be corrected as suggested.

L.27-29: *Depending on the purpose, some modellers will use pH in combination with C_T ; I suggest to write “most modellers” instead.*

OK – will be changed as suggested.

L.38-39: *Not sure what is meant with “this best had to be one pair of input data only”.*

This means that users should only have to provide the absolutely necessary information (i. e., the pair of data), but no further auxiliary information, such as a bracketing interval or starting values for an iterative process. As in SOLVESAPHE v. 1, the algorithm should be able to derive that kind of information autonomously without having to rely on user input.

L.40-44: *I would suggest to finish the introduction and start a new manuscript section after presenting the aim.*

The section heading “2 Theoretical Considerations” will be moved before the current line 44. The now initial part of that section will be headed by a new subsection title “2.1 Revisiting the mathematics of the alkalinity-*p*H equation” and rephrased for a smoother start.

L.187: *better write “I” instead of “we” (single author)*

OK.

L.193: *[H +] >> (something appears to be missing here)*

See reply to the same comment by AR#1.

L.270-271: *I suggest to provide one sentence here to explain the difference between both solvers, for example by moving the current L.324-326 which explains that one is the Newton-Raphson solver, while the other uses the secant scheme.*

The paragraph starting at line 270 will be reformulated along the following lines:

“The SOLVESAPHE Fortran 90 library from Munhoven (2013) – hereafter SOLVESAPHE v. 1 – has been revised, cleaned up and upgraded to allow the processing of the additional three pairs. For the purpose of this paper, only the two main solvers have been kept: these are `solve_at_general`, which uses a Newton-Raphson method, and `solve_at_general_sec`, which uses the secant method. Both can be still be used with the same Application Programming Interface (API) as in v. 1. The instances in SOLVESAPHE-r2 are nevertheless only wrappers to the newly added Newton-Raphson based `solve_at_general2` and secant (or more precisely regula falsi) based `solve_at_general2_sec` both of which are able to process problems that have two roots. They return the number of roots of the problem, as well as their actual values, if any.”

References

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