Review on SolveSAPHE-r2: revisiting and extending the Solver Suite for Alkalinity-pH Equations for usage with CO₂, HCO₃⁻ or CO₃²⁻ input data by Guy Munhoven

Guy Munhoven has investigated the number of solutions (pH values) of the carbonate system for the pairs AlkT-CO₂, AlkT-HCO₃⁻, and AlkT-CO₃²⁻. Using detailed mathematical analysis he has shown that for reasonable values for the variables in the first two pairs one obtains a unique (one and only) physically sensible solution (positive concentration of all compounds). In contrast, the pair AlkT-CO₃²⁻ is more of a challenge: (1) Depending on the concentration of CO₃²⁻ three cases have to been discerned; although all three cases have been properly analyzed by Munhoven, the third one (with γ > 0) is the most relevant (the only relevant in the ocean). (2) For CO₃²⁻ concentrations > 1 µmol kg⁻¹ (implying γ > 0) either two or no physically sensible solution exists.

Based on his detailed mathematical insight, Munhoven has developed algorithms to solve the various equations (in order to be efficient, good bounds and initial values are useful). The algorithms were coded in FORTRAN-90 and extensively tested.

After Munhoven (2013) this is another outstanding contribution by Guy Munhoven. It is clearly written, however, not ‘easy reading’. With respect to mathematical analysis, the work can be considered as the capstone (a heavy one!) to the arc of all 15 possible pairs of carbonate system parameters.

I have only one major comment (which is beyond mathematics) and a few minor points.

When calculating pH from alkalinity and carbonate ion concentration in typical seawater (let’s say at AlkT = 2300 µmol kg⁻¹ and 100 µmol kg⁻¹ < [CO₃²⁻] < 600 µmol kg⁻¹) one obtains two solutions and the question is ‘Which one to take?’. In order to shed some light on this problem I have calculated the concentrations of all carbonate system parameters for a fixed alkalinity (AlkT = 2300 µmol kg⁻¹) as a function of pH (Fig. 1). For [CO₃²⁻] = 500 µmol kg⁻¹ one obtains two solutions: pH₁ = 8.70 and
pH$_2$ = 10.75 with quite different DIC values. The higher pH value is discarded because the DIC is ‘unrealistically’ low and that pH = 8.70 would be the chosen answer. This choice has been taken, for example, by Zeebe & Wolf-Gladrow (2001, p. 277, ‘use the larger one’): they recommend using the real solution with the largest H$^+$ concentration (lowest pH). Although this choice works out fine in common seawater, it has not been properly justified. And the justification is actually beyond mathematics.
Figure 1: Illustration of varying number of solution for given TA (black dash-dotted line; TA = 2300 µmol kg\(^{-1}\) is a typical/characteristic oceanic value) and carbonate ion concentration, \([\text{CO}_3^{2-}]\). The results are plotted over pH (surface ocean pH is slightly above 8, lower values can be found in deeper layers, higher values in the surface during algal blooms (up to 9) or in sea ice brines (above 10, however, at different TA values). At pH = 7 most of TA is in the form of bicarbonate whereas \([\text{CO}_3^{2-}]\) is relative small. Above pH = pK\(_2\) (here = 9.1) the concentration of \(\text{CO}_3^{2-}\) is larger than that of \(\text{HCO}_3^-\) and clearly dominates the contribution to TA. However, with further increasing pH the concentration of OH\(^-\) becomes larger and larger and at pH ≈ 11 is dominating by far the contribution to TA; this is only possible when the concentrations of bicarbonate and carbonate ions go down. Thus whereas the pair TA-\(\text{CO}_3^{2-}\) possesses always two solutions at pH < 11 (as an example: for TA = 2300 µmol kg\(^{-1}\) and \([\text{CO}_3^{2-}]\) = 500 µmol kg\(^{-1}\) pH = 8.70 and pH = 10.75 are solutions) there does not exist a solution at pH > 11.
Minor points:
Units of alkalinity: I suggest replacing meq (outdated) by mmol (compare, for example, Dickson et al., 2007, Chapter 5, Table 2)
L50 typo: whoe → whose
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
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
L174 typo: eq. (12then → eq. (12) then
L193 [H+] ≫: something missing here
L210 H₁ < Hₘᵟᵣ and H₂ > Hₘᵟᵣ might be shortened to H₁ < Hₘᵟᵣ < H₂
L229 ‘exact knowledge determination’ ???
L271 API = ???
L275 ‘In the course of the development s related to ...’ ??? something missing here?
L291 ‘equation function’ ???
Fig. legend: ‘two roots The’ dot missing after roots

Sup. Mathematical and Technical Details
Typos:
2.3.1 B(OH₃) → B(OH)₃
2.3.3 H₃(PO)₄ → H₃PO₄
2.3.4 H₄(SiO)₄ → H₄SiO₄
MATLAB code for Fig. 1:

\[
K_1 = 1.1 \times 10^{-6}; \quad K_2 = 7.8 \times 10^{-10}; \quad K_W = 2.3 \times 10^{-14}; \quad K_B = 1.9 \times 10^{-9}; \quad \% \text{use rounded values}
\]
\[
b_{\text{bor}} = 0; \quad \% \text{contribution by borate ignored}
\]
\[
\text{alk} = 2300 \times 10^{-6}; \quad \% \text{(mol/kg) typical sea water value}
\]
\[
p_{\text{Ha}} = 7.0:0.1:12; \quad L = \text{length}(p_{\text{Ha}});
\]
\[
\text{for } i = 1:L
\]
\[
\quad \text{pH} = p_{\text{Ha}}(i); \quad h = 10^{-\text{pH}};
\]
\[
\quad \% \text{Zeebe & Wolf-Gladrow (2001):}
\]
\[
\quad s = (\text{alk} - K_W / h + K_B * b_{\text{bor}} / (K_B + h)) / (K_1 / h + 2 * K_1 * K_2 / h^2); \quad \% [\text{CO}_2]
\]
\[
\quad \text{dic} = s * (1 + K_1 / h + K_1 * K_2 / h^2);
\]
\[
\quad \text{hco}_3 = \text{dic} / (1 + h / K_1 + K_2 / h);
\]
\[
\quad \text{co}_3 = \text{dic} / (1 + h / K_1 + K_2 / h);
\]
\[
\quad \text{CO}_2(i) = s; \quad \text{HCO}_3(i) = \text{hco}_3; \quad \text{CO}_3(i) = \text{co}_3; \quad \text{DIC}(i) = \text{dic};
\]
\[
\quad \text{Hp}(i) = h; \quad \text{OH}(i) = K_W / h;
\]
\[
\text{end}
\]
\[
\% \text{2 solutions for a single CO}_3: \text{example}
\]
\[
\text{CO}_3\text{ex} = 500 \times 10^{-6};
\]
\[
\% \text{------------- CO}_3 \text{ and ALK given ---------------}
\]
\[
\text{co}_3 = \text{CO}_3\text{ex};
\]
\[
\text{p}_5 = -\text{co}_3 / K_2 + 1.;
\]
\[
\text{p}_4 = \text{alk} - \text{co}_3 * (K_1 / K_2 + (K_B + 2 * K_2) / K_2) + K_B + K_1;
\]
\[
\text{p}_3 = \text{alk} * (K_B + K_1) / \text{co}_3 * (K_1 / K_2 + (K_B + 2 * K_2) / K_2 + 2 * \text{KB}) ... \nonumber
\quad + (\text{-KB} * b_{\text{bor}} - K_W / K_1 + K_B / K_1 + K_2);
\]
\[
\text{p}_2 = \text{alk} * (K_B / K_1 + K_1 / K_2) / \text{co}_3 * (K_1 / K_2 + (K_B + 2 * K_2) + 2 * \text{KB}) K_1 ... \nonumber
\quad + (\text{-KW} * K_B - K_1 * K_B * b_{\text{bor}} - K_1 * K_W / K_1 * K_2 * K_B);
\]
\[
\text{p}_1 = \text{alk} * K_B / K_1 * K_2 / \text{co}_3 / 2 * \text{KB} / K_1 * K_2 / K_1 * K_W / K_B ... \nonumber
\quad + (\text{-K_1} * K_2 / K_B * b_{\text{bor}} - K_1 / K_2 * K_W);
\]
\[
\text{p}_0 = -K_1 * K_2 * K_W / K_B;
\]
\[
\text{p} = [\text{p}_5 \text{ p}_4 \text{ p}_3 \text{ p}_2 \text{ p}_1 \text{ p}_0];
\]
\[
\text{r} = \text{roots}(\text{p});
\]
\[
\% \text{2 real solutions?}
\]
\[
\text{isol} = 0;
\]
\[
\text{for } j = 1:5
\]
\[
\quad \text{if } (\text{real}(\text{r}(j)) > 0) \&\& (\text{imag}(\text{r}(j)) == 0)
\]
\[
\quad \quad \text{isol} = \text{isol} + 1; \quad \text{pHsol(isol)} = \text{round}(-\text{log10}(\text{r}(j)),2)
\]
\[
\quad \text{end}
\]
\[
\end
References

