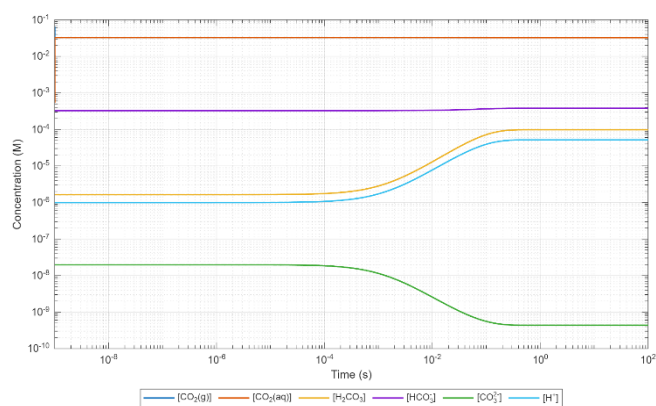


CO₂ Uptake Analysis in Seawater: Phase Equilibrium, Field Data and Reaction Kinetics



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Abstract

The ocean has absorbed roughly a quarter of the CO₂ released by human activity, which buffers climate change and also acidifies seawater. This project builds a two-part MATLAB model of that process. The first part is a phase-equilibrium model. It couples Raoult's law for water and Henry's law for CO₂ with Peng-Robinson fugacity coefficients and reduces the problem to a 4×4 linear system in the phase mole fractions. An analytical singularity analysis shows that the system fails only when the water and CO₂ equilibrium relations become proportional, which corresponds to near-critical behaviour, and that this condition is not reached in practice. The model reproduces literature vapour-pressure (3.17 kPa) and Henry's-constant (162 MPa) values at 25 °C. It agrees closely with published solubility data at low temperature. Its deviation grows towards 80 °C, where the absolute solubility approaches zero. Driven by 184 monthly means of atmospheric CO₂ measured at the Great Barrier Reef between 2009 and 2024, the model predicts a +6.6 % rise in equilibrium dissolved CO₂, with a clear seasonal cycle. The second part is a reaction-kinetics model. It solves the stiff six-species carbonate system with ode15s and conserves total carbon to within 0.011 %. The model identifies CO₂ hydration ($\tau \approx 0.05$ s) as the rate-limiting step, about nine orders of magnitude slower than gas-liquid transfer ($\tau \approx 5 \times 10^{-11}$ s). Every species is within 1 % of steady state by 0.35 s. Taken together, the two models show how much CO₂ the ocean takes up and how quickly that CO₂ turns into acidity.

Introduction

Atmospheric CO₂ has risen from about 280 ppm before industrialisation to more than 420 ppm today [4]. The ocean has absorbed roughly 25–30 % of these emissions [4, 5]. That uptake slows warming, but it comes at a cost. Dissolved CO₂ reacts with water to form carbonic acid, which releases hydrogen ions. Surface-ocean pH has already fallen by about 0.1 units, which corresponds to a ~30 % increase in acidity [5]. Coral reefs are among the most exposed ecosystems, because a lower carbonate-ion concentration makes it harder for corals to build their calcium-carbonate skeletons.

Two separate questions follow from this:

- How much CO₂ dissolves at a given temperature, pressure and atmospheric concentration? This is a thermodynamic equilibrium problem.
- How fast does dissolved CO₂ move through the carbonate system, and which step controls the rate? This is a reaction-kinetics problem.

Each question needs a different kind of model. This project builds both and connects them. It has four objectives:

1. Formulate the water–CO₂ vapour–liquid equilibrium as a linear system, and determine analytically when that system has no solution.
2. Implement the model in modular MATLAB using the Peng-Robinson equation of state, and validate it against published solubility data [1].
3. Apply the model to 15 years of atmospheric CO₂ measurements from the Great Barrier Reef to estimate the long-term trend in equilibrium dissolved CO₂.
4. Solve the time-dependent carbonate reaction system, identify the rate-limiting step, and compare what the two models can and cannot predict.

Theory

1.1 Phase Equilibrium

The system has two components, water (1) and CO₂ (2), distributed between a liquid phase (mole fractions x_i) and a vapour phase (mole fractions y_i) at temperature T and pressure P .

Water follows a modified Raoult's law, because it is the solvent and is present in near-pure form:

$$P_{v1} x_1 = \phi_1 P y_1 \quad (1)$$

CO₂ follows Henry's law, because it is a dilute, supercritical solute:

$$H_{21} x_2 = \phi_2 P y_2 \quad (2)$$

Each phase must sum to one:

$$y_1 + y_2 = 1, \quad x_1 + x_2 = 1 \quad (3,4)$$

Here P_{v1} is the vapour pressure of water and H_{21} is the Henry's constant of CO₂ in water. ϕ_1 and ϕ_2 are fugacity corrections that account for non-ideal gas behaviour. All four are functions of T and P only, not of composition.

At fixed T and P , Eqs. (1)–(4) are therefore linear in the four unknowns and can be written as $\mathbf{Az} = \mathbf{b}$:

$$\begin{pmatrix} P_{v1} & -\phi_1 P & 0 & 0 \\ 0 & 0 & H_{21} & -\phi_2 P \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ x_2 \\ y_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 1 \end{pmatrix} \quad (5)$$

1.2 Vapour Pressure of Water

P_{v1} is taken from the IAPWS-95 saturation-pressure equation [3]:

$$\ln \left(\frac{P_{v1}}{P_c} \right) = \frac{T_c}{T} (a_1 \vartheta + a_2 \vartheta^{1.5} + a_3 \vartheta^3 + a_4 \vartheta^{3.5} + a_5 \vartheta^4 + a_6 \vartheta^{7.5}), \quad \vartheta = 1 - \frac{T}{T_c} \quad (6)$$

with $T_c = 647.096$ K, $P_c = 22.064$ MPa, $a_1 = -7.85951783$, $a_2 = 1.84408259$, $a_3 = -11.7866497$, $a_4 = 22.6807411$, $a_5 = -15.9618719$ and $a_6 = 1.80122502$.

1.3 Henry's constant of Carbon Dioxide

H_{21} is taken from the correlation of Carroll et al. [1], which is valid for $273 \text{ K} < T < 433 \text{ K}$ and $P < 1 \text{ MPa}$:

$$\ln \left(\frac{H_{21}}{\text{MPa}} \right) = -6.8346 + \frac{1.2817 \times 10^4}{T} - \frac{3.7668 \times 10^6}{T^2} + \frac{2.997 \times 10^8}{T^3} \quad (7)$$

At 25 °C, Eqs. 6 and 7 give $P_{v1} = 3.17$ kPa and $H_{21} = 162$ MPa, which match standard reference values.

1.4 Fugacity Coefficients: Peng-Robinson Equation of State

Real gases deviate from the ideal-gas law because their molecules have finite size and attract each other. The Peng-Robinson equation of state [2] captures both effects:

$$P = \frac{RT}{v-b} - \frac{a\alpha(T)}{v^2 + 2bv - b^2} \quad (8)$$

$$a = 0.45724 \frac{R^2 T_c^2}{P_c}, \quad b = 0.07780 \frac{RT_c}{P_c} \quad (9)$$

$$\alpha = [1 + \kappa(1 - \sqrt{T/T_c})]^2, \quad \kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (10)$$

In terms of the compressibility factor $Z = Pv/RT$, Eq.8 becomes a cubic:

$$Z^3 - (1-B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0, \quad A = \frac{a\alpha P}{(RT)^2}, \quad B = \frac{bP}{RT} \quad (11)$$

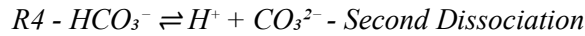
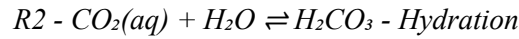
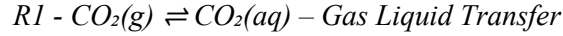
The largest real root corresponds to the vapour and the smallest to the liquid. The fugacity coefficient for a given root is:

$$\ln \phi = Z - 1 - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \ln \left(\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right) \quad (12)$$

For water, $\phi_1 = \phi_1^V / \phi_1^L$, the ratio of the vapour-root to liquid-root coefficients. For CO₂, which is supercritical and has a single real root under these conditions, $\phi_2 = \phi_2^V$.

1.5 Carbonate Reaction Kinetics

When CO₂ enters water, it moves through four reversible reactions:



Applying mass-action kinetics to each species gives six coupled ODEs. Water is in vast excess, so its concentration is absorbed into k_{2f} :

$$\frac{d[CO_2(g)]}{dt} = -k_{1f}[CO_2(g)] + k_{1b}[CO_2(aq)] \quad (13)$$

$$\frac{d[CO_2(aq)]}{dt} = k_{1f}[CO_2(g)] - k_{1b}[CO_2(aq)] - k_{2f}[CO_2(aq)] + k_{2b}[H_2CO_3] \quad (14)$$

$$\frac{d[H_2CO_3]}{dt} = k_{2f}[CO_2(aq)] - k_{2b}[H_2CO_3] - k_{3f}[H_2CO_3] + k_{3b}[H^+][HCO_3^-] \quad (15)$$

$$\frac{d[HCO_3^-]}{dt} = k_{3f}[H_2CO_3] - k_{3b}[H^+][HCO_3^-] - k_{4f}[HCO_3^-] + k_{4b}[H^+][CO_3^{2-}] \quad (16)$$

$$\frac{d[CO_3^{2-}]}{dt} = k_{4f}[HCO_3^-] - k_{4b}[H^+][CO_3^{2-}] \quad (17)$$

$$\frac{d[H^+]}{dt} = k_{3f}[H_2CO_3] - k_{3b}[H^+][HCO_3^-] + k_{4f}[HCO_3^-] - k_{4b}[H^+][CO_3^{2-}] \quad (18)$$

Adding Eqs. 13–17 gives zero, so total carbon is conserved exactly. This identity is used as a check on the numerical solution.

Characteristic time. Each reaction relaxes towards equilibrium on a timescale

$$\tau = \frac{1}{k_f + k_b} \quad (19)$$

For R3 and R4, the backward step involves H^+ , so the effective backward rate is $k_b[H^+]$ and τ shortens as acidity rises. A species settles to within 1 % of equilibrium after approximately $\ln(100) \tau \approx 4.6 \tau$.

The rate constants span about ten orders of magnitude. This makes the system stiff: an explicit solver would need time steps small enough to resolve R1 ($\sim 10^{-11}$ s) over the whole run, even though the interesting behaviour happens over ~ 1 s. An implicit solver (MATLAB's `ode15s`) avoids this restriction.

1.6 From Atmospheric Data to Model Input

Atmospheric CO_2 is reported in ppm by volume. For an ideal-gas mixture this equals the mole fraction, so the vapour-phase input $y_2 = 10^{-6} \times CO_2$ (ppm). Equation (2) is then rearranged to give the equilibrium dissolved mole fraction for each month:

$$x_2 = \frac{\phi_2 P y_2}{H_{21}(T)} \quad (20)$$

Equilibrium Model

2.1 Solvability Analysis

Unless it is singular, A will always have a unique solution, for example, $\det(A) \neq 0$. However, when expanding $\det(A)$ by cofactor expansion along the first column, it gives us:

$$\det(A) = P_{v1} \cdot (-\phi_2 P) + 1 \cdot (-\phi_1 P) \cdot H_{21} \cdot (-1)$$

$$\det(A) = \phi_1 P \cdot H_{21} - P_{v1} \cdot \phi_2 P = P(\phi_1 \cdot H_{21} - P_{v1} \cdot \phi_2)$$

As a result, this shows that $Az=b$ cannot be solved, or in other words, A is singular when:

$$P = 0 \quad \text{or} \quad \phi_1 H_{21} = \phi_2 P_{v1}$$

However, it is easy to notice that $P=0$ is when the model is in a vacuum, which is not very meaningful for this model so we can set this aside and mainly focus our attention on the second condition stated.

Implications for the real-life system

The second condition that was stated reveals that the two-phase equilibrium relations become proportional to one another rather than being independent of each other (In the case of water, Raoult's law and for CO_2 , Henry's law). This means:

Eqs 1 and 2 stop giving 2 separate constraints. What happens is they both collapse into a single independent relation. This results in 3 independent equations with only 4 unknowns, which as a result means that water and CO2 become indistinguishable with how they partition between their phases. The behaviour just stated is exactly what is expected of a mixture approaching the critical point, where the liquid and vapour phase merge, and result in fixed equilibrium splits no longer being a meaningful concept. Overall, the singularity is a physical limit of the phase equilibrium assumption

Another thing to consider is the likelihood of hitting the exact condition stated; since these come from independently fitted empirical correlations, the condition stated would be unlikely to occur. Running Eq.7 outside its fitted range (1) is a much more likely failure mode. The Henry's-constant correlation (Eq. 7) is valid only for 273–433 K, and furthermore the whole two-phase model in Eqs: 1,2,3 and 4 is limited to P being smaller than 1MPa. Anything above the stated maximum would result in liquid phase non-idealities becoming prominent.

Solutions beyond $\det(A)=0$

When looking at $\det(A)=0$, this only tells us that the solution isn't unique, however, it doesn't tell us if a solution exists at all. As a result, for us to check this, we need to have 4 equations that are in agreement at singularity and not just dependent. (The existence argument $\text{rank}(A) = \text{rank}([A/b])$)

What was done was that the 4 rows were multiplied by ϕ_2 , ϕ_1 , $\phi_1\phi_2 p$ and $-\phi_2 p_{v1}$ then added together, which results in the whole left-hand side vanishing completely, only when $\phi_1 H_{21} = \phi_2 P_{v1}$ (The previously stated condition). As a result, this confirms exactly where the equations become dependent. Leading on, if you do the same for the right-hand side, this gives $\phi_2(\phi_1 P P_{v1})$, which is required to be 0 for a solution to exist. This differs from the singularity itself, meaning there's no reason for to hold at once. As a result, we can deduce that at a singularity the 4 equations contradict each other rather than have infinite solutions, meaning the model predicts no equilibrium state exists at that Temperature and Pressure, but only are rare cases where both conditions coincide.

2.2 MATLAB Implementation

Figure 1 shows how each model component feeds into the linear solver. As stated before, the only two free inputs I have will be T and P, as Eqs. 6,7, 8-12 calculations rely only on the 2 variables stated and are all independent of each other. As a result, this means they can all be evaluated in any order, with their outputs then converging into a single step, which is assembling A and b, checking it is nonsingular and then finally solving the system.

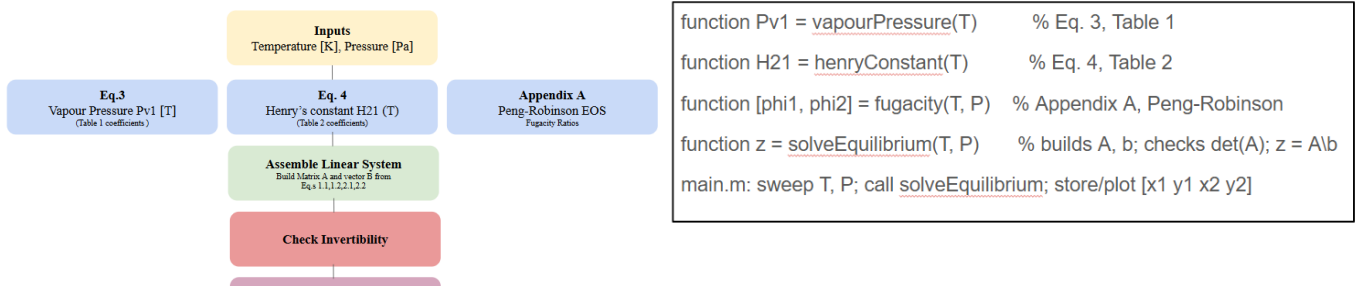


Figure 1: Schematic of MATLAB Code Structure

The structure in Figure 1 maps directly onto the MATLAB implementation shown in Figure, as four self-contained functions in addition to a driver script that assembles and solved the system (in the context for any T or P). I was able to keep the empirical correlations separate from the linear algebra step by using solveEquilibrium; this doesn't care how the values for the variables are obtained, it only receives them. Carroll et al. [1] used the Redlich-Kwong equation of state. This project uses Peng-Robinson [2] instead, which predicts liquid densities more accurately. As a result, I had to use a modular fugacity(T,P), which makes the swap possible without touching solveEquilibrium. at all.

Figure 2: Pseudocode structure for MATLAB implementation, mapping each equation set to its corresponding function.

Model Validation

3.1 Temperature Dependence of Model Inputs

Figure 3 shows how the four model inputs vary between 10 and 80 °C at atmospheric pressure. Firstly, H_{21} and P_{v1} both simply follow Eqs. 6-7 directly. When looking at the variables ϕ_2 and ϕ_1 we know they both follow Peng-Robinson equations [2]. For each of the pure components, Eq. 8-12 must be solved for its real roots. In addition, $\phi_2 = \phi_2^v$ can use only the CO₂ vapour root. CO₂ is supercritical at these conditions, so the cubic (Eq. 11) has a single real root.

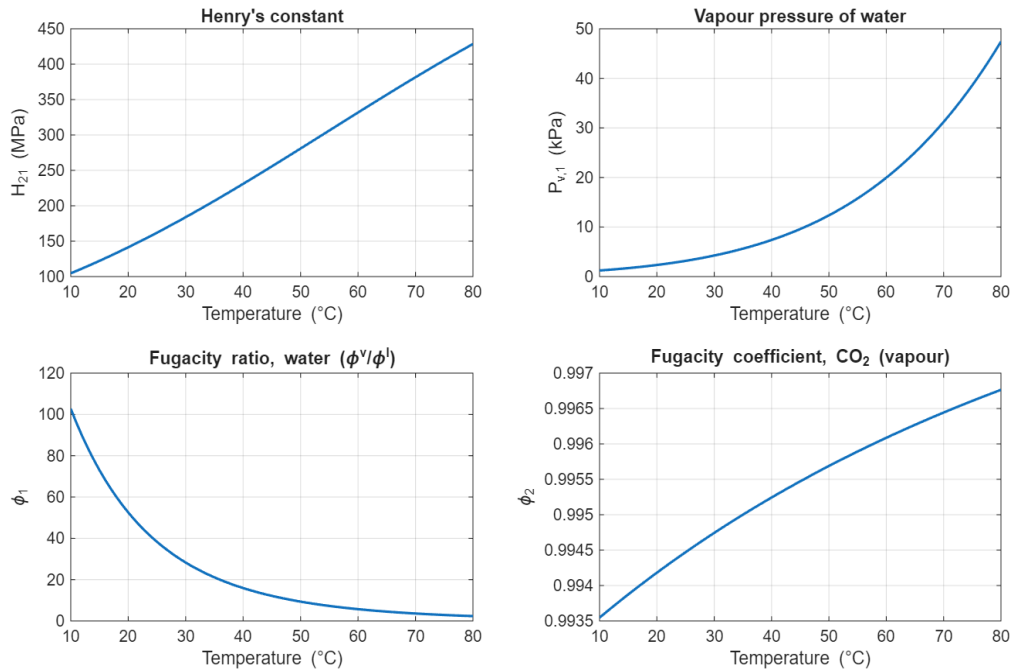


Figure 1: The specified quantities vs temperature at atmospheric pressure (101.325kPa)

As we can see, H_{21} rises at a steady rate. Additionally, we can see P_{v1} rises exponentially, which is to be expected from a pure component vapour pressure curve. ϕ_1 showcases an extreme fall, starting at a value of around 103 at the 10°C to eventually dropping down to around 2 at the 80°C. This rapid drop is unsurprising; this is because ϕ_1^i it is a ratio of the vapour fugacity coefficient divided by the liquid fugacity coefficient; the liquid number doesn't change much with temperature, but the vapour number rises and approaches the liquid number. As a result, the ratio must shrink, which is seen in the graph. On the other hand, ϕ_2 stays relatively close to 1, which indicates that the CO₂ gas must behave like an ideal gas.

3.2 Comparison with Experimental Data

After having plotted the validation graph and compared it to the experimental data of Carroll et al. [1], the similarities at low temperatures are very high across the 3 pressures. However, as the temperature grows, so does the error, at 80°C, P=101.325kPa reaches 48.3%, for P=50kPa it reaches 248.7%, and 23.2% for P=200kPa. These errors are not due to the model breaking down at lower pressures, but instead the absolute solubility itself shrinking near 0, small absolute errors are exaggerated in percentage terms. In addition, the model uses pure component coefficients with no mixing rule, which weakens CO₂ approximations at its critical temperature.

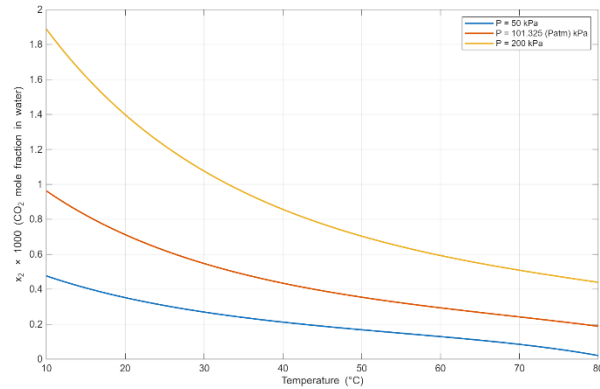


Figure 2: CO₂ solubility vs temperature

Case Study: Great Barrier Reef, 2009-2024

Atmospheric CO₂ data were obtained through UCL, covering 5 stations around Australia. This study uses the GBRWIS reference station at the Great Barrier Reef, the rest provided are other stations around Australia. Once the sentinel values and unexpectedly high CO₂ spikes were removed, the remaining hourly readings were aggregated to 184 monthly means, all to smooth sensor noise. Once the Atmospheric CO₂ concentration was converted into mole fractions, it was used directly as the input that drives y_2 in Eq 2 (which was also rearranged to solve for x_2 at each month).

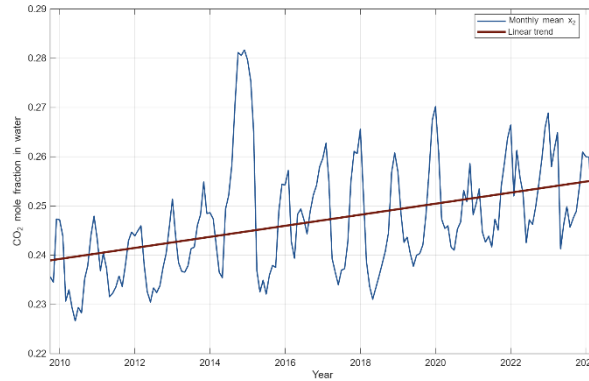


Figure 3: Modelled Equilibrium CO₂ in seawater, GBRWIS (2009-2024)

This plot shows a seasonal cycle of Equilibrium CO₂ in seawater; in addition, it shows a long-term rise of around +6.6% over the entire data set of CO₂ equilibrium in seawater. However, the large 6 month anomaly in 2014 shows signs of being a local event rather than a sensor fault (gradual rise and fall and coincides with the 2015-16 El Niño). The net rise indicates multiple things, primarily confirming that atmospheric CO₂ rise outpaces warming, the main mechanism of ocean acidification

Reaction Kinetics Model

5.1 Numerical Method

To plot this graph, the MATLAB function used to solve Eqs. 13 to 18 was ode15s. The reason a stiff solver is used is because of the table spanning 10 orders of magnitude. In addition, for the initial conditions, the data on page 1 was used as recommended. A log spacing for the time output was used; this is because if a linear one was used, it wouldn't show anything but a sharp jump at $t=0$, given the speed of the reactions. FinalAbsTol and RelTol were set to 1e-12 and 1e-6, due to how low some initial concentrations go down to around 1.97e-8M.

Additionally, two numerical checks were carried out to confirm that the numerical solution is valid. Firstly, total carbon contents across all 5 carbon-containing species are conserved to within 0.0105% between the times $t=0$ and $t=100$. Secondly, testing was redone, however with looser tolerances ($\text{AbsTol}=1\text{e-}6$, $\text{RelTol}=1\text{e-}3$) to test the tolerance sensitivity. The results obtained were physically invalid, as it produced a negative concentration, which as a result, confirms that the recommended tight tolerances are necessary.

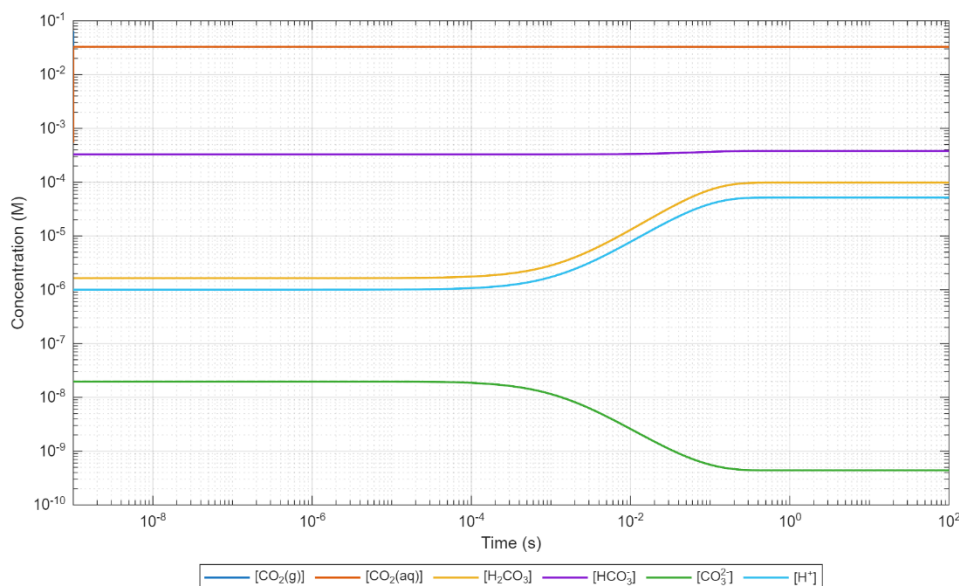


Figure 4: Time dependent solution of Eqs. 13-18

5.2 Timescales and the Rate-Limiting Step

When comparing the characteristic times, Eq 19, we are able to see that: $\text{CO}_2(\text{g})$ to $\text{CO}_2(\text{aq})$ (R1) has a time of $\tau = 5\text{e-}11$ seconds, which is by far the quickest time we can observe. Second fastest is H_2CO_3 to $\text{H}^+ + \text{HCO}_3^-$ (R3) with a $\tau = 8\text{-}10\text{e-}8\text{s}$. Then HCO_3^- to $\text{H}^+ + \text{CO}_3^{2-}$ (R4) with $\tau = 0.4\text{-}20\text{e-}6\text{s}$, but increases in speed as the H^+ ions increase. Slowest of all is $\text{CO}_2(\text{aq})$ to H_2CO_3 (R2) with $\tau = 5\text{e-}2\text{s}$, with an order of magnitude 6 to 9 orders lower than the other 3. These results obtained from the plot showcase textbook carbonate chemistry; from textbooks, we are able to understand that CO_2 hydration to carbonic acid is a slow step in this whole system. The $\text{CO}_2(\text{g})$ and (aq) both overlap each other and then very quickly plateau, like the rest of the plot until around $1\text{e-}4\text{s}$, which is when

H_2CO_3 , HCO_3^- , CO_3^{2-} and H^+ all start to cascade; the reason is that they are waiting on the slow step to produce H_2CO_3 has occurred before any other step can occur. When analysing every specimen, every one is within 1% of its $t=100\text{s}$ value by $t = 0.19\text{-}0.35\text{s}$, with H_2CO_3 by far being the slowest to settle at 0.346s . This is backed up by math: R2's time constant (τ) is 0.0499s , which is 7 times smaller than 0.35 ; this is consistent with exponential relaxation, which is about a multiple of 5τ .

Discussion: Comparing the Two Models

When we start to compare the the equilibrium model (Section 3) and the kinetics model (Section 6), we are able to see they both describe the same physical event from different angles about CO_2 entering seawater. The Phase Equilibrium, given a fixed temperature and pressure, finds how much CO_2 is dissolved; however, it is a static snapshot, with no sense of time included. However, the Reaction Kinetics starts from a sudden injection of CO_2 , sees how the system changes second by second as it reacts with the substance. Unlike the first method, it is a transit method of looking at the system, and works more like a timeline, tracking the starting reactant if the CO_2 all the way through to carbonic acid, bicarbonate, carbonate and pH.

The moment in which both models meet is exactly at one point, which is during R1. This process is the same physical process that is described in Eq. 1-2 as an equilibrium. As shown in section 6.2, we are able to see that R1 is extremely fast, with a time of around 50 picoseconds. This is extremely fast and justifies Phase Equilibriums' core assumption, which is treating gas-liquid CO_2 exchange as instantaneous.

The key ways in which both of these models differ are in a few different ways; firstly, Phase Equilibrium provides us with an answer on how much CO_2 dissolves in total, unlike Reaction Kinetics, which showcases how fast, and what the CO_2 turns into. In addition, Phase Equilibrium is a static snapshot which stops at dissolved CO_2 , unlike Reaction Kinetics, which is more of a full-time evolution which also showcases and tracks the full cascade to H^+ a CO_3^{2-} . The use cases for both are: for Phase Equilibrium, it showcases the effects of warming on the oceans' CO_2 capacity, whereas the Reaction Kinetics showcases which step is rate-limiting.

The assumptions made in Phase Equilibrium are that it assumes activity coefficients at 1, in addition to having a negligible Poynting correction, and no reaction past the CO_2 being dissolved. This means that the model has nothing to say about the carbonate chemistry for ocean acidification. On the other hand, the assumptions made on the Reaction Kinetics model are that it assumes a well-mixed system, with a constant temperature and that water is held in vast excess. It mainly assumes that CO_2 arrives as a single injection instead of something that is able to keep on arriving as the atmosphere keeps changing.

Future Works

The most important improvement is a salinity correction. The Henry's constant in Eq. (7) applies to pure water, but seawater contains about 35 g/kg of dissolved salt, which reduces CO_2 solubility by roughly 15–20 % through the “salting-out” effect. Replacing Eq. (7) with the seawater solubility function of Weiss [6] would make the reef case study physically consistent with the water it describes.

The thermodynamic model could also be improved by adding mixing rules. At present the Peng-Robinson coefficients are calculated separately for each pure component. Van der Waals one-fluid mixing rules with a binary interaction parameter k_{ij} would capture the interaction between water and CO_2 in the vapour phase, and should reduce the high-temperature error seen during validation.

The two models could then be coupled. Feeding the monthly equilibrium CO_2 from the reef case study into the kinetics model as a boundary condition would produce a predicted seawater pH time series for 2009–2024, directly linking how much CO_2

dissolves with how quickly it becomes acidity. That coupling would also be more realistic if the single CO₂ injection were replaced by a continuous air–sea flux driven by the difference between atmospheric and dissolved CO₂, which is closer to how the ocean surface actually behaves. Applying Arrhenius scaling to the rate constants would further show how warming changes the speed of the carbonate system, not just its capacity.

The equilibrium model could be extended beyond two components to include N₂, O₂ and Ar. Each additional gas needs its own Henry’s-law relation, critical properties and interaction parameters, as well as $N - 1$ closure relations, because the current formulation is determined only for a single solute. Finally, applying the model to the other Australian monitoring stations would test whether the reef trend is regional or local, and a sensitivity analysis on temperature, pressure and the correlation coefficients would put error bars on the predictions.

Conclusions

This project modelled CO₂ uptake by water from two complementary angles: how much dissolves, and how fast it reacts.

Framing the vapour–liquid equilibrium as a 4×4 linear system made the problem simple to solve and to analyse. The system becomes singular only when $\phi_1 H_{21} = \phi_2 P_{v1}$, a near-critical condition that real ocean conditions never approach. Even at that point, a solution would exist only if $\phi_1 P = P_{v1}$ also held. The model reproduces reference property values at 25 °C and agrees closely with published solubility data at low temperature. The larger percentage errors near 80 °C come mainly from the near-zero absolute solubility at that temperature and from the absence of a mixing rule.

Applied to 15 years of Great Barrier Reef data, the model predicts a +6.6 % rise in equilibrium dissolved CO₂. This shows that rising atmospheric CO₂ has outweighed the loss of solubility caused by warming, which is the mechanism behind ocean acidification. The kinetics model shows that the carbonate system reaches steady state within about 0.35 s, with CO₂ hydration as the bottleneck. Gas–liquid transfer is around nine orders of magnitude faster, which justifies treating dissolution as instantaneous in the equilibrium model.

Neither model is complete on its own. The equilibrium model gives the CO₂ load but stops at dissolved CO₂, while the kinetics model tracks the full cascade to H⁺ and carbonate but needs that load as an input. Coupling the two and adding a salinity correction is the natural next step towards predicting reef pH directly from atmospheric measurements.

References

- [1] Carroll, J.J., Slupsky, J.D. and Mather, A.E. (1991) 'The Solubility of Carbon Dioxide in Water at Low Pressure', *Journal of Physical and Chemical Reference Data*, 20(6), pp. 1201–1209.
- [2] Peng, D.Y. and Robinson, D.B. (1976) 'A New Two-Constant Equation of State', *Industrial & Engineering Chemistry Fundamentals*, 15(1), pp. 59–64.
- [3] Wagner, W. and Pruß, A. (2002) 'The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use', *Journal of Physical and Chemical Reference Data*, 31(2), pp. 387–535.
- [4] IPCC (2021) *Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge: Cambridge University Press.
- [5] Doney, S.C., Fabry, V.J., Feely, R.A. and Kleypas, J.A. (2009) 'Ocean acidification: the other CO₂ problem', *Annual Review of Marine Science*, 1, pp. 169–192.
- [6] Weiss, R.F. (1974) 'Carbon dioxide in water and seawater: the solubility of a non-ideal gas', *Marine Chemistry*, 2(3), pp. 203–215.
- [7] Zeebe, R.E. and Wolf-Gladrow, D. (2001) *CO₂ in Seawater: Equilibrium, Kinetics, Isotopes*. Amsterdam: Elsevier.