Simple Ocean Chemistry

CO2,Calcium and Sulfate

Start with the Henry Law,

$$CO_2(\text{gas}) \rightleftharpoons \ CO_2(\text{dissolved}) \implies \frac{P_{[CO2]}}{[CO_2 \text{ dissolved}]} \quad = k_{\text{Henry}} \ \simeq \ 29.76 \text{ atm}/(\text{mol}/\text{liter}) \tag{1}$$

and the basic water - carbonate - Calcium equilbrium as before:

$$H_2\,O + CO_2 \rightleftharpoons H_2\,CO_3 \implies K_h = \frac{[H_2\,CO_3]}{[CO_2]} \simeq 1.7 \times 10^{-3}\ (dimensionless) \tag{2}$$

$$H_2\,CO_3 \rightleftharpoons HCO^-{}_3 + H^+ \implies \ K_{a1} = \frac{[HCO^-{}_3][H^+]}{[H_2\,CO_3]} \simeq 2.5 \times 10^{-4} \text{ mol}/\text{liter} \tag{3}$$

$$HCO^-{}_3 \rightleftharpoons \ CO_3{}^{2-} \ + \ H^+ \implies K_{a2} = \frac{[CO_3{}^{2-}][H^+]}{[HCO_3{}^-]} \ \simeq 4.69 \times 10^{-11} \text{ mol}/\text{liter} \tag{4}$$

$$H_2\,O \rightleftharpoons H^+ + OH^- \implies K_w = \left[H^+\right][OH^-] \simeq 1.0 \times 10^{-14} \text{ mol}^2 \big/ \text{liter}^2 \tag{5}$$

but, increase the solubility product by a factor of 100:

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3{}^{2-} \implies K_{Ca} = \left[Ca^{2+}\right] + \left\{CO_3{}^{2-}\right] = 100 \times 4.47\ \times 10^{-9} \text{ mol}^2 \big/ \text{liter}^2 \tag{6}$$

Also, to refine the results throw in 30 miliMoles/Liter of Sulfate. The Sulfate ion acidfies the mixture a bit (obviously there is neglible combination of $HSO^-{}_4$ with H^+) :

$$[HSO^-{}_4] \rightleftharpoons \left[SO4_4{}^{2-}\ \right] \ + \ \left[H^+\right] \implies K_{a2} = \frac{[SO4_4{}^{2-}][H^+]}{[HSO^-{}_4{}^-]} \ \simeq 1.2 * 10^{-2} \text{ mol}/\text{liter} \tag{7}$$

$$\left[SO4_4{}^{2-}\right] + [HSO^-{}_4] = \text{Total Sulfate} = 30 \times 10^{-3} \text{ mols}/\text{liter} \tag{8}$$

The sulfate ions modify the charge balance condition:

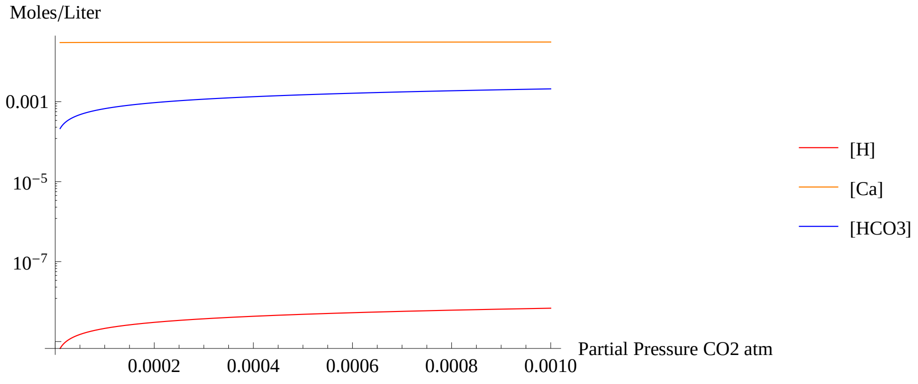
$$2\left[Ca^{2+}\right] + \left[H^+\right] = [OH^-] + [HCO_3{}^-] + 2\left[CO_3{}^{2-}\right] + 2\ \ SO4_4{}^{2-} + HSO^-{}_4 \tag{9}$$

Equations 1-9 are nine equations for the nine unknowns [Ca],[SO4][,HSO4],CO2],[H2CO3],[HCO3],[CO3],[H],[OH] in terms of the P_{CO2}-- **Once the partial pressure of $CO_2$is established concentrations of the nine components are determined.**

For example, at 350 μ atm (350 ppmv) the undissociated dissolved CO_2 calculates immediately from eq 1 as $\texttt{"CO2dissolved=", "1.17608"} \times 10^{\texttt{"-5"}}$ and the remaining components calculate to $\texttt{h} \to 4.00852 \times 10^{-9}$, $\texttt{oh} \to 2.49469 \times 10^{-6}$, $\texttt{ca} \to 0.0306393$, $\texttt{co3} \to 0.0000145891$, .(all in units of moles/liter) $\texttt{hco3} \to 0.00124692$, $\texttt{h2co3} \to 1.99933 \times 10^{-8}$, $\texttt{so4} \to 0.03$, $\texttt{hso4} \to 2.39941 \times 10^{-8}$

The total dissolved carbon $\texttt{"TDIC=", "1.27161"} \times 10^{\texttt{"-3"}}$mol/liter (see eq 10 below)

Partial graph:

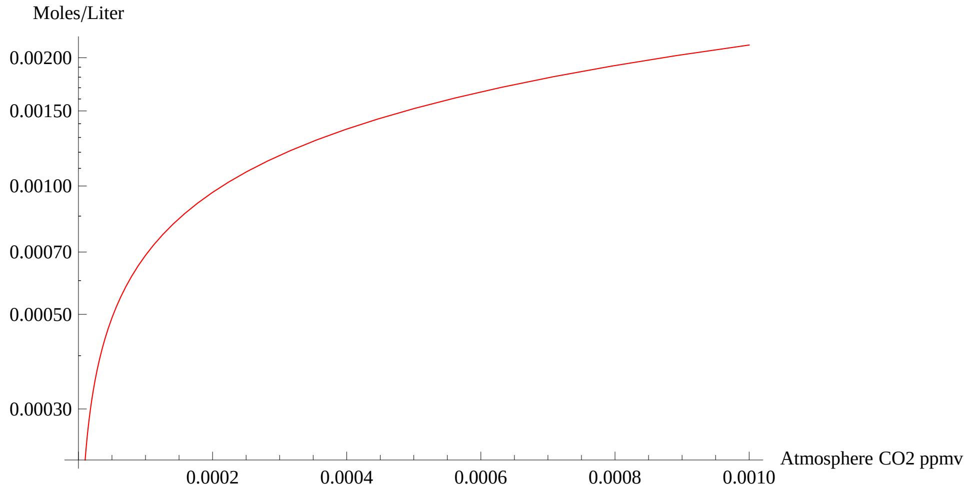


Revelle Effect

Total dissolved inorganic carbon is defined as:

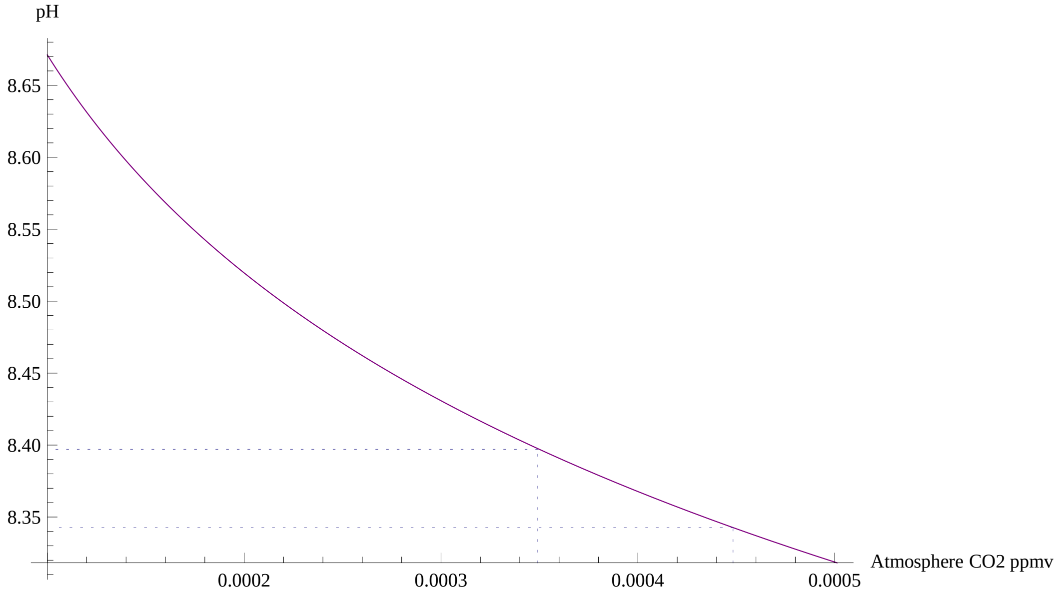
$$\text{TDIC} = \text{CO}_2(\text{dissolved}) + [H_2\,\text{CO}_3] + [\text{HCO}_3{}^-] + \left[\text{CO}_3{}^{2-}\right] \tag{10}$$

And here is plot around present atmospheric levels, clearly showing saturation of the total dissolved carbon components the so called Revelle effect: (Actually, first noted by K. Buch in 1933 see the 1957 Revelle-Suess paper)



Total Dissolved Carbon=CO_2(dissolved) $+ [H_2\,\text{CO}_3] + [\text{HCO}_3{}^-] + \left[\text{CO}_3{}^{2-}\right]$ vs Atmospheric CO_2

And here is plot of pH vs atmospheric CO2 showing the dreaded ocean acidification:



References

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Wikipedia “Calcium carbonate” under section “Solubility” http://en.wikipedia.org/wiki/Calcium_carbonate# With_varying _pH

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Revelle and Suess: Tellus IX (1957),1 “Carbon Dioxide Exchange Between Atmosphere and Ocean...” www.uscentrist.org/about/issues/environment/docs/Revelle-Suess1957.pdf

1. Wikpedia “Carbonic Acid”
2. Wikipedia “Calcium carbnate” under section “Solubiity”